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Thermodynamic Models of Aqueous Solutions Containing Inorganic Electrolytes and Dicarboxylic Acids at 298.15 K. 1. The Acids as Nondissociating Components

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Atmospheric aerosols contain a significant fraction of water-soluble organic compounds, including dicarboxylic acids. Water activities at ∼298.15 K (including data for highly supersaturated solutions) of oxalic, malonic, succinic, glutaric, maleic, malic, and methyl succinic acids are first correlated as a function of concentration, treating the acids as nondissociating components. Methods proposed by Clegg et al. (*J. Aerosol. Sci.* **2001**, *32*, 713−738), and by Clegg and Seinfeld (*J. Phys. Chem. A* **2004**, *108*, 1008−1017) for estimating water activities and solute activity coefficients in aqueous mixtures containing both electrolytes and uncharged solutes are then evaluated from comparisons with literature data. These data include water activities, solubilities, and determinations of the eutonic points of solutions containing up to five acids, and solutions containing one or more acids and the salts $(NH_4)_2SO_4$, NH_4NO_3, or NaCl. The extended Zdanovskii−Stokes−Robinson approach of Clegg and Seinfeld yields the more accurate predictions for aqueous mixtures containing dicarboxylic acids only, and for aqueous mixtures of the acids and salts (though by a lesser margin). A number of hybrid modeling approaches, which contain elements of both methods, are outlined.

1. Introduction

Atmospheric aerosols can contain a large fraction of organic material, from both anthropogenic and natural sources.[1] Dicarboxylic acids are found in aerosols,[2,3] and their properties and behavior are likely to be typical of many polar atmospheric organic compounds that are soluble in water. In addition to chamber experiments investigating organic aerosol formation[4,5] there are consequently a large number of studies of the deliquescence, nucleation, and water uptake properties of aqueous dicarboxylic acids and their mixtures with salts.

Water and solute activities, and gas/liquid/solid equilibrium, of atmospheric aerosols containing dissolved organic compounds are currently modeled in quite a simple way (e.g., see Pun et al.[6] and Griffin et al.[7]). This is partly because of a lack of information regarding the properties and reactions of the compounds that are present, and partly because of the lack of a suitable general method of representing the thermodynamic properties of aqueous solutions containing both ions and uncharged solutes to very high concentration (low equilibrium relative humidity).[8]

Clegg et al.[9,10] and Clegg and Seinfeld[11] have described two possible solutions to this problem, in which models for the different components of the aqueous aerosols—the ionic or electrolyte component, and the uncharged organic solutes—are combined in a self-consistent way. Both approaches allow existing, established, models to be used for the inorganic component of the mixture, and a choice of methods for the uncharged organic solutes. The approach of Clegg et al.[9] (hereafter referred to as CSB) is analogous to a species interaction model such as that of Pitzer,[12] while that of Clegg and Seinfeld[11] is based upon an extended Zdanovskii−Stokes−Robinson (ZSR) scheme. This method, in a somewhat simpler form, is already widely used in atmospheric models to estimate aerosol water content.[13,14] A number of other models have recently been reviewed by Raatikainen and Laaksonen,[8] who identified a lack of experimental thermodynamic data as a major constraint to the development of accurate models.

In this work, we first correlate the available water activity and osmotic coefficient data for aqueous solutions of seven dicarboxylic acids at 298.15 K. Then we use these correlations to test the CSB and extended ZSR approaches for calculating water activities and solubilities in aqueous mixtures of the acids and of aqueous mixtures of the acids and salts. Here the acids are treated as nondissociating solutes in most calculations, which is satisfactory for weakly dissociating acids and is also a reasonable approximation for atmospheric aerosols already acidified by H_2SO_4. In the following study (ref 15), we develop models of activity and osmotic coefficients in aqueous solutions containing succinic and malonic acids, including both dissociation equilibria. These models can be used to test more practical, approximate, methods and are used to suggest a possible hybrid modeling approach that incorporates elements of both the CSB and extended ZSR methods.

2. Theory

The differences between the CSB modeling approach[9] and the extended ZSR method[11] are best illustrated by an example. Consider an aqueous mixture containing ammonium sulfate, sulfuric acid, and two nondissociating organic solutes N_1 and N_2. In the CSB approach, solvent and solute activities for the electrolyte component ($(NH_4)_2SO_4 + H_2SO_4$) and then the nonelectrolytes ($N_1 + N_2$) are first calculated separately at their molalities in the mixture. The aerosol inorganics model (AIM) might be used for the acid ammonium sulfate, and UNIFAC

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for the mixture of N_1 and N_2. This calculation yields a set of activity coefficients $\gamma_i^{(\mathbf{e})}$, and water activity contribution $a_w^{(\mathbf{e})}$, for the electrolyte component **e**; and $\gamma_j^{(\mathbf{N})}$ and $a_w^{(\mathbf{N})}$ for the mixture of N_1 and N_2. Where there are no interactions between the inorganic ions and organic solutes then the water activity of the mixture is equal to $a_w^{(\mathbf{e})}a_w^{(\mathbf{N})}$, and each solute activity coefficient γ_i or γ_j is unchanged from the previously calculated value $\gamma_i^{(\mathbf{e})}$ or $\gamma_j^{(\mathbf{N})}$ respectively (see eq 1 of Clegg et al.[9]). Where such interactions do exist—for example the salting in or salting out of the organic species by dissolved electrolytes—then the effects on solute activity coefficients and the water activity (or osmotic coefficient ϕ) can be expressed by additional terms, which in the work of Clegg et al.[9] are drawn from the Pitzer molality-based model. This approach has the advantage of not being restricted in the choice of methods used to represent the thermodynamic properties of the electrolyte, and nonelectrolyte, elements of the solution. However, it remains limited by the use of mixture terms from the Pitzer model which can take unrealistically large values in concentrated solutions. Parsons et al.[16] have used the method to predict the equilibrium water activities of solutions of organic compounds saturated with respect to ammonium sulfate.

A scheme based on the ZSR relationship is an alternative to that described above. Clegg and Seinfeld[11] have shown how to incorporate submodels for different groups of solutes within the overall approach, and have derived additional terms to correct for the effects (mainly on activity coefficients) of the presence of solutes of different charge types. Thus, to return to the above example, the AIM model could again be used to calculate the properties of the acid ammonium sulfate component ($(NH_4)_2SO_4 + H_2SO_4$), and UNIFAC for the nonelectrolytes ($N_1 + N_2$). However, in this case the calculations would be carried out for each component at the water activity of the mixture and not for the actual solution concentrations. The calculated quantities would be the water amounts associated with each component, and the activity coefficients $\gamma_i^{(\mathbf{e}),\circ}$ and $\gamma_j^{(\mathbf{N}),\circ}$ in aqueous solutions of the two components each at the water activity of the mixture. Their total water content, and the solute activity coefficients in the mixture γ_i and γ_j, are given by eqs 31−34 of Clegg and Seinfeld.[11] If only the concentration of the mixture is known initially, and not the equilibrium water activity, then the equations must be iterated until the calculated solution concentration is equal to the actual one. This method yields different estimates of water and solute activities from the CSB approach even where there are no parameters for interactions between the solution components. Also, dissociation equilibria are difficult to implement within the ZSR equations, as noted by Clegg et al.[10] and discussed in ref 15.

In this work, osmotic coefficients (ϕ) and solute activity coefficients (γ_i) are on the molal scale, molalities are indicated by prefix m, and activities (equal to the product $m\gamma$ for each species i) by prefix a. The stepwise dissociation constants of the dicarboxylic acid H_2X, K_1 (mol kg^{-1}) and K_2 (mol kg^{-1}), are defined by

$$H_2X(aq) \leftrightarrow H^+(aq) + HX^-(aq) \tag{1a}$$

$$K_1 = aH^+\, aHX^-/aH_2X = mH^+\, mHX^-\, \gamma_H\, \gamma_{HX}/(mH_2X\, \gamma_{H_2X}) \tag{1b}$$

$$HX^-(aq) \leftrightarrow H^+(aq) + X^{2-}(aq) \tag{2a}$$

$$K_2 = aH^+\, aX^{2-}/aHX^- = mH^+\, mX^{2-}\, \gamma_H\, \gamma_X/(mHX^-\, \gamma_{HX}) \tag{2b}$$

The activity product K_S of a salt $M_{\nu+}X_{\nu-}{\cdot}nH_2O_{(cr)}$ in equilibrium with an aqueous solution containing cation M^{z+} and anion X^{z-} is given by

$$M_{\nu+}X_{\nu-}{\cdot}nH_2O(s) \leftrightarrow \nu_+M^{z+}(aq) + \nu_-X^{z-}(aq) + nH_2O(l) \tag{3a}$$

$$K_S = aM^{\nu+}aX^{\nu-}a_w^n/a(M_{\nu+}X_{\nu-}{\cdot}nH_2O) \tag{3b}$$

where ν_+ and ν_- are the numbers of moles of M^{z+} and anion X^{z-} in 1 mol of the salt, n is the moles of water of hydration (if any) and a_w is the water activity. Because the activity of the pure solid phase $a(M_{\nu+}X_{\nu-}{\cdot}nH_2O)$ is by definition unity, only the activity product of the ions and solvent in eq 3b is significant.

In the ZSR model, uncharged solutes and electrolytes, or groups of electrolytes, are treated as solution components and not individual ions. Consequently, activity coefficients derived using the model are mean stoichiometric values ($\gamma_\pm$), which are related to those of the individual ions for electrolyte $M_{\nu+}X_{\nu-}$ by[17]

$$\gamma_\pm = (\gamma_M{}^{\nu+}\,\gamma_X{}^{\nu-})^{1/(\nu+ + \nu-)} \tag{4}$$

The activity of $M_{\nu+}X_{\nu-}$ in solution is therefore equal to $mM\, mX\, \gamma_\pm^{(\nu+ + \nu-)}$. The relationship between the stoichiometric activity coefficient of the atmospherically important acid H_2SO_4 and the activity coefficients of H^+, HSO_4^-, and SO_4^{2-} in aqueous solution is given in section 3.4 of Clegg et al.[10]

Water and solute activities in pure aqueous solutions of the dicarboxylic acids are represented by the following set of equations:[18]

$$g^e/RT = x_s(1 - x_s)(c_1 + \Sigma_{i=2,m}\, c_i(1 - x_s)^{i-1}) \tag{5a}$$

$$\begin{aligned} d(g^e/RT)/d(x_s) = {} & (1 - 2x_s)(c_1 + \Sigma_{i=2,m}\,(1 - x_s)^{i-1}) + \\ & x_s(1 - x_s)(-2c_2 - \Sigma_{i=3,m}\, 2(i - 1)c_i(1 - 2x_s)^{i-2}) \end{aligned} \tag{5b}$$

$$\ln(f_s) = g^e/RT + (1 - x_s)\, d(g^e/RT)/d(x_s) \tag{5c}$$

$$\ln(f_w) = g^e/RT - x_s\, d(g^e/RT)/d(x_s) \tag{5d}$$

where g^e is the excess Gibbs energy of the solution per mole of total material, x_s is the stoichiometric mole fraction of the acid solute (equal to $n_s/(n_s + n_w)$ where n is the number of moles). Symbols c_i ($i = 1,m$) are the fitted coefficients, f_w is the mole fraction based activity coefficient of the solvent, water, and f_s is the activity coefficient of the solute. The reference state for f_s is the hypothetical pure liquid s, and f_s is converted to a value based on a reference state of infinite dilution in water (f_s^*) by dividing by the value of f_s calculated for $x_s = 0$. The activity coefficient f_s^* is related to the molality based activity coefficient γ_s by $\gamma_s = f_s^*(1 - x_s)$.

The stoichiometric osmotic coefficient ϕ_{st} of a solution containing a dissolved dicarboxylic acid is defined by

$$\ln(a_w) = -(M_w/1000)m_{st}\phi_{st} \tag{6}$$

where M_w (18.0152 g) is the molar mass of water, and m_{st} (mol kg^{-1}) is the stoichiometric (total) molality of the acid assuming no dissociation. For a dicarboxylic acid H_2X, which dissociates into the ions H^+, HX^-, and X^{2-}, the limiting value of ϕ_{st} as $m_{st} \to 0$ is 3.0, rather than 1.0. While eq 5 always yields ϕ_{st} equal to 1.0 for m_{st} equal to 0.0, the error in terms of the calculated water activity is very small, as will be seen. In ref 15, the dissociation of the acids is considered explicitly.

TABLE 1: Dissociation Constants of the Dicarboxylic Acids at 298.15 K (Units: mol kg^{-1})

acid	formula	CAS Registry No.	K_1[a]	K_2[b]	ref.
oxalic	(HOOC)(COOH)	144-62-7	5.2906×10^{-2}	5.3306×10^{-5}	53
malonic	(HOOC)CH_2(COOH)	141-82-2	1.4223×10^{-3}	2.0172×10^{-6}	54
succinic	(HOOC)$(CH_2)_2$(COOH)	110-15-6	6.1659×10^{-5}	2.3014×10^{-6}	55
glutaric	(HOOC)$(CH_2)_3$(COOH)	110-94-1	4.5710×10^{-5}	3.8904×10^{-6}	56
malic	(HOOC)CH_2CHOH(COOH)	6915-15-7	3.9811×10^{-4}	7.7625×10^{-6}	57
maleic	(HOOC)$(CH)_2$(COOH)	110-16-7	1.1995×10^{-2}	5.9566×10^{-7}	17
methyl succinic	(HOOC)$(CH_2)_2CH_3$(COOH)	498-21-5	7.4132×10^{-5}	2.2909×10^{-6}	58

[a] For the reaction $H_2X(aq) \leftrightarrow H^+(aq) + HX^-(aq)$. [b] For the reaction $HX^-(aq) \leftrightarrow H^+(aq) + X^{2-}(aq)$.

In our analysis, we have also estimated values of the osmotic coefficient ϕ_{H_2X} of a hypothetical solution containing only the undissociated acid molecule. This enables data for the more strongly dissociating acids in dilute solution to be more easily assessed, and it was performed by assuming that the stoichiometric osmolality of each acid could be expressed as the sum of two terms, one for the ionic contribution and one for the undissociated acid:

$$\phi_{st} m_{st} = \phi_{ions}(mH^+ + mHX^- + mX^{2-}) + \phi_{H_2X} mH_2X \quad (7a)$$

hence

$$\phi_{H_2X} = (\phi_{st} m_{st} - \phi_{ions}(mH^+ + mHX^- + mX^{2-}))/mH_2X \quad (7b)$$

where $\phi_{st} m_{st}$ is obtained from the experimental water activity (and is equal to $-1000 \ln(a_w)/M_w$), and the individual species molalities are calculated using the dissociation constants of the acids given in Table 1. It is assumed that $\gamma_{H_2X} = 1.0$ in all solutions, and the Pitzer molality based model[12] is used to determine iteratively the activity coefficients and molalities of the ions. The species HSO_4^- and SO_4^{2-} are taken as analogues of HX^- and X^{2-}, respectively, and the equations of Clegg et al.[19] (and their parameters for $H^+-HSO_4^-$ and $H^+-SO_4^{2-}$ interactions) were used in the calculations. The osmolality contribution of the ions in eq 7 is given by

$$\phi_{ions}(mH^+ + mHX^- + mX^{2-}) = mH^+ + mHX^- + mX^{2-} + 2(-A^{\phi} I^{3/2}/(1 + 1.2I^{1/2})) + mH^+ mHX^-(B^{\phi}_{H,HX} + ZC^{T\phi}_{H,HX}) + mH^+ mX^{2-}(B^{\phi}_{H,X} + ZC^{T\phi}_{H,X}) + mHX^- mX^{2-}\, \Phi^{\phi}_{HX,X} \quad (8)$$

where A^{ϕ} is the Debye–Huckel constant (0.3915 at 298.15 K[20]), I is the ionic strength, and the other functions are as defined in appendix I of Clegg et al.[19] This approach to estimating ϕ_{H_2X} is broadly similar to that of Robinson et al.,[21] although their intent was to estimate the true osmotic coefficient taking into account the actual speciation (H^+, HX^-, X^{2-}, and H_2X) rather than to isolate the contribution of the undissociated acid.

3. Aqueous Solutions of Single Dicarboxylic Acids

In this section, we correlate the available activity data for aqueous solutions of seven dicarboxylic acids at room temperature. The dissociation constants of the dicarboxylic acids are listed in Table 1. The effect of ignoring dissociation is mainly a function of the first dissociation constant K_1. Values range from 1.1995×10^{-2} mol kg^{-1} for maleic acid to only 4.571×10^{-5} mol kg^{-1} for glutaric acid. The effects are likely to be greatest in solutions containing maleic or malonic acids and sulfate salts, where the formation of aqueous HSO_4^- will tend to increase the dissociation of the acid. This effect is discussed in section 5. We note that oxalic acid ($K_1 = 5.291 \times 10^{-2}$ mol kg^{-1}) also dissociates strongly. However, the properties of its mixtures with other acids and salts are not considered in this work.

Solubilities of the dicarboxylic and hydroxy-dicarboxylic acids treated here range from about 0.7 (succinic acid) to 15.8 mol kg^{-1} (malonic acid) at 298.15 K and are listed in Table 2, together with sources of data leading to water activities and solute activity coefficients. The equilibrium solubilities adopted in this study are given in Table 3 together with the calculated activity of the acid in a saturated pure aqueous solution.

Measurements of water activities of bulk solutions have been used as listed by the authors, and the data from the very few isopiestic studies have been generally recalculated using modern values of the osmotic coefficients of the reference standards. The uncertainties associated with the different types of measurement are taken from the original papers, or are estimated here, and are shown as error bars in the figures. The electrodynamic balance (edb) experiments of Chan and co-workers[22,23] yield data for supersaturated solutions. The ambient relative humidity in the edb chamber is either measured directly,[22] or is known from the results of calibration experiments in the case of the "scanning" edb technique.[23] The solute concentration in the suspended particle (in mass units) is determined indirectly from the dc balancing voltage, which is proportional to the mass/charge ratio of the particle (on which the total charge is assumed to remain constant). Absolute values of concentration are obtained by standardizing relative to the measured water activities of bulk solutions whose concentrations are known.[24] In this study we have either used the concentrations (mass fractions of solute, mfs) tabulated by Chan and co-workers[79] or have restandardized them to achieve a closer match with osmotic coefficients from bulk solution measurements. The procedure is equivalent to varying the assumed mass fraction of solute in the particle, which alters both the molality and osmotic coefficient of the solution (though the product, the osmolality, remains the same). This standardization adds an additional uncertainty to the concentrations calculated from the experimental data and will be greatest for those systems for which the data are most scattered at high relative humidity.

The dissociation of the dicarboxylic acids is mostly ignored in the ZSR-based calculations of deliquescence properties in this section, and the water activity and solute activity coefficients of pure aqueous solutions of each of the acids are represented by eq 5. We now discuss the available water activity data for each acid at 298.15 K, and the fit of eq 5. Parameters for all the acids are listed in Table 4.

3.1. Oxalic Acid. This C2 dicarboxylic acid (IUPAC name: ethanedioic acid) is the most strongly dissociating of all the acids considered here, and has a solubility of about 1.26 mol kg^{-1} (Table 2). Consequently the bulk solution measurements are restricted to low molalities and, of these, the direct

TABLE 2: Sources of Solubility and Water Activity Data for Dicarboxylic Acids

acid	t/°C	m^{a} min	m^{a} max	used^{b}	data^{c}	source
oxalic	25	–	1.208^{d,e}		sol	59
	25	–	1.248^{d}		sol	27
	25	–	1.307^{d}		sol	60
	25	–	1.265^{d}		sol	61
	various	–	–		sol^{f}	62
	25	0.200	0.927	yes	a_w	22
	25	3.42	38.9	yes	edb^{g}	22
	25	0.231	1.235	yes	a_w	31
	25	0.44	1.4	yes	a_w	30
	various	0.849	1.331	no	vp^{h}	62
	25	–	–	yes	DRH	27
	25	0.436	1.125	yes	iso	63
malonic	25	–	15.81		sol	59
	25	–	15.22		sol	27
	25	–	15.44		sol	60
	various	–	–		sol^{i}	62
	various	–	–		sol^{j}	64
	25	0.499	7.984	yes	a_w	22
	25	5.533	209.3	yes	edb^{k}	22
	23.3			no	edb^{l}	23
	25	0.504	9.545	yes	a_w	31
	various	0.57	14.0	no	vp^{m}	62
	25	0.461	4.838	yes	vpl	28
	25	0.61	15.8	no	a_w	30
	25	–	–	yes	DRH	27
	various	–	–	no	DRH^{n}	65
	<0	–	–	no	fp	64
succinic	25	–	0.707		sol^{o}	59
	25	–	0.752		sol^{o}	60
	25	0.096	0.683	no	a_w	22
	25	5.98	81.2	yes	edb^{g}	22
	25	1.73	25.7	no	edb^{p}	25
	25	<1	∼65	no	edb^{q}	26
	25	0.399	0.602	yes	iso	21
	25	0.399	0.602	yes	vpl	28
	25	0.128	0.489	no	a_w	31
	25	0.105	0.669	yes	vpo	29
	25	0.3	0.83	no	a_w	30
	100	1.177	8.182	no	vp^{r}	33
	various	–	–	no	DRH^{s}	65
glutaric	25	–	10.5^{d,t}		sol	59
	25	–	10.57^{d}		sol	66
	25	–	10.8^{d}		sol	27
	25	0.200	11.96	yes	a_w	22
	25	9.779	98.14	yes	edb^{g}	22
	25	0.493	4.114	yes	vpl	28
	25	0.44	11.5	no	a_w	30
	20	–	–	no	DRH	48
	25	–	–	yes	DRH	27
	various	–	–	no	DRH^{u}	65
malic	25	–	10.3^{d,e}		sol	59
	25	–	10.21^{d}		sol	60
	25	–	10.05^{d}		sol	27
	24	–	19.46^{v}		sol	34
	25	1.006	7.906	no	$a_w{}^{w}$	22
	25	5.19	122	yes	edb^{k}	22
	25	0.528	6.420	yes	iso	21
	25	0.500	3.00	yes	vpl	28
	25	0.392	7.369	no	a_w	31
	25	0.098	10.86	no	a_w	29
	25	0.500	19.48	no	$a_w{}^{v}$	30
	25	0.186	4.330^{x}	no	a_w	67
	25	–	–	yes	DRH	68
	25	–	–	yes	DRH	27
	24	–	–	no	DRH^{v}	34
maleic	25	–	6.85^{d,e}		sol	59
	25	–	6.924^{d}		sol	60
	25	–	6.769^{d}		sol	27
	22	0.987	5.499	no	$a_w{}^{w}$	23
	22.7	4.357	33.29	yes	edb^{k}	23
	25	0.473	3.262	yes	iso	21
	25	0.500	3.00	yes	vpl	28
	25	0.611	6.050	no	a_w	30
	25	–	–	yes	DRH	27
methyl succinic	25	–	4.184^{d}		sol	27
	25	0.300	1.00	yes	vpl	28
	25	–	–	yes	DRH	27

[a] Molality range of the data. Where the data have been used in fits described in section 3, then the range given is for nonzero weighted data only. [b] Used in the fit of the model. See Table 3 regarding the use of solubility data. [c] Type of measurement: sol, solubility; a_w, water activity of bulk aqueous solutions; edb, aqueous phase concentration as a function of ambient relative humidity using an electrodynamic balance; iso, isopiestic determination of water activity; DRH, relative humidity at which deliquescence of the solid acid occurs (equivalent to the equilibrium relative humidity above a saturated aqueous solution); vpl, vapor pressure lowering; vp, direct determination of vapor pressure; vpo, vapor pressure osmometry; fp, freezing point depression with respect to ice which yields the water activity of the solution at the freezing temperature. [d] Molal solubility at 298.15 K. [e] Given by Marcolli et al.[27] in their Table 1. [f] The fitted equation in Table 1F of Braban et al.[62] gives a solubility of 1.23 mol kg^{-1} at 298.15 K. [g] The original data have been re-standardized (which affects the molalities), see text. [h] The measurements were made from 283 to 318 K (Table 1 of Braban et al.[62]). [i] The fitted equation in Table 1C of Braban et al.[62] gives a solubility of 15.3 mol kg^{-1} at 298.15 K. [j] Hansen and Beyer[64] have determined liquid/solid-phase transitions involving the solid acid, ice and malonic acid hexahydrate. [k] Tabulated data (see http://ihome.ust.hk/∼keckchan/hygroscopic.html) used directly, without adjustment. [l] These later data were not used here, but agree very closely with the earlier work of Peng et al.[22] [m] The measurements were made from 274.1 to 293.1 K (Table 1 of Braban et al.[62]). [n] Parsons et al.[65] have measured the deliquescence relative humidities of several dicarboxylic acids, and summarize the available data. Their fitted equation gives a DRH of 72.1% at 298.15 K, in good agreement with the 72.4% determined by Marcolli et al.[27] [o] There are numerous other measurements of solubility, often obtained as a part of larger studies of the solubility of the acid in mixtures (see, for example, the work of Marshall and Bain tabulated by Linke[69] (Vol. II)). The lower of these two values appears to be more nearly correct. [p] These data appear to be in error: see text, and also Peng et al.[22] [q] The results are presented as a fitted equation, and agree well with the re-standardized data of Peng et al.[22] [r] Boiling point elevations of aqueous succinic acid are also listed in the compilation,[33] and could be used to calculate osmotic coefficients at the boiling temperature. [s] Because of the low solubility of succinic acid, and the large uncertainty of the DRH, the measurements are of limited value. [t] Interpolated from Table 1244. [u] The equation of Parsons et al.[65] yields a DRH of 88.2%, agreeing closely with the 88.8% measured by Marcolli et al.[27] [v] For L-malic acid. [w] Inadvertently omitted. [x] The solution concentrations given by the authors, and listed here, are in mol dm^{-3}.

measurements of water activity have a large uncertainty when expressed as osmotic coefficients.

The edb data for aqueous oxalic acid are quite scattered (see Figure 2 of Peng et al.[22]) and are not consistent with the bulk solution data at low aqueous phase concentrations. A simple restandardization of the data (varying all mfs by a constant amount) did not yield plausible results. The measured relative humidities in the edb chamber are uncertain to about ±1%, and evaporation of oxalic acid from the particle at low RH is also a possibility. Some test calculations were carried out, in which it was assumed that the mass of oxalic acid in the suspended particle decreased (due to evaporative loss) with decreasing RH rather than remained constant. (An overall net loss of 17% of the oxalic acid was assumed in these calculations.) The apparent step change in water activity, or equilibrium RH, shown in Figure 2 of Peng et al.[22] suggested that there might also be a

TABLE 3: Dicarboxylic Acid Solubilities and Activity Products in Saturated Aqueous Solutions at 298.15 K (Units: mol kg^{-1})

acid	solubility[a]	activity product[b]	a_w(sat.)[c]
oxalic	1.265	1.237[d]	0.9777[d]
succinic	0.707	0.588	0.9885
malonic	15.3	17.28	0.725
glutaric	10.68	3.12	0.878
malic	10.2	16.95	0.786
L-malic	19.5	62.3	0.559
maleic	6.86	6.73	0.885
methyl succinic	4.18	2.05	0.948

[a] The value is either selected from those listed in Table 2 or is a mean of two or more values: oxalic acid, evaluation of Clegg et al.;[61] succinic acid, data from the compilation of Stephen and Stephen;[59] malonic acid, mean of the two lower values in Table 2; glutaric and maleic acids, means of the solubilities determined by Marcolli et al.[27] and by Apelblat and Manzurola;[66] malic acid, mean of the values listed in Table 2; L-malic and methyl succinic acids, values listed in Table 2. Preference was given to those values of solubility that appeared to be consistent with measurements for mixed solutions, and which agreed closely with other, independent, determinations. [b] This quantity (K_s) is the product of the stoichiometric acid molality in the saturated solution multiplied by the molal activity coefficient γ calculated from eq 5. [c] The equilibrium water activity of the saturated solution, from eq 5. [d] Obtained using the listed solubility and assuming Raoult's law (and no dissociation of the acid).

small negative error in the determination of RH in the edb chamber. Adjusting for such an error, together with the possible particle evaporation noted above, yields the osmotic coefficients and water activities plotted in Figure 1 and satisfactory overall consistency. We have adopted these values. Note that the error bars in Figure 1a do not reflect the uncertainties associated with these changes, and we must also point out that we have no direct evidence that supports the adjustments we have made to the measurements, beyond the large inconsistency with the bulk solution data that is shown in the work of Peng et al. and confirmed by other literature studies listed in Table 2.

In Figure 1a the trend to high values of ϕ_{st} as $\sqrt{m_{st}}$ tends to zero is due to the dissociation of the acid. Rather than fit eq 5 to these data without taking dissociation into account explicitly, and in view of the overall uncertainty in the edb data, we have simply assumed that Raoult's law applies for this acid. The line is plotted in Figure 1a and agrees reasonably well with the edb measurements, given this limitation, as is also clear from the water activity plot (see Figure 1b).

Estimated osmotic coefficients ϕ_N for solutions containing only the undissociated acid, shown in Figure 1c, extrapolate to unity at zero molality, as expected. Within the uncertainty in the data, it is not possible to tell whether there are any features in the ϕ_{st} or ϕ_N curves other than a monotonic decline with increasing molality. However, it should be remembered that the edb data have been adjusted based on the assumption of a smooth transition between bulk and particle data, and therefore both ϕ_{st} and m_{st} from these measurements to some degree depend on this.

3.2. Succinic Acid. This acid (butanedioic acid) is one of the least soluble of the short chain dicarboxylic acids, and bulk solution measurements of water activities at room temperature are restricted to molalities of less than about 0.7 mol kg^{-1}. Electrodynamic balance measurements have been made for supersaturated aerosol droplets by Peng et al.,[22] by Na et al.,[25] and by Mohan and Myerson.[26] The results of the latter two studies are presented as fitted equations only. The results of Na et al. do not extrapolate to unit water activity at zero molality, and Peng et al. have suggested that they are affected by solute evaporation from the suspended particle. The results of Peng et al. were restandardized by adding +0.06 to their listed mfs to agree better with the bulk solution measurements. However, this adjustment is probably uncertain by as much as 50%. The error bars in Figure 2a do not reflect this and could be 2 to 3 times greater than shown.

Equation 5 has been fitted to the bulk solution measurements and to the results of Peng et al.[22] The data and predictions of the fitted equation are shown in Figure 2a as ϕ_{st}, and as a_w in Figure 2b. Water activities from the equation of Mohan and Myerson[26] are also plotted in Figure 2b and agree moderately well with the work of Peng et al.[22]

For all the acids studied here, eq 5 is unconstrained at water activities below which the particle crystallizes, and the calculated values should be regarded only as plausible extrapolations to $x_s = 1$ and $a_w = 0$. However, the extrapolation can be important in calculations of the water content of multicomponent solutions using the ZSR relationship. This is because the method requires the water content (or molality) of pure aqueous solutions at the water activity of the mixture, and very low values can be attained in solutions containing several components.[27]

Osmotic coefficients of aqueous succinic acid from bulk solution measurements are shown in Figure 2c. These were obtained using the isopiestic method,[21] by vapor pressure difference,[28] vapor pressure osmometry,[29] or by dew point determination.[22,30,31] At low molalities the water activity is close to unity—a_w is equal to 0.9915 at 0.5 mol kg^{-1}, and $\phi_{st} = 0.95$. Measurements using meters based on dew point determination that have an accuracy of no better than ±0.003 in a_w, equivalent to ±0.34 in ϕ_{st} at this molality, are therefore of limited value. Three sets of results[22,30,31] that use this technique have been omitted from Figure 2c. Isopiestic measurements of water activity[32] are the most accurate at low molalities, but it is possible that solute evaporation from the sample cups could affect the results for volatile solutes such as the dicarboxylic acids. For this reason, we have assumed an uncertainty of ±0.01

TABLE 4: Coefficients for Eq 5[a]

acid	a_i	i	a_i	i	a_i	i	a_i	i
oxalic	Raoult's law is assumed[b]							
malonic	−0.149445	(1)	−0.403222	(2)	−0.571432	(3)	0.628461	(6)
succinic	0.291972	(2)	0.452397	(8)				
glutaric	−0.209091	(1)	0.353220	(2)	0.755191	(7)		
malic	−3.72769	(1)	−1.54008	(2)	1.567 24	(3)		
maleic	−0.939821	(1)	0.174880	(2)				
methyl succinic	−0.454105	(1)	0.164341	(2)	0.244702	(3)	0.217680	(4)
	0.829461	(7)	0.136151	(8)	−1.89197	(9)	2.15157	(11)
	−0.872404	(13)						

[a] The subscript number i of each parameter a_i is given in parentheses after each value. Thus, for example, activities in aqueous succinic acid are calculated using only c_2 and c_8 in eq 5, whereas for aqueous glutaric acid parameters c_1, c_2, and c_7 are used. [b] For Raoult's law both solvent and solute mole fraction activity coefficients f_w and f_s^* are equal to unity at all concentrations. This is equivalent to all parameters $c_i = 0$ in eq 5.

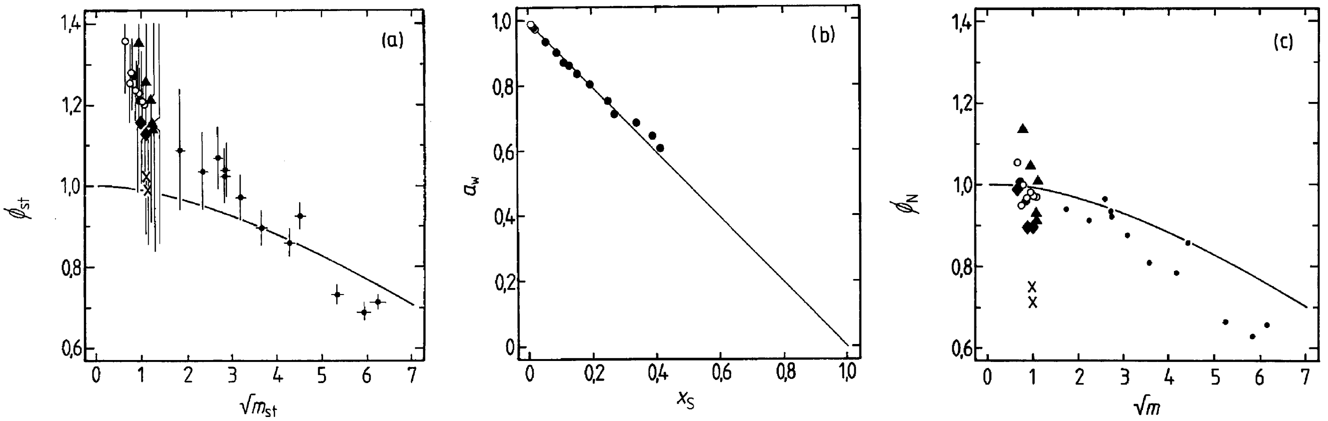

Figure 1. Osmotic coefficients and water activities of aqueous oxalic acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, Kirsch and Maurer;[63] filled circle, Peng et al.[22] (bulk measurements); triangle, Wise et al.;[30] diamond, Maffia and Meirelles;[31] cross, Marcolli et al.;[27] dot, Peng et al.[22] (edb measurements for supersaturated solutions); line, Raoult's law. (b) Water activities (a_w) plotted against oxalic acid mole fraction x_s. Key: open circle, bulk solution data; dot, Peng et al.[22] (supersaturated solutions); line, Raoult's law. (c) Osmotic coefficients (ϕ_N) of solutions containing only the undissociated acid molecule, calculated using eqs 7 and 8. Values are plotted against the square root of the calculated molality of the undissociated acid (m_N), the symbols are the same as in part a, and the line is ϕ_{st} from eq 5 plotted against $\sqrt{m_{st}}$.

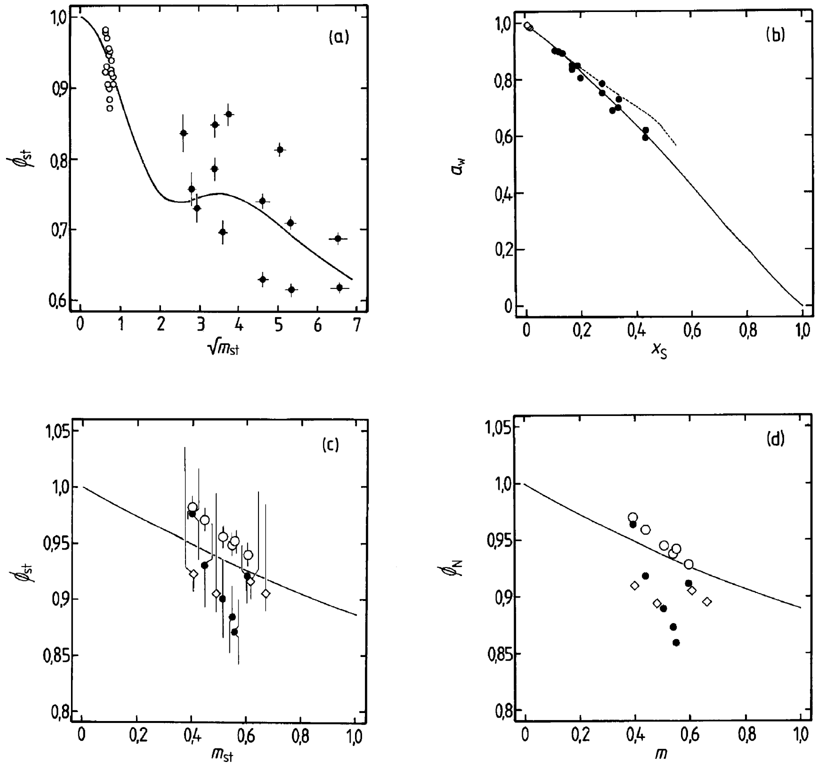

Figure 2. Osmotic coefficients and water activities of aqueous succinic acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, all bulk solution data; dot, edb measurements of Peng et al.[22] for supersaturated solutions. (b) Water activities (a_w) plotted against succinic acid mole fraction x_s. Key: open circle, bulk solution data; dot, edb measurements of Peng et al.;[22] solid line, eq 5 with coefficients from Table 4; dotted line, equation of Mohan and Myerson.[26] (c) Bulk solution measurements of ϕ_{st}. Key: open circle, Robinson et al.;[21] dot, Davies and Thomas;[28] diamond, Carlo;[29] solid line, eq 5. (d) Osmotic coefficients (ϕ_N) of solutions containing only the undissociated acid molecule, calculated using eqs 7 and 8. Values are plotted against the calculated molality of the undissociated acid (m_N), the symbols are the same as in part c, and the line is ϕ_{st} from eq 5 plotted against m_{st}.

in the ϕ_{st} data of Robinson et al.,[21] which is a factor of 2−3 lower than can be obtained under the best possible conditions. The vapor pressure osmometry measurements of Carlo[29] have been assessed by comparing the results of that author for L-malic and citric acids with data from other sources. Values of ϕ_{st} are essentially correct at 1 mol kg^{-1}, the highest molality at which this technique was used, but below this are too low by an amount that increases with decreasing molality (to about −0.09 at 0.4 mol kg^{-1}). The upper error bars in Figure 2c have been assigned based on the assumption that this error varies linearly with molality. It is also worth noting that the vapor pressure measurements of Tamman[33] yield osmotic coefficients at 373.15 K of 0.90 to 0.92, from 1.18 to 8.18 mol kg^{-1}, suggesting only a small variation in ϕ_{st} with temperature.

Finally, values of ϕ_N, the hypothetical osmotic coefficient of the pure aqueous undissociated succinic acid, are shown in Figure 2d. The decrease relative to ϕ_{st} is small, as this is one of the more weakly dissociated of the acids.

3.3. Malonic Acid. This C3 dicarboxylic acid (propanedioic acid) has a solubility of 15.3 mol kg^{-1} at 298.15 K, and water

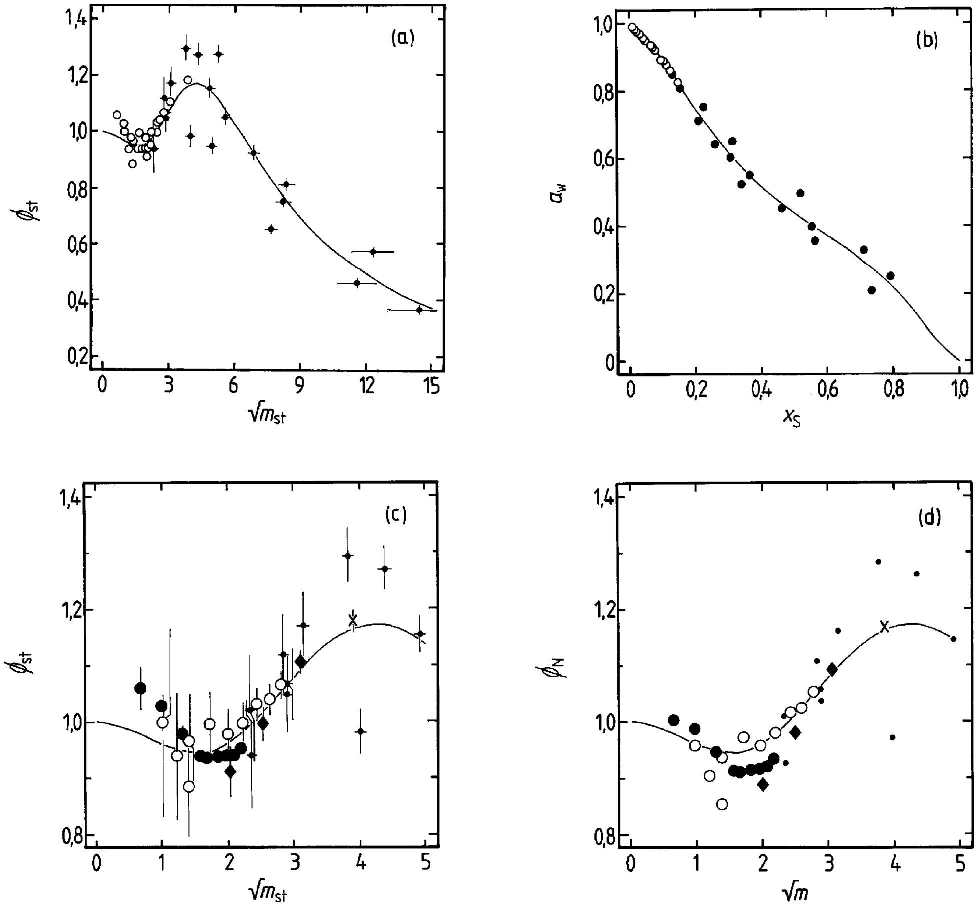

Figure 3. Osmotic coefficients and water activities of aqueous malonic acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, all bulk solution data; dot, edb measurements of Peng et al.[22] for supersaturated solutions. (b) Water activities (a_w) plotted against malonic acid mole fraction x_s. Key: open circle, bulk solution data; dot, edb measurements of Peng et al.;[22] solid line, eq 5 with coefficients from Table 4. (c) Values of ϕ_{st} at low to moderate molalities. Key: open circle, Peng et al.[22] (bulk solution data); filled circle, Davies and Thomas;[28] diamond, Maffia and Meirelles;[29] cross, Marcolli et al.;[27] dot, Peng et al.[22] (edb data); solid line, eq 5. (d) Osmotic coefficients (ϕ_N) of solutions containing only the undissociated acid molecule, calculated using eqs 7 and 8. Values are plotted against the square root of the calculated molality of the undissociated acid (m_N), the symbols are the same as in part c, and the line is ϕ_{st} from eq 5 plotted against $\sqrt{m_{st}}$.

activity data are available from several different sources; see Table 2. The results of the different studies of bulk solutions are reasonably consistent and are shown in Figure 3a, together with the electrodynamic balance data of Peng et al.[22] for supersaturated solutions, and the fitted eq 5. The equation represents all the data satisfactorily. Figure 3c shows mainly the bulk solution data, with error bars. The uncertainty in the data varies considerably, and increases as the solutions become more dilute. The fitted models, and bulk solution and edb data, are shown in Figure 3b as a_w over the entire concentration range.

The first dissociation constant of malonic acid is about 20× greater than that of succinic acid. Estimated osmotic coefficients of the pure aqueous undissociated acid, ϕ_N, are shown in Figure 3d. Values are clearly reduced relative to ϕ_{st}, and extrapolate well to 1.0 at infinite dilution.

3.4. Glutaric Acid. Glutaric acid (pentanedioic acid) has a solubility of 10.68 mol kg^{-1} at 298.15 K, and the measurements of Davies and Thomas[28] and Peng et al.[22] are the principal sources of data for subsaturated solutions. These are shown in Figure 4a, together with electrodynamic balance data for supersaturated solutions and the fitted eq 5. Figure 4b shows the same data, but as water activities, and the extrapolation of the equation to a solute mole fraction of unity.

Glutaric acid has a similar first dissociation constant to succinic acid, and estimated values of ϕ_N for solutions containing only the undissociated acid molecule differ only slightly from ϕ_{st}; see Figure 4c.

3.5. Malic Acid. This C4 dicarboxylic acid (hydroxybutanedioic acid) has an −OH group attached to the carbon chain and the measured osmotic coefficients ϕ_{st} are all greater than unity; see Figure 5a,b. There are two forms of the acid, and the measurements of both Wise et al.[30] and of Carlo[29] are for solutions of L-malic acid. Data of other workers are presumably for the racemic mixture. Robinson et al.[21] concluded from their isopiestic study of DL-tartaric and D-tartaric acid aqueous solutions that there was no measurable difference between the water activities, and here aqueous solutions of the two forms of malic acid are treated as having the same thermodynamic properties. However, we do note that the solubility of L-malic acid at 297.15 K (19.5 mol kg^{-1})[34] is almost double that for the racemic mixture.

The osmotic coefficient data shown in Figure 5, parts a and b, agree well, although there is some suggestion that values of ϕ_{st} for solutions at or above the saturation molality (and based largely on values from edb experiments) may be too high. Data of Carlo[29] and of Maffia and Meirelles,[31] which were not fitted, are shown in Figure 5c.

The data and fitted eq 5 are plotted as a_w against solute mole fraction in Figure 5d. The curve is more typical of an electrolyte solution than are those of the other acids, with a significant

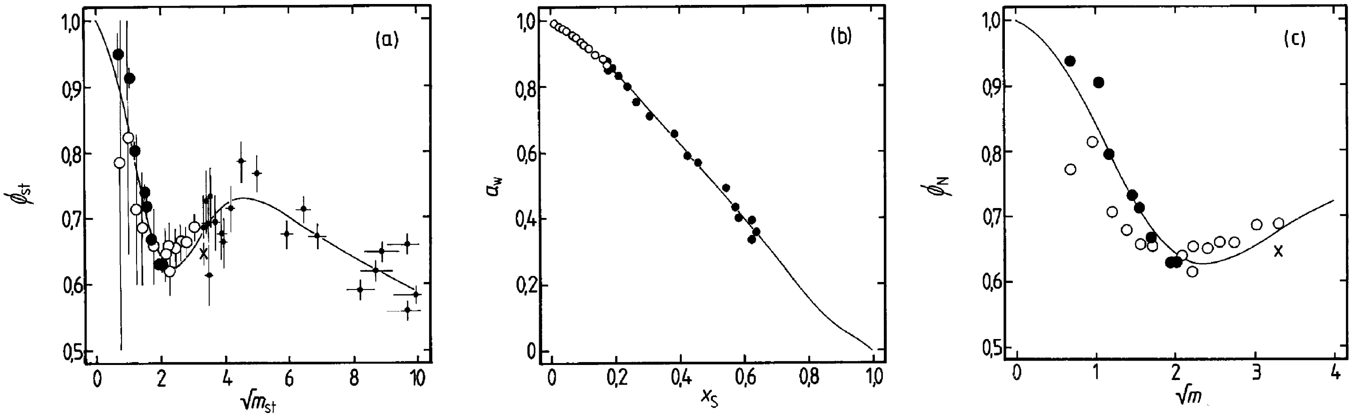

Figure 4. Osmotic coefficients and water activities of aqueous glutaric acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, Peng et al.[22] (bulk solution data); filled circle, Davies and Thomas;[28] cross, Marcolli et al.;[27] dot, Peng et al.[22] (edb data); solid line, eq 5 with coefficients from Table 4. (b) Water activities (a_w) plotted against glutaric acid mole fraction x_s. Key: open circle, bulk solution data; dot, edb measurements of Peng et al.;[22] solid line, eq 5. (c) Osmotic coefficients (ϕ_N) of solutions containing only the undissociated acid molecule, calculated using eqs 7 and 8. Values are plotted against the square root of the calculated molality of the undissociated acid (m_N), the symbols are the same as in part a, and the line is ϕ_{st} from eq 5 plotted against $\sqrt{m_{st}}$.

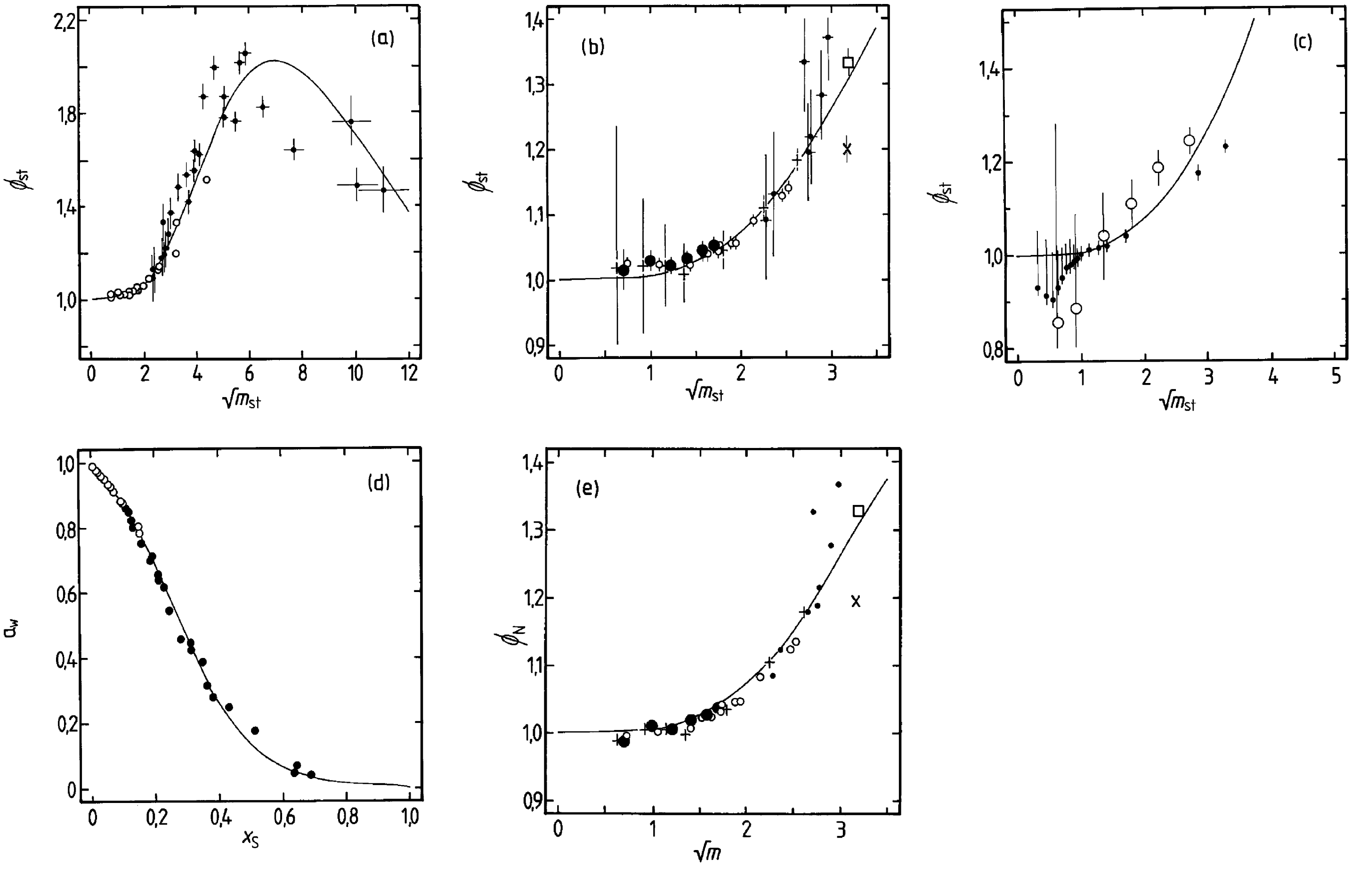

Figure 5. Osmotic coefficients and water activities of aqueous malic acid and L-malic acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, all bulk solution data; dot, Peng et al.[22] (edb measurements of supersaturated solutions). (b) Values of ϕ_{st} at low to moderate molalities. Key: open circle, Robinson et al.;[21] filled circle, Davies and Thomas;[28] plus, Velezmoro and Meirelles;[67] square, Apelblat et al.;[68] cross, Marcolli et al.;[27] dot, Peng et al.[22] (edb data); line, eq 5 with coefficients from Table 4. (c) Values of ϕ_{st} that were not included in the fitted model. Key: open circle, Carlo;[29] dot, Maffia and Meirelles.[31] (d) Water activities (a_w) plotted against malic acid mole fraction x_s. Key: open circle, bulk solution data; dot, edb measurements of Peng et al.;[22] solid line, eq 5. (e) Osmotic coefficients (ϕ_N), calculated using eqs 7 and 8, of solutions containing only the undissociated acid molecule. Values are plotted against the square root of the calculated molality of the undissociated acid (m_N), the symbols are the same as in (b), and the line is ϕ_{st} from eq 5 plotted against $\sqrt{m_{st}}$.

negative deviation from Raoult's law. Aqueous malic acid solutions clearly have a lower water activity, for a given concentration, than the other acids and this feature may be due to the greater degree of polarity of the molecule. Calculated values of ϕ_N for solutions of the undissociated acid are shown in Figure 5e, and extrapolate smoothly to unity with little difference from the stoichiometric values.

3.6. Maleic Acid. This dicarboxylic acid (*cis*-butenedioic acid) has the same number of carbon atoms as succinic acid, but also a central double bond. It has a first dissociation constant

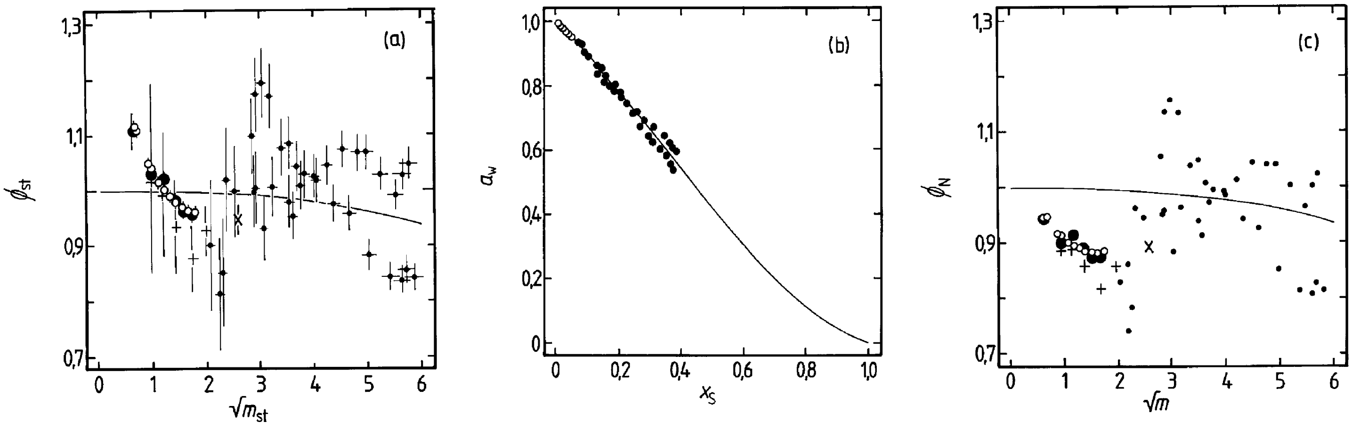

Figure 6. Osmotic coefficients and water activities of aqueous maleic acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, Robinson et al.;[21] filled circle, Davies and Thomas;[28] plus, Peng et al.[22] (bulk solution measurements); cross, Marcolli et al.;[27] dot, Peng et al.[22] (edb data); line, eq 5 with coefficients from Table 4. (b) Water activities (a_w) plotted against maleic acid mole fraction x_s. Key: open circle, bulk solution data; dot, edb measurements of Peng et al.;[22] solid line, eq 5. (c) Osmotic coefficients (ϕ_N) of solutions containing only the undissociated acid molecule, calculated using eqs 7 and 8. Values are plotted against the square root of the calculated molality of the undissociated acid (m_N), the symbols are the same as in part a, and the line is ϕ_{st} from eq 5 plotted against $\sqrt{m_{st}}$.

of 1.2 × 10^{-2} mol kg^{-1} (Table 1), almost 200 times greater than that of succinic acid. Stoichiometric osmotic coefficients are shown in Figure 6a, and there is a clear upward trend in ϕ_{st} to values greater than unity as m_{st} tends to zero, a feature that is due chiefly to the dissociation of the acid. The fitted eq 5 does not reproduce this—because the calculated ϕ_{st} always tend to 1.0 at infinite dilution—but the equation does satisfactorily represent the edb data within its relatively large uncertainty. The same results are shown as water activities in Figure 6b. At x_s equal to about 0.2 the water activity of aqueous maleic acid is similar to that of succinic acid, but at x_s equal to 0.4 it is lower by about 0.1. Calculated values of ϕ_N for hypothetical solutions of the aqueous undissociated acid are shown in Figure 6c. The osmotic coefficient now approaches 1.0 as molality tends to zero, and there is some suggestion that the overall shape of the curve, with a trough at about $\sqrt{m_{st}} = 2$ and a peak at $\sqrt{m_{st}} = 4$, is similar to that of the other acids.

3.7. Methyl Succinic Acid. The thermodynamic properties of aqueous methyl succinic acid appear to have been little studied, and the only data available are those of Davies and Thomas,[28] and the water activity of the saturated aqueous solution determined by Marcolli et al.[27] These data are insufficient to fit eq 5, and we have therefore generated values of water activity over the entire concentration range using UNIFAC[35,36] and the modified parameter values listed in Table 3 of Peng et al.[22] Equation 5 was fitted to the generated a_w and represents these values essentially exactly. The results are shown in Figure 7a,b. The UNIFAC-based ϕ_{st} are reasonably consistent with the available experimental data, which is encouraging. Methyl succinic acid is quite weakly dissociating, and the estimated values of ϕ_N differ relatively little from ϕ_{st} and are not shown.

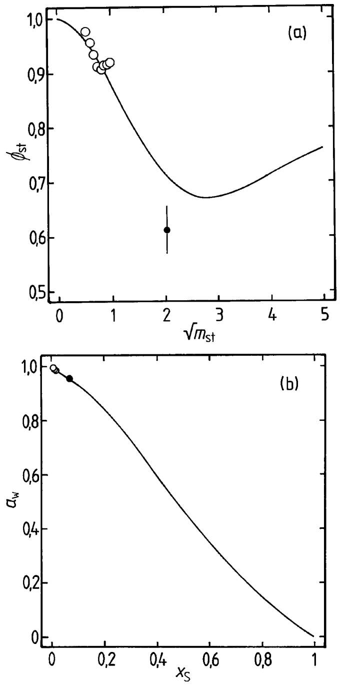

Figure 7. Osmotic coefficients and water activities of aqueous methyl succinic acid at 298.15 K. (a) Stoichiometric osmotic coefficients (ϕ_{st}) plotted against the square root of the stoichiometric molality (m_{st}). Key: open circle, Robinson et al.;[21] dot, Marcolli et al.;[27] line, eq 5 with coefficients from Table 4, fitted to values generated using UNIFAC with the modified parameter values listed by Peng et al.[22] (b) Water activities (a_w) plotted against methyl succinic acid mole fraction x_s. Key: open circle, bulk solution data; dot, Marcolli et al.;[27] solid line, eq 5.

4. Aqueous Mixtures of Dicarboxylic Acids

Here we compare measurements of the deliquescence properties of mixtures of the dicarboxylic acids discussed in the previous section with predictions of both the extended ZSR model[10,11] and the CSB approach.[9] The acids are treated as nondissociating solution components, and eq 5 with the parameters listed in Table 4 is used to calculate water and solute activities of the individual pure aqueous solutions. The data used in these comparisons are mainly those of Marcolli et al.[27] These authors have measured water activities and the aqueous phase compositions of eutonic solutions at 298.15 K (i.e., solutions saturated simultaneously with respect to all dissolved solutes at the specified temperature) containing up to six acids, and also the properties of mixtures containing the salts NaCl, $(NH_4)_2SO_4$, and NH_4NO_3.

4.1. Malic (1) + Malonic (2) Acids. A solution containing 7.3 mol kg^{-1} malic acid and 13.5 mol kg^{-1} of malonic acid is saturated with respect to both solids at 298.15 K and has a water activity of 0.618 (Table 2 of Marcolli et al.[27]). We have calculated the deliquescence curve for this mixture using eqs 7

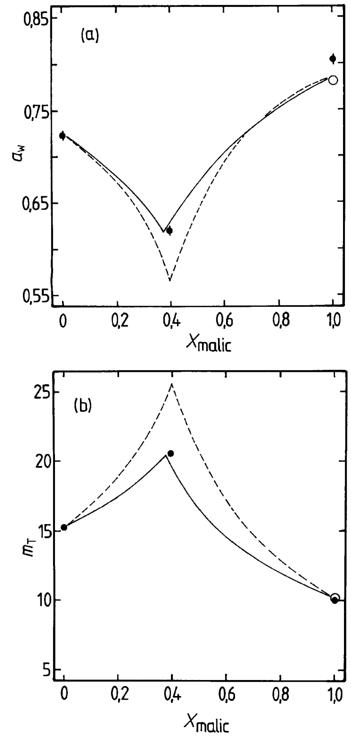

Figure 8. Deliquescence relative humidities of mixtures of malonic and malic acids (M2 of Marcolli et al.[27]) at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions plotted against the dry mole fraction of malic acid (X_{malic}). Key: open circle, Apelblat et al.;[68] dot, Marcolli et al.;[27] solid line, extended ZSR model with mixture parameters set to zero; dashed line, CSB method. (b) Total molality of the two acids (m_T) of the saturated aqueous solutions. The symbols and lines have the same meanings as in part a.

and 9 of Clegg et al.[10] (the ZSR method) for the solution water content and solute activity coefficients in the mixture. The three mixture parameters A^0, A^1, and B, are set to zero so that the predicted properties of the mixture are based only on those of the two pure aqueous solutions. The activity products (K_s) of the two acids in saturated solution are taken from Table 3. The calculated deliquescence curve is shown in Figure 8a,b together with the measurements of Marcolli et al. for the mixture, plotted against the dry mole fraction of malic acid $X(H_2Malic)$, which is defined for a solute s as $X_s = n_s/\Sigma_i n_i$, where n_s is the number of moles of solute s and the summation is over all solutes i. The predicted values of $X(H_2Malic)$, a_w, and the solute molalities at the eutonic point all agree well with the measurements.

In the alternative CSB approach[9] the activity coefficient of each solute species in the mixture is, in the absence of solute–solute interaction terms, equal to that in a pure aqueous solution at the same solute molality. The corresponding relationship for the water activity of the mixture is

$$a_w = \Pi_i \, a_{w(i)} \tag{9}$$

where $a_{w(i)}$ is the water activity of a pure aqueous solution of i at the same molality as in the mixture. The equation is equivalent to eq 3 of Clegg et al.,[9] which is given in terms of the osmotic coefficient. This approach can also be applied to groups of solutes, for example all ions in one group i_1 and all uncharged solutes in a second group i_2 in which case $a_w = a_{w(i_1)}a_{w(i_2)}$. These relationships for solute and solvent activities can be modified by the use of parameters for the interactions between solutes.[9,15]

In the absence of interaction parameters the CSB method implies that the molality of malic acid in a solution saturated with respect to the acid at 298.15 K is always equal to 10.2 mol kg^{-1} (its value in a pure aqueous solution), and similarly for malonic acid it is 15.31 mol kg^{-1}. The water activity of the eutonic solution is then 0.728 × 0.788 = 0.570, which is the product of the water activities of the two pure aqueous solutions. This value is clearly much too low, and the calculated total solute molality in the eutonic solution is also too high, by about 5 mol kg^{-1}; see Figure 8b. An interaction parameter $\lambda_{1,2}$ can be used to improve the predictions, contributing a factor $\exp((-M_w/1000)m_1m_2\lambda_{1,2})$ to the water activity, and the addition of $\ln(2m_2\lambda_{1,2})$ to $\ln(\gamma_1)$, and $\ln(2m_1\lambda_{1,2})$ to $\ln(\gamma_2)$. Values of $\lambda_{1,2}$ equal to 0.01 and 0.02 yield water activities of 0.623 and 0.602, respectively, for the eutonic solution. These agree much better with the measured value. However, the ZSR method is clearly preferable in this example as it yields satisfactory predictions based only on the properties of the pure aqueous solutions.

TABLE 5: Saturation in the Ternary System Malic (1) + Malonic (2) + Maleic (3) Acids at 298.15 K

quantity	measured	ZSR[a]	ZSR[b]	CSB[c]
m(malic)	7.3	7.37	7.28	10.2
m(malonic)	13.1	12.27	13.44	15.31
m(maleic)	4.4	4.61	5.83	6.85
a_w	0.564	0.572	0.560	0.467
m(malic)	7.3	7.59	7.59	10.2
m(malonic)	13.5	12.76	12.76	15.31
a_w	0.618	0.619	0.619	0.570
m(malonic)	–	15.34	14.24	15.31
m(maleic)	–	6.3	4.95	6.85
a_w	–	0.650	0.666	0.641
m(malic)	–	9.37	9.37	10.2
m(maleic)	–	5.48	5.48	6.85
a_w	–	0.714	0.714	0.697

[a] The mixture parameter $A^0_{2,3} = 0.784$ was used in the equations for both solvent content and solute activity coefficients. [b] Calculated from the properties of the three pure aqueous solutions only (mixture parameter $A^0_{2,3}$ set to zero). [c] Mixture parameters were set to zero. Consequently the solubilities are predicted to be the same as in the three pure aqueous solutions, and the calculated mixture water activity is equal to the product of the values for the pure aqueous solutions.

Measured and calculated eutonic compositions and water activities are listed in Table 5 for this mixture, and for the ternary system discussed below.

4.2. Malic (1) + Malonic (2) + Maleic (3) Acids. The experimental water activity of the eutonic solution is 0.564,[27] and the value calculated using the ZSR model is 0.560 which agrees well. However, the predicted composition of the eutonic solution (Table 5) differs somewhat from the measurement, with a maleic acid molality of 5.83 mol kg^{-1} compared to the measured 4.4 mol kg^{-1}. We therefore investigated the use of solute interaction parameter A^0 in eqs 7 and 9 of the extended ZSR model[10] to improve this result. Choi and Chan[23] have already shown that the water activities of 1:1 mixtures of malic and maleic acids are satisfactorily predicted using the ZSR method to relative humidities of 40% or lower (see their Figure 9) without further parameters. This leaves a possible interaction between maleic and malonic acids. A fit of the logarithms of the activity products of all three acids for the eutonic mixture, together with the water activity, yields $A^0_{2,3} = 0.784 \pm 0.06$. This improves the calculated molality of maleic acid in the saturated solution (to 4.61 mol kg^{-1}), although it does also reduce the predicted malonic acid solubility by about 9%. The calculated water activity is now 0.572, 0.008 greater than the measured value.

The water activity of the eutonic solution calculated using the CSB model, without mixture parameters, is only 0.504. This is largely because the measured solubilities in the mixture are

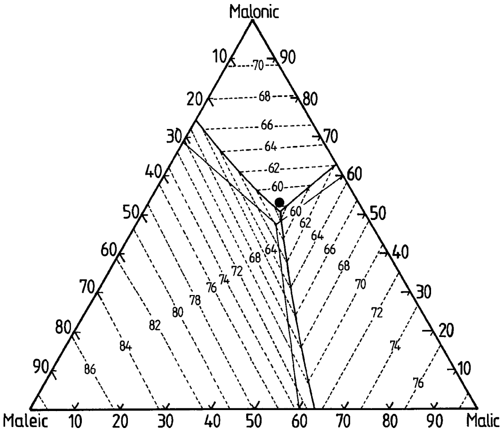

Figure 9. Water activities and saturation with respect to solids in mixtures of malonic, malic, and maleic acids (M3 of Marcolli et al.[27]) at 298.15 K. Key: filled circle, composition of an aqueous solution saturated with respect to all three acids, measured by Marcolli et al.;[27] thick solid lines, saturation with respect to pairs of solids, calculated using the extended ZSR model with mixture parameters listed in Table 9; thin solid lines, saturation with respect to pairs of solids, calculated using the CSB method; dashed lines, contours of equilibrium relative humidity (in percent), calculated using the extended ZSR model including mixture parameters.

lower than those in the pure aqueous solutions, implying a mutual "salting out" behavior in which the activity coefficient of each solute is increased by the presence of the others. This could be accounted for by introducing solute−solute mixture parameters, in the same way as for the previous mixture, but it is not done here.

Water activities and concentrations of mixtures saturated with respect to one, two, or all three components are shown in Figure 9. The water activity contours and the main set of saturation lines (phase boundaries) have been calculated using the extended ZSR model including the $A^0_{2,3}$ parameter. The deliquescence pathways of ternary mixtures can be determined as follows. First, for any ternary solution composition the water activity at saturation with respect to the first precipitating solid can be read directly from the contour lines for that composition. As solution concentration is increased, a_w decreases and more of the first precipitating solid forms. The solution composition then follows a straight line projected through the initial composition from the apex of the composition region in which it lies. When the solution composition reaches one of the phase boundaries between two acids, indicating that the solution is simultaneously saturated with respect to both, further increases in concentration will cause the composition to follow the phase boundary toward the eutonic point (the ternary phase boundary). Here the solution is simultaneously saturated with respect to all three acids. For an aqueous aerosol droplet of this composition any decrease in ambient relative humidity below the equilibrium value at the ternary phase boundary (0.572 at 298.15 K, Table 5) will result in a solid particle.

4.3. Malic (1) + Malonic (2) + Maleic (3) + Glutaric (4) Acids. The water activity of the eutonic solution, calculated using the ZSR model without mixture parameters, is 0.461 which agrees quite well with the measured 0.488, although the calculated molalities all slightly exceed the measured values (Table 6). Such differences are to be expected, both because the models are likely to be less accurate as concentrations increase, and also because the properties of the pure aqueous solutions on which the ZSR predictions are based are more uncertain at low relative humidities.

We have investigated the use of mixture parameters to improve the result for this system. A value of $A^0_{2,3}$ has already been determined using the data for the ternary system in section 4.2, and measurements of Choi and Chan[23] suggest that for the pairs of acids 1,3 and 2,4 the parameters are likely to be small or negligible. This leaves only the acid pairs 1,4 (malic + glutaric) and 3,4 (maleic + glutaric). We have fitted the logarithms of the activity products of the acids, and the water activity at the eutonic composition, to obtain $A^0_{1,4} = 0.423 \pm 0.03$ and $A^0_{3,4} = 0.505 \pm 0.03$. The model then yields a eutonic composition that agrees well with the measured values, see Table 6, and a water activity of 0.484 with differs negligibly from the measurement.

The CSB model yields a water activity of the eutonic solution of 0.443, again too low due to the neglect of interaction parameters and the consequent assumption that the saturation molalities of the acids are the same as in pure aqueous solutions.

A calculated deliquescence curve for an equimolar mixture of the acids is shown in Figure 10, in terms of the moles of liquid water per mole of total acid. This was calculated using the ZSR model including the mixture parameters noted above. The solution remains fully liquid until a water activity of about 0.64 at which point maleic acid begins to precipitate, followed by malic acid at just over 0.56, glutaric acid at about 0.53, and finally malonic acid at the eutonic point. The predicted amount of water associated with 1 mol of $(NH_4)_2SO_4$ is also shown in Figure 10 (for a supersaturated solution below the deliquescence relative humidity of about 0.8). This emphasizes the point that the water uptake of these soluble, polar, organic compounds is still significantly less than that of a typical electrolyte found in atmospheric aerosols.

The deliquescence curve calculated using the ZSR model without mixture parameters (not shown) differs little from the result in Figure 10. Over the region where the system is fully liquid the maximum difference in the predicted water content is about 4%, and at lower relative humidities the water content predicted by the model without mixture parameters is higher by up to 12%. This increase is mainly due to the slightly different relative humidities at which precipitation of the various solids is predicted to occur. The water content predicted by the CSB model of Clegg et al.[9] is less than that shown in Figure 10 for all water activities >0.52, by a maximum of about 17%. Below a_w equal to 0.52, the alternative model predicts somewhat higher water contents than the ZSR method.

4.4. Malic (1) + Malonic (2) + Maleic (3) + Glutaric (4) + Methyl Succinic (5) Acids. This mixture contains the additional component methyl succinic acid, and its water activities in pure aqueous solution have been estimated using UNIFAC, as described in section 3.7. Consequently the predicted deliquescence properties of this mixture might be expected to be less accurate than in the other examples. Nonetheless, the water activity of the eutonic solution calculated using ZSR is 0.431 (with mixture parameters) and 0.407 (without) which compares reasonably well with the measured value of 0.454. The CSB model yields a water activity of 0.42, which agrees better with the measured value than was the case for mixtures containing fewer components. Measured and calculated water activities and compositions of eutonic solutions of all possible combinations of solutes 1−5 are shown in Table 6.

Marcolli et al.[27] have also measured the water activities of subsaturated mixtures of eutonic composition, over a range of total molalities, and shown that they agree well with ZSR predictions (their Figure 8). Our calculations using the ZSR

TABLE 6: Saturation in the Quinary System Malic (1) + Malonic (2) + Maleic (3) + Glutaric (4) + Methyl Succinic (5) Acids at 298.15 K

acids					ZSR^a						ZSR^b						CSB^c
i	j	k	l	m	a_w	m_i	m_j	m_k	m_l	m_m	a_w	m_i	m_j	m_k	m_l	m_m	a_w
1	2				(0.618	7.3	13.5)^d										
1	2				0.619	7.58	12.76				0.619	7.58	12.76				0.570
1	3				0.714	9.37	5.48				0.714	9.37	5.48				0.695
1	4				0.694	9.51	7.97				0.685	10.00	8.72				0.690
1	5				0.733	10.10	4.17				0.733	10.10	4.17				0.745
2	3				0.666	14.24	4.95				0.650	15.34	6.30				0.642
2	4				0.613	17.16	10.89				0.613	17.16	10.89				0.637
2	5				0.667	15.95	5.00				0.667	15.95	5.00				0.688
3	4				0.759	7.55	10.04				0.750	8.23	10.84				0.777
3	5				0.815	7.80	5.15				0.815	7.80	5.15				0.839
4	5				0.786	11.88	6.49				0.786	11.88	6.49				0.833
1	2	3			(0.564	7.3	13.1	4.4)^d									
1	2	3			0.572	7.37	12.27	4.61			0.560	7.28	13.44	5.83			0.504
1	2	4			0.530	7.15	15.19	10.16			0.524	7.69	15.19	10.85			0.501
1	2	5			0.571	7.51	13.63	4.82			0.571	7.51	13.63	4.82			0.541
1	3	4			0.625	8.60	5.92	8.40			0.611	9.06	6.51	9.82			0.611
1	3	5			0.660	9.13	5.93	4.61			0.660	9.13	5.93	4.61			0.659
1	4	5			0.634	9.07	9.19	5.29			0.626	9.56	9.93	5.30			0.655
2	3	4			0.556	16.38	5.54	11.56			0.535	18.02	7.70	12.70			0.564
2	3	5			0.606	14.94	5.48	5.52			0.591	16.21	6.92	5.61			0.609
2	4	5			0.548	18.36	12.74	6.63			0.548	18.36	12.74	6.63			0.604
3	4	5			0.679	7.86	11.46	6.57			0.670	8.63	12.34	6.66			0.737
1	2	3	4		(0.488	7.0	14.6	5.2	10.3)^d								
1	2	3	4		0.484	6.88	14.94	5.15	10.78		0.461	7.38	16.77	7.44	12.68		0.443
1	2	3	5		0.523	7.27	13.24	5.10	5.31		0.511	7.20	14.61	6.45	5.43		0.478
1	2	4	5		0.476	7.02	16.83	11.94	6.38		0.470	7.58	16.86	12.66	6.41		0.475
1	3	4	5		0.567	8.14	6.33	9.59	5.70		0.553	8.61	7.00	11.09	5.78		0.579
2	3	4	5		0.492	17.86	6.14	13.52	7.25		0.471	19.95	8.86	14.97	7.58		0.535
1	2	3	4	5	(0.454	6.8	14.8	5.3	12.4	5.5)^d							
1	2	3	4	5	0.431	6.71	16.78	5.72	12.66	6.97	0.407	7.24	19.10	8.38	14.85	7.35	0.420

[a] Water activities (a_w) and acid molalities (m_{i-m}) of the saturated solutions calculated using the ZSR mixture parameters as derived in section 4 and listed in Table 9. [b] Calculated using the ZSR model without mixture parameters. [c] Calculated using the CSB approach. In the absence of mixture parameters, the acid molalities and activity coefficients are the same as in saturated pure aqueous solutions of the acids. [d] Measured values, see Table 2 of Marcolli et al.[27]

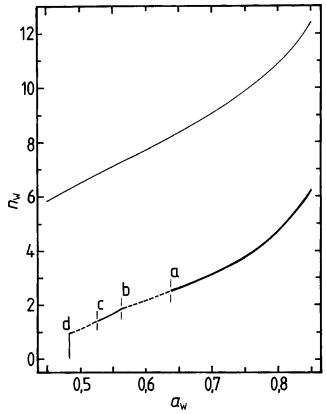

Figure 10. Deliquescence curve of an equimolar mixture of malonic, glutaric, malic and maleic acids at 298.15 K, calculated using the extended ZSR model. The moles of liquid water (n_w) for 1 mol of total acid are plotted against the water activity (a_w) of the aqueous mixture. As a_w is decreased, formation of the solid acids occurs in the following order: a, maleic acid; b, malic acid; c, glutaric acid; d, malonic acid. The upper solid line is the calculated water content of a solution of $(NH_4)_2SO_4$ containing 1 mol of the salt.[38] (This solution is supersaturated with respect to the salt at water activities below 0.8.)

model both with and without mixture parameters, and also the CSB model, are compared with the data in Figure 11. The latter model yields water activities that are too high by up to about 0.04, whereas both sets of ZSR predictions match the data closely.

In summary, Choi and Chan[23] have shown that the ZSR method yields satisfactory estimates of the water content of solutions of pairs of dicarboxylic acids, and Marcolli et al.[27] have demonstrated that the water activities of mixtures containing up to five acids are also predicted well. The comparisons here have both confirmed this result and shown that saturation of solutions with respect to the acids—and therefore the deliquescence properties of the system—can also be calculated. The use of mixture parameters in the ZSR model improves predictions by a small amount. It seems reasonable to assume that these conclusions will extend to systems containing an arbitrary number of similar, soluble, nonelectrolytes.

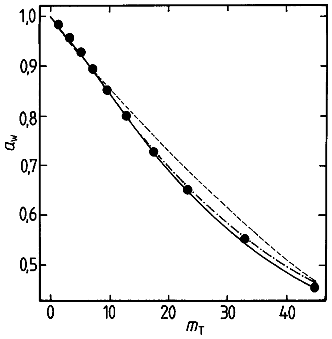

Figure 11. Measured and calculated water activities (a_w) of a mixture of malonic, glutaric, malic, maleic, and methyl succinic acids (M5 of Marcolli et al.[27]) at 298.15 K. Key: filled circle, measurements of Marcolli et al. from their Table 3 and also the a_w (0.454) at the eutonic point; solid line, calculated using the extended ZSR model including mixture parameters; dash dot line, extended ZSR model without mixture parameters; dashed line, calculated using the CSB method.

TABLE 7: Eutonic Points Calculated Using the CSB Method[a]

	NH_4NO_3		$(NH_4)_2SO_4$		NaCl	
acid	X_a	a_w	X_a	a_w	X_a	a_w
succinic	0.0262	0.6069	0.109	0.7918	0.103	0.7443
malonic	0.368	0.4452	0.725	0.5807	0.714	0.5459
glutaric	0.289	0.5391	0.648	0.7033	0.635	0.6611
malic	0.280	0.4826	0.638	0.6296	0.624	0.5919
L-malic	0.426	0.3432	0.771	0.4478	0.760	0.4209
maleic	0.207	0.5434	0.542	0.7089	0.528	0.6664
methyl succinic	0.137	0.5821	0.419	0.7593	0.405	0.7138

[a] Key: X_a, dry mole fraction of acid in a solution saturated with respect to both acid and salt; a_w, water activity of the saturated solution. These values were calculated without mixture interaction parameters, as described in the text.

The CSB model predicts water activities of eutonic solutions that are lower than measured values, and it is only by using parameters for solute−solute interactions that these can be improved. For relatively dilute solutions, with water activities above about 0.75, experience suggests that this approach can yield very accurate results for systems for which there are sufficient data to determine the parameters. For nonelectrolyte systems over extended ranges of concentration the comparisons in this section suggest that the ZSR approach is superior. However, it should be remembered that the method requires pure solution properties at the water activity of the mixture. In the above examples, this information has been available from electrodynamic balance experiments, but for many applications this is not likely to be the case.

5. Aqueous Mixtures of Dicarboxylic Acids and Salts.

The ZSR method, in its standard form, is most accurate for solutions containing either all nondissociating compounds or electrolytes all of the same charge type, for reasons given by Mikhailov.[37] The inclusion of the correction terms proposed by Clegg and Seinfeld[11] mainly affects the calculation of solute activity coefficients, and therefore the predicted deliquescence points. In this section, the available data for water uptake and deliquescence relative humidities (DRH) of aqueous mixtures of dicarboxylic acids and salts are used to test the application of the extended ZSR model to such systems. We have not carried out detailed comparisons with the CSB model. However, values of the DRH can be calculated from the saturated solution molalities and water activities of the acids listed in Table 3 and the following values for the salts at 298.15 K: 26.3 mol kg^{-1} and 0.614 (NH_4NO_3), 5.80 mol kg^{-1} and 0.801 ($(NH_4)_2SO_4$), and 6.14 mol kg^{-1} and 0.753 (NaCl). In the CSB approach (without ternary mixture parameters) the molality of an acid or salt in a saturated solution mixture is equal to its value in a pure aqueous solution, and the water activity of the mixture is equal to $a_{w(acid)}a_{w(salt)}$ where the two water activities are the values for pure aqueous saturated solutions. Compositions and water activities of the eutonic points of several acid/salt mixtures, calculated using the CSB method, are listed in Table 7 and may be compared with the other results discussed below.

It is also worth noting that the measured behavior of aqueous mixtures of single salts and dicarboxylic acids cannot always be described in terms of simple salting in, or salting out, where the solubilities of both components are either increased or decreased by their mutual interaction. (Salting out behavior also corresponds to a decrease in water activity for a given solution composition, relative to the case in which the activity coefficients of the solutes are unaffected by each other's presence. The opposite is true where salting in occurs.) For example, the measurements of Wise et al.[30] of the water activities of solutions containing dicarboxylic acids and $(NH_4)_2SO_4$ at their eutonic points show the following: salting in of both solutes occurs for mixtures containing glutaric acid; with malonic acid the solubility of the acid is decreased while that of the salt is increased, and with L-malic acid there is a slight salting in of the acid, but a very large increase in the solubility of the salt. Solubilities of both acid and salt are slightly increased for mixtures with maleic acid, but this seems likely to be due to the dissociation of the acid (enhanced by the formation of bisulfate) and may not represent a strong interaction between the $(NH_4)_2SO_4$ and the undissociated acid molecule.

The data, see Table 8, include measurements for binary aqueous mixtures of dicarboxylic acids and the salts NH_4NO_3, $(NH_4)_2SO_4$, and NaCl, and also mixtures of five acids with the salts. We consider first the binary mixtures. The acids are treated as nondissociating compounds, as before. While this is likely to be a reasonable assumption for mixtures of the acids with NH_4NO_3 and NaCl, it is less likely to be true for mixtures with $(NH_4)_2SO_4$, because dissociation will be enhanced by the formation of HSO_4^- in solution. The magnitude of this effect has been estimated by calculating the fraction of total acid existing in undissociated form in mixtures with aqueous $(NH_4)_2SO_4$ over a range of concentrations; see Figure 12a,b. The calculations were carried out using the CSB approach, with eq 5 and parameters from Table 4 used to calculate the activity coefficients of the undissociated acid molecules (H_2X), and the AIM model[38] for the ions (H^+, NH_4^+, HSO_4^-, SO_4^{2-}, HX^-, and X^{2-}). The parameters for interactions between the two cations and the ions HX^- and X^{2-} were assumed to be the same as for HSO_4^- and SO_4^{2-}, respectively. The most strongly dissociating acids are malonic ($K_1 = 1.42 \times 10^{-3}$ mol kg^{-1}) and maleic ($K_1 = 1.2 \times 10^{-2}$) acids. Even in a 1:1 (mole ratio) mixture the proportion of undissociated maleic acid is predicted to be mostly less than 80%, and in a 1:10 mixture (acid:salt) no more than 50% of the total. While these calculations are subject to some uncertainty they suggest that in systems containing significant molalities of sulfate it is important to account for the dissociation of acids with high K_1.

In the calculations in this section, the thermodynamic properties of aqueous NH_4NO_3 were calculated using the AIM model,[38] and those of aqueous $(NH_4)_2SO_4$ and NaCl using functions that reproduce critically assessed values of ϕ and γ for subsaturated solutions,[39,40] the available edb data for supersaturated solutions,[24,41] and then smoothly extrapolate to $x_s = 1.0$.

5.1. Succinic Acid + NaCl. The primary data for this mixture are the edb and bulk a_w measurements of Choi and Chan[42] for a 1:1 (mole ratio) mixture. The edb data have been restandardized, by reducing all mass fractions of solute (mfs) by 0.02, to agree with total concentrations at about 80% relative humidity calculated using the Pitzer model developed in ref 15.

The extended ZSR model, without mixture parameters, predicts succinic acid solubilities in aqueous NaCl that rise slightly with NaCl molality if the constant b in eqs 7 and 18 of Clegg and Seinfeld[11] for the unsymmetrical correction term is set equal to 1.2. However, measurements of Herz[43] and of Linderstrom-Lang[44] show that succinic acid solubility decreases. The data are shown in Figure 13 together with predictions of the ZSR model both without the unsymmetrical correction term (which yields the highest solubilities), and with the correction term for $b = 1.2$ and also $b = 0.5$. Best agreement with the data is obtained with the lower value of b, combined with a NaCl−H_2Succ interaction parameter $A^0 = 2.75$ or $B = 3.44$. It

TABLE 8: Sources of Water Activity Data for Aqueous Mixtures of Dicarboxylic Acids and Salts[g]

acid	salt	t/°C	used[a]	data[b]	source
succinic	NH_4NO_3	25	c	edb	45
succinic	$(NH_4)_2SO_4$	24, 4, −10	c	DRH	34
succinic	$(NH_4)_2SO_4$	22, 20−23	f	edb, a_w	42
succinic	$(NH_4)_2SO_4$	25	f	DRH, a_w^c	30
succinic	NaCl	22, 20−23	c	edb, a_w	42
malonic	$(NH_4)_2SO_4$	22, 20−23	f	edb, a_w	42
malonic	$(NH_4)_2SO_4$	24, 4, −10	f	DRH	34
malonic	$(NH_4)_2SO_4$	20	f	DRH	16
malonic	$(NH_4)_2SO_4$	25	f	DRH, a_w^c	30
malonic	NaCl	22, 20−23	f	edb, a_w	42
glutaric	$(NH_4)_2SO_4$	20	f	DRH	48
glutaric	$(NH_4)_2SO_4$	22, 20−23	f	edb, a_w	42
glutaric	$(NH_4)_2SO_4$	25	f	DRH, a_w^c	30
glutaric	$(NH_4)_2SO_4$	24, 4, −10	f	DRH	34
glutaric	NaCl	22, 20−23	c	edb	42
glutaric	NaCl	room temp	f	DRH	47
glutaric	NaCl	20	c	DRH	48
maleic	$(NH_4)_2SO_4$	24, 4, −10	c	DRH	34
maleic	$(NH_4)_2SO_4$	25	f	DRH, a_w^c	30
L-malic	$(NH_4)_2SO_4$	24, 4, −10	c	DRH	34
L-malic	$(NH_4)_2SO_4$	25	f	DRH, a_w^c	30
maleic + malic	−	20−23	−	edb	23
malonic + glutaric	−	20−23	−	edb	23
malonic + malic (M2)	−	25	c	a_w^d	27
M2 + maleic (M3)	−	25	f	a_w^d	27
M3 + glutaric (M4)	−	25	f	a_w^d	27
M4 + methylsuccinic (M5)	−	25	c	a_w^d	27
M5 + oxalic	−	25	−	a_w^e	27
M5 + succinic	−	25	−	a_w^e	27
M5	NH_4NO_3	25	c	a_w^f	27
M5	$(NH_4)_2SO_4$	25	c	a_w^f	27
M5	NaCl	25	c	a_w^f	27

[a] Key: c, these data are compared with ZSR model predictions only; f, used to obtain values of ZSR interaction parameters. [b] Key: edb, electrodynamic balance measurements of water activities of supersaturated aqueous solutions; DRH, relative humidity of deliquescence, equivalent to the water activity of a solution saturated with respect to one or more solutes; a_w, water activity. [c] Water activities of the aqueous eutonic mixture over a range of total molalities, including the saturated solution. [d] For the eutonic solution composition only. [e] Water activities of a series of solutions saturated with respect to the named acid. [f] Water activities of a series of solutions saturated with respect to the salt. [g] Other sources of data are listed here, and given as system composition(s), followed by the types of measurement in parentheses: [glycerol, citric acid] + [$(NH_4)_2SO_4$, NaCl], (edb, a_w);[42] [glycerol, levoglucosan, fulvic acid] + $(NH_4)_2SO_4$, (DRH);[16] pyruvic acid + NaCl, (DRH);[47] oxalic acid + $(NH_4)_2$SO4, (DRH, a_w);[30,34] adipic acid + $(NH_4)_2$SO4, (DRH);[34] malonic acid + $(NH_4)_2SO_4$, (DRH and phase transitions);[70] fulvic acids + [$(NH_4)_2SO_4$, NaCl], (edb);[71] [oxalic, succinic, malonic, glutaric, adipic acids] + $(NH_4)_2SO_4$, (DRH, growth factor);[72] [glutaric, pinonic acids] + [$(NH_4)_2SO_4$, NaCl], (DRH, growth factor);[73] [humic acids + [$(NH_4)_2SO_4$], (DRH, growth factor);[74] maleic acid + [$(NH_4)_2SO_4$], (DRH, phase transitions);[75] [oxalic, adipic acids] + $(NH_4)_2SO_4$, (DRH);[34] [succinic, malonic, adipic, phthalic acids] + $(NH_4)_2SO_4$, (growth factor);[76] [glutaric, maleic, L-malic acids] + $(NH_4)_2SO_4$, (freezing temperatures), (a_w, crystallization relative humidity).[77]

is important to realize that the same value of b would not be satisfactory for a 2:1 electrolyte such as $(NH_4)_2SO_4$ since the possible values of b and their effects depend on the charge type of the electrolyte. However, the results here suggest that some experimentation with different values of b is worthwhile, in which case the equations given in the Appendix of Clegg and Seinfeld[11] should be used for the unsymmetrical correction term. This is because they permit different values of b to be assigned to individual electrolytes.

Stoichiometric osmotic coefficients ϕ_{st} calculated using the extended ZSR model with $B = 3.44$ are compared with values from bulk solution water activity measurements in Figure 14, together with calculations using the full Pitzer model (including acid dissociation) from ref 15. The bulk solution measurements appear to be too low by a small amount, similar to the quoted accuracy of the measurement (±0.003 in a_w). We have not attempted to take into account the fact that the measurements of Choi and Chan[42] were conducted at 22 °C as this seems likely to make only a small difference to the osmotic coefficients.

The edb data of Choi and Chan are shown in Figure 15, together with the results of various calculations using the extended ZSR model. There are a number of points to be made. First, the predicted mfs values for the fully liquid particles at water activities greater than about 0.73 agree well with the predicted values that include either of the two mixture parameters. In this work, we most often use the parameter B, as its effect on calculated solution water content is proportional to a_w whereas that of A^0 is constant, which leads to a very large effect on the solution water content at low water activities. (We do not use the third possible parameter, A^1.)

Second, neither of the ZSR model predictions, with or without the mixture parameter B, accurately represent the observed mfs below $a_w \approx 0.7$ for the evaporation experiments (in which the suspended particles are presumed to exist as supersaturated aqueous solutions). The reasons for this are unclear. Furthermore, at the lowest a_w the observed mfs approach the values expected for a solution containing aqueous NaCl and succinic acid in equilibrium with the solid acid (the consequent reduction in liquid water leads to a higher mfs value).

Third, the measured solubilities of succinic acid in aqueous NaCl suggest that salting *in* may occur at very high concentrations. The decrease in the activity coefficient of the solute implies a corresponding change in solvent activity that is equivalent to an *increase* in mfs, though the magnitude of the

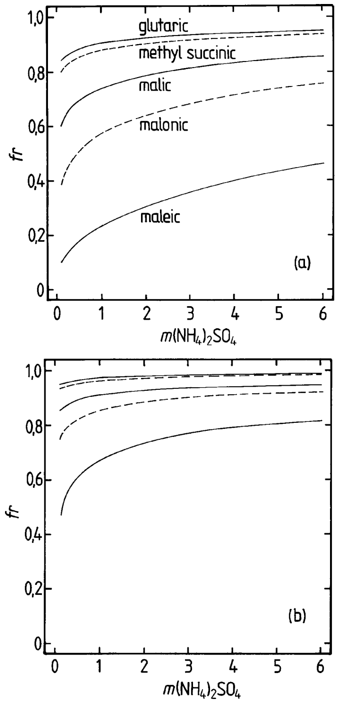

Figure 12. Calculated fractions of dicarboxylic acids in undissociated form (*fr*), in aqueous mixtures with $(NH_4)_2SO_4$ at 298.15 K and plotted against $(NH_4)_2SO_4$ molality $m(NH_4)_2SO_4$: (a) for acid:salt molar ratios of 1:10; (b) for acid:salt ratios of 1:1 (the lines for each acid are in the same order as in part a).

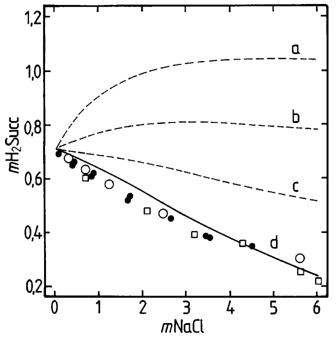

Figure 13. Solubilities of succinic acid in aqueous NaCl at 298.15 K. Key: open circle, Herz;[43] dot, Linderstrom-Lang;[44] square, Doosaj and Bhagwat;[78] line a, calculated using the ZSR model without mixture parameters and without the unsymmetrical correction to the activity coefficients; line b, calculated using the ZSR model with the unsymmetrical correction (and $b = 1.2$) but without mixture parameters; line c, calculated using the ZSR model with the unsymmetrical correction (and $b = 0.5$) but without mixture parameters; line d, calculated using the ZSR model with the unsymmetrical correction (and $b = 0.5$), and with $A^0 = 2.75$.

difference between the observed and calculated mfs for the fully liquid particles in Figure 15 seems far too large to be explained by this effect.

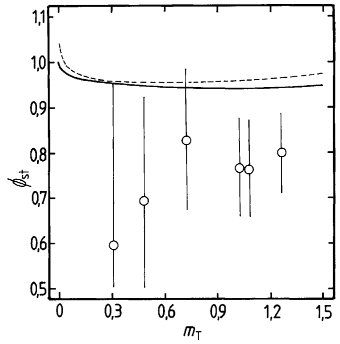

Figure 14. Stoichiometric osmotic coefficients (ϕ_{st}) of an equimolar mixture of succinic acid and NaCl at 298.15 K (the data were obtained at 22 °C but the small temperature difference is ignored). Key: circle, measurements of Choi and Chan;[42] solid line, calculated using the extended ZSR model with $b = 0.5$ in the unsymmetrical correction term and interaction parameter $B = 3.44$; dashed line, calculated using the Pitzer model developed in ref 15.

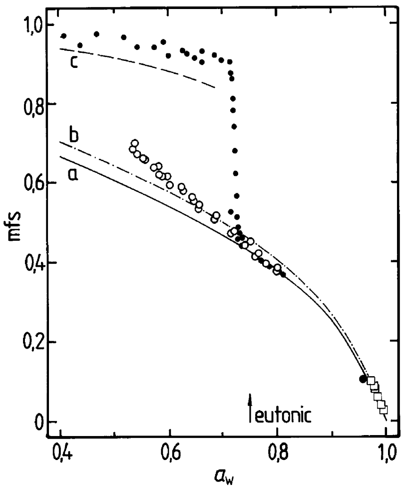

Figure 15. Water uptake of 1:1 (mole ratio) mixtures of succinic acid and NaCl at approximately 298 K, plotted as mass fraction of solute (mfs) against equilibrium water activity (a_w). Key: square, bulk solution measurements of Choi and Chan;[42] open circle, edb (evaporation) measurements of Choi and Chan for supersaturated aqueous droplets; dot, edb (growth) measurements of Choi and Chan; line a, calculated using the extended ZSR model with mixture parameter $B = 3.44$ and $b = 0.5$ in the unsymmetrical correction term; line b, calculated using the extended ZSR model without mixture parameters; line c, calculated using the extended ZSR model, assuming the particle consists of solid NaCl and aqueous succinic acid. The calculated water activity of the eutonic solution is marked.

Last, the results of the particle growth experiments shown in Figure 15 indicate that the uptake of water at very low relative humidities is slight. The fact that the measured mfs are greater than values calculated assuming solid undissolved NaCl and fully dissolved succinic acid is consistent with particles consisting of the solid salt, largely solid acid, plus a small amount of water probably associated with the acid. Deliquescence occurs in the growth experiments at $0.713 \leq a_w \leq 0.728$ (Table 2 of Choi and Chan[42]), with a consequent steep reduction in mfs. The extended ZSR model, with $B = 3.44$, predicts a water activity of 0.715 for a 1:1 solution saturated with respect to NaCl (in which all succinic acid is dissolved) and 0.75 for the eutonic composition. Given the fact that the particles in the growth experiments appear to exist in a partially liquid state at water activities below 0.7 (for which mfs is just over 0.9) the former figure is probably the most appropriate one for the transition and agrees well with the observed value.

5.2. Succinic Acid + $(NH_4)_2SO_4$. Wise et al.[30] have measured the water activities of solutions of eutonic composition (dry mole fraction of acid equal to 0.0409), and Choi and Chan[42] have carried out both bulk solution and edb measurements for 1:1 (mole ratio) mixtures. Because the eutonic solution contains only a small fraction of succinic acid, water activities differ very little from those of solutions containing only $(NH_4)_2SO_4$ (see Figure 8 of ref 15) and are not shown here. The data of Choi and Chan are plotted in Figure 16, together with the results of several sets of calculations. First of all, mass fractions of solute for supersaturated aqueous solutions calculated using the full Pitzer model (described in ref 15) agree closely with the

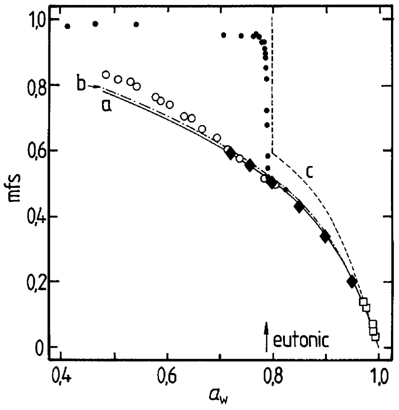

Figure 16. Water uptake of 1:1 (mole ratio) mixtures of succinic acid and $(NH_4)_2SO_4$ at approximately 298 K, plotted as mass fraction of solute (mfs) against equilibrium water activity (a_w). Key: square, bulk solution measurements of Choi and Chan;[42] open circle, edb (evaporation) measurements of Choi and Chan for supersaturated aqueous droplets; dot, edb (growth) measurements of Choi and Chan; diamond, calculated using the Pitzer model of the system developed in ref 15; line a, calculated using the extended ZSR model with mixture parameter $B = -0.88$ and $b = 0.8$ in the unsymmetrical correction term; line b, calculated using the extended ZSR model without mixture parameters; line c, calculated using the extended ZSR model, assuming the particle consists of aqueous $(NH_4)_2SO_4$ above the eutonic point (marked), and aqueous succinic acid in equilibrium with the solid acid.

measurements, which is a good result. However, both sets of calculations using the extended ZSR model predict mfs that are too low at water activities below about 0.7. This is also the case for a number of other acids. Agreement at low water activities could not be improved using mixture parameters A and B without affecting the fit at water activities above 0.7. The particle growth results in Figure 16 suggest a small amount of water uptake (mfs less than unity) at low relative humidity, which is probably associated with the acid content of the particle. This is followed by complete dissolution at about the eutonic point. This general behavior is common to all the acids studied by Choi and Chan, but is not what would be expected for a system at thermodynamic equilibrium. Line c on the plot shows that, at the eutonic point, all the $(NH_4)_2SO_4$ but only a small part of the succinic acid should dissolve. This would produce a particle with an aqueous phase of the eutonic composition, and solid succinic acid. This acid would then gradually dissolve as relative humidity increased. However, it is clear from the figure that the particles in the growth experiments are entirely liquid above the eutonic point, and they are consequently in a metastable state.

5.3. Succinic Acid + NH_4NO_3. Lightstone et al.[45] have determined the water content of NH_4NO_3 + succinic acid particles of various relative compositions using an electrodynamic balance. The particles in the experiments were thought to include a solid core of succinic acid in equilibrium with the liquid phase. The measured water content of the particles, per mole of NH_4NO_3, would therefore be expected to be the same for the different particle compositions,[45] and this is what was found. The data are shown in Figure 17 together with water contents calculated using the extended ZSR model and the assumption of an aqueous particle containing solid succinic acid in equilibrium with the liquid phase. The predicted amount of water in the particles is almost invariant with respect to the mixture parameters A^0 and B, because of the very low concentration of acid in the aqueous phase.

In Figure 18, we show calculated succinic acid solubilities in aqueous NH_4NO_3 for three different values of parameter B for interactions between NH_4NO_3 and succinic acid. A solubility at 298.15 K estimated from the polytherm of Yunusov et al.[46] is also shown, but is quite uncertain due both to the scatter in the original measurements and the interpolation required. We note that this study lists one of the solids formed in the system as mNH$_4$NO$_3$.nH$_2$Succ(s), but no other references to it have been found in the literature.

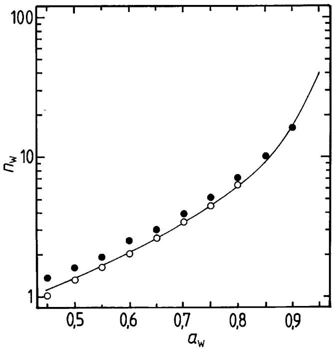

Figure 17. Water content (n_w) of aqueous droplets containing succinic acid and NH_4NO_3 at 298.15 K,[45] plotted against water activity (a_w). The water content is expressed as moles of water per mole of NH_4NO_3 in the mixture. Key: open circle, 12.5 mass % of succinic acid; dot, 25 mass % of succinic acid; line, calculated using the extended ZSR model.

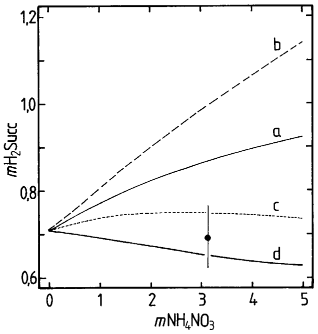

Figure 18. Solubilities of succinic acid in aqueous NH_4NO_3 at 298.15 K. Dot, estimated from the solubility polytherm of Yunusov et al.,[46] with an assumed error of ±10%; line a, calculated using the extended ZSR model without mixture parameters and with $b = 0.5$ in the unsymmetrical correction term; line b, calculated using the extended ZSR model with mixture parameter $B = -2.0$; line c, calculated using the extended ZSR model with mixture parameter $B = 2.0$; line d, calculated using the Pitzer model developed in ref 15.

The data of Yunusov et al. suggest that dissolved NH_4NO_3 has little effect on succinic acid solubility, at least at low molalities. Solubilities calculated using the full Pitzer model of the system (from ref 15) are also shown in Figure 18 and indicate a small decrease with increasing mNH$_4$NO$_3$. We conclude from this comparison that the extended ZSR model is consistent with the available data when B is positive. The optimum value of B probably lies in the range 2.0 to 3.0. The calculated deliquescence relative humidity (DRH) curve is shown in Figure 19a. The predicted eutonic point ranges from a_w equal to 0.608 for $B = 2.0$, to 0.584 for $B = -2.0$. Calculated total molalities, m_T, corresponding to solutions at the deliquescence point are shown in Figure 19b. There is quite a large dependence of m_T on the value of B at XH$_2$Succ = 0.05 to 0.1, and solubility measurements in this region would be useful for improving the accuracy of models of the $NH_4NO_3-H_2Succ-H_2O$ system.

Lightstone et al.[45] note that it is not possible to reconcile their observations of a dependence of DRH on XH$_2$Succ with the properties of a particle in which solid H$_2$Succ exists at

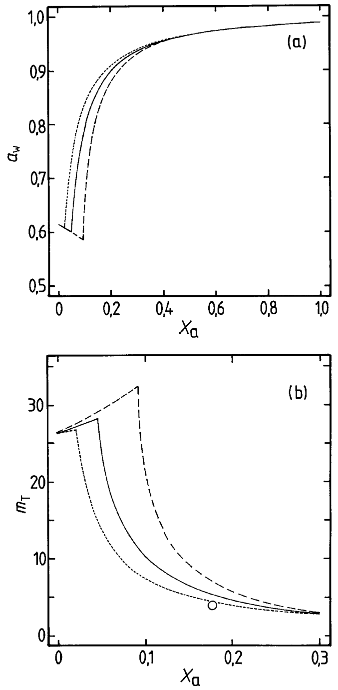

Figure 19. Deliquescence curve of a mixture of succinic acid and NH_4NO_3 at 298.15 K. (a) Water activities of the saturated aqueous solutions plotted against the dry mole fraction of acid (X_a) in the mixture. Key: solid line, calculated using the extended ZSR model without mixture parameters and with $b = 0.5$ in the unsymmetrical correction term; dashed line, calculated using the extended ZSR model with mixture parameter $B = -2.0$; dotted line, calculated using the extended ZSR model with mixture parameter $B = 2.0$. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. Key: open circle, estimated from the solubility polytherm of Yunusov et al.;[46] lines, as in plot a.

equilibrium with the liquid phase. (The deliquescence relative humidity should always be that of the eutonic point and therefore invariant with overall particle composition.) It is possible that the observed behavior is related to the mixed solid, or solid solution, $m\mathrm{NH_4NO_3}\cdot n\mathrm{H_2Succ(s)}$ apparently found by Yunusov et al.[46] in solutions also saturated with respect to the acid.

5.4. Malonic Acid + NaCl. The available data for this system consist of bulk solution and edb water activity measurements carried out at 20−23 °C.[42] A fit of the combined data with the extended ZSR model, but using the edb results for evaporation experiments only, yields $B = -1.292$ and predicted water contents (mfs) that agree well with the data (Figure 20). The calculated eutonic point is at $a_w = 0.599$ at $X\mathrm{H_2Malo} = 0.70$.

Using the extended ZSR model with this value of *B*, the edb growth curve in Figure 20 was calculated by assuming that the particle contained aqueous malonic acid under all conditions, but that NaCl was in equilibrium with the solid salt at all relative humidities below the DRH value of 65.8% ($a_w = 0.658$).[42] The result again agrees well with the data.

The particles in the growth portion of the curve in Figure 20 are calculated to be supersaturated with respect to the solid acid at all relative humidities below 61%. The slight change in slope (in the data) at a water activity of about 0.57 corresponds to the onset of deliquescence observed by Choi and Chan[42] and is also quite close to the calculated eutonic point for this system. However, this may not be significant as the particle has clearly taken up a significant amount of water at lower relative humidities and therefore contains dissolved malonic acid.

The calculated DRH curve for the malonic acid + NaCl mixture is shown in Figure 21.

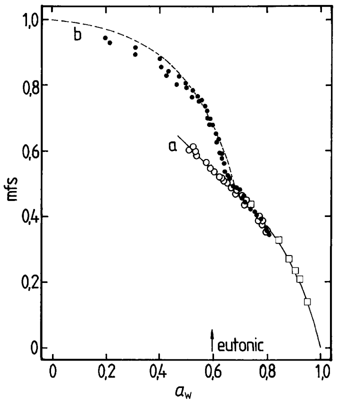

Figure 20. Water uptake of 1:1 (mole ratio) mixtures of malonic acid and NaCl at approximately 298 K, plotted as mass fraction of solute (mfs) against equilibrium water activity (a_w). Square, bulk solution measurements of Choi and Chan;[42] open circle, edb (evaporation) measurements of Choi and Chan for supersaturated aqueous droplets; dot, edb (growth) measurements of Choi and Chan; line a, calculated using the extended ZSR model with mixture parameter $B = -1.292$; line b, calculated using the extended ZSR model with $B = -1.292$, assuming the particle consists of aqueous malonic acid and NaCl in equilibrium with the solid salt. The calculated water activity of the eutonic solution is marked.

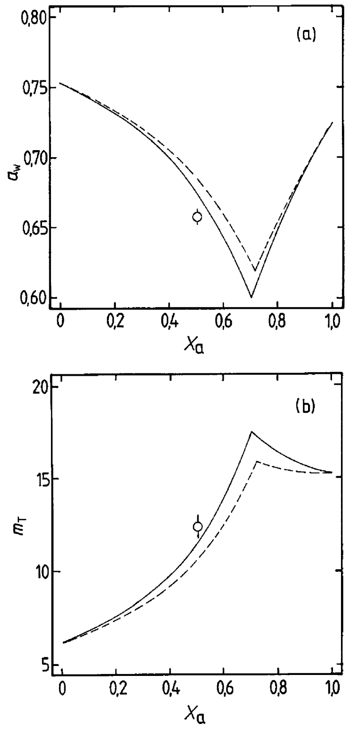

Figure 21. Deliquescence curve of a mixture of malonic acid and NaCl at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions are plotted against the dry mole fraction of acid (X_a) in the mixture. Key: open circle, $\mathrm{DRH_{complete}}$ from Table 2 of Choi and Chan;[42] solid line, calculated using the extended ZSR model with mixture parameter $B = -1.292$; dashed line, calculated using the extended ZSR model without mixture parameters. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. The symbol and lines have the same meanings as in plot a.

5.5. Malonic Acid + $(NH_4)_2SO_4$. The deliquescence relative humidities of mixtures of these compounds have been studied by several authors, see Table 8, and the water activities of bulk solution mixtures have been measured by Wise et al.[30] and by Choi and Chan.[42] A fit of all these data with the extended ZSR model, giving a higher weight to the results of Choi and Chan,

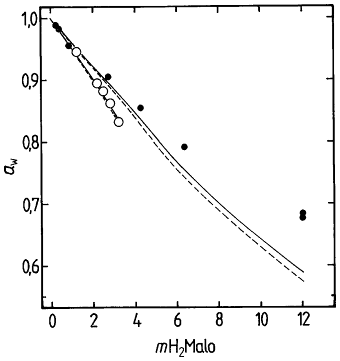

Figure 22. Water activities (a_w) of aqueous mixtures of malonic acid and $(NH_4)_2SO_4$, plotted against the molality of malonic acid (mH$_2$Malo). Key: open circle, bulk solution measurements of Choi and Chan[42] at 295.15 K for a 1:1 (mole ratio) mixture; dot, data of Wise et al.[30] for mixtures of eutonic composition (dry mole fraction of acid = 0.6154) at 298.15 K; solid lines, calculated using the extended ZSR model with mixture parameter $B = -1.26$; dashed lines, calculated using the extended ZSR model with mixture parameters set equal to zero.

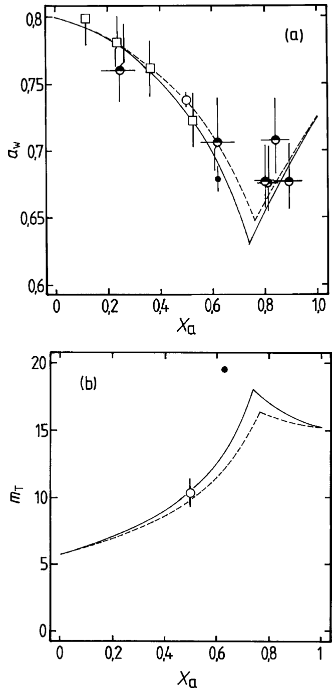

Figure 23. Deliquescence curve of a mixture of malonic acid and $(NH_4)_2SO_4$ at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions plotted against the dry mole fraction of acid (X_a) in the mixture. Key: open circle, DRH$_{complete}$ from Table 2 of Choi and Chan;[42] half-filled circle, measurements of Brooks et al.;[34] square, data of Parsons et al.,[16] adjusted to 298.15 K; dot, measurement of Wise et al.[30] for the eutonic mixture; solid line, calculated using the extended ZSR model with mixture parameter $B = -1.26$; dashed line, calculated using the extended ZSR model with mixture parameters set equal to zero. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. The symbols and lines have the same meanings as in plot a.

yields $B = -1.260$ and the results shown in Figures 22 and 23. Fitted water activities, shown in Figure 22, are generally too low especially at the highest molality which corresponds to the eutonic point determined by Wise et al.[30]

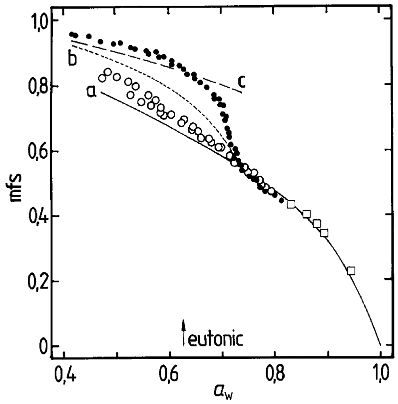

Figure 24. Water uptake of 1:1 (mole ratio) mixtures of malonic acid and $(NH_4)_2SO_4$ at approximately 298 K, plotted as mass fraction of solute (mfs) against equilibrium water activity (a_w). Key: square, bulk solution measurements of Choi and Chan;[42] open circle, edb (evaporation) measurements of Choi and Chan for supersaturated aqueous droplets; dot, edb (growth) measurements of Choi and Chan; line a, calculated using the extended ZSR model with mixture parameter $B = -1.126$; line b, calculated using the extended ZSR model with $B = -1.126$, assuming the particle consists of aqueous malonic acid and $(NH_4)_2SO_4$ in equilibrium with the solid salt; line c, calculated using the extended ZSR model with $B = -1.126$, assuming the particle consists of aqueous malonic acid and solid $(NH_4)_2SO_4$. The calculated water activity of the eutonic solution is marked. The calculated mfs for $B = 0$ differ very little from those shown.

Measured and fitted DRH at 298.15 K are shown in Figure 23a, and also values predicted using the extended ZSR model without the fitted parameter B. Both sets of calculations agree reasonably well with the measurements, except that the eutonic point is predicted to be at a higher XH$_2$Malo and lower a_w than measured. It appears that there may be some inconsistency between the water activity and the deliquescence data, although uncertainties in the latter are quite large. It should also be remembered that the calculations shown in Figure 12 suggest that a significant fraction of malonic acid (10 to 20% for a 1:1 mixture) may be dissociated in mixtures with $(NH_4)_2SO_4$, and this has not been taken into account here. The calculated eutonic point for $B = -1.26$ is $a_w = 0.628$, $m(NH_4)_2SO_4 = 4.86$ mol kg^{-1} and mH$_2$Malo = 13.48 mol kg^{-1}, compared to a measured value of $a_w = 0.675$, $m(NH_4)_2SO_4 = 7.5$ mol kg^{-1} and mH$_2$Malo = 12.0 mol kg^{-1}.[30] Calculated total molalities in saturated solutions at the DRH are shown in Figure 23b.

Model predictions are next compared with the edb data of Choi and Chan[42] for a 1:1 (mole ratio) mixture. The mass fractions of solute of evaporating particles, which exist as supersaturated aqueous solution droplets, are under-predicted below 70−80% RH, see Figure 24, which is consistent with the fit of the model to the bulk solution data shown in Figure 22. To model the particle growth measurements we initially assumed an aqueous droplet in which only solid $(NH_4)_2SO_4$ forms (line b). The complete dissolution of $(NH_4)_2SO_4$ at a relative humidity of about 74% is quite well predicted, and the measured and calculated mfs agree in that region. However, at lower relative humidities the particle is calculated to contain much more water than is measured, yielding mfs values that are too low. For relative humidities less than 65% the measured mfs exceed what would be expected for a particle containing only dissolved acid plus undissolved solid $(NH_4)_2SO_4$ (see Figure 24). It is therefore likely that, although the particle contains some liquid water at all relative humidities below the eutonic point, the malonic acid in the particle is not completely dissolved. This is consistent with the observation of Choi and Chan that malonic acid absorbs water reversibly at very low relative humidities, without crystallization occurring.

5.6. Glutaric Acid + NaCl. There are two sources of data for deliquescence relative humidities: measurements of Chen and Lee[47] for XH$_2$Glut up to 0.4 at room temperature, and of Pant et al.[48] at 293.15 K over the entire composition range. An additional point for saturation with respect to NaCl can be

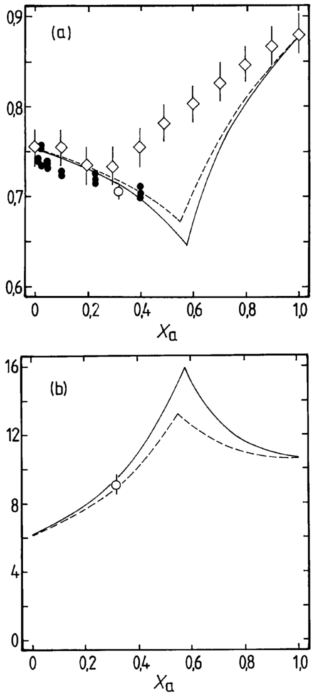

Figure 25. Deliquescence curve of a mixture of glutaric acid and NaCl at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions plotted against the dry mole fraction of acid (X_a) in the mixture. Key: open circle, $DRH_{complete}$ from Table 2 of Choi and Chan;[42] dot, measurements of Brooks et al.;[34] square, data of Parsons et al.,[16] adjusted to 298.15 K; dot, measurements of Chen and Lee;[47] diamond, data of Pant et al.[48] (not fitted); solid line, calculated using the extended ZSR model with mixture parameter $B = -1.791$; dashed line, calculated using the extended ZSR model with mixture parameters set equal to zero. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. The symbol and lines have the same meanings as in plot a.

estimated from the edb measurements of Choi and Chan.[42] (Note that Figure 10 of Choi and Chan shows both measured and calculated mfs incorrectly due to an arithmetical error. The correct values are shown here; see also ref 79 for the revised data.)

The measurements of Pant et al.,[48] for saturation with respect to the solid acid, imply very large positive values of the ZSR mixture parameter B which are inconsistent with other data. The results of Chen and Lee,[47] and the point estimated from the measurements of Choi and Chan,[42] were fitted to obtain $B = -1.791$. Th results are shown in Figure 25a. The predicted eutonic point occurs at $a_w = 0.648$, $m\text{NaCl} = 6.77$ mol kg^{-1}, and $mH_2\text{Glut} = 9.10$ mol kg^{-1}. Calculated total molalities of the saturated aqueous solutions are shown in Figure 25b.

The model has also been used to calculate particle growth and evaporation curves for a 1:1 (by mass) mixture of NaCl and glutaric acid to compare to the edb measurements Choi and Chan.[42] For this pair of solutes, there are no bulk solution measurements with which to standardize the edb data. However, saturation of the aqueous mixtures with respect to NaCl is predicted well by the extended ZSR model, and it was therefore used to standardize the data to agree with the model at $a_w = 0.8$. We excluded the evaporation data for particle number 2 as they were discordant with the other data by a small amount. The overall consistency of the standardized data, in particular the agreement of both evaporation and growth data at high relative humidities and the close approach of the growth measurements to mfs = 1 at low relative humidity, gives confidence in the results. Measured and predicted values of mfs are shown in Figure 26. There is very good agreement for the evaporation measurements at all water activities.

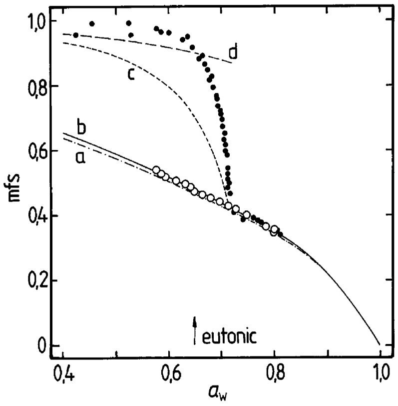

Figure 26. Water uptake of 1:1 (mass ratio) mixtures of glutaric acid and NaCl at approximately 298 K, plotted as mass fraction of solute (mfs) against equilibrium water activity (a_w). Key: open circle, edb (evaporation) measurements of Choi and Chan[42] for supersaturated aqueous droplets; dot, edb (growth) measurements of Choi and Chan; line a, calculated using the extended ZSR model with mixture parameters equal to zero; line b, calculated using the extended ZSR model with mixture parameter $B = -1.791$; line c, calculated using the extended ZSR model with $B = -1.791$, assuming the particle consists of aqueous glutaric acid and NaCl in equilibrium with the solid salt; line d, calculated using the extended ZSR model with $B = -1.791$, assuming the particle consists of aqueous glutaric acid and solid NaCl. The calculated water activity of the eutonic solution is marked.

The particles in the growth experiments take up very little water below $a_w = 0.6$ suggesting that both solid NaCl and H_2-Glut are present. This appears to be confirmed by the fact that for $a_w < 0.65$ the water content of the particles is less than predicted for either the aqueous acid plus NaCl in equilibrium with the solid salt (line c), or a particle containing aqueous acid plus nondissolving solid NaCl (line d). The fall in mfs as a_w is increased to about 0.7 is consistent with both the acid and salt dissolving to produce an entirely aqueous droplet at the predicted water activity of about 0.72.

5.7. Glutaric Acid + $(NH_4)_2SO_4$. Deliquescence relative humidity measurements are available from three sources, see Table 8, and bulk solution water activities have been determined by Wise et al.[30] and by Choi and Chan[42] who have also made edb measurements of the 1:1 (mole ratio) mixture.

The results for the mixture succinic acid + NaCl have shown that deliquescence properties calculated using the extended ZSR model can be sensitive to the parameter b in the Debye−Huckel equations used for the unsymmetrical mixture correction (eq 7 and eq 18 of Clegg and Seinfeld[11]). This sensitivity is mainly in the calculated activity coefficients, not the water activity. Most of the calculations for this mixture were carried out using the usual value of 1.2.[12] However, some additional tests were also made with $b = 0.8$, and these are discussed at the end of this section.

The extended ZSR model was first fitted to all the data (including edb measurements), giving the bulk solution data higher weights, and the results are shown in Figures 27 and 28. The fit yields $B = 4.456$, and a reasonable prediction of the eutonic point, which is calculated to be $a_w = 0.758$ and XH_2-Glut = 0.54 compared to the measured water activity of 0.767, and $XH_2\text{Glut} = 0.57$. However, the predicted bulk solution water activities are too low for the most concentrated solutions (Figure 28) and the data are more consistent with a lower value of B (1.01) which was obtained by fitting the water activity and edb measurements of Choi and Chan[42] only; see Figure 29.

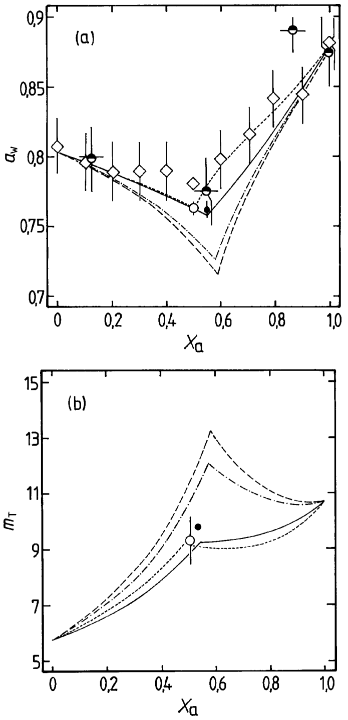

Figure 27. Deliquescence curve of a mixture of glutaric acid and $(NH_4)_2SO_4$ at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions plotted against the dry mole fraction of acid (X_a) in the mixture. Key: open circle, $DRH_{complete}$ from Table 2 of Choi and Chan;[42] dot, measurement of the water activity of the eutonic mixture by Wise et al.;[30] half-filled circle, data of Brooks et al.;[34] diamond, data of Pant et al.;[48] solid line, calculated using the extended ZSR model with mixture parameter $B = 4.456$; dashed line, calculated using the extended ZSR model with mixture parameters set equal to zero; dash−dot line, calculated using the extended ZSR model with $B = 1.01$; dotted line, calculated using the extended ZSR model with mixture parameters set equal to zero, but $b = 0.8$ in the unsymmetrical correction term. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. The symbols and lines have the same meanings as in plot a.

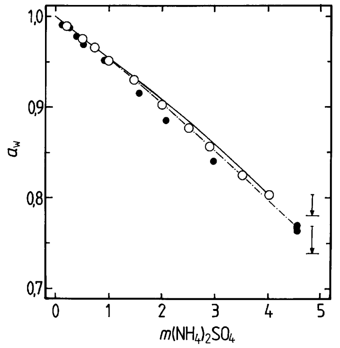

Figure 28. Water activities (a_w) of aqueous mixtures of glutaric acid and $(NH_4)_2SO_4$, plotted against the molality of the salt ($m(NH_4)_2SO_4$). Key: open circle, bulk solution measurements of Choi and Chan[42] at 295.15 K for a 1:1 (mole ratio) mixture; dot, data of Wise et al.[30] for mixtures of eutonic composition (dry mole fraction of acid = 0.5334) at 298.15 K; lines, calculated using the extended ZSR model with mixture parameter $B = 4.456$. The vertical arrows indicate the reduction in calculated a_w, for the two measurements at the highest molalities, for $B = 0.0$.

Model calculations using both values of B are compared with the edb data in Figure 29. The water content of the fully liquid evaporating particles is, as noted above, most accurately reproduced with $B = 1.01$. The edb data are predicted well to $a_w = 0.6$, the limit of the measurements for supersaturated aqueous particles. However, this value of B also yields DRH

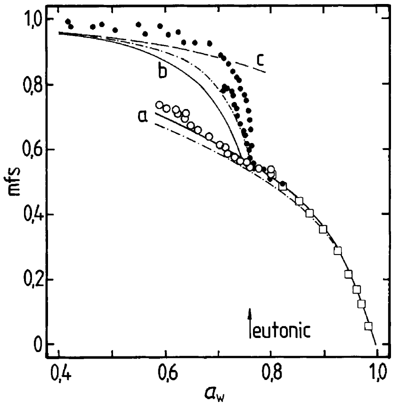

Figure 29. Water uptake of 1:1 (mass ratio) mixtures of glutaric acid and $(NH_4)_2SO_4$ at approximately 298 K, plotted as mass fraction of solute (mfs) against equilibrium water activity (a_w). Key: open circle, edb (evaporation) measurements of Choi and Chan[42] for supersaturated aqueous droplets; dot, edb (growth) measurements of Choi and Chan; lines a, calculated using the extended ZSR model with mixture parameter $B = 1.01$ (solid line), and $B = 4.456$ (dash−dot line); lines b, the same as for lines a, but assuming the particle consists of aqueous glutaric acid and $(NH_4)_2SO_4$ in equilibrium with the solid salt; line c, calculated for a particle consisting of aqueous glutaric acid and solid $(NH_4)_2SO_4$. The calculated water activity of the eutonic solution is marked.

that are too low, as shown in Figure 27. This apparent inconsistency may be caused by limitations in the model, and appears to be at least partly reconciled by a change in the value of the parameter b, which is further discussed below.

Turning to the edb growth measurements, at the lowest water activities the particles take up a small amount of water, but comparison with the line for aqueous acid plus solid nondissolving salt suggests that the liquid water present is insufficient to dissolve all of the acid for $a_w < 0.7$.

The water content of the particles in the growth cycle, including the water activity at which the particles become fully liquid (0.766) is most accurately predicted using the model with $B = 4.456$. This is consistent with the fact that DRH data from other sources, shown in Figure 27, are best represented using this value. Also, the fact that the measured mfs for growth particle 1 are much higher than predicted for a particle containing all aqueous acid plus dissolved salt in equilibrium with the solid is consistent with the droplet containing both solid and dissolved acid even though the water activity is below that at the eutonic point. It is unclear as to how this occurs—Chan and Choi[42] note that separate experiments in which the RH in the edb chamber is changed in discrete steps, rather than in scanning mode, yield the same overall growth curve. Consequently it is unlikely that the cause is a lack of equilibrium between the particles and surrounding water vapor.

Last, we have repeated the DRH calculation for the mixture using the extended ZSR model without the mixture parameter B, but with the parameter b in the unsymmetrical correction assigned a reduced value of 0.8. The results are shown in Figure 27 as a fine dotted line and agree very well with the data, better than for the earlier fit with $B = 4.456$. The effect of using the lower value of b is mainly confined to the activity coefficients, so there would be very little change in calculated mfs for the edb evaporation experiments shown in Figure 29 (or the water activities in Figure 28). Calculations for the edb growth experiments yield very similar results to those shown for the $B = 4.456$ (and $b = 1.2$) case. The optimum models for this mixture are therefore either based on $b = 1.2$ and $B = 4.456$, or $b = 0.8$ and a low value of B in the range 0 to 1.01.

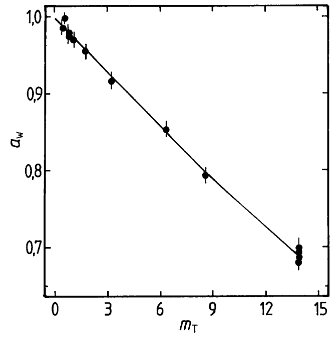

Figure 30. Water activities (a_w) of aqueous mixtures of maleic acid and $(NH_4)_2SO_4$, plotted against the total molality (m_T). Symbol: data of Wise et al.[30] for mixtures of eutonic composition (dry mole fraction of acid = 0.5500) at 298.15 K. Line: the extended ZSR model with fitted mixture parameter $B = -1.732$.

5.8. Maleic Acid + $(NH_4)_2SO_4$. Deliquescence relative humidities and water activities of mixtures of these compounds have been determined by Brooks et al.[34] and by Wise et al.;[30] see Table 8. A fit of the water activity data (using $b = 1.2$ in the unsymmetrical correction terms) yields $B = -1.732$, see Figure 30, and the model represents the data well. The calculated eutonic composition using the extended ZSR model with $B = -1.732$ is 0.723, with $m(NH_4)_2SO_4 = 5.736$ mol kg^{-1} and mH_2-Maleic = 5.484 mol kg^{-1}. The measured value of Wise et al.[30] is $a_w = 0.685$, $m(NH_4)_2SO_4 = 6.24$ mol kg^{-1} and mH_2Maleic = 7.63 mol kg^{-1}. Predicted deliquescence relative humidities are compared with the available data in Figure 31a and appear to be too high for the eutonic composition, which corresponds to the data point for the highest total molality in Figure 30. Thus, the model quite accurately predicts the water activity of this solution, but also that it is supersaturated with respect to both solutes. This also explains why the calculated total molality for the eutonic solution, see Figure 31b, is lower than measured.

The reason for these differences is likely to be the dissociation of maleic acid in these solutions, discussed at the beginning of this section. This causes a reduction the molality of the undissociated acid, and also that of SO_4^{2-} (due to the formation of HSO_4^-) implying that a model that does not take this into account will predict solubilities that are too low, and therefore DRH values that are too high.

5.9. L-Malic Acid + $(NH_4)_2SO_4$. Deliquescence relative humidities have been measured by Brooks et al.,[34] and water activities of solutions of eutonic composition were obtained by Wise et al.[30] Fits of the extended ZSR model to the water activities of Wise et al. showed that it was not possible to reproduce the data satisfactorily to the highest total molality (34 mol kg^{-1}). Omitting the data at this concentration yields the result shown in Figure 32, and $B = -7.03$. The calculated DRH curve, shown in Figure 33a, agrees only moderately well with the data, but is an improvement on the result without the mixture parameter. Calculated total molalities corresponding to the DRH curve are shown in Figure 33b. Tests using different values of b in the unsymmetrical correction term did not yield any significant improvements in calculated properties.

6. Multicomponent Aqueous Mixtures of Dicarboxylic Acids and Salts

Marcolli et al.[27] have measured the water activities of saturated solutions containing each of the salts NH_4NO_3, $(NH_4)_2SO_4$, NaCl, and the five acids malic, malonic, maleic, glutaric, and methyl succinic (M5 in Table 2 of Marcolli et al.[27]). Here we compare predictions of the extended ZSR model, including the interaction parameters determined above, with these data. The complete set of model parameters, of which 12 are known out of a possible total of 25, are listed in Table 9.

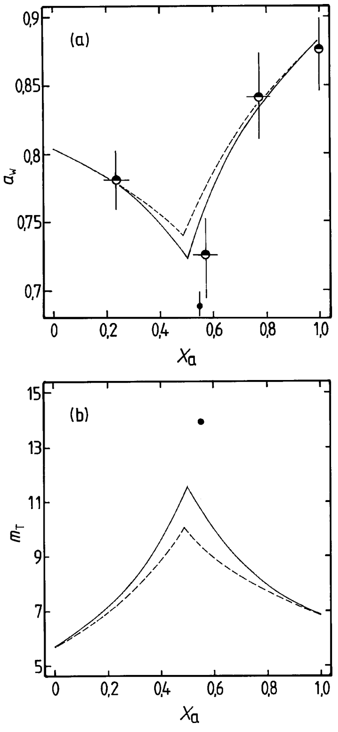

Figure 31. Deliquescence curve of a mixture of maleic acid and $(NH_4)_2SO_4$ at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions plotted against the dry mole fraction of acid (X_a) in the mixture. Key: dot, measurement of the water activity of the eutonic mixture by Wise et al.;[30] half-filled circle, data of Brooks et al.;[34] solid line, calculated using the extended ZSR model with mixture parameter $B = -1.732$; dashed line, calculated using the extended ZSR model with mixture parameters set equal to zero. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. The symbol and lines have the same meanings as in plot a.

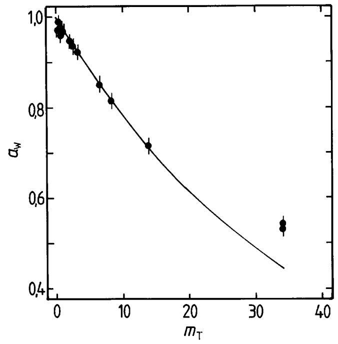

Figure 32. Water activities (a_w) of aqueous mixtures of L-malic acid and $(NH_4)_2SO_4$, plotted against the total molality (m_T). Symbols: data of Wise et al.[30] for mixtures of eutonic composition (dry mole fraction of acid = 0.6579) at 298.15 K. Line: the extended ZSR model with fitted mixture parameter $B = -7.03$. Note that the pair of points at the highest total molality were not fitted.

The results for solutions saturated with respect to NH_4NO_3(s) are shown in Figure 34. The measured and calculated water activities agree well over the measured range $0.374 \le a_w \le 0.599$, even though all the acid-salt interaction parameters are unknown. Setting the acid−acid parameters to zero also has little effect. Calculated NH_4NO_3(s) solubilities in the acid mixture, also shown in Figure 34, are greater than those measured by about 1 mol kg^{-1} (3.5%). It is possible that the

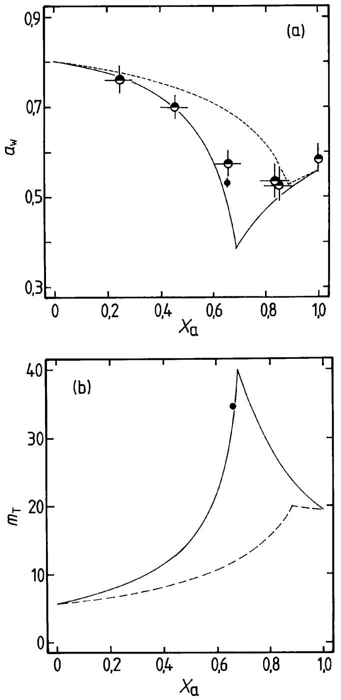

Figure 33. Deliquescence curve of a mixture of L-malic acid and $(NH_4)_2SO_4$ at 298.15 K. (a) Water activities (a_w) of the saturated aqueous solutions plotted against the dry mole fraction of acid (X_a) in the mixture. Dot, measurement of the water activity of the eutonic mixture by Wise et al.;[30] half-filled circle, data of Brooks et al.;[34] solid line, calculated using the extended ZSR model with mixture parameter $B = -7.03$; dashed line, calculated using the extended ZSR model with mixture parameters equal to zero. (b) Total molality of the two solutes (m_T) in the saturated aqueous solutions. The symbol and lines have the same meanings as in plot a.

measured values are too low, as they do not appear to extrapolate to the correct value of 26.3 mol kg^{-1} in a pure aqueous solution.

Water activities of mixtures of the acids with NaCl are shown in Figure 35. There is reasonable agreement, with calculated values being too low by up to about 0.03 in a_w and with little sensitivity to the values of the mixture parameters. There is more variation in the predicted NaCl solubilities in the acid mixture, with the known parameters for interactions with malonic and glutaric acids having too great an effect in reducing the predicted solubility.

The measurements of Marcolli et al.[27] for mixtures containing $(NH_4)_2SO_4$ include water activities of solutions both saturated and subsaturated with respect to the salt. Measured and predicted water activities for the subsaturated solutions are shown in Figure 36a. Agreement is satisfactory, with predictions being too low by about 0.04 in a_w for the most concentrated solutions. The sensitivity to the presence of the mixture parameters is quite small.

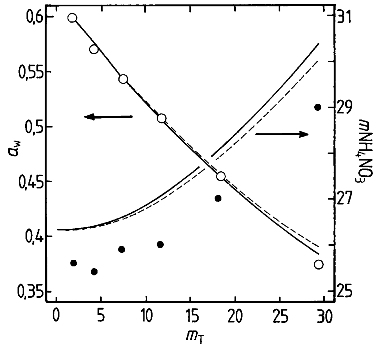

Figure 34. Water activities (a_w) of aqueous mixtures of dicarboxylic acids saturated with respect to NH_4NO_3, plotted against the total acid molality (m_T). Key: open circle (left-hand axis), data of Marcolli et al.[27] at 298.15 K from their Table 3; dot (right-hand axis), molalities of NH_4NO_3 in the saturated aqueous solutions (from the same data set); solid lines, calculated using the extended ZSR model including the acid−acid mixture parameters in Table 9; dashed lines, calculated using the extended ZSR model with all mixture parameters set to zero.

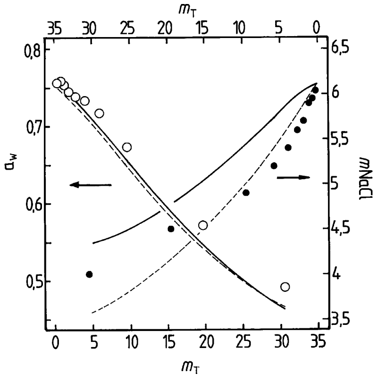

Figure 35. Water activities (a_w) of aqueous mixtures of five dicarboxylic acids saturated with respect to NaCl, plotted against the total acid molality (m_T). The mixtures contain malic, malonic, maleic, glutaric and methyl succinic acids. Key: open circle (left-hand and bottom axes), data of Marcolli et al.[27] at 298.15 K from their Table 3; dot (right-hand and top axes), molalities of NaCl in the saturated aqueous solutions; solid lines, calculated using the extended ZSR model including the mixture parameters in Table 9; dashed lines, calculated using the extended ZSR model with all mixture parameters set to zero.

Calculated water activities of solutions saturated with respect to $(NH_4)_2SO_4$ are shown in Figure 36b, both for the tabulated solution compositions (Table 3 of Marcolli et al.) and for the listed acid molalities but with $m(NH_4)_2SO_4$ calculated to be in equilibrium with the solid salt. These are lower than the

TABLE 9: Parameters for Interactions between Components of the M5 Acid Mixture and the Salts NH_4NO_3, $(NH_4)_2SO_4$, and NaCl[d]

	A^0					B		
	malic	malonic	maleic	glutaric	methyl succinic	NH_4NO_3	$(NH_4)_2SO_4$	NaCl
malic	*c*	0[a]	0	0.423	*c*	*c*	−7.03	*c*
malonic	*c*	*c*	0.784	0[a]	*c*	*c*	−1.260	−1.292
maleic	*c*	*c*	*c*	0.505	*c*	*c*	−1.732	*c*
glutaric	*c*	*c*	*c*	*c*	*c*	*c*	1.01[b]	−1.791
methyl succinic	*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*

[a] From results of Choi and Chan,[23] see section 4 above. [b] This value was determined by fitting the data of Choi and Chan,[42] a larger value of 4.456 was obtained from data for deliquescence relative humidities. [c] Interactions for which no data are available. [d] All acid−acid parameters are A^0, and all acid-salt parameters are B. The extended ZSR equations incorporating A^0 and B are given by Clegg et al.[10] and by Clegg and Seinfeld.[11]

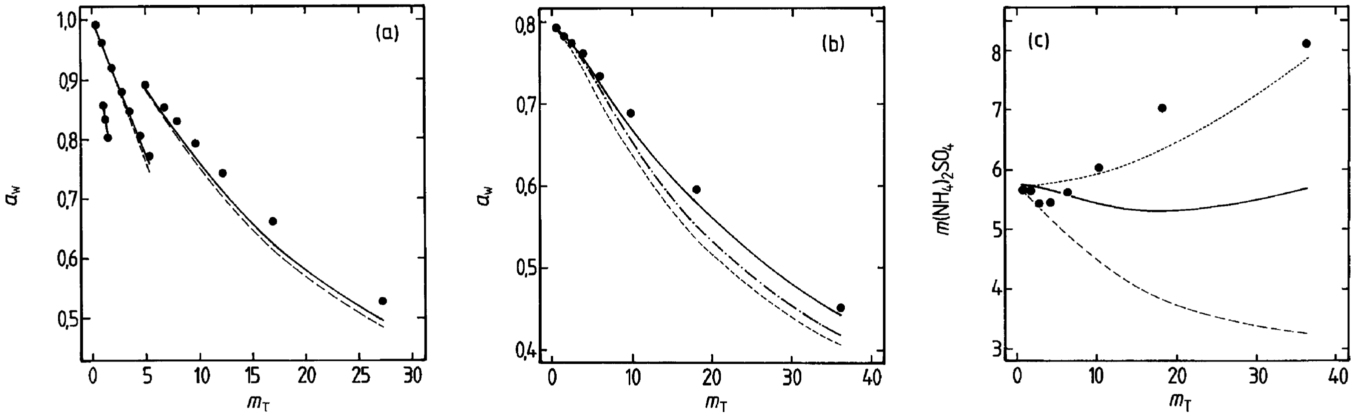

Figure 36. Water activities (a_w) and solubilities in aqueous mixtures of dicarboxylic acids and $(NH_4)_2SO_4$, plotted against the total acid molality (m_T). The mixtures contain malic, malonic, maleic, glutaric and methyl succinic acids. (a) Key: dot, water activities of solutions not saturated with respect to the salt, from Table 3 of Marcolli et al.;[27] solid line, calculated using the extended ZSR model with mixture parameters listed in Table 9; dashed line, calculated using the extended ZSR model without mixture parameters. (b) Key: dot, water activities of solutions saturated with respect to the salt, from Table 3 of Marcolli et al.; solid line, calculated using the extended ZSR model with mixture parameters listed in Table 9, for acid molalities listed by Marcolli et al. but $(NH_4)_2SO_4$ molalities calculated to be in equilibrium with the solid salt; dash−dot line, calculated using the extended ZSR model with mixture parameters listed in Table 9, for acid and salt molalities listed by Marcolli et al.; dotted line, the same as for the dash−dot line but with mixture parameters set to zero. (c) Key: dot, the measured solubilities of $(NH_4)_2SO_4$ in the acid mixture, from Table 3 of Marcolli et al.; solid line, calculated using the extended ZSR model with the mixture parameters in Table 9; dashed line (bottom), calculated using the extended ZSR model without mixture parameters; dotted line, calculated using the extended ZSR model without mixture parameters but with $b = 2.0$ in the unsymmetrical correction terms.

measured $m(NH_4)_2SO_4$, and result in higher calculated a_w which agree quite closely with the data in Figure 36b. Water activities calculated for the saturated solution compositions given by Marcolli et al. are too low, as was the case for the subsaturated solutions shown in Figure 36a.

Measured and calculated $(NH_4)_2SO_4$ solubilities are plotted in Figure 36c. The measurements indicate that solubilities of $(NH_4)_2SO_4$ increase from 5.8 mol kg^{-1} in pure aqueous solution to about 8 mol kg^{-1} at 36 mol kg^{-1} total acid molality. In contrast, the predicted solubilities vary very little with acid molality for the case where mixture parameters are used in the model, and decrease when no mixture parameters are used. We investigated whether this could be due to the formation of HSO_4^- in solution, by carrying out a calculation using the CSB model. As before, the parameters for interactions between H^+ and hydrogen carboxylate and carboxylate anions were assumed to be the same as those for and HSO_4^- and SO_4^{2-} respectively. No organic/inorganic mixture parameters were used. The effect on the calculated $(NH_4)_2SO_4$ solubility of allowing the organic acids to dissociate was found to be small, less than 10% at the highest total acid molality. Further test calculations using the extended ZSR model showed that the predicted solubilities were sensitive to the value of b used in the unsymmetrical correction. Increasing b from 1.2 to 2.0 resulted in a predicted $(NH_4)_2SO_4$ solubility of 7.87 mol kg^{-1} at the highest total acid molality, which is close to the measured value.

In this section, and in section 5, the extended ZSR model has been tested in calculations of solubilities, water activities, and deliquescence relative humidities of aqueous acid−salt mixtures. In most cases the results are satisfactory, and the parameters B for acid−salt interactions are generally of greater magnitude than those for acid−acid interactions. It has also been found that predicted activity coefficients, hence deliquescence properties, are sensitive to the value of parameter b in the unsymmetrical correction terms. We have not examined in detail the effect of varying b for different electrolytes and different mixtures, but our results suggest that eqs A7−A9 of Clegg and Seinfeld[11] should probably be used as they permit the use of different values of b for each electrolyte in a multicomponent mixture.

The eutonic points of acid/salt mixtures estimated using the CSB approach and listed in Table 7 generally have lower water activities than calculated using the extended ZSR model, with the exceptions of L-malic acid + $(NH_4)_2SO_4$, and glutaric acid + NaCl, for which they are comparable. It appears that the ZSR model yields more accurate predictions of the compositions and water activities of the saturated solutions, but by a smaller margin than was found for the acid mixtures discussed in section 4. We note that the predicted water activity of the eutonic point for maleic acid + $(NH_4)_2SO_4$ by the CSB approach is close to the value measured by Wise et al.[30] However, this agreement is probably fortuitous because dissociation of the acid is likely to be significant in these solutions but is not included in either model.

The edb measurements for evaporating (supersaturated) particles are quite well reproduced by the ZSR model, particularly for mixtures with NaCl. The data for the growth particles, for which RH is increased in the chamber from dryness, are not always easy to interpret because a number of the acids are evidently able to take up water at relative humidities below the eutonic point of the mixture. However, even for these particles the relative humidities at which the particles become completely liquid (with no solid present) is predicted well.

7. Modeling Schemes

In this work we have tested the CSB[9] and extended ZSR[10,11] methods for calculating activity and osmotic coefficients of multicomponent solutions containing both inorganic and organic components. Both approaches allow the incorporation of existing models of inorganic aqueous mixtures, and of organic mixtures, into the overall schemes. The different possibilities for modeling are most easily illustrated by considering the example shown in Figure 37. This is an aqueous solution mixture containing two cations c_1 and c_2, two anions a_1 and a_2, and four nondissociating organic solutes N_1, N_2, O_1, and O_2. The solute content of the solution can be considered as an electrolyte element **e**, and elements **N** (solutes N_1 and N_2) and **O** (solutes O_1 and O_2). For the purpose of this example it is assumed that N_1 and N_2 are solutes whose thermodynamic properties in

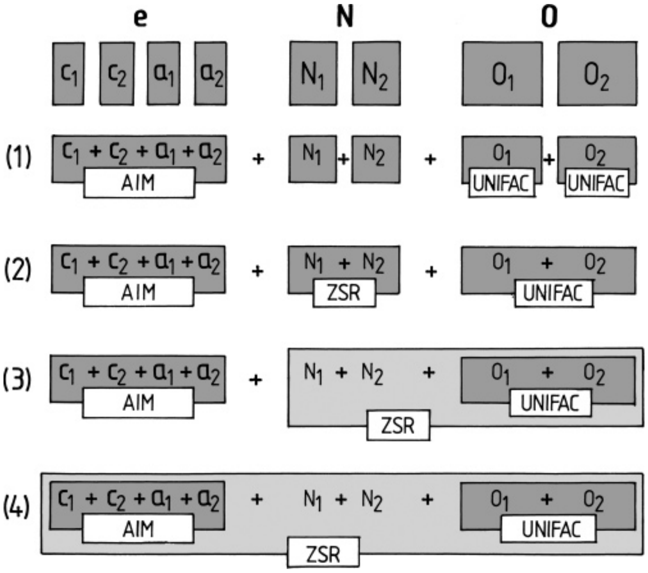

Figure 37. Schematic diagram of an aqueous system consisting of an electrolyte element (**e**), and organic elements **N** and **O**, containing the ions and uncharged solutes listed in the boxes along the top row. The numbered rows (1−4) illustrate approaches for calculating water activities and solute activity coefficients, and are described in the text.

aqueous solution are well established (such as the dicarboxylic acids treated here), but O_1 and O_2 are water-soluble compounds whose properties are not known. The number of solutes in each element **e**, **N**, and **O** is arbitrary, and we have assigned four ions and two solutes each in Figure 37 for simplicity.

Four different approaches are summarized in Figure 37. In all of these, we assume that the activity coefficients and water activity contribution of the electrolyte element **e** (i.e., just the four ions and neglecting solution elements **N** and **O**) are calculated using AIM[38] or some other established electrolyte solution model. The first three approaches are variants of the CSB method, and the last one is a full application of ZSR to both water activity and solute activity coefficients.

Approach 1: Here the water activity contributions of solutes N_1 ($a_{w(N_1)}$) and N_2 ($a_{w(N_2)}$) are calculated individually from their known thermodynamic properties. Thus, for example, $a_{w(N_1)}$ is the water activity of a pure aqueous solution of N_1 at its molality in the mixture. The water activity contributions of solutes O_1 and O_2 are analogous, except that their water activities in pure aqueous solutions are estimated using a model, such as UNIFAC. In the simplest form of the CSB approach interactions between the solutes in the three solution elements are neglected, and the water activity of the mixture (a_w) is given by: $a_w = a_{w(\mathbf{e})}a_{w(N_1)}a_{w(N_2)}a_{w(O_1)}a_{w(O_2)}$, where $a_{w(\mathbf{e})}$ is the water activity contribution of the electrolyte element of the solution. The activity coefficient of each solute N_1, N_2, O_1, and O_2 is simply equal to its value in a pure aqueous solution at its molality in the mixture. Activity coefficients of the cations and anions are those calculated by AIM[38] (or some other electrolyte model) for a solution containing only the ions, at their molalities in the mixture.

Approach 2: Properties of the pairs of solutes N_1 and N_2, and O_1 and O_2, are now calculated together, using ZSR for ($N_1 + N_2$) and UNIFAC for ($O_1 + O_2$). This yields water activity contribution $a_{w(\mathbf{N})}$, calculated using ZSR for a solution containing only solutes N_1 and N_2 at their molalities in the mixture; and $a_{w(\mathbf{O})}$, similarly calculated using UNIFAC for a solution containing O_1 and O_2. The water activity of the solutions is then given by: $a_w = a_{w(\mathbf{e})}a_{w(\mathbf{N})}a_{w(\mathbf{O})}$. The activity coefficients of the ions are the same as in Approach 1, and the activity coefficients of N_1 and N_2 are values calculated using ZSR (eq 18 of Clegg et al.[10]) for the solution of N_1 and N_2. Similarly, the activity coefficients of O_1 and O_2 in the mixture are equal to the values calculated using UNIFAC for a solution containing only O_1 and O_2.

Approach 3: in this case the use of ZSR is extended to both **N** and **O** solution components, using the equations derived by Clegg et al.[9] for the case where the thermodynamic properties of a subgroup of solutes (here O_1 and O_2) are calculated using a second model. For this case the water content (and, by iteration, the water activity $a_{w(\mathbf{N},\mathbf{O})}$) of a solution containing N_1, N_2, O_1, and O_2 is given by eq 14 of Clegg et al.,[10] the activity coefficients of N_1 and N_2 are given by their eq 18, and the activity coefficients of O_1 and O_2 by their eq 15. The water activity of the mixture is $a_w = a_{w(\mathbf{e})}a_{w(\mathbf{N},\mathbf{O})}$. The activity coefficients of the ions in the mixture are again the same as in Approach 1, and the activity coefficients of the four organic solutes are those calculated using ZSR and just described.

Approach 4: Last, the ZSR approach is extended to all the solutes, and it includes both solution elements **e** and **O** as subgroups of solutes whose activity coefficients and contributions to the total water content of the solution are calculated by other models. The total water content of the solution is now given by eq 31 of Clegg and Seinfeld,[11] which contains additional terms (the unsymmetrical correction) to account for the fact that the system being treated contains both neutral solutes and ions. Neglecting the solute−solute interaction terms, eq 31 can be written for this example:

$$W_{\text{total}} = w^{\circ,r_1} + w^{\circ,r_2} + w_{N_1}{}^{\circ} + w_{N_2}{}^{\circ} + (W'_{\text{total}} - w^{\circ,r_{1'}} - w^{\circ,r_{2'}} - w_{N_1}{}^{\circ'} - w_{N_2}{}^{\circ'}) \quad (10)$$

where the subgroup of solutes r_1 is solution element **e** (the ions) and r_2 is element **O** (solutes O_1 and O_2). The definitions of symbols are the same as given by Clegg and Seinfeld.[11] The activity coefficients of solutes N_1 and N_2 in the mixture are given by eq 33 of Clegg and Seinfeld, and those of O_1 and O_2 by eq 34 in which each activity coefficient $\gamma_R{}^{\circ,r}$ (where R is solute O_1 or O_2) is calculated using UNIFAC. Equation 34 of Clegg and Seinfeld[11] also applies to the ionic solutes (element **e**), but in terms of stoichiometric mean activity coefficients of the four cation−anion combinations rather than single ion activity coefficients. This is because the ZSR approach treats electrolytes (salts or acids) and uncharged solutes as solution components and not ions. This is described in more detail by Clegg et al.,[10] and has implications for the calculation of dissociation equilibria, which are discussed further in ref 15.

The model calculations and tests in earlier sections have shown the following. First, that for solutions containing only uncharged components ZSR yields more accurate water activities and solute activity coefficients than the CSB method in which each solute is treated as an individual component (N_1, N_2, N_3, etc.). That is to say, Approach 2 in Figure 37 is better than Approach 1 for such systems.

Second, water activities and deliquescence properties of mixtures containing electrolytes are estimated more accurately using the extended ZSR method (Approach 4) than by the CSB model (Approaches 1−3). However, the comparisons of DRH values noted at the end of section 6 suggest that the advantages of ZSR for calculating deliquescence properties of mixtures containing both electrolytes and acids are less clear than for either (i) the water activities of aqueous mixtures or, (ii) the deliquescence properties of mixtures containing only acids. This is probably due to the limitations of ZSR for calculating activity coefficients in mixtures containing solutes of different charge types, which are only partially addressed by the correction term proposed by Clegg and Seinfeld.[11]

Third, the models have not been applied to mixtures which include the additional group of solutes **O** in Figure 37. However, it seems reasonable that for such mixtures (which again do not contain an electrolyte element) Approach 3—treating all the uncharged solutes, both **N** and **O**, within the ZSR framework—would be likely to give better results than Approaches 1 and 2. In Approach 3, UNIFAC (or some other suitable model) is used to calculate activity coefficients and water activity of the mixture of O_1 and O_2, which are then incorporated into the ZSR calculation using eqs 14 and 15 of Clegg et al.[10]

Last, the CSB and the extended ZSR models contain interaction parameters that can be determined from water or solute activity data for solutions containing two solutes. Our calculations have shown that the use of these parameters can significantly improve model accuracy. In the ZSR model the parameters are $A^0_{i,j}$, $A^1_{i,j}$ and $B_{i,j}$, and in the CSB method they are the ion−neutral and neutral−neutral interaction parameters from the Pitzer model.[12] For systems of moderate concentration, and for which mixture parameters are available, the CSB method (or Pitzer model) are to be preferred to ZSR even in its extended form. We base this conclusion on the extensive literature of applications of the Pitzer equations to aqueous systems.[12,50,51]

The ZSR approach is also limited by its treatment of dissociation equilibria. Consider a solution containing aqueous H_2SO_4 (component 1) and a nondissociating organic compound (component 2). The water content W of the mixture (or, by iteration, the water activity for a fixed solution concentration) can be calculated using extended ZSR:

$$W = w^{\circ,1} + w^{\circ,2} + (n_1 + n_2)X_1X_2(A^0 + Ba_w) \qquad (11)$$

where $w^{\circ,i}$ is the mass of water solvent in a pure aqueous solution of component i, n_i is the number of moles of i present, and X_i is the dry mole fraction of each solute. For the purpose of this example, we ignore the unsymmetrical correction of Clegg and Seinfeld[11] (the terms in parentheses on the first line of their eq 31). The corresponding expression for solute activity coefficients is their eq 32, but omitting the last term on the first line. It is obtained by integration of the water activity of the mixture, calculated using eq 10 above, for a fixed mole ratio of the two solutes.[52] The activity coefficients so derived are stoichiometric or total values. In the case of the solute H_2SO_4 nothing is therefore implied about the concentrations of the individual species H^+, HSO_4^-, and SO_4^{2-} in the mixture because the ZSR method treats electrolytes and nondissociating solutes as components, not individual ions. The stoichiometric activity coefficient of H_2SO_4 is related to those of the ions by eq 22 of Clegg et al.,[10] and can still be used in calculations of equilibrium partial pressures and saturation ratios of solids, as shown in section 3.4 of Clegg et al. However, the limitations of the extended ZSR approach when applied to all three solution elements **e**, **N**, and **O** are more serious where it is also necessary to consider the dissociation of the organic compound. This is examined further in ref 15.

Finally, we note that the modeling approaches we have investigated have some features in common with the recent work of Topping et al.[49] These authors estimate the water content of the aerosol solutions using ZSR, but calculated activity coefficients are based on the amounts of water associated with each group of solutes (inorganic ions, or dissolved organic compounds) at the specified RH rather than the total water content of the solution.

8. Summary

Water activity data for solutions of seven dicarboxylic acids at 298.15 K have been critically examined and fitted to an excess Gibbs energy equation to high (supersaturated) molalities. The CSB model of Clegg et al.[9] and the extended ZSR model of Clegg et al.[10] and Clegg and Seinfeld[11] have been tested against extensive water activity and deliquescence relative humidity data for multicomponent solutions of dicarboxylic acids. The extended ZSR model was found to yield more accurate predictions, and it has been applied to aqueous mixtures of salts and dicarboxylic acids. Measured deliquescence relative humidities and water activities of supersaturated aqueous droplets are generally quite well represented by the model but often require the use of additional parameters for the interactions between pairs of solutes. Calculated activity coefficients showed some sensitivity to the value of parameter b in the unsymmetrical correction term of Clegg and Seinfeld.[11]

A few of the dicarboxylic acids dissociate strongly enough to affect their deliquescence behavior—notably maleic acid—and some calculations have been carried out using the CSB model to estimate qualitatively the effect of this on model predictions.

Different possible approaches to estimating solute and water activities of complex mixtures, using the CSB and extended ZSR methods, have been discussed. The extended ZSR method is generally to be preferred for solutions of nondissociating solutes, but the treatment of dissociation equilibria remains a problem for this type of model. In ref 15, we develop ion-interaction models of multicomponent aqueous solutions including dissociated dicarboxylic acids, and use these to suggest practical approaches for modeling solute and solvent activities in solutions containing ions, and both dissociating and nondissociating neutral (organic) solutes.

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Note Added in Proof. Many of the data used in this work have been tabulated and are available at: http://www.uea.ac.uk/~e770/aim.html.

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