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Thermodynamic Models of Aqueous Solutions Containing Inorganic Electrolytes and Dicarboxylic Acids at 298.15 K. 2. Systems Including Dissociation Equilibria

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Atmospheric aerosols contain a significant fraction of water-soluble organic compounds, including dicarboxylic acids. Pitzer activity coefficient models are developed, using a wide range of data at 298.15 K, for the following systems containing succinic acid (H_2Succ) and/or succinate salts: $\{H^+, Li^+, Na^+, K^+, Rb^+, Cs^+\}Cl^-{-}H_2Succ{-}H_2O$, $HNO_3{-}H_2Succ{-}H_2O$, $H^+{-}NH_4^+{-}HSucc^-{-}Succ^{2-}{-}NH_3{-}H_2Succ{-}H_2O$, $NH_4Cl{-}(NH_4)_2Succ{-}H_2O$, $H^+{-}Na^+{-}HSucc^-{-}Succ^{2-}{-}Cl^-{-}H_2Succ{-}H_2O$, $NH_4NO_3{-}H_2Succ{-}H_2O$, and $H_2SO_4{-}H_2Succ{-}H_2O$. The above compositions are given in terms of ions in the cases where acid dissociation was considered. Pitzer models were also developed for the following systems containing malonic acid (H_2Malo): $H^+{-}Na^+{-}HMalo^-{-}Malo^{2-}{-}Cl^-{-}H_2Malo{-}H_2O$, and $H_2Malo{-}H_2SO_4{-}H_2O$. The models are used to evaluate the extended Zdanovskii−Stokes−Robinson (ZSR) model proposed by Clegg and Seinfeld (*J. Phys. Chem. A* **2004**, *108*, 1008−1017) for calculating water and solute activities in solutions in which dissociation equilibria occur. The ZSR model yields satisfactory results only for systems that contain moderate to high concentrations of (nondissociating) supporting electrolyte. A practical modeling scheme is proposed for aqueous atmospheric aerosols containing both electrolytes and dissociating (organic) nonelectrolytes.

1. Introduction

Atmospheric aerosols contain both inorganic components, such as sea salt and acid ammonium sulfate, and an organic fraction consisting of a wide range of compounds with diverse physical and thermodynamic properties.[1] The more polar, and therefore water-soluble, organic compounds with two or more −COOH and −OH functional groups are likely to influence the water uptake of atmospheric aerosols. Dicarboxylic acids are examples of such compounds and occur in significant concentrations in aerosols.[2,3] In the preceding work,[4] Clegg and Seinfeld tested two thermodynamic modeling approaches[5−7] for calculating water activities and deliquescence properties (solubilities and water activities of saturated aqueous solutions) of aqueous dicarboxylic acids and their mixtures with salts. In that study, the dicarboxylic acids were treated as nondissociating compounds.

Soluble dicarboxylic acids can potentially affect the pH of aqueous aerosols, by dissociation, and thus gas/aerosol equilibrium of important volatile components such as NH_3 and HNO_3. In some systems solid dicarboxylate or hydrogen carboxylate salts may also form. It is therefore necessary to incorporate dissociation equilibria of the organic components of aerosols into thermodynamic models used to calculate water and solute activities and solid/liquid and gas/liquid equilibrium.

In this work we develop thermodynamic models of multicomponent solutions containing succinic and malonic acids, at 298.15 K. These models use the Pitzer equations to calculate osmotic and activity coefficients, and can serve as references for testing the methods used in atmospheric gas/aerosol partitioning codes. The extended Zdanovskii−Stokes−Robinson (ZSR) model of Clegg and Seinfeld[7] is also evaluated for calculations involving the dissociation of organic solutes, and possible hybrid methods incorporating elements of different models are suggested.

2. Theory

Osmotic coefficients (ϕ), water activities (a_w), and solute activity coefficients γ_i in aqueous solutions are calculated in this work mainly using the molality-based model of Pitzer.[8] The equations used are as given by Clegg et al.[9] (ion−ion interaction terms), and by eqs 62−64 and eqs F6−F9 of Pitzer[8] (neutral−neutral and ion−neutral terms). We also employ extensions to the model proposed by Fernandez-Merida et al.,[10] which add ionic strength dependent neutral−ion parameters $\lambda^*_{n,i}$ and a molality dependent neutral−neutral self-interaction parameter λ^*_n. These extensions were found to be useful by Fernandez-Merida et al. for representing the properties of electrolyte− polar nonelectrolyte mixtures, and they are given in general form in the Appendix.

Hybrid approaches to calculating water activities and solute activity coefficients, in aqueous solutions containing both electrolytes and nonelectrolytes, have been proposed by Clegg et al.[5] (referred to hereafter as CSB) and by Clegg and Seinfeld[7] (the extended ZSR method). They are discussed in section 4 of this work. Descriptions of the methods are not reproduced here and the original papers[5,7] should be consulted for details.

Equations for the first dissociation constants K_1 (for $H_2X(aq) \leftrightarrow H^+(aq) + HX^-(aq)$) and second dissociation constants K_2 (for $HX^-(aq) \leftrightarrow H^+(aq) + X^{2-}(aq)$) of the dicarboxylic acids are given in section 2 of ref 4. The general expression for the

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activity product of a solid (K_s) in a saturated aqueous solution is also given there, and values of the dissociation constants and K_s at 298.15 K are listed in Tables 1 and 3 of that work.

3. Models of Aqueous Dicarboxylic Solutions Including Dissociation

In ref 4, the water uptake and deliquescence properties of aqueous solutions of dicarboxylic acids, and their mixtures with salts, have been treated using the extended ZSR model without considering the dissociation of the acids. Although the primary effect of soluble organic compounds is likely to be on the water content of aerosols—which is effectively addressed using the ZSR approach—it is also possible that the dissociation of organic acids will affect aerosol pH. We have therefore developed thermodynamic models for aqueous mixtures containing succinic and malonic acids at 298.15 K, using the Pitzer molality-based equations.[8] These models are intended as a reference against which to test practical atmospheric codes, and are described below.

3.1. The System $H^+-Na^+-NH_4^+-\{Li^+, K^+, Rb^+, Cs^+\}-HSucc^--Succ^{2-}-Cl^--HSO_4^--SO_4^{2-}-H_2Succ-H_2O$. The available data for aqueous mixtures containing succinic acid are summarized in Table 1. Most of the data are solubilities, usually for mixtures of succinic acid and common salts and inorganic acids. The solubilities of many succinate and hydrogen succinate salts are not known, and there are few data that yield osmotic and activity coefficients of their aqueous solutions. These are needed to determine the primary interaction parameters in the Pitzer model (β^0, β^1, $C^{0\phi}$, and $C^{1\phi}$ between each cation and anion).[8,9] Esteso et al.[11−13] have determined activity coefficients of Na_2Succ, and of NaCl, in aqueous mixtures of the salt with NaHSucc and Na_2Succ. However, we have not adopted their Pitzer model treatment of the systems[12] because the authors determined the parameters for $Na^+-HSucc^-$ interactions from measurements of stoichiometric osmotic coefficients of NaHSucc(aq) without recognizing that aqueous solutions of this salt exist as a mixture of Na^+, H^+, $HSucc^-$, and $Succ^{2-}$ ions, and undissociated succinic acid.

Some assumptions regarding cation−anion interaction parameters are necessary because of the paucity of data. We have assumed that interactions between H^+ and $HSucc^-$, and between H^+ and $Succ^{2-}$, are the same as those between H^+ and HSO_4^- and SO_4^{2-}, respectively. The parameters for these interactions are listed by Clegg et al.[9] Sulfuric acid was chosen because the two anions have the same charges as $HSucc^-$ and $Succ^{2-}$ and are both relatively large, and the interaction parameters have been quite accurately determined. Calculations using these parameters should produce satisfactory results in dilute solutions in which the acids will be most strongly dissociated. In concentrated solutions, any inaccuracies in the calculated strength of the interactions between the H^+ ion and the two organic anions are likely to be subsumed into fitted parameters.

Where data are lacking we have extended the above assumption to include other cations, and used the appropriate cation−HSO_4^- and cation−SO_4^{2-} parameters given by Pitzer.[8] In this study we have determined values of β^0, β^1, $C^{0\phi}$, and $C^{1\phi}$ for interactions between Na^+ and NH_4^+ and the ions $HSucc^-$ and $Succ^{2-}$.

The Pitzer model treatments of osmotic and activity coefficients of pure aqueous solutions of H_2Succ and NH_4NO_3 have been extended to high molalities using the additional terms proposed by Fernandez-Merida et al.,[10] and given the Appendix. All parameter values for solutions containing dissolved succinic acid are listed in Table 2. The development of the model is described below.

TABLE 1: Sources of Solubility and Activity Data for Na^+ and NH_4^+ Succinates and for Aqueous Acid Succinate Mixtures[a]

solute 1	solute 2	t (°C)	used	data[b]	source
NaHSucc	−	0−75	yes	solu	61
NaHSucc	−	25	yes	f	62
Na_2Succ	−	0−75	yes	solu	61
Na_2Succ	−	25	yes	edb, a_w	63
Na_2Succ	−	25	no	emf	11
H_2Succ	Na_2Succ	0−75	yes	solu	61
H_2Succ	HCl	25	yes	solu	64
H_2Succ	H_2SO_4	25	yes	solu	31
H_2Succ	HNO_3	25−100	yes	solu	65
H_2Succ	LiCl	25	yes	solu	66
H_2Succ	LiCl	11.85−23.75	yes	solu	67
H_2Succ	NaCl	5−225	yes	K^*	20
H_2Succ	NaCl	18	yes	K^*	21
H_2Succ	NaCl	25	yes	solu	66
H_2Succ	NaCl	11.85−23.75	yes	solu	67
H_2Succ	NaCl	25	yes	solu	68
H_2Succ	NaCl	22, 20−23	yes	edb, a_w	17
H_2Succ	KCl	25	yes	solu	66
H_2Succ	KCl	11.85−23.75	yes	solu	67
H_2Succ	K_2SO_4	−2 to +60	no	solu	69
H_2Succ	RbCl	11.85−23.75	yes	solu	67
H_2Succ	CsCl	11.85−23.75	yes	solu	67
H_2Succ	NH_3	25	yes	solu	23
H_2Succ	$(NH_4)_2SO_4$	22, 20−23	yes	edb,a_w	17
H_2Succ	$(NH_4)_2SO_4$	25	yes	a_w	32
H_2Succ	$(NH_4)_2SO_4$	4, 9, 24	no	DRH	33
H_2Succ	NH_4NO_3	25	yes	edb	29
H_2Succ	NH_4NO_3	−16.5 to +36.5	yes	solu	30
NaHSucc	HCl	0−50	yes	emf	18
NaHSucc	Na_2Succ + NaCl	0−50	yes	emf	19
NaHSucc	NaCl	25	yes	emf	12
Na_2Succ	NaCl	25	yes	emf	13
$(NH_4)_2Succ$	NH_4Cl	25.2	yes	solu	31

[a] Additional sources of data either not used, or for interactions with other salts: H^+−succinate equilibria in Na^+ and K^+ salt solutions;[70] solubilities in the systems $H_2Succ-MgCl_2-H_2O$ at 25 °C,[71] $H_2Succ-KOH-H_2O$ at 25 °C;[72] H_2Succ solubilities in NaI, KBr, and KI aqueous solutions;[67] formation and stability of dicarboxylic acid−NH_4^+ complexes;[73] protonation of dicarboxylates in aqueous NaCl;[22] salt effects on the dissociation of dicarboxylic acids;[74] freezing point depressions of Na^+ salts of dicarboxylic acids;[75] densities and surface tensions of Na_2Succ and Na_2Malo in very dilute solutions;[39] acidity functions for aqueous solutions containing NaHSucc + NaCl, NaHSucc + Na_2Succ, and NaHSucc + HCl;[76] the influence of dissolved salts on the dissociation of aqueous succinic acid.[77] [b] Key: solu, solubility in water; ϕ, stoichiometric osmotic coefficient; edb, electrodynamic balance measurements of water activities of supersaturated aqueous solutions; a_w, water activities of bulk aqueous solutions; emf, electromotive force measurements yielding activities or activity coefficients; K^*, stoichiometric dissociation constant; DRH, relative humidity of deliquescence, equivalent to the water activity of a solution saturated with respect to one or more solutes.

3.1.1. Aqueous Succinic Acid. The model, including dissociation to form $HSucc^-$ and $Succ^{2-}$ ions, was fitted to the same data as used for the extended ZSR model (Table 2 of ref 4), and the result is shown in Figure 1. (See Figure 2 of ref 4 for uncertainties associated with the osmotic coefficients from bulk solution measurements.) For subsaturated solutions there is little difference from the result obtained with eq 5 in ref 4, mainly because the acid is only weakly dissociated. The degree of dissociation α is calculated to be <0.1 for all molalities greater than 0.01 mol kg^{-1}; see Figure 1a. The uncertainties in the values of ϕ obtained from edb experiments, discussed in ref 4, only affect the model for high (supersaturated) molalities of succinic acid.

TABLE 2: Pitzer Model Parameters for Aqueous Solutions Containing Succinic Acid and Malonic Acid, at 298.15 K[e]

(a) Cation−Anion Interaction Parameters

cation	anion	b^0	b^1	$C^{0\phi}$	$C^{1\phi}$	note or source
Na	HMalo	0.0387	0.1777	−0.002949	0.0	*a*
Na	Malo	0.2058	1.3243	−0.013910	−0.8267	*a*
Na	HSucc	0.0495	0.2772	−0.000160	0.0	*a*
Na	Succ	0.2078	1.9020	−0.010440	0.0263	*a*
NH_4	HSucc	0.1600	0.4000	0.007000	0.0	*a*
NH_4	Succ	0.0750	1.4990	−0.004794	0.0	*a*
NH_4	HMalo	0.0328	0.4684	0.002307	−0.6974	*b*
NH_4	Malo	0.0374	0.5345	−0.000616	0.4646	*b*
H	HMalo	0.2959	0.4005	−0.011316	−0.8187	*b*
H	Malo	−0.0084	0.3147	0.028828	−0.9155	*b*
H	HSucc	0.2959	0.4005	−0.011316	−0.8187	*b*
H	Succ	−0.0084	0.3147	0.028828	−0.9155	*b*
H	SO_4	−0.0084	0.3147	0.028828	−0.9155	9
H	HSO_4	0.2959	0.4005	−0.011316	−0.8187	9
H	Cl	0.1873	0.2970	−0.000667	−0.1234	8
H	NO_3	0.1168	0.3546	−0.005390	0.0	*c*
Na	SO_4	−0.0173	0.7534	0.011745	0.0	78
Na	HSO_4	0.0454	0.3980	0.0	0.0	79
Na	Cl	0.0806	0.2631	0.000525	−0.0201	80
Na	OH	0.0864	0.2528	0.004255	0.0	9
NH_4	SO_4	0.0374	0.5345	−0.000616	0.4646	81
NH_4	HSO_4	0.0328	0.4684	0.002307	−0.6974	81
NH_4	Cl	0.0548	0.2132	−0.003304	−0.0694	*c*
NH_4	NO_3	−0.0020	0.0879	−0.000086	−0.0230	*a*

(b) Dicarboxylic Acids

acid	$\lambda_{n,n}$	λ_n^*	α_n	$\mu_{n,n,n}$	acid	$\lambda_{n,n}$	λ_n^*	α_n	$\mu_{n,n,n}$
H_2Succ	−0.01575	−0.40160	1.5	0.000080	H_2Malo	0.126 50	−0.28000	0.4	−0.001835

(c) Ion−Ion Mixture Parameters

ion	ion	$\theta_{i,i'}$	source	ion	ion	$\theta_{i,i'}$	note or source
H	Na	0.0360	8	Cl	HMalo	0.0146	*a*
H	NH_4	−0.0190	8	Cl	Malo	0.0583	*a*
Na	NH_4	0.0044	24	Cl	HSucc	0.0366	*a*
				Cl	Succ	0.0549	*a*
				Cl	OH	−0.0500	8

ion	ion	ion	$\psi_{i,i',j}$	source	ion	ion	ion	$\psi_{i,i',j}$	note or source
H	Na	Cl	−0.00400	8	SO_4	HSO_4	NH_4	−0.00842	81
H	NH_4	SO_4	−0.02245	81	Cl	HMalo	Na	−0.00914	*a*
H	NH_4	HSO_4	−0.00865	81	Cl	Malo	Na	−0.01160	*a*
H	NH_4	Cl	−0.00910	24	Cl	HSucc	Na	−0.00386	*a*
H	NH_4	NO_3	−0.01000	82	Cl	Succ	Na	−0.01692	*a*
					Cl	Succ	NH_4	−0.00047	*a*
					Cl	OH	Na	−0.00600	8
					HSucc	Succ	NH_4	0.007 00	*a*

(d) Neutral−Ion Mixture Parameters

neutral	ion	$\lambda_{n,c}$	note or source	neutral	ion	$\lambda_{n,a}$	note or source
H_2Succ	H	0.1000	*a*	H_2Succ	SO_4	−0.0265	*a*
H_2Succ	Na	0.0212	*a*	H_2Succ	HSO_4	0.0436	*a*
H_2Succ	NH_4	0.0600	*a*	H_2Succ	Cl	0.077 87	*a*
H_2Succ	Li	0.0587	*a*	H_2Succ	NO_3	−0.0504	*a*
H_2Succ	K	−0.0700	*a*	H_2Succ	HSucc	−0.1355	*a*
H_2Succ	Rb	−0.0938	*a*	H_2Malo	HSO_4	−0.00098	*a*
H_2Succ	Cs	−0.1152	*a*	H_2Malo	Cl	−0.0055	*a*
H_2Malo	H	0.1070	*a*	H_2Malo	HMalo	−0.1250	*a*
H_2Malo	Na	0.0446	*a*	NH_3	Succ	0.1335	*a*
NH_3	NH_4	0.0500	*d*, 27	NH_3	OH	0.1030	27

neutral	ion	ion	$\zeta_{n,c,a}$	note or source	neutral	ion	ion	$\zeta_{n,c,a}$	note or source
H_2Succ	H	SO_4	−0.01760	*a*	H_2Succ	NH_4	SO_4	−0.00747	*a*
H_2Succ	H	HSO_4	−0.01760	*a*	H_2Malo	H	Cl	−0.00412	*a*
H_2Succ	H	Cl	−0.04492	*a*	H_2Malo	Na	Cl	−0.00400	*a*
H_2Succ	H	NO_3	−0.001616	*a*	NH_3	NH_4	SO_4	−0.00918	27
H_2Succ	Na	Cl	−0.008112	*a*					

[a] Determined in this study. [b] Assumed to be the same as for the corresponding sulfate (malonate or succinate), or bisulfate (hydrogen malonate or hydrogen succinate). [c] Determined by the authors from osmotic and activity coefficients given by Hamer and Wu.[83] [d] The parameter $\mu_{NH_3,NH_3,NH_4} = -0.000750$. [e] The activity products K_s, at 298.15 K, determined in this work are as follows: $H_2Succ(s)$, 0.5568 (0.7074 mol kg^{-1}); $NaHSucc\cdot 3H_2O(s)$, 1.164 (2.84 mol kg^{-1}); $Na_2Succ\cdot 6H_2O(s)$, 1.698 (2.15 mol kg^{-1}); $(NH_4)_2Succ\cdot H_2O$, 3.372 (7.19 mol kg^{-1}); $NH_4HSucc(s)$, 6.3 (for $\lambda_{H_2Succ,NH_4} = 0.06$, and see text regarding limitations of the model). Parameter α_1 in the Pitzer model is equal to 2.0 for all cation−anion pairs above except Na−SO_4, for which it is equal to 1.4.

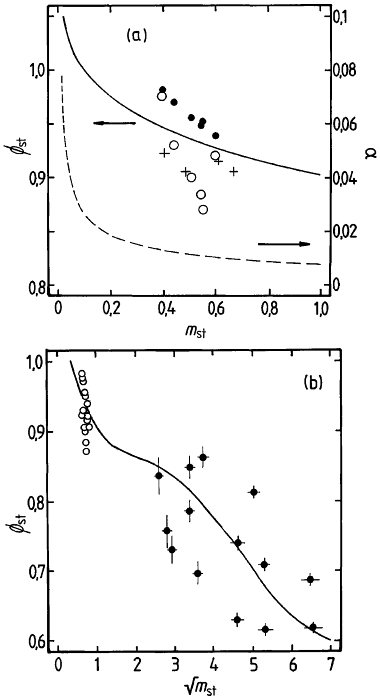

Figure 1. Osmotic coefficients (ϕ_{st}) and calculated degrees of dissociation α of aqueous succinic acid at 298.15 K, plotted against stoichiometric molality (m_{st}). (a) Bulk solution measurements. Key: dot, Robinson et al.;[88] open circle, Davies and Thomas;[89] plus, Carlo;[90] solid line, fitted model; dashed line, calculated degrees of total dissociation (α), right-hand scale. (b) All data. Key: open circle, all bulk solution measurements; dot, edb results of Peng et al.[91] for supersaturated solutions.

3.1.2. {H^+, Li^+, Na^+, K^+, Rb^+, Cs^+}Cl^-−H_2Succ−H_2O and HNO_3−H_2Succ−H_2O. Solubilities of succinic acid have been measured in aqueous solutions of the chlorides by a number of groups; see Table 1. The weak dissociation of H_2Succ means that the effect of each electrolyte on the acid solubility can be expressed simply in terms of interactions between the uncharged acid molecule, and the cations (c) and anions (a) of the salt, using the parameters $\lambda_{H_2Succ,c}$, $\lambda_{H_2Succ,a}$, and $\zeta_{H_2Succ,c,a}$. In an aqueous solution containing molality m of salt $M_{\nu+}X_{\nu-}$ the contribution of these interactions to the activity coefficient of H_2Succ is[8]

$$\ln(\gamma_{H_2Succ}) = ... + 2m(\nu_+\lambda_{H_2Succ,M} + \nu_-\lambda_{H_2Succ,X}) + \nu_+\nu_-m^2\zeta_{H_2Succ,M,X} \quad (1)$$

There are corresponding effects (involving the same parameters) on the osmotic coefficient of the solution, and activity coefficients of the ions M^{z+} and X^{z-}.[8] Thus, data for the solubility of the acid in the salt solution yield, indirectly, the effect of the acid on salt solubility and the effects of salt−acid interactions on the water activity of the mixture. Because the parameters $\lambda_{H_2Succ,M}$ and $\lambda_{H_2Succ,X}$ can only be determined in pairs, due to the constraint of electroneutrality, it is usual to arbitrarily assign the parameter value involving a single cation or anion. The choice of value has no effect on calculated activity coefficients of the uncharged species, or on mean activity coefficients of pairs of cations and anions. In this study, we adopt $\lambda_{H_2Succ,Succ} = 0.0$.

Measured and fitted solubilities of the acid in all seven electrolytes are shown in Figure 2, and the fitted $\lambda_{H_2Succ,i}$ and $\zeta_{H_2Succ,c,a}$ interaction parameters are listed in Table 2. For the alkali metal chlorides, the influence of the salt varies from a strong salting out by LiCl and NaCl, to salting in by RbCl and CsCl. These effects, and how they relate to the properties of the salt solutions, have been discussed by Long and McDevit,[14] Millero,[15] and others. The small difference between measured and fitted solubilities in aqueous NaCl is due to the fact that the parameters $\lambda_{H_2Succ,Na}$ and $\lambda_{H_2Succ,Cl}$ were optimized as a part of more comprehensive fits that also included other data.

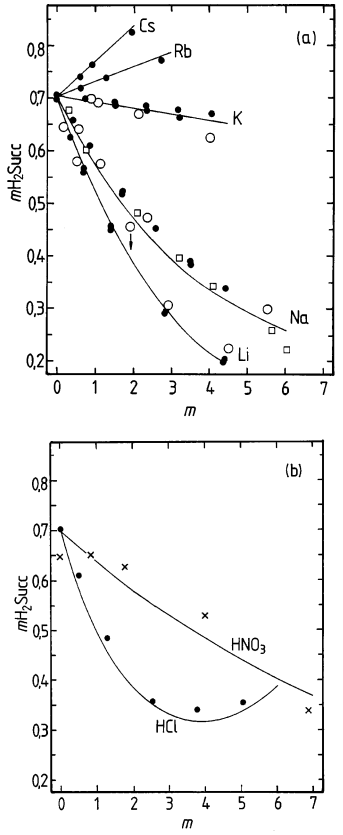

Figure 2. Succinic acid solubilities (mH_2Succ) in alkali metal chloride and inorganic acid solutions at 298.15 K, plotted against the molality (m) of the salt or acid. (a) Alkali metal chlorides. Key: dot, Linderstrom-Lang;[67] open circle, Herz;[66] square, Doosaj and Bhagwat;[68] lines, the fitted model. (b) Hydrochloric and nitric acids. Key: dot, Herz;[64] cross, Sepp and Rajalo;[65] lines, the fitted model.

The results for HNO_3, see Figure 2b, show an almost linear decrease in solubility with $mHNO_3$, but for aqueous HCl there is a change to salting in at high molalities. This behavior is also shown in aqueous H_2SO_4 at high molality and by other dicarboxylic acids such as oxalic acid in aqueous mineral acids.[16]

Model predictions of stoichiometric osmotic coefficients of H_2Succ−NaCl aqueous mixtures are compared with bulk solution and electrodynamic balance data of Choi and Chan[17] for 1:1 (mole ratio) mixtures in Figure 3. At low molalities, the data and model differ by an amount equivalent to a little more than 0.003 in water activity, which is the accuracy of the instrument used. It is likely that the model is more nearly correct because the data, if accurate, imply very large interactions between the acid and salt in dilute solutions. This is inconsistent with other measurements for the system. At high molality, for solutions supersaturated with respect to the acid, the agreement is reasonable considering the uncertainty related to the standardization of the edb data. Note that the error bars shown in Figure 3 take into account only the uncertainty in the measured relative humidity in the balance chamber, and an approximate ±0.01 uncertainty in the mass fraction of solute in the suspended particle. The limit of validity of the model is about 6 mol kg^{-1} of NaCl. The calculated osmotic coefficient is too high above

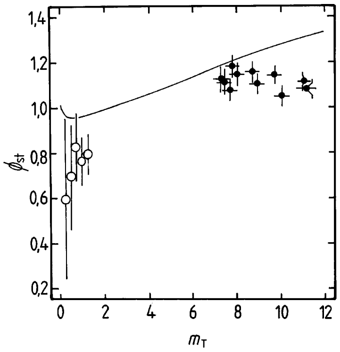

Figure 3. Stoichiometric osmotic coefficients (ϕ_{st}) of 1:1 (mole ratio) aqueous mixtures of NaCl and succinic acid at approximately 298 K, plotted against total molality (m_T). Key: open circle, Choi and Chan[17] (bulk solution water activities); dot, Choi and Chan[17] (edb measurements); line, calculated using the Pitzer model developed in this work.

this molality and for relative humidities less than 70−75%. An error of ±0.2 in the osmotic coefficient (observed for the highest molalities shown in Figure 3) is equivalent to ±0.044 in the water activity.

3.1.3. $H^+-Na^+-HSucc^--Succ^{2-}-Cl^--H_2Succ-H_2O$. The data for this system, Table 1, include emf measurements of HCl, NaCl, and Na_2Succ activities, stoichiometric osmotic coefficients of aqueous NaHSucc, bulk solution and edb water activity data for aqueous Na_2Succ, solubilities in aqueous $H_2Succ-Na_2Succ$ mixtures, and measurements of stoichiometric dissociation constants K_1^* and K_2^* in aqueous NaCl. The Pitzer model of this system was developed by initially fitting interaction parameters for solutions in which only a few of the solution species dominate and then combining all the data for an overall fit with weights reflecting the relative uncertainties of the different measurements. All the results are shown in Figure 4, and the fitted model parameters are listed in Table 2.

Stoichiometric osmotic coefficients of aqueous NaHSucc and Na_2Succ are shown in Figure 4a,b. The data for NaHSucc(aq) were obtained from isopiestic experiments for which the uncertainty is low, and the model agrees well with the data. Calculations show that a 1 mol kg^{-1} solution of NaHSucc contains about 0.63 mol kg^{-1} $HSucc^-$, 0.18 mol kg^{-1} $Succ^{2-}$ and 0.18 mol kg^{-1} H_2Succ. The primary sources of data for pure aqueous Na_2Succ are bulk solution measurements of water activity and, at high molality, edb experiments, see Figure 4b. The dotted line in the figure shows values of the osmotic coefficient determined from emf measurements of Na_2Succ activities by Esteso et al.[11] (their Table 2) which were obtained using an Na^+ glass electrode paired with a novel mercurous succinate electrode. This electrode has not, to our knowledge, been used elsewhere, and its accuracy cannot be assessed. Inclusion of the data of Esteso et al. in the fits resulted in a worsening of predictions of other measured properties, for example, dissociation constants in aqueous NaCl, and so these data were given zero weight.

The emf measurements of Pinching and Bates,[18,19] using the cell Pt|H_2(g, 1 atm)|*test solution*|AgCl;Ag, yield very accurate values of HCl activities ($mH^+ mCl^- \gamma_H \gamma_{Cl}$) and were used by the authors to obtain the dissociation constants of the acid (K_1 and K_2). The compositions of the solutions studied by Pinching and Bates[19] are such that $Succ^{2-}$ and $HSucc^-$ are the two dominant succinate species in the experiments to determine K_2, and we calculate the molality of free H^+ to be about 3×10^{-6} mol kg^{-1} in their series 1 experiments, and 2.5×10^{-5} mol kg^{-1} in series 2. The error plots in Figure 4c show that the HCl activities are predicted satisfactorily for both sets of measurements, for a likely uncertainty of ±0.2 mV in $E - E°$. The results are not as good for the first dissociation of succinic acid, also shown in Figure 4c. In this case deviations increase to about −0.6 mV at an ionic strength of 0.25 mol kg^{-1}. For these experiments the principal succinate species are H_2Succ and $HSucc^-$. At the highest ionic strengths, mH_2Succ is calculated to be equal to about 0.1 mol kg^{-1}, and it is possible that the error in the predicted emf is associated with errors in the predicted activity coefficient of the undissociated acid (hence its dissociation to produce H^+), because the osmotic coefficient data for pure aqueous H_2Succ at low molality are quite scattered (Figure 1) and therefore uncertain. An error of 0.6 mV corresponds to an error of about 2.5% in HCl activity.

Emfs yielding activity coefficients of NaCl in $NaCl-Na_2Succ$ and $NaCl-NaHSucc$ solutions have been determined by Esteso et al.[12,13] These experiments involve the use of Na^+ glass electrodes paired with an AgCl;Ag electrode, and also a separate reference cell. The measured quantity is the difference in emf between the test solution and a pure aqueous NaCl solution at the same stoichiometric ionic strength. The experiments were carried out for 0.5−3.0 mol kg^{-1} ionic strength solutions ($NaCl-Na_2Succ$), and for 0.1−3.0 mol kg^{-1} ionic strength ($NaCl-Na_2HSucc$). The results are shown as mean activity coefficients of NaCl in Figure 4d,e. The model predictions agree with the measured emfs to within ±0.2 mV in all cases, a good result.

Stoichiometric dissociation constants of H_2Succ in NaCl media have been determined by a number of different groups,[20−22] and are defined by

$$K_1^* = mH^+ mHSucc^-/mH_2Succ = K_1\gamma_{H_2Succ}/(\gamma_H\gamma_{HSucc}) \quad (2)$$

$$K_2^* = mH^+ mSucc^{2-}/mHSucc^- = K_2\gamma_{HSucc}/(\gamma_H\gamma_{Succ}) \quad (3)$$

where K_1 and K_2 are the thermodynamic values of the constants, listed in Table 1 of ref 4. The data of Adell,[21] obtained at 291.15 K, were converted to 298.15 K using enthalpies tabulated by Kettler et al.[20] Values of dissociation constants from these sources were found to agree well, but those of Crea et al.[22] were inconsistent with those of the other two groups and were therefore rejected. The results of the model are shown in Figure 4f. Both dissociation constants vary very steeply at low molalities of NaCl, rise to maxima at $m\mathrm{NaCl} \approx 0.75$ mol kg^{-1}, and then decline at higher molalities. The acid is present at very low molalities in the solutions studied by Adell and by Kettler et al., and their data mainly provide information on the interactions of Na^+ and Cl^- with $HSucc^-$, $Succ^{2-}$, and H_2Succ. Parameters for these interactions are also constrained by the solubility data shown in section 3.1.2, and the ternary parameters $\theta_{H,Na}$ and $\psi_{H,Na,Cl}$, which are known from other data (see Table 2). Both dissociation constants are satisfactorily represented by the model over the entire molality range.

The succinate solids that can occur in the system at room temperature are H_2Succ(s), $NaHSucc\cdot 3H_2O$(s), and $Na_2Succ\cdot 6H_2O$(s). Measured and calculated solubilities in aqueous $H_2Succ-Na_2Succ$ mixtures are shown in Figure 4g. The addition of Na_2Succ to the aqueous acid causes its solubility to increase, largely due to the increased dissociation and formation of $HSucc^-$. The acid succinate salt forms over the composition range $mH_2Succ{:}mNa_2Succ = 1{:}0.67$ to 1:4.8, and the solubility of the hexahydrate salt is increased by the addition of H_2Succ probably because of $HSucc^-$ formation (and a consequent reduction in $Succ^-$ molality). The values of the activity products K_s of the acid, and the two salts, in saturated solution are listed in the notes to Table 2.

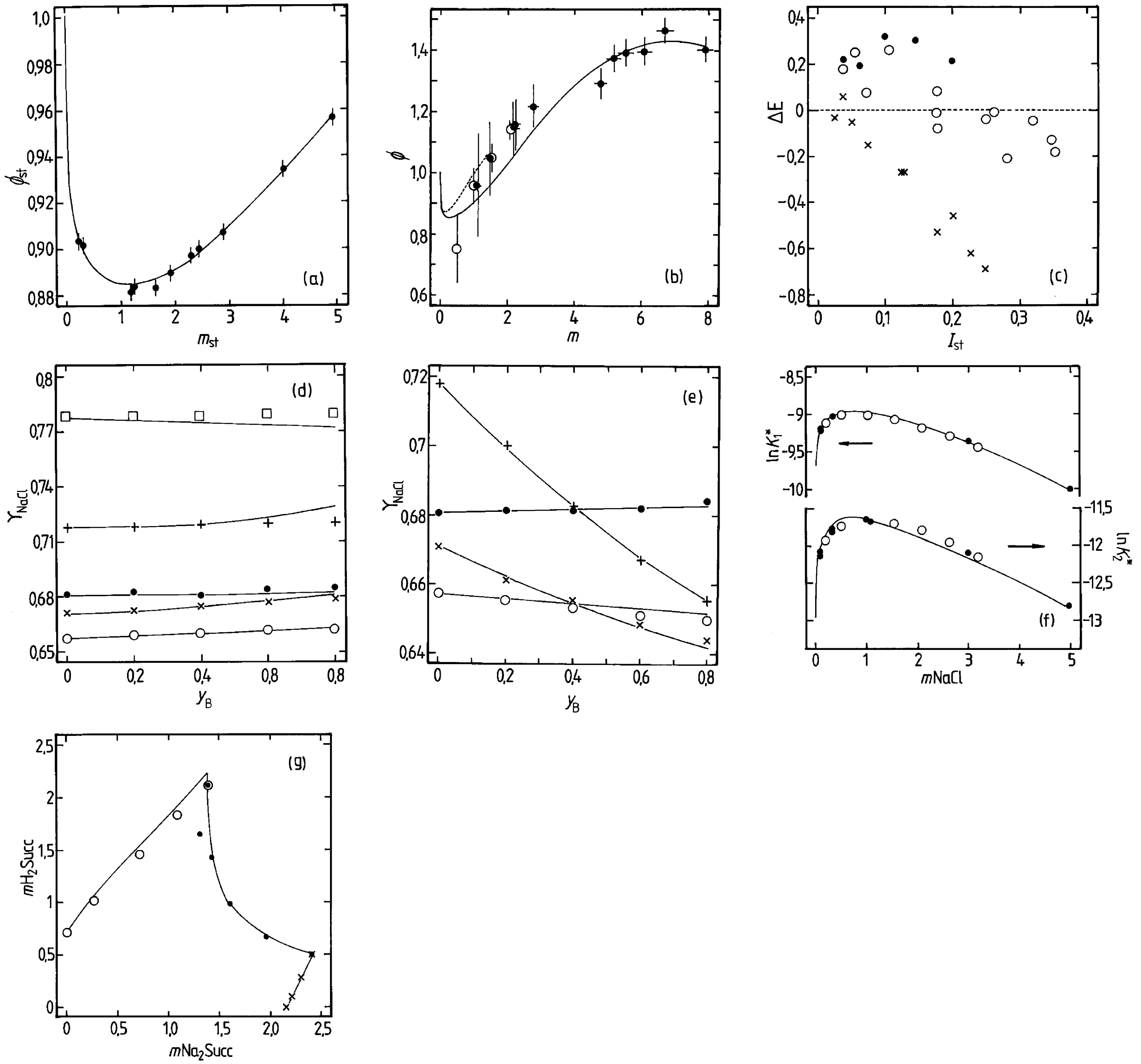

Figure 4. Measured and fitted quantities for solutions containing succinic acid. (a) Stoichiometric osmotic coefficients of aqueous NaHSucc (treated as a 1:1 electrolyte) at 298.15 K, plotted against molality (m_{st}). Key: dot, Stokes;[62] line, the fitted model. (b) Osmotic coefficients of aqueous Na_2Succ at 298.15 K, plotted against molality (m). Key: open circle, Peng and Chan[62] (bulk solution measurements); dot, Peng and Chan[62] (edb measurements); solid line, the fitted model; dotted line, from results of Esteso et al.[11] (not fitted). (c) Differences between measured and fitted emfs (ΔE/mV), from experiments yielding HCl activities in aqueous solution at 298.15 K, plotted against the stoichiometric ionic strength (I_{st}). Key: dot, Pinching and Bates[19] (series 2 experiments, to determine K_2 of succinic acid); open circle, Pinching and Bates[19] (series 1 experiments); cross, Pinching and Bates[18] (series 1 experiments, to determine K_1 of succinic acid). (Note that the ionic strength I_{st} was calculated on the basis of NaHSucc as a 1:1 electrolyte.) (d) Mean activity coefficients of NaCl in aqueous NaCl−NaHSucc mixtures at 298.15 K, plotted against the ionic strength fraction (y_B) of NaHSucc (treating this salt as a 1:1 electrolyte). Data are from Esteso et al.[12] at the following ionic strengths: square, 0.1; dot, 0.5; open circle, 1.0; cross, 2.0; plus, 3.0. The lines represent the fitted model. (e) Mean activity coefficients of NaCl in aqueous NaCl−Na_2Succ mixtures at 298.15 K, plotted against the ionic strength fraction (y_B) of Na_2Succ. Data are from Esteso et al.[13] at the following ionic strengths: dot, 0.5; open circle, 1.0; cross, 2.0; plus, 3.0. The lines represent the fitted model. (f) Stoichiometric first (K_1^*) and second (K_2^*) dissociation constants of succinic acid in aqueous NaCl at 298.15 K, plotted against NaCl molality. Key: dot, Kettler et al.;[20] open circle, Adell;[21] lines, the fitted model. (g) Solubilities in aqueous H_2Succ−Na_2Succ mixtures at 298.15 K. All data are from Marshall and Bain.[61] Key: open circle, solid phase H_2Succ(s); dot, solid-phase NaHSucc·3H_2O(s); cross, solid-phase Na_2Succ·6H_2O(s); lines, the fitted model.

3.1.4. H^+−NH_4^+−HSucc$^-$−Succ^{2-}−NH_3−H_2Succ−H_2O, and NH_4^+−Cl^-−Succ^{2-}−H_2O. Solubilities in aqueous mixtures of NH_3 and H_2Succ have been measured by Druzhinin et al.[23] at 298.15 K. The solids formed are H_2Succ(s), $(NH_4)_2$Succ·H_2O(s), and NH_4HSucc(s). The data and fitted model are plotted in Figure 5, and thr data have been converted into molalities of $(NH_4)_2$Succ (y axis), and an excess of either H_2Succ (x axis, to the right) or NH_3 (x axis, to the left). Thus, for example, a mixture of 1.5 mol kg^{-1} H_2Succ and 3.0 mol kg^{-1} NH_3 is equivalent to 1.5 mol kg^{-1} $(NH_4)_2$Succ (and no excess of either acid or NH_3), whereas 1.6 mol kg^{-1} H_2Succ plus 3.0 mol kg^{-1} NH_3 is equivalent to 1.5 mol kg^{-1} $(NH_4)_2$Succ plus 0.1 mol kg^{-1} H_2Succ. Note that the acid dissociation of NH_3 (NH_4^+(aq) ↔ H^+(aq) + NH_3(aq)) was included in the model

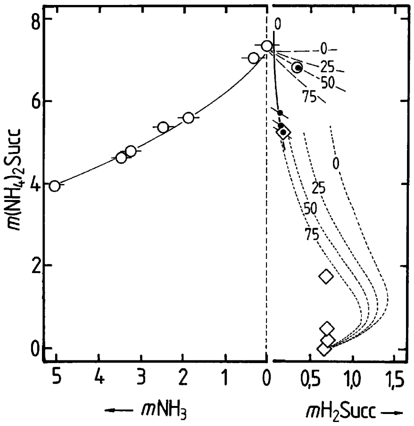

Figure 5. Solubilities in aqueous $H_2Succ-NH_3$ mixtures at 298.15 K. Left hand side: solutions in which NH_3 is in excess. Key: open circle, solid phase $(NH_4)_2Succ\cdot H_2O(s)$; line, the fitted model. The vertical dashed line (at zero on the *x* axis) corresponds to a solution of pure aqueous $(NH_4)_2Succ$. Right-hand side: solutions in which H_2Succ is in excess. Key: diamond, solid-phase $H_2Succ(s)$; dot, solid-phase $NH_4HSucc(s)$; open circle, solid phase $(NH_4)_2Succ\cdot H_2O(s)$; dashed lines, calculated solubilities of $(NH_4)_2Succ\cdot H_2O(s)$ for different assumed values of λ_{H_2Succ,NH_4}; solid line, calculated solubility of $NH_4HSucc(s)$ for $\lambda_{H_2Succ,NH_4} = 0$; dotted lines, calculated solubilities of $H_2Succ(s)$ for different assumed values of λ_{H_2Succ,NH_4}. The numbers on the plot are $1000 \times \lambda_{H_2Succ,NH_4}$ so, for example, the lines marked 75 were calculated using $\lambda_{H_2Succ,NH_4} = 0.075$.

in all calculations for this mixture. The dissociation constant is 5.694×10^{-10} mol kg^{-1} at 298.15 K[24,25] and the Pitzer model parameters for interactions between undissociated NH_3 and ions were taken from Clegg and Whitfield.[24,26] See Clegg and Brimblecombe[27] for a detailed treatment of the thermodynamic behavior of NH_3 in water and in aqueous salt solutions.

The data in Figure 5 show that $(NH_4)_2Succ\cdot H_2O(s)$ is salted out by both NH_3 and by H_2Succ (although there is only a single point in the acid region). The main aqueous species in solutions containing an excess of NH_3 are NH_4^+, $Succ^{2-}$, and NH_3, but in acid mixtures NH_4^+, $HSucc^-$, $Succ^{2-}$, and H_2Succ can all be present at significant molalities. For mixtures of $(NH_4)_2Succ$ and NH_4Cl the speciation is much simpler, as NH_4^+, $Succ^{2-}$, and Cl^- are the main species present.

We consider first the nonacidic solutions. Parameters for interactions between NH_4^+ and Cl^-, between NH_3 and NH_4^+ and Cl^-, and between $Succ^{2-}$ and Cl^- are known and are listed in Table 2. This leaves β^0, β^1, and $C^{0\phi}$ for $NH_4^+-Succ^{2-}$, $\lambda_{NH_3,Succ}$, and $\psi_{Cl,Succ,NH_4}$ to be determined. Pitzer and Mayorga[8,28] have shown that values of β^0 and β^1 are related for electrolytes of the same charge type, for example see Figures 2−4 of Pitzer and Mayorga.[28] In the absence of data for dilute solutions from which β^0 and β^1 can be determined unambiguously, we fix $\beta^0 = 0.075$ and then $\beta^1 = 1.499$ from the equation $\beta^1 = 1.74 + 3\beta^0$. This relationship was estimated by determining the slope from values of the parameters for inorganic 2:1 electrolytes, and the intercept from the β^0, β^1 pair determined for Na^+-Succ^{2-} in this study. These values can only be an approximation, especially as the relationship is weaker for organic electrolytes than inorganic ones. Parameters $C^{0\phi}$, $\lambda_{NH_3,Succ}$ and $\psi_{Cl,Succ,NH_4}$ were determined by fitting measured $(NH_4)_2Succ(s)$ solubilities in NH_3 and in NH_4Cl, and are listed in Table 2. The calculated solubilities are shown in Figure 5 (left-hand side) and in Figure 6.

For the $(NH_4)_2Succ-H_2Succ$ solutions the principal unknown interaction parameters are β^0, β^1, $C^{0\phi}$, and $C^{1\phi}$ for $NH_4^+-HSucc^-$ interactions, $\psi_{HSucc,Succ,NH_4}$, and λ_{H_2Succ,NH_4}. Unfortunately there seems to be no clear relationship between β^0 and β^1 for 1:1 organic electrolytes (Figure 3 of Pitzer and Mayorga[28]), only a range of plausible values. A number of combinations of parameter values were tested and $\beta^0 = 0.16$, $\beta^1 = 0.40$, $C^{0\phi} = 0.007$, and $\psi_{HSucc,Succ,NH_4} = 0.007$ were selected based on the representation of $H_2Succ(s)$ and $NH_4HSucc(s)$ solubilities in the mixtures. Calculated solubilities are shown in Figure 5 (right-hand side) for this set of parameters combined with a range of assumed λ_{H_2Succ,NH_4}. Varying λ_{H_2Succ,NH_4} has a very large effect on the calculated solubilities of the acid. It is apparent from the plot that λ_{H_2Succ,NH_4} lies between about 0.05 and 0.075 for the current model parameter set, as this range yields the best predictions of simultaneous saturation with respect to $H_2Succ(s)$ and $NH_4HSucc(s)$, and also of the solubility of $(NH_4)_2Succ\cdot H_2O(s)$ in the acid region. The value of λ_{H_2Succ,NH_4} selected (0.06) appears to be consistent with other data (solubilities of H_2Succ in aqueous HNO_3, and NH_4NO_3) and is discussed in the section below. While this is a partial confirmation of the validity of the model for this system the parameters for the important $NH_4^+-HSucc^-$ interaction remain very uncertain. It has been found that the chosen values lead to very large γ_{HSucc} in concentrated solutions which may not be realistic, even though they appear to be necessary to represent the observed solubilities in this system. It is recommended that the model for this system not be used for mH_2Succ greater than about 1.5 mol kg^{-1}.

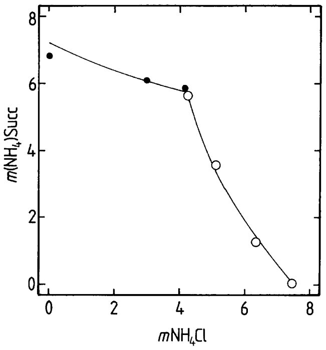

Figure 6. Solubilities in aqueous $(NH_4)_2Succ-NH_4Cl$ mixtures at 298.15 K. Data are from the compilation of Stephen and Stephen.[31] Key: open circle, solid-phase $NH_4Cl(s)$; dot, solid phase $(NH_4)_2Succ\cdot H_2O(s)$; lines, the fitted model.

There are two features of the data shown in Figure 5 that are not represented well by the model and are difficult to explain. First is the fact that H_2Succ solubility is almost invariant with added $(NH_4)_2Succ$ below about 2 mol kg^{-1} of salt. It would be expected that the addition of succinate ion to the solution would increase acid solubility due to increased dissociation and $HSucc^-$ formation. Second, there are the points of simultaneous saturation with respect to $NH_4HSucc(s)$ and the other two solids. Although the solution composition at which the succinate salt forms in the acid region is satisfactorily predicted, solubility with respect to $NH_4HSucc(s)$ is calculated to decline monotonically as $m(NH_4)_2Succ$ is increased, as would be expected from the steadily increasing NH_4^+ molality (pushing the equilibrium $NH_4^+(aq) + HSucc^-(aq) \leftrightarrow NH_4HSucc(s)$ to the right). This is not what is observed.

3.1.5. $NH_4NO_3-H_2Succ-H_2O$. The water uptake of particles containing NH_4NO_3 and succinic acid has been measured in an edb by Lightstone et al.,[29] and they tabulate their results as moles of water per mole of NH_4NO_3. Lightstone et al. note that the particles were likely to contain a solid core of H_2Succ, with which the aqueous acid would be expected to be in equilibrium. Lightstone et al. point out that the particle water content (per mole of NH_4NO_3) should then be invariant with the total amount

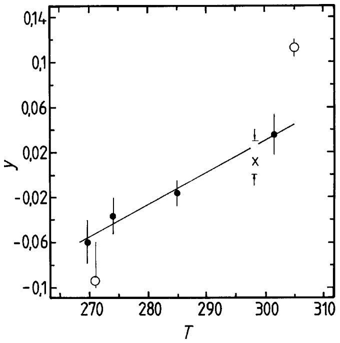

Figure 7. Estimates of the combined salting parameter (λ_{H_2Succ,NH_4} + λ_{H_2Succ,NO_3}) (y) estimated as a function of temperature (T/K) from the solubility measurements of Yunusov et al.[30] Key: dot, estimates from tabulated solubilities including uncertainties based on possible errors in the measured H_2Succ molalities; line, fitted equation (values of y plotted as open circle were not fitted); cross, value of y for λ_{H_2Succ,NH_4} = 0.06 and $\lambda_{H_2Succ,NO_3} = -0.050$, including the range for $0.05 \le \lambda_{H_2Succ,NH_4} \le 0.075$ (limits marked above and below).

of succinic acid present. Also, because of the very low solubility of succinic acid the effect of the acid on the water content would be very small.

Yunusov et al.[30] have determined the solubility polytherm of $H_2Succ + NH_4NO_3$ and, as noted in ref 4, find the solids ice, NH_4NO_3(s), H_2Succ(s), and $mH_2Succ{\cdot}nNH_4NO_3$(s). The data have been used to estimate the interaction between H_2Succ and NH_4NO_3 in the following way: we first calculated the saturated solution activity of H_2Succ using measured solubilities[31] over a range of temperatures, and assuming that the activity coefficient parameters $\lambda_{H_2Succ,H_2Succ}$, $\lambda^*_{H_2Succ}$ and $\mu_{H_2Succ,H_2Succ,H_2Succ}$ in Table 2 are the same at all T. The total activity product in a saturated solution, K_s, must be the same whether it is expressed on a total acid or a free (dissociated) basis and is given by

$$K_s = mH_2Succ_{st}\,\gamma_{st} = mH_2Succ_{fr}\,\gamma_{fr} \qquad (4)$$

where subscript st indicates a stoichiometric or total quantity, and fr the same quantity but for the free acid molecule in a system in which dissociation is calculated. Since H_2Succ is only slightly dissociating the difference between the activity coefficients is small. Using the measured H_2Succ solubilities in aqueous NH_4NO_3, the stoichiometric activity coefficient of H_2Succ in the mixture can be estimated from

$$\gamma_{H_2Succ(mix,st)} = K_s/mH_2Succ_{mix,st} \qquad (5)$$

where $mH_2Succ_{mix,st}$ is the stoichiometric concentration of succinic acid in the mixture. If the stoichiometric activity coefficient in a pure aqueous acid solution at the molality of the acid in the mixture (γ^*_{st}) is calculated, then values of the combined salting parameters ($\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,NO_3}$) can be determined from

$$\ln(\gamma_{H_2Succ(mix,st)}) = \ln(\gamma^*_{st}) + 2mNH_4NO_3(\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,NO_3}) \qquad (6)$$

We have plotted values of the combined salting parameters derived from the data of Yunusov et al.[30] in Figure 7. The results shown in Figure indicate that salting in occurs at low temperatures (negative values of the parameter sum) but that this changes to salting out at about 290 K.

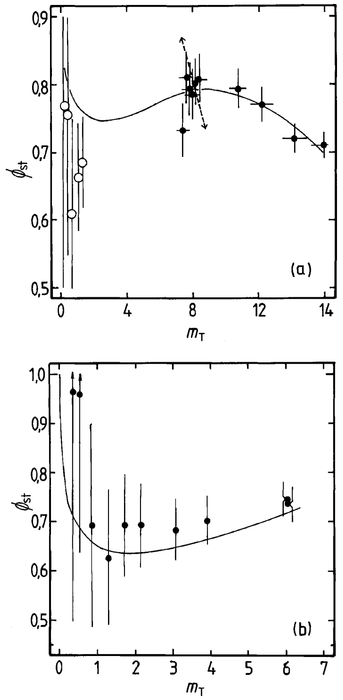

Figure 8. Stoichiometric osmotic coefficients (ϕ_{st}) of aqueous mixtures of $(NH_4)_2SO_4$ and succinic acid at approximately 298 K, plotted against total molality (m_T). (a) 1:1 mole ratio mixtures. Key: open circle, Choi and Chan[17] (bulk solution water activities); dot, Choi and Chan[17] (edb measurements); line, calculated using the Pitzer model developed in this work. (b) Mixtures of eutonic composition (dry mole fraction of acid equal to 0.0409). Key: dot, Wise et al.;[32] line, calculated by the model.

The value of λ_{H_2Succ,NO_3} determined from solubilities in HNO_3 solutions is −0.0504. The data for solubilities in solutions of NH_3 and succinic acid, discussed above, suggest that λ_{H_2Succ,NH_4} lies in the range 0.05 to 0.075. Adding the values together yields a combined salting parameter at 298.15 K that agrees well with the estimates determined from the solubility polytherm and is shown in Figure 7. This consistency between interaction parameters determined from different data sets is encouraging.

3.1.6. $(NH_4)_2SO_4-H_2Succ-H_2O$. Choi and Chan[17] have measured water activities of 1:1 (molar ratio) mixtures in both bulk solution and edb experiments. Water activities of the eutonic mixture ($XH_2Succ = 0.0409 \pm 0.001$ at 297.15 K) have been determined by Wise et al.[32] We have used the results of Choi and Chan to determine $(2\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,SO_4}) = 0.0935$ and $\zeta_{H_2Succ,NH_4,SO_4} = -0.00747$, see Figure 8a. The bulk solution data, all at very low molality, appear to be in error by a small amount, and the values of the parameters are determined almost entirely from the edb measurements for supersaturated solutions. These have been standardized to agree with ZSR predictions of particle water content at a relative humidity of about 80%,[17] and the osmotic coefficients shown in Figure 8 are dependent upon this. For a total molality $m_T = 8$ mol kg^{-1} the value of ϕ_{st} is about 0.8. A moderate change of +0.02 in the mass fraction of solute in the edb particles would change m_T to 8.66 and decrease ϕ to 0.739. Similarly, a decrease of −0.02 in the mass fraction of solute changes m_T to 7.38 mol kg^{-1} and ϕ_{st} to 0.867. These variations are shown on Figure and clearly would be great enough to influence the fitted values of the parameters.

A second source of uncertainty, though somewhat less important, is the effect of the dissociation of H_2Succ which is enhanced by the presence of SO_4^{2-} (and consequent formation of HSO_4^-). Speciation in the solutions has been calculated using the full set of parameters listed in Table 2. Substitution of

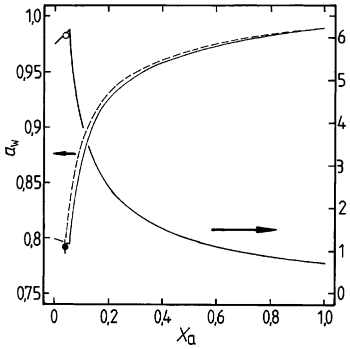

Figure 9. Deliquescence of a mixture of succinic acid and $(NH_4)_2SO_4$ at 298.15 K. Left-hand axis: water activities (a_w) of the saturated aqueous solutions are plotted against the dry mole fraction of acid (X_a). Key: dot, Wise et al.,[32] for the eutonic point; solid line, calculated using the model with $\lambda_{H_2Succ,NH_4} = 0.06$; dashed line, calculated using the model with $\lambda_{H_2Succ,NH_4} = 0.075$. Right-hand axis, total molality (m_T) of the saturated aqueous solutions. Key: open circle, Wise et al.,[32] for the eutonic point; solid line, calculated using the model with $\lambda_{H_2Succ,NH_4} = 0.06$.

$NH_4^+{-}HSO_4^-$ and $NH_4^+{-}SO_4^{2-}$ parameters in place of those involving NH_4^+ and $HSucc^-$ and $Succ^{2-}$, to simulate a variation in the strongest interactions affecting the speciation, yielded ($2\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,SO_4}) = 0.106$ and $\zeta_{H_2Succ,NH_4,SO_4} = -0.0081$. These values do not differ greatly from those previously determined and suggest a limited sensitivity to the effects of dissociation. Adopting $\lambda_{H_2Succ,NH_4} = 0.06$ (see previous section) we obtain $\lambda_{H_2Succ,SO_4} = 0.0935 - 0.12 = -0.0265$.

Calculated osmotic coefficients of solutions of eutonic composition are compared with values from the water activity measurements of Wise et al.[32] in Figure 8b. There is good agreement, as would be expected for a solution that contains mostly $(NH_4)_2SO_4$.

The calculated DRH curve of the mixture is shown in Figure 9, together with the water activity of the eutonic solution measured by Wise et al.[32] The predicted eutonic composition, using the Pitzer model parameter set listed in Table 2, is 0.058 at 297.15 K, a little greater than determined by Brooks et al.[33] ($XH_2Succ = 0.0409 \pm 0.001$, at the same temperature). The calculated eutonic composition is quite sensitive to the value of the combined mixture parameters ($2\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,SO_4}$). Increasing λ_{H_2Succ,NH_4} from 0.06 to 0.075 yields a predicted eutonic composition of $XH_2Succ = 0.041$ which agrees with the measured value. This higher value of λ_{H_2Succ,NH_4} is within the range estimated in section 3.1.4, suggesting both that the parameters determined from the different data sets are reasonably consistent, and possibly that the sum ($2\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,SO_4}$) determined here is too low by about $2 \times 0.015 = 0.03$. While this is possible, the value of λ_{H_2Succ,NH_4} determined from other data is not certain enough to draw firm conclusions. Measurements of the solubility of succinic acid in aqueous ammonium chloride would be valuable, as they would allow the sum ($\lambda_{H_2Succ,NH_4} + \lambda_{H_2Succ,Cl}$), hence λ_{H_2Succ,NH_4}, to be determined directly.

3.1.7. $H_2SO_4{-}H_2Succ{-}H_2O$. Solubilities of H_2Succ in aqueous H_2SO_4 were taken from the compilation of Stephen and Stephen.[31] Assigning $\lambda_{H_2Succ,SO_4} = -0.0265$ and $\lambda_{H_2Succ,H} = 0.1$, a fit of the measured solubilities to 6.6 mol kg^{-1} H_2SO_4 yielded $\lambda_{H_2Succ,HSO_4} = 0.0436$ and $\zeta_{H_2Succ,H,HSO_4} = -0.0176$. The SO_4^{2-} ion is present in the solutions at a lower molality than HSO_4^- and it was assumed that ζ_{H_2Succ,H,SO_4} has the same value as ζ_{H_2Succ,H,HSO_4}, because the two cannot be determined independently from the data. The value of ζ_{H_2Succ,H,SO_4} might be expected to be the greater in magnitude of the two parameters, because of the higher charge on the SO_4^{2-} ion, but it is not possible to assign a value to this. The results of the fit are shown in Figure 10.

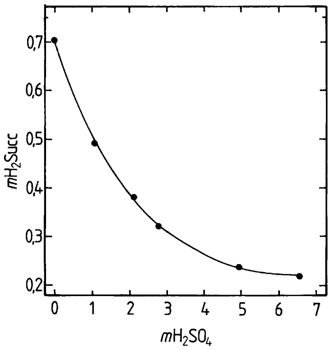

Figure 10. Succinic acid solubilities in aqueous H_2SO_4 at 298.15 K. Key: dot, data from the compilation of Stephen and Stephen;[31] line, the fitted model.

The dissociation of succinic acid and the other dicarboxylic acids, yielding H^+(aq) and two organic ions, means that there are a large number of possible ion−ion and neutral−ion interactions even in mixtures containing only one or two other solutes. However, there are also relatively few data from which parameters can be determined. This means that the thermodynamic properties of solutions containing most of the dicarboxylic acids, particularly those that are more strongly dissociated, can only be calculated if some approximations are adopted. In dilute aqueous solutions the use of analogue parameters such as those for interactions between cations and HSO_4^- and SO_4^{2-} (for hydrogen carboxylate and carboxylate), are likely to give reasonable results.

The parameterization developed here for solutions containing succinic acid should be used only over the ranges of molality of the data used for fitting. A number of the ion−neutral $\lambda_{n,i}$ parameters have large values compared to the corresponding parameters for less strongly interacting species such as NH_3(aq), and they may have an unrealistically large effect on calculated activity coefficients in concentrated solutions.

3.2. Systems $H^+{-}Na^+{-}HMalo^-{-}Malo^{2-}{-}Cl^-{-}H_2Malo{-}H_2O$ and $H_2Malo{-}H_2SO_4{-}H_2O$. The availability of data for solution mixtures containing these components is summarized in Table 3. The principal unknown parameters for the first system are β^0, β^1, $C^{0\phi}$, and $C^{1\phi}$ for $Na^+{-}HMalo^-$ and $Na^+{-}Malo^{2-}$ interactions, $\lambda_{H_2Malo,H}$, $\lambda_{H_2Malo,Na}$, and $\lambda_{H_2Malo,Cl}$. There are also a number of possible binary and ternary ion−ion parameters ($\theta_{i,i'}$ and $\psi_{i,i',j}$) and neutral−ion parameters ($\zeta_{H_2Malo,i,j}$). Values of parameters involving only the ions H^+, Na^+, Cl^-, and OH^- were taken from the literature, as before, and are listed in Table 2. All others were determined in this study.

There are fewer solubility data for solutions containing malonic acid than for systems containing succinic acid. The only measurements for mixtures appear to be those of Knox and Richards[35] for malonic acid solubilities in aqueous HCl and H_2SO_4 solutions, and compositions of eutonic mixtures determined by Brooks et al.[33] and by Wise et al.[32] Knox and Richards[35] tabulate saturated solution compositions in terms of normality (equal to the molarity of a monobasic acid such as HCl, and twice the molarity for diacids H_2Malo and H_2SO_4). These values were converted to molality using densities of dilute solutions of malonic acid tabulated by Timmermans,[36] combined with an estimate for the pure aqueous saturated solution derived from the normality listed by Knox and Richards and the molality in Table 3 of ref 4. Densities of pure aqueous HCl and H_2SO_4

TABLE 3: Sources of Solubility and Activity Data for Na^+ Malonates and for Aqueous Acid Malonate Mixtures[f]

solute 1	solute2	t (°C)	used	data type[a]	source
NaHMalo	−	25	yes	ϕ	62
Na_2Malo	−	25	yes	edb, a_w	63
H_2Malo	NaCl	0−100	yes	K*	51
H_2Malo	NaCl	18	yes	K*	21
H_2Malo	NaCl	22, 20−23	yes	edb, a_w	17
H_2Malo	HCl	25	yes	solu[b]	35
H_2Malo	H_2SO_4	25	yes	solu[b]	35
H_2Malo	$(NH_4)_2SO_4$	22, 20−23	no	edb, a_w	17
H_2Malo	$(NH_4)_2SO_4$	25	no	a_w, DRH	32
H_2Malo	$(NH_4)_2SO_4$	4, 9, 24	no	DRH	33
H_2Malo	$(NH_4)_2SO_4$	20	no	DRH	84
H_2malo	$(NH_4)_2SO_4$	30	no	gf	85
NaHMalo	NaCl	25	no[c]	emf	50
NaHMalo	Na_2Malo + NaCl	25	yes	emf[d]	49
NaHMalo	Na_2Malo + NaCl	0−60	yes	emf[d]	53
Na_2Malo	NaCl	25	yes	emf[e]	52

[a] Key: ϕ, stoichiometric osmotic coefficient; edb, electrodynamic balance measurements of water activities of supersaturated aqueous solutions; a_w, water activities of bulk aqueous solutions; solu, solubility in water; emf, electromotive force measurements yielding activities or activity coefficients; K*, stoichiometric dissociation constant; DRH, relative humidity of deliquescence, equivalent to the water activity of a solution saturated with respect to one or more solutes; gf, hygroscopic growth factor of aerosol particles. [b] Solution compositions given as normalities. [c] See text. [d] Data yielding activities of HCl. [e] Data yielding γ_{NaCl}. [f] Additional sources of data either not used, or for interactions with other salts: Freezing point depressions of Na^+ salts of dicarboxylic acids;[75] phase transitions in $(NH_4)_2SO_4/H_2$Malo aerosols studied by spectrometry;[86] densities and surface tensions of Na_2Malo in very dilute solutions;[39] heat capacities and densities of Na_2Malo solutions;[38] salt effects on the dissociation of malonic and other dicarboxylic acids.[73,74,87]

were taken from Sohnel and Novotny,[37] and the densities of the mixtures estimated as described in ref 4.

Solubilities of sodium and ammonium malonate and hydrogen malonate salts in water do not appear to have been measured. Densities and heat capacities of aqueous Na_2Malo have been determined by Tromans[38] to about 4 mol kg^{-1} at 298.15 K. Tromans[34] was unable to prepare a 5 mol kg^{-1} solution, suggesting that the solubility lies between these two molalities at room temperature. Solid sodium malonate is available in both anhydrous form and as a monohydrate. Presumably the latter is the equilibrium form at 298.15 K, as is the corresponding succinate salt. Sodium malonate also has a solubility of at least 1 mol kg^{-1} at 273.15 K, since densities, viscosities, and freezing point depressions of aqueous solutions of the salt have been measured at this temperature.[39] McPherson[40] states that solutions of sodium malonate at neutral pH have solubilities of about 4 M (this appears to be a molality, not a molarity), though it is unclear whether this is at the temperature of 17 °C at which his experiments were carried out. It is worth noting that the neutral pH mentioned would require the addition of some acid to the solution, as calculations suggest that a solution of pure aqueous sodium malonate would have a pH ($-\log 10(mH^+)$) of about 9.5 due to the formation of hydrogen malonate ion in solution. The solubility of 14.8 M in McPherson's Table 2 appears to be a typographical error, or may be the solubility of malonic acid. No data have been found for sodium hydrogen malonate solubilities.

McMaster and co-workers[41−43] have described the preparation, and some of the properties, of ammonium salts of a number of organic acids including the dicarboxylic acids of interest here. Behavior such as a tendency to deliquesce (generally only those compounds with carboxylate groups on the same carbon atom), or to give off ammonia, are noted but the solubilities in water are not determined. No other data have been found for ammonium malonate or hydrogen malonate salts although Chapuis et al.,[44] citing McMaster[41] and Finkelstein,[45] have stated that re-crystallization of commercial ammonium malonate from water yields the acid salt. It is also worth noting that lithium and sodium superacid malonate salts can be formed (formula {Li or Na}H_3(Malo)$_2$), and that their crystallization−and/or that of the simple dimalonate salts−from aqueous solution can depend on whether the solution is evaporated or cooled.[46,47] The formation of the superacid potassium succinate salt has been investigated by Marshall and Cameron.[48]

The emf studies of Esteso and co-workers[49,50,52] are of particular importance for defining the properties of the system. We have excluded one data set[50] for γ_{NaCl} in aqueous NaHMalo−NaCl mixtures. During the development of the model it became clear that these data were inconsistent with other measurements for the system. A possible reason is the use of a glass Na^+ electrode and a reference cell (containing pure aqueous NaCl) which could not have been at the same ionic strength as the test solutions, because of the dissociation of the hydrogen malonate ion. Esteso and co-workers[49,50] have also applied the Pitzer model to represent activity and osmotic coefficients in the systems they measured. However, their parameters for Na^+−HMalo$^-$ interactions are incorrect due to the neglect of malonate dissociation equilibria, as was the case for the succinic acid system discussed earlier. We have therefore not made use of their model treatment.

Water activities and deliquescence relative humidities are the principal data for mixtures of malonic acid and ammonium sulfate; see Table 3. We have not attempted to develop a Pitzer model of the system H^+−NH_4^+−HMalo$^-$−Malo^{2-}−SO_4^{2-}−H_2O because the available data are insufficient to determine the NH_4^+−HMalo$^-$ and NH_4^+−Malo^{2-} interaction parameters. In acid sulfate systems, these are more important than would be the case for the corresponding succinates because of the greater degree of dissociation of malonic acid. However, the thermodynamic data for this system have been used for a number of model comparisons and tests.

We have assumed that parameters for interactions between H^+ and HMalo$^-$, and between H^+ and Malo^{2-}, are the same as those between the cation and HSO_4^- and SO_4^{2-}, respectively. All of the Pitzer model parameters used or determined in this section are listed in Table 2, and the treatment of the different systems is described below.

3.2.1. Aqueous Malonic Acid. The Pitzer model was fitted to the same data as were used in ref 4 (see Table 2 of that work for sources), up to the saturation concentration of 15.3 mol kg^{-1}. The result is shown in Figure 11. The trend in the stoichiometric osmotic coefficient of the solution to a value of 3.0 at infinite dilution is now correctly reproduced because the dissociation of the acid is here treated explicitly.

3.2.2. {HCl, H_2SO_4}−H_2Malo−H_2O. These two systems have been studied by Knox and Richards.[35] Malonic acid is salted out by both electrolytes at low to moderate concentration, changing to salting in—increases in solubility—above about 8 to 10 mol dm^{-3} of acid. In these solutions the dissociation of malonic acid is effectively suppressed, and the solutions can be treated as containing only the undissociated acid molecule. Thus, in pure aqueous HCl, the activity coefficient of malonic acid is given by (see eq A4):

$$\ln(\gamma_{H_2Malo}) = 2mH_2Malo(\lambda_{H_2Malo,H_2Malo} + \lambda^*_{H_2Malo}(g(x) + g'(x))) + 3mH_2Malo^2\,\mu_{H_2Malo,H_2Malo,H_2Malo} + 2mHCl(\lambda_{H_2Malo,H} + \lambda_{H_2Malo,Cl}) + mHCl^2\zeta_{H_2Malo,H,Cl} \quad (7)$$

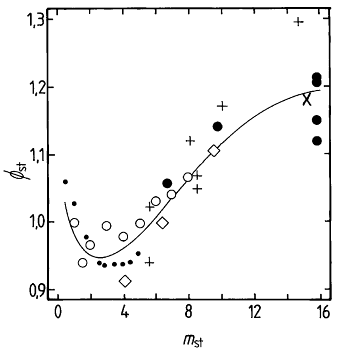

Figure 11. Osmotic coefficients (ϕ_{st}) of aqueous malonic acid at 298.15 K, plotted against the stoichiometric molality (m_{st}). Key: open circle, Peng et al.[91] (bulk solution data); dot, Davies and Thomas;[89] diamond, Maffia and Meirelles;[90] cross, Marcolli et al.;[92] plus, Peng et al.[91] (edb data); filled circle, Wise et al.;[32] line, the fitted model. See Figure 3c of ref 4 for the uncertainties associated with each data point.

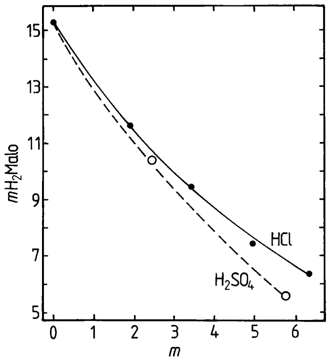

Figure 12. Malonic acid solubilities (mH_2Malo) in acid solutions at 298.15 K, plotted against the molality (m) of the inorganic acid. Key: dot, Knox and Richards[35] for aqueous HCl; open circle, Knox and Richards[35] for aqueous H_2SO_4; lines, the fitted model.

TABLE 4: Values of the Parameter λ_{H_2Malo,HSO_4} Determined from Malonic Acid Solubilities in Aqueous H_2SO_4[a]

λ_{H_2Malo,SO_4} (fixed)	λ_{H_2Malo,HSO_4} (fitted)
−0.125	0.0282
−0.10	0.005 39
−0.05	−0.00149
0.0	−0.00098
0.05	0.000535
0.10	0.001 99
0.125	0.002 62

[a] The value of $\lambda_{H_2Malo,H}$ is fixed at 0.107.

where prefix m denotes molality, and functions $g(x)$ and $g'(x)$ (where $x = \alpha_{H_2Malo}\sqrt{mH_2Malo}$) are given in the appendix of Clegg et al.[9] Values of $(\lambda_{H_2Malo,H} + \lambda_{H_2Malo,Cl}) = 0.1015$ and $\zeta_{H_2Malo,H,Cl} = -0.00412$ were determined from the solubilities in aqueous HCl, and the results are shown in Figure 12. Work with the system discussed in the next section showed that a value of $\lambda_{H_2Malo,Cl} = -0.0055$ was optimum, hence $\lambda_{H_2Malo,H} = 0.107$.

The model treatment of malonic acid solubilities in aqueous H_2SO_4 is complicated by the fact that both HSO_4^- and SO_4^{2-} ions are present, and both λ_{H_2Malo,HSO_4} and λ_{H_2Malo,SO_4} can be expected to have nonzero values. Table 4 shows the results of fits carried out to determine λ_{H_2Malo,HSO_4} for a range of fixed λ_{H_2Malo,SO_4}. Values of λ_{H_2Malo,HSO_4} are generally small. The fact that they do not appear to vary in a regular way with λ_{H_2Malo,SO_4} is probably because the calculated speciation (i.e., $mHSO_4^-$ and mSO_4^{2-}) is dependent upon both interaction parameters and because there are only two data points to fit. The plotted line in Figure 12 is for the parameter pair $\lambda_{H_2Malo,HSO_4} = -0.00098$, $\lambda_{H_2Malo,SO_4} = 0$. The optimum value of λ_{H_2Malo,SO_4} could be best determined from malonic acid solubilities in aqueous Na_2SO_4, because parameters for the $Na^+-HMalo^-$, Na^+-Malo^{2-}, and Na^+-H_2Malo interactions have been determined from other data. However, no such measurements are available.

3.2.3. $H^+-Na^+-HMalo^--Malo^{2-}-Cl^--H_2Malo-H_2O$.

The data for this system, see Table 3, are comparable in extent to those for the analogous system containing succinic acid except for the lack of solubility data for malonate salts. The measurements include K_1^* and K_2^* in aqueous NaCl, emf data yielding γ_{HCl} and HCl activities in aqueous mixtures containing NaHMalo and Na_2Malo, and data for water activities of aqueous Na_2Malo, NaHMalo and $NaCl-H_2Malo$ mixtures from isopiestic and edb measurements. The Pitzer model of the system was developed first for a few individual mixtures, and then optimized in a single fit of all the nonzero-weighted data. The model parameters for this system are listed in Table 2, and all the results shown in Figure 13.

Stoichiometric osmotic coefficients of aqueous Na_2Malo and NaHMalo, shown in Figures 13a,b, are fitted well though there is quite a large uncertainty associated with the bulk solution and edb data for Na_2Malo.

The K_1^* and K_2^* measurements of Adell[21] were converted to 298.15 K using enthalpies and heat capacities given by Kettler et al.[51] and were found to agree with the dissociation constants of Kettler et al. The data are represented well by the fitted model, see Figure 13c.

Emfs of $NaCl-Na_2Malo$ aqueous mixtures,[52] for a range of compositions and total ionic strengths, were fitted as γ_{NaCl} and are shown in Figure 13d,e. The emf measurements of Hamer et al.[53] are for dilute aqueous solutions, and the compositions were chosen in order to determine the second dissociation constant of malonic acid. Consequently $HMalo^-$ and $Malo^{2-}$ are the dominant malonate species. This is also true of the measurements of Fernandez-Merida et al.[49] at higher molalities. Both data sets were fitted directly as emfs and the results are shown in Figure 13f. A small offset of −0.255 mV was applied to the data of Fernandez-Merida et al. to bring them into agreement with those of Hamer et al.[53] This small difference is probably due to the electrode systems used, and is not unusual even for different preparations of the same electrode. Both sets of measurements are represented to within about ±0.2 mV, which is typical of the overall uncertainty associated with such studies.

The last set of measurements used to develop the model are water activities from bulk solution and edb experiments on aqueous $H_2Malo-NaCl$ (1:1 mole ratio). This stoichiometry is equivalent to $NaHMalo-HCl$, and such solutions may have a significant HCl vapor pressure. However, the edb measurements of Choi and Chan[17] were made using the rapid “step” (SEDB) technique, which would tend to minimize HCl loss from the suspended particles. The treatment of the data over the full concentration range using the ZSR method, described in ref 4, did not find evidence that HCl loss occurred to any significant extent. The data are fitted well by the Pitzer model, see Figure 13g, up to 6 mol kg^{-1} molality for each component.

This parameterization for malonic acid mixtures enables speciation, activity coefficients, and water activities to be calculated for solutions containing up to about 6 mol kg^{-1} of salts. We base this limit on both the general capabilities of the model, and the concentration ranges for which the data for the solution mixtures are available.

The parameterization presented here for malonic acid mixtures is not unique, as was also the case for mixtures containing

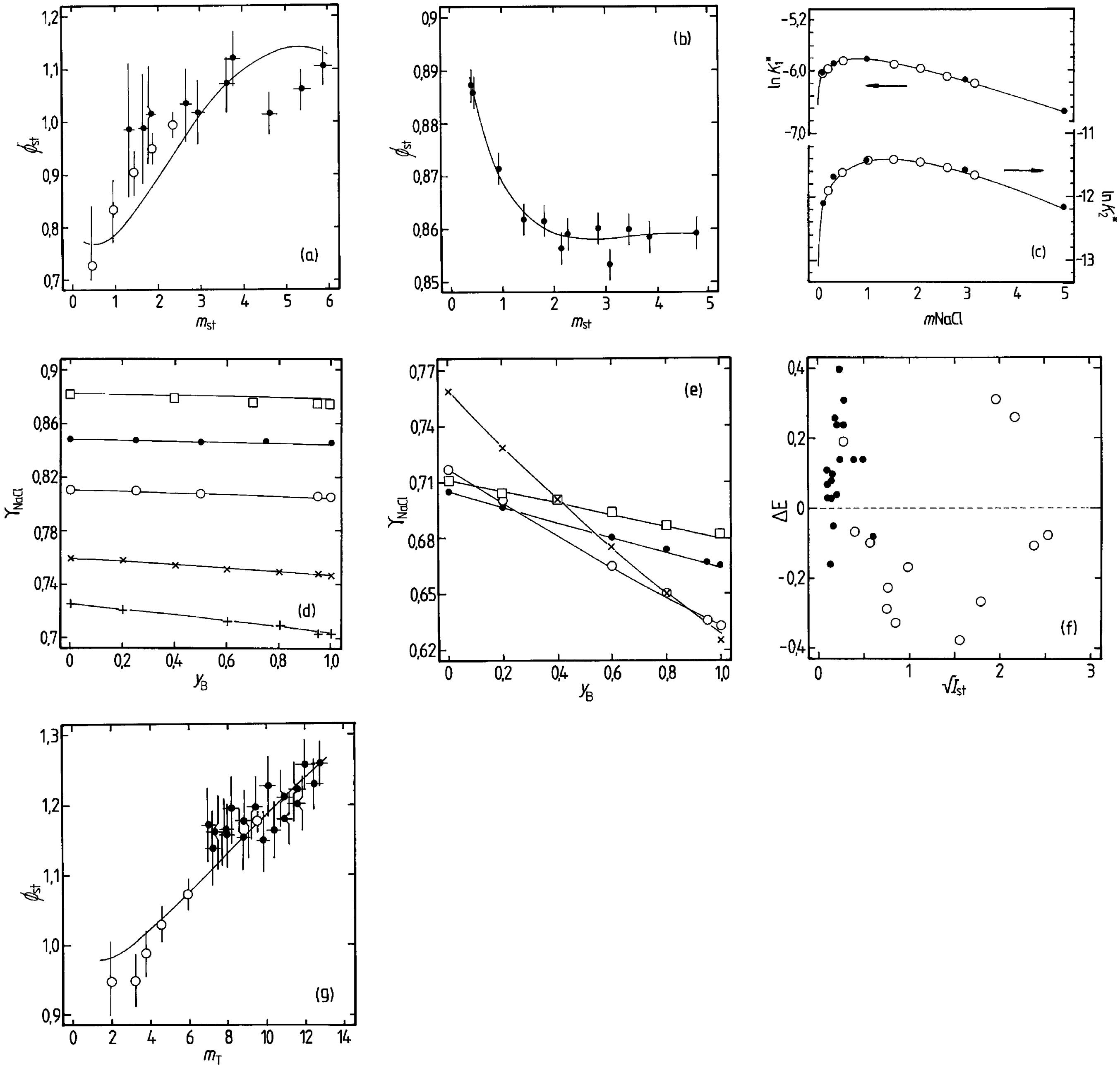

Figure 13. Measured and fitted quantities for solutions containing malonic acid. (a) Stoichiometric osmotic coefficients (ϕ_{st}) of aqueous Na_2Malo at 298.15 K, plotted against molality (m_{st}). Key: open circle, Peng and Chan[62] (bulk solution measurements); dot, Peng and Chan[62] (edb measurements); solid line, the fitted model. (b) Stoichiometric osmotic coefficients of aqueous NaHMalo (treating NaHMalo as a 1:1 electrolyte) at 298.15 K, plotted against molality (m_{st}). Key: dot, Stokes;[62] line, the fitted model. (c) Stoichiometric first (K_1^*) and second (K_2^*) dissociation constants of malonic acid in aqueous NaCl at 298.15 K, plotted against NaCl molality. Key: dot, Kettler et al.;[20] open circle, Adell;[21] lines, the fitted model. (d) Mean activity coefficients of NaCl in aqueous NaCl−Na_2Malo mixtures at 298.15 K, plotted against the ionic strength fraction (y_B) of Na_2Malo. Data are from Fernandez-Merida et al.[52] at the following ionic strengths: square, 0.025; dot, 0.05; open circle, 0.10; cross, 0.25; plus, 0.50. The lines represent the fitted model. (e) Same as for part d, but at the following ionic strengths: square, 0.75; dot, 1.0; open circle, 2.0; cross, 3.0. (f) Differences between measured and fitted emfs (ΔE/mV), for experiments yielding HCl activities in NaCl−NaHMalo−Na_2Malo aqueous solutions at 298.15 K, plotted against the square root of the stoichiometric ionic strength (I_{st}). Key: dot, Hamer et al.;[53] open circle, Fernandez-Merida et al.[49] (For plotting, the ionic strength I_{st} was calculated on the basis of complete dissociation of NaHMalo.) (g) Stoichiometric osmotic coefficients (ϕ_{st}) of 1:1 (mole ratio) aqueous mixtures of NaCl and malonic acid at approximately 298 K, plotted against total molality (m_T). Key: open circle, Choi and Chan[17] (bulk solution water activities); dot, Choi and Chan[17] (edb measurements); line, the fitted model.

succinic acid. In particular, we note that the data could be fitted almost equally well for a range of different values of $\lambda_{H_2Malo,HMalo}$. We also note that the $\lambda_{H_2Malo,H}$ and $\lambda_{H_2Malo,HMalo}$ parameters determined here affect calculated osmotic and activity coefficients of pure aqueous H_2Malo. However, the fact that dissociation is relatively slight and that the parameters have opposite signs (so that the effects of the two ions on the undissociated acid almost cancel) means that their net effect is small. Further improvements to the model would probably require measurements that provide further information on the speciation in solution, such as emfs yielding HCl activities.

4. Modeling Schemes

In this work, we have developed activity coefficient models of aqueous solutions containing succinic acid, and malonic acid, in which both dissociation equilibria are treated explicitly. Because data are limited, even for these two common acids, the models are useful mainly as a test of approximations and assumptions to be applied in more complex systems rather than as elements of a practical atmospheric model.

In ref 4, the method of Clegg et al.[5] and the extended ZSR model of Clegg and Seinfeld[7] were tested in applications to multicomponent mixtures of dicarboxylic acids and salts. The extended ZSR approach gave generally more accurate results but, for reasons noted in ref 4, is not readily applied to dissociation equilibria. This problem is now explored further, using one of the Pitzer models developed above as a reference. First, consider a system in which aqueous H_2SO_4 is one component and a dissociating dicarboxylic acid is the second. In the extended ZSR model the inorganic ions H^+, HSO_4^-, and SO_4^{2-} would be treated as a subgroup of *r* solutes, and the stoichiometric activity coefficient of H_2SO_4 and water activity contributions of the ions would be calculated using a model such as AIM.[55] The dicarboxylic acid could readily be treated as a separate, undissociated, component *q*. The more general case where the electrolyte element of the solution contains multiple ions in addition to those from H_2SO_4, and there are an arbitrary number of uncharged nondissociating solutes, is also straightforwardly treated by ZSR.

However, difficulties arise when one or more of the uncharged solutes dissociate. Taking malonic acid as an example, the ions $HMalo^-$, $Malo^{2-}$, and additional H^+ arising from the dissociation would be included in electrolyte subgroup *r*, leaving the remaining undissociated H_2Malo as individual solute *q*. The degree of dissociation of the malonic acid of course varies with solution composition and concentration. However, the derivation of the ZSR expression for activity coefficients (eqs 32 and 34 of Clegg and Seinfeld[7]) requires that the relative amounts of the different solutes be fixed. In the present example these would be the stoichiometric quantities of each solute in the electrolyte element of the solution, and the number of moles of undissociated malonic acid. Test calculations involving direct integration of water activities using the McKay−Perring equation[54] have confirmed this, showing that activity coefficients calculated using eqs 31 and 32 of Clegg and Seinfeld[7] are thermodynamically consistent with the solution water activity only if the degree of dissociation is fixed (i.e., has the same value) at all water activities. This inconsistency appears to be significant, but it is unclear whether it entirely precludes the use of extended ZSR to estimate both water activities and solute activity coefficients in systems in which the organic components dissociate. We have therefore carried out a number of calculations to test this, and these are described below.

Case 1. We first consider a system of pure aqueous malonic acid. In the extended ZSR model the ions H^+, $HMalo^-$, and $Malo^{2-}$ are treated as an electrolyte subgroup r of solutes and the undissociated form of the acid is considered as a separate component. Activity coefficients are calculated from eqs 33 and 34 of Clegg and Seinfeld,[7] using eq 5 of ref 4 (with parameters from Table 4 of that work) for the undissociated acid and the Pitzer model for the $H^+-HMalo^--Malo^{2-}$ component. The amounts of H_2Malo and each of the ions are varied iteratively until both dissociation equilibria are obeyed.

The calculated degrees of total dissociation α, equal to $(mHMalo^- + mMalo^{2-})/mH_2Malo_{(T)}$, are shown as a function of total molality in Figure 14a together with the results of a reference calculation using the Pitzer model. The Pitzer model predicts a steadily increasing mH^+ as total concentration increases, see Figure 14b, and α that approaches 0.012 at the highest total molality. This is reasonable, because the increasing activity of H_2Malo pushes the primary dissociation equilibrium $H_2Malo \leftrightarrow H^+ + HMalo^-$ to the right. By contrast, the extended ZSR model predicts mH^+ that varies little over the entire concentration range, and a degree of dissociation that falls as low as 0.02. The main reason for this is that the activity coefficients of the ions calculated by extended ZSR are based upon values for the $H^+-HMalo^--Malo^{2-}$ component at the water activity of the mixture (the first term in eq 34 of Clegg and Seinfeld[7]). These are then modified by further terms in the water contents of the two components, and an unsymmetrical mixing correction. For systems at low water activity, the calculation for the $H^+-HMalo^--Malo^{2-}$ component therefore requires activity coefficients in very concentrated solutions whose ionic strength exceeds by far that in the real mixture. These activity coefficients appear to be much too high, yielding mH^+ and a degree of dissociation that is unrealistically low. Thus, while the predicted a_w of a pure aqueous dicarboxylic acid, or acid mixture, could be quite accurately estimated using the extended ZSR model (because the undissociated molecules are the dominant species), both mH^+ and α are very poorly predicted for the reasons given above.

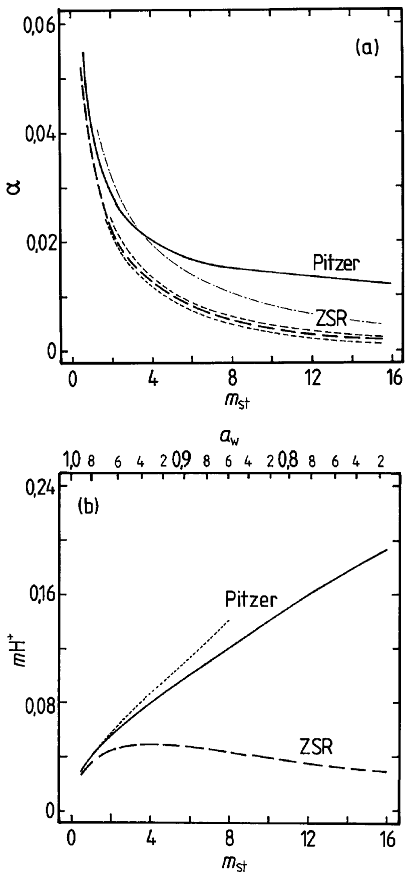

Figure 14. Calculated dissociation of malonic acid in pure aqueous solution at 298.15 K. (a) Degrees of total dissociation (α), plotted against stoichiometric molality (m_{st}). Key: solid line, reference calculation using the Pitzer model developed in this work; heavy dashed line, extended ZSR model (the light dashed lines on either side show the effect of parameter A^0 equal to +2.0 and −2.0 for $H_2Malo-(H^+, HMalo^-)$ interactions); dash−dot line, extended ZSR model without unsymmetrical correction terms. Note that in the Pitzer model calculation the parameters $\lambda_{H_2Malo,H}$ and $\lambda_{H_2Malo,HMalo}$ were set to zero because their effect is likely to be too great at high molality. (b) Calculated H^+ molalities (mH^+) plotted against stoichiometric molality (m_{st}). Key: solid line, reference calculation using the Pitzer model as in (a); dashed line, extended ZSR model; dotted line, Pitzer model with $\lambda_{H_2Malo,H}$ and $\lambda_{H_2Malo,HMalo}$ equal to the values given in Table 2.

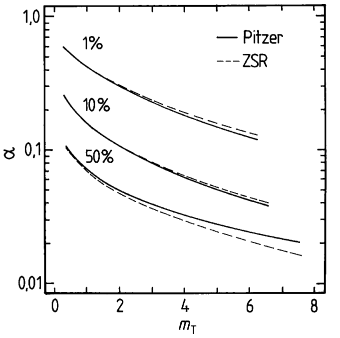

Figure 15. Calculated degrees of total dissociation (α) of malonic acid in aqueous NaCl at 298.15 K, plotted against total molality m_T. Results are shown for solutions containing 1, 10, and 50 mol % malonic acid, using both the Pitzer model (with parameters from Table 2) and extended ZSR models.

Case 2. The above limitations might not apply to the more atmospherically realistic case of small amounts of dicarboxylic acid dissolved in an aqueous electrolyte solution. We therefore carried out a second set of calculations of the degree of dissociation of malonic acid in aqueous solutions of NaCl containing 1, 10, and 50 mol % malonic acid. The undissociated form of the acid is again treated as an independent component *q*, but the electrolyte element of the solution *r* now contains both the ions H^+, $HMalo^-$, and $Malo^{2-}$ and the NaCl supporting electrolyte.

Calculated degrees of dissociation of the acid are compared with reference values obtained using the Pitzer model in Figure 15. The two sets of calculations agree quite well, because the NaCl portion of the electrolyte mixture component mainly determines its water activity. Consequently, the stoichiometric mean activity coefficients of $H^+{-}HMalo^-$ and $H^+{-}Malo^{2-}$ in the electrolyte solution component are calculated at concentrations that are representative of the mixture as a whole, and not at extreme values as in case 1. This is most true of the 1 mol % solution and it is for this composition that the two degrees of dissociation closely agree.

For $NaCl{-}H_2Malo{-}H_2O$, and just a few other simple systems, the ion interaction parameters needed to calculate dissociation using the Pitzer model are known. However, this is not the case for most dicarboxylic acids and other soluble acids that occur in the atmosphere. Consequently analogue parameters, such as HSO_4^- for hydrogen carboxylate and SO_4^{2-} for carboxylate, would generally be used, and mixture parameters such as those listed in Table 2 (both ion−ion and ion−neutral) would be set to zero. To estimate the effects of these uncertainties we have repeated the calculation of α in Figure 15, but using the analogue parameters as noted above. The results, see Figure 16, show that in this particular case the degree of dissociation is reduced, relative to the reference value, by a factor of up to 1.5 at a water activity of 0.75. The calculated activity of the undissociated acid molecule (not shown) is decreased by up to about 25% at the highest molalities.

If the above differences are typical of the effects of uncertainties in the thermodynamic properties of aqueous solutions containing salts and soluble organic acids then the following can be said. First, these differences are of similar magnitude to those between reference calculations of the degree of dissociation and those obtained using the extended ZSR model. This suggests that the thermodynamic inconsistency introduced into extended ZSR by incorporating dissociation equilibria between the organic acid components and electrolyte subgroup may be similar in magnitude to more fundamental uncertainties regarding the thermodynamic properties of the mixture. However, this is only likely to apply to systems in which inorganic electrolytes are major components.

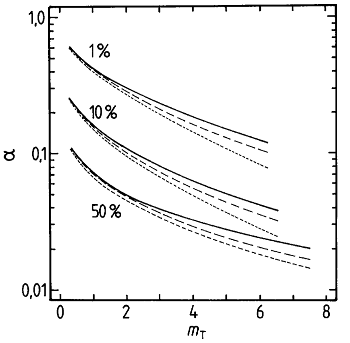

Figure 16. Degrees of total dissociation (α) of malonic acid in aqueous NaCl at 298.15 K and plotted against total molality m_T. Results are shown for solutions containing 1, 10, and 50 mol % percent malonic acid, and were all obtained using the Pitzer models. Key: solid lines, reference calculation, the same as in Figure 15; dashed lines, with all H_2Malo—ion interaction parameters set to zero; fine dashed lines, the same as for the previous case, but also substituting $Na^+{-}HSO_4^-$ and $Na^+{-}SO_4^{2-}$ interaction parameters for $Na^+{-}HMalo^-$ and $Na^+{-}Malo^{2-}$ parameters, respectively.

Second, the lower values of α plotted in Figure 16 for each mol % of acid are equivalent to those that would be obtained using the CSB approach in which the activity coefficients of ions, and the group of neutral solutes, are calculated separately at their molalities in the mixture without any interactions between the neutral solutes and ions. Because these are quite similar to the values obtained from the ZSR predictions, it appears that the extended ZSR method may not have any particular advantage over CSB for estimating dissociation in many practical calculations. This is probably due to a combination of two things: (a) the fact that ZSR is simply an empirical mixing rule, which is not formulated in terms of ions as solution components; (b) the correction for the presence of solutes of different charge type in solution is necessarily approximate, and it has been shown in ref 4 that results are quite sensitive to the parameter *b* in the terms used for this.

Results presented in ref 4 for aqueous dicarboxylic acid mixtures, and mixtures of the acids with salts, have shown that the extended ZSR model is generally more successful than the CSB approach at predicting water activities and deliquescence relative humidities of concentrated aqueous mixtures. The calculations presented above suggest that this advantage does not extend to the prediction of activity coefficients in mixtures that include dissociation equilibria, particularly between different solution components.

A further possibility for a practical model, which we have not investigated here, is the combination of the extended ZSR approach to estimate the water content of solution mixtures, and perhaps the activity coefficients of the uncharged organic solutes, and the CSB approach for all the ions. This is illustrated in Figure 17 for the system shown in Figure 37 of ref 4 and discussed in section 7 of that work. Figure 17 shows three numbered groupings of the solutes to indicate how calculations of water activity and solute activity coefficients could be carried out under this scheme. First is the water activity which can be calculated using the extended ZSR model with N_1 and N_2 as individual solutes, O_1 and O_2 as a subgroup whose combined contribution to water content is calculated by UNIFAC, and the ions as a second subgroup whose contribution to water content would be calculated using AIM[55] or some other electrolyte model. The individual solutes N_1 and N_2 would be components *q* in eq 31 of Clegg and Seinfeld,[7] and the ions

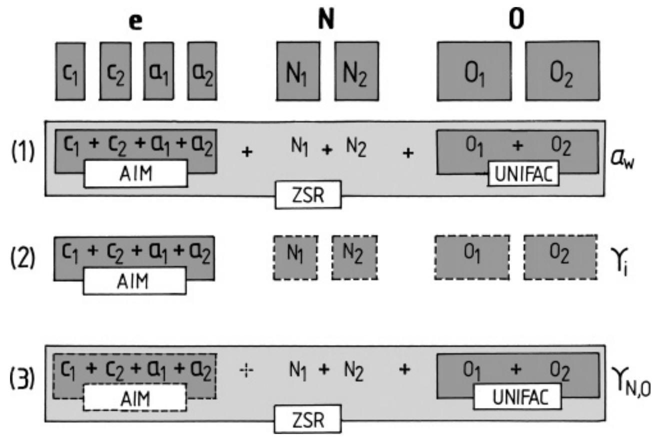

Figure 17. Schematic diagram of an aqueous system consisting of an electrolyte element (**e**), and organic elements **N** and **O**, containing the ions and uncharged solutes listed in the boxes along the top row. The numbered rows (1−3) illustrate approaches for calculating water activities (row number 1) and solute activity coefficients (rows 2 and 3), and are described in the text.

and the pair of solutes O_1 and O_2 would be two subgroups *r* in the equation. The second solute grouping in Figure 17 illustrates the calculation of the ion activity coefficients. These are calculated with the AIM model at the actual ion molalities in the mixture (not at the water activity of the mixture, as would have been the case for a ZSR calculation). In the absence of known interactions between the ions and the other solutes the presence of N_1, N_2, O_1, and O_2 is effectively ignored in this calculation, except that the dissociation of any of these solutes would result in the addition of further ions to the group treated by AIM. The third solute grouping in Figure 17 illustrates the calculation of the activity coefficients of the uncharged solutes. In this case, the extended ZSR approach is used for the entire system, and the presence of the ions affects the calculated activity coefficients through their influence on the total water content of the system (see eqs 33 and 34 in Clegg and Seinfeld[7]). While this approach breaks the link of thermodynamic consistency between solute and solvent activities it may be necessary when either no single model can adequately represent all the properties of the solution, or when one model (ZSR) yields generally better estimates of water activity—a key property for atmospheric aerosol calculations—and is known to be robust.

The method outlined above is similar to the approach taken by Pun et al.,[56] who combined aerosol water contents calculated using ZSR and activity coefficients calculated using SCAPE[57,58] or, more recently, ISORROPIA[59] (Pun[93]). In the model of Pun et al. the activity coefficients of the undissociated organic species are calculated by UNIFAC,[60] at their molalities in the aqueous mixture and ignoring the presence of the ions. The hydrogen carboxylate and dicarboxlyate ions produced by dissociation are added to the electrolyte element of the solution but are assigned activity coefficients of unity. This approach is essentially the same as the CSB method for the calculation of activity coefficients, but coupled with ZSR (without the unsymmetrical correction term, or interaction parameters) for the calculation of solution water content. The tests and comparisons shown in ref 4 suggest that the use of ZSR to estimate the activity coefficients of the organic solutes (case 3 in Figure 17 for solutes O_1 and O_2) might be an improvement on the approach of Pun et al. Also, better estimates of the activity coefficients of the organic anions would certainly be obtained at low to moderate molality by using analogue ions (such as HSO_4^-, and SO_4^{2-}) rather than the assumption of unit activity coefficients.

5. Summary

In this work, we have developed Pitzer ion-interaction models of aqueous solutions containing succinic and malonic acids, including the dissociation of both acids. Their main function is to serve as references, based upon available thermodynamic data, for testing practical models for atmospheric calculations. Even for these common dicarboxylic acids the solubilities of some of the sodium and ammonium salts are unknown, and data are lacking for interactions with some atmospherically important ions such as NH_4^+ and NO_3^-.

These Pitzer models have been used to evaluate the extended ZSR approach for the calculation of activity coefficients and degrees of dissociation in systems containing dissociating acids. It was shown in ref 4 that the extended ZSR generally yields more accurate estimates of water activities and solubilities in multicomponent solutions than the CSB method, for systems not involving dissociation. However, where dissociation does occur a hybrid method of estimating water activities and solute activity coefficients may be best, given the large uncertainties in the properties of atmospheric organic compounds, even though calculated activity coefficients are no longer thermodynamically consistent with water activities.

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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.

Appendix

Fernandez-Merida et al.[10] have proposed extensions to the Pitzer model for the self-interactions of polar uncharged (neutral) species, and between uncharged species and ions. An ionic strength dependent term containing the new parameter $\lambda^*_{n,i}$ is added for neutral−ion interactions, and a molality dependent term (and parameter λ^*_{n}) for the self-interaction of neutral species *n*. Their contributions to the excess Gibbs energy (G^{ex}) of the solution per kilogram of solvent is given by

$$G^{\mathrm{ex}}/w_{\mathrm{w}}RT = \Sigma_{\mathrm{n}}\, m_{\mathrm{n}}^{2}\lambda^*_{\mathrm{n}} g(\alpha_{\mathrm{n}}\sqrt{m_{\mathrm{n}}}) + 2\Sigma_{\mathrm{n}}\Sigma_{\mathrm{c}}\, m_{\mathrm{n}}m_{\mathrm{c}}\lambda^*_{\mathrm{n,c}} g(\alpha_{\mathrm{n,c}}\sqrt{I}) + 2\Sigma_{\mathrm{n}}\Sigma_{\mathrm{a}}\, m_{\mathrm{n}}m_{\mathrm{a}}\lambda^*_{\mathrm{n,a}} g(\alpha_{\mathrm{n,a}}\sqrt{I}) \quad \text{(A1)}$$

where w_{w} (kg) is the mass of solvent, *R* is the gas constant, *T* (K) is temperature, and *m* is molality. Subscript n indicates an uncharged solute species, c an cation, and a an anion. The summations are over all solute species as indicated. Functions $g(x)$ and $g'(x)$ (in the equations below) are given by Pitzer,[8] and α_{n}, $\alpha_{\mathrm{n,c}}$, and $\alpha_{\mathrm{n,a}}$ are coefficients that are usually set to the same values for many solutes, but which can be varied individually if necessary. Symbol *I* (mol kg^{-1}) represents ionic strength. Note that values of $\alpha_{\mathrm{n,c}}$ and $\alpha_{\mathrm{n,a}}$, and $\lambda^*_{\mathrm{n,c}}$ and $\lambda^*_{\mathrm{n,a}}$, cannot be determined independently because of electroneutrality constraints.

Contributions to the osmotic coefficient (ϕ) of the solution, and cation activity coefficient γ_M are obtained by differentiation in the usual way[8] and are given below:

$$\phi - 1 = (2/\Sigma_i\, m_i) \times (0.5\Sigma_\mathrm{n}\, m_\mathrm{n}{}^2\lambda^*_\mathrm{n} \exp(-\alpha_\mathrm{n}\sqrt{m_\mathrm{n}}) + \Sigma_\mathrm{n}\Sigma_\mathrm{c}\, m_\mathrm{n}m_\mathrm{c}\lambda^*_\mathrm{n,c} \exp(-\alpha_\mathrm{n,c}\sqrt{I}) + \Sigma_\mathrm{n}\Sigma_\mathrm{a}\, m_\mathrm{n}m_\mathrm{a}\, \lambda^*_\mathrm{n,a} \exp(-\alpha_\mathrm{n,a}\sqrt{I})) \quad \text{(A2)}$$

$$\ln(\gamma_\mathrm{M}) = z_\mathrm{M}{}^2(\Sigma_\mathrm{n}\Sigma_\mathrm{c}\, m_\mathrm{n}m_\mathrm{c}\, \lambda^*_\mathrm{n,c}\, g'(\alpha_\mathrm{n,c}\sqrt{I})/I + \Sigma_\mathrm{n}\Sigma_\mathrm{a}\, m_\mathrm{n}m_\mathrm{a}\, \lambda^*_\mathrm{n,a}\, g'(\alpha_\mathrm{n,a}\sqrt{I})/I) + 2\Sigma_\mathrm{n}\, m_\mathrm{n}\lambda^*_\mathrm{n,M}\, g(\alpha_\mathrm{n,M}\sqrt{I}) \quad \text{(A3)}$$

where z_M is the magnitude of the charge on cation M. The contributions of the terms in eq A1 to the logarithm of the activity coefficient of an anion X can be obtained from eq A3 by swapping X for M, c for a, and a for c.

The additional terms for the activity coefficient of uncharged solute N are given by

$$\ln(\gamma_\mathrm{N}) = 2m_\mathrm{N}\, \lambda^*_\mathrm{n}(g(\alpha_\mathrm{n}\sqrt{m_\mathrm{N}}) + g'(\alpha_\mathrm{n}\sqrt{m_\mathrm{N}})/2) + \Sigma_\mathrm{c}\, 2m_\mathrm{c}(\lambda^*_\mathrm{n,c}\, g(\alpha_\mathrm{n,c}\sqrt{I})) + \Sigma_\mathrm{a}\, 2m_\mathrm{a}(\lambda^*_\mathrm{n,a}\, g(\alpha_\mathrm{n,a}\sqrt{I})) \quad \text{(A4)}$$

The Pitzer model, in its standard form, uses the interaction parameters $\lambda_{n,i}$ and $\zeta_{n,c,a}$ to express salting-in or salting-out behavior, and terms containing both parameters can produce unrealistically large contributions to osmotic and activity coefficients in highly concentrated solutions. The use of parameters $\lambda^*_{n,i}$ should enable salting effects to be expressed over a wider range, because the expression has an ionic strength dependence.

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