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A Generic and Updatable Pitzer Characterization of Aqueous Binary Electrolyte Solutions at 1 bar and 25 °C

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S *Supporting Information*

ABSTRACT: The thermodynamic properties of the binary aqueous solutions of 183 electrolytes at 25 °C and 1 bar have been fitted using a standard form of the Pitzer equations. Where possible, all thermodynamic properties have been treated simultaneously, in contrast to previous compilations of Pitzer parameters. Prior to fitting, a critical assessment of the available information for each system was made using the JESS database and software. Employing linear regression with singular value decomposition and using an appropriate objective function criterion, more than two-thirds of the systems could be satisfactorily fitted to the upper concentration limit of the available data. Only six electrolytes proved to be completely intractable using the present Pitzer model. All of these systems (which included HF, H_2SO_4, and H_3PO_4) are known to exhibit significant changes in chemical speciation at low concentrations (even though ion association per se does not preclude a satisfactory fit). The present Pitzer ion-interaction parameters provide a coherent, up-to-date set of empirical coefficients that can be combined in a self-consistent manner to produce multicomponent electrolyte solution models having a minimum of computational uncertainty in bulk solution properties such as density, heat capacity, and water activity.

INTRODUCTION

Reliable computational models of the thermodynamic properties of electrolyte solutions are in high demand for industrial,[1−3] analytical,[4] geochemical,[5] and environmental[6−9] purposes and in particular for addressing a variety of globally important problems such as the safe storage of radioactive wastes,[8] ocean acidification,[9] and desalination.[10] However, modeling the thermodynamic properties of *multicomponent* electrolyte solutions, which is required for virtually all practical applications, still remains problematic.[11] Specifically, due to the empirical nature of such models, it is essential to make the data correlation and modeling processes more robust, that is, less sensitive to errors and gaps in the available data.[12,13]

Some success in modeling multicomponent electrolyte solutions has been achieved using Pitzer ternary interaction parameters,[6,7,13] but this approach is limited by the "combinatorial explosion" of parameters required when the number of components is increased.[13] On the other hand, it is well-known[14] that simple mixing rules, such as those of Young for solution densities (molar volumes) or heat capacities[2] and of Zdanovskii for osmotic coefficients (water activities),[15] provide reasonable and robust estimates of the thermodynamic properties of multicomponent strong electrolyte solutions of arbitrary composition at constant temperature and pressure.[2,12,14,15] However, implementation of such mixing rules requires accurate, thermodynamically consistent descriptions of all of the relevant properties of the corresponding *binary* electrolyte solutions. These binary solution properties should be based on a standard, well-proven, and widely accessible theoretical framework, so as to smooth and harmonize the available data. Moreover, it is desirable that the underlying raw (experimental) information should be critically assessed and be as comprehensive and up-to-date as possible.

Despite the plethora of published correlations for the thermodynamic properties of binary strong electrolyte solutions in water, none meets all of the above criteria. Of the many approaches described in the open literature,[16] only the Pitzer formalism[17,18] has been applied to a broad range of modeling applications by researchers who are independent of the model's originator(s). Even so, no comprehensive set of Pitzer coefficients determined simultaneously for all relevant thermodynamic quantities has been published. The major collections of Pitzer parameters are now over 15 years old,[17−23] and many of the more recent studies use "extended" Pitzer equations with empirical coefficients that provide excellent fits but which are inherently incompatible with earlier variants and with each other.

In this work, ion-interaction parameters of over 180 aqueous binary (mostly strong) electrolyte systems have been calculated using a standardized Pitzer model. A least-squares regression analysis of the literature data was employed that simultaneously covered activity coefficients, osmotic coefficients, relative enthalpies, heat capacities, volumes, and absolute or relative densities, at 1 bar and 25 °C. From this self-consistent collection of coefficients, it is possible to calculate with a good degree of confidence any required thermodynamic property for a specified range of electrolyte concentrations, limited only by the availability of good quality data in the literature. A sound, up-to-date platform is thus provided for modeling the thermodynamic properties of multicomponent

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electrolyte solution mixtures, based on either the Pitzer ternary functions or on robust electrolyte mixing rule(s), such as those of Young or Zdanovskii.

■ THEORY

The Pitzer formalism has been described in detail in numerous publications (e.g., refs 17−23), so only a brief outline is presented here. The Pitzer equations relevant to this study of binary strong electrolyte solutions MX(aq) are most conveniently derived[17] from an expression for the excess Gibbs energy, eq 1:

$$G^{E}/(w_{w}RT) = -A_{\varphi}(4Ib^{-1})\ln(1 + bI^{1/2}) + 2\nu_{M}\nu_{X}(m^{2}B_{MX} + m^{3}\nu_{M}z_{M}C_{MX}) \qquad (1)$$

where R and T have their usual meanings, w_w is the mass in kilograms of the solvent (water), A_ϕ is the Debye−Hückel constant for osmotic coefficients (at 25 °C, $A_\phi = 0.39126\ \mathrm{kg^{1/2}\cdot mol^{-1/2}}$), m is the molality of the solute MX, I is the stoichiometric molality-based ionic strength, $\nu = \nu_M + \nu_X$, where ν_M and ν_X are the stoichiometric coefficients of the cation and anion, respectively, and z_i is the formal charge of the ion i. The constant b is temperature- and pressure-independent and is given the value 1.2 for all solutes. The ionic-strength dependence of the second virial coefficient B_{MX} is represented by eq 2, whereas the third virial coefficient C_{MX} is taken to be independent of ionic strength.

$$\begin{aligned} B_{MX} = {} & \beta_{MX}^{(0)} \\ & + 2\beta_{MX}^{(1)}[1 - (1 + \alpha_{1}I^{1/2})\exp(-\alpha_{1}I^{1/2})](\alpha_{1}{}^{2}I)^{-1} \\ & + 2\beta_{MX}^{(2)}[1 - (1 + \alpha_{2}I^{1/2})\exp(-\alpha_{2}I^{1/2})](\alpha_{2}{}^{2}I)^{-1} \end{aligned} \qquad (2)$$

In the original Pitzer equations, α_1 and α_2 are taken as temperature- and pressure-independent; $\alpha_1 = 2$ and $\alpha_2 = 0$ (i.e., $\beta_{MX}^{(2)}$ is not needed) unless both ions are divalent or more highly charged, in which case $\alpha_1 = 1.4$ and $\alpha_2 = 12$ (for 2:2 electrolytes) or $\alpha_1 = 2$ and $\alpha_2 = 50$ (for 3:2 electrolytes) and $\beta_{MX}^{(2)}$ is included. Thus at a fixed pressure and temperature, G^E is expressed in terms of up to four adjustable parameters: $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}, per binary electrolyte.

Expressions for other excess thermodynamic quantities can be derived from G^E in a thermodynamically consistent manner.[17] The osmotic coefficient of the solvent, ϕ, and the activity coefficients of the solutes, γ_i, are obtained by appropriate partial differentiation of G^E with respect to composition. Apparent molar enthalpies, heat capacities, volumes, and compressibilities are related to the first and second partial derivatives of G^E with respect to temperature and pressure. Since these differentiations are carried out only on the Debye−Hückel coefficient and the Pitzer parameters (but not on the temperature- and pressure-independent molalities and constants α_1, α_2, and b), the mathematical form of eq 1 is retained.

For a binary electrolyte solution at a fixed temperature and pressure, the pertinent thermodynamic equations for the osmotic coefficient, mean ionic activity coefficient, apparent molar relative enthalpy, ${}^{\phi}L$, apparent molar heat capacity, ${}^{\phi}C_p$, and apparent molar volume, ${}^{\phi}V$, are:[8]

$$\phi = 1 - A_{\varphi}|z_{M}z_{X}|I^{1/2}/(1 + bI^{1/2}) + m(2\nu_{M}\nu_{X}/\nu)B_{MX}^{\varphi} + m^{2}[2(\nu_{M}\nu_{X})^{3/2}/\nu]C_{MX}^{\varphi} \qquad (3)$$

$$\begin{aligned} \ln\gamma_{\pm} = {} & -A_{\varphi}|z_{M}z_{X}|[I^{1/2}/(1 + bI^{1/2}) \\ & + (2/b)\ln(1 + bI^{1/2})] + m(2\nu_{M}\nu_{X}/\nu)[B_{MX} + B_{MX}^{\varphi}] \\ & + m^{2}[3(\nu_{M}\nu_{X})^{3/2}/\nu]C_{MX}^{\varphi} \end{aligned} \qquad (4)$$

$${}^{\phi}L = \nu|z_{M}z_{X}|(A_{L}/2b)\ln(1 + bI^{1/2}) + \nu_{M}\nu_{X}R[2mB_{MX}^{L} + m^{2}(\nu_{M}\nu_{X})^{1/2}C_{MX}^{\varphi L}] \qquad (5)$$

$${}^{\phi}C_{p} = C_{p}^{0} + \nu|z_{M}z_{X}|(A_{J}/2b)\ln(1 + bI^{1/2}) - \nu_{M}\nu_{X}R[2mB_{MX}^{J} + m^{2}(\nu_{M}\nu_{X})^{1/2}C_{MX}^{\varphi J}] \qquad (6)$$

$${}^{\phi}V = V^{0} + \nu|z_{M}z_{X}|(A_{V}/2b)\ln(1 + bI^{1/2}) + \nu_{M}\nu_{X}RT[2mB_{MX}^{V} + m^{2}(\nu_{M}\nu_{X})^{1/2}C_{MX}^{\varphi V}] \qquad (7)$$

The Debye−Hückel constants are given by A_L (at 25 °C, $A_L/RT = 0.7956\ \mathrm{kg^{1/2}\cdot mol^{-1/2}}$) for enthalpy, A_J (at 25 °C, $A_J/RT = 3.82\ \mathrm{kg^{1/2}\cdot mol^{-1/2}}$) for heat capacity, and A_V (at 25 °C, $A_V = 1.898\ \mathrm{cm^{3}\cdot kg^{1/2}\cdot mol^{-3/2}}$) for volume. Useful relations required in the above equations are:

$$B_{MX}^{\varphi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}\exp(-\alpha_{1}I^{1/2}) + \beta_{MX}^{(2)}\exp(-\alpha_{2}I^{1/2}) \qquad (8)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}g(\alpha_{1}I^{1/2}) + \beta_{MX}^{(2)}g(\alpha_{2}I^{1/2}) \qquad (9)$$

$$B_{MX}^{D} = \beta_{MX}^{(0)D} + \beta_{MX}^{(1)D}g(\alpha_{1}I^{1/2}) + \beta_{MX}^{(2)D}g(\alpha_{2}I^{1/2}) \qquad (10)$$

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^{2} \qquad (11)$$

$$C_{MX} = C_{MX}^{\varphi}(2|z_{M}z_{X}|^{1/2})^{-1} \qquad (12)$$

where the superscript D denotes the relevant apparent molar quantity: the relative enthalpy, L, heat capacity, J, or volume, V. Therefore, for complete characterization of thermodynamic properties for a binary electrolyte solution at **one** temperature and pressure, up to 18 parameters: $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, C_{MX}^{ϕ}, $\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, $\beta_{MX}^{(2)L}$, $C_{MX}^{\phi L}$, C_p°, $\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$, $\beta_{MX}^{(2)J}$, $C_{MX}^{\phi J}$, V°, $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and $C_{MX}^{\phi V}$, may need to be optimized. As described above, the $\beta^{(2)}$ coefficients are required only for electrolytes where both ions have divalent or higher charges; otherwise, just the remaining 14 parameters are needed. The known dependences between some of these coefficients[8] do not apply when the analysis is confined to data only at a single temperature and pressure (i.e., 25 °C and 1 bar here).

Note that the way the equations for the apparent molar quantities are presented above differs slightly from those of Pitzer (ref 17, pp 95−97). First, the expressions are given in terms of C^{ϕ}, not C. Second, in the case of the apparent molar relative enthalpy and apparent molar heat capacity, the optimized coefficients (excluding $C_p{}^{\circ}$ and V°) here incorporate factors of $-T^2$ and T^2, respectively, a scaling which facilitates the regression analysis.

Table 1. Summary List of Solutes Investigated at 1 bar and 25 °C[a]

solute name	electrolyte formula	upper conc.	optim. conc.	OF	C_p^o	V^o	comments/footnotes
aluminum chloride	$AlCl_3$						*b*
aluminum nitrate	$Al(NO_3)_3$						*b*
aluminum sulfate	$Al_2(SO_4)_3$	1.1	1.1	10	−1112	−42.4	
ammonium bromide	NH_4Br	7.5	7.5	0.24	−61	42.6	
ammonium chloride	NH_4Cl	7.4	7.4	0.28	−57	35.7	
ammonium hydrogen - phosphate	$(NH_4)_2HPO_4$	3.1	3.1	0.10	−104	43.5	
ammonium iodide	NH_4I	7.5	7.5	0.14	−51	54.1	
ammonium nitrate	NH_4NO_3	25.9	20.0	0.61	−2.0	46.9	
ammonium perchlorate	NH_4ClO_4	2.1	2.1	2.6	45	62.0	
ammonium sulfate	$(NH_4)_2SO_4$	5.5	5.5	1.5	−140	49.8	
barium acetate	$Ba(C_2H_3O_2)_2$	3.5	3.5	5.6	6	68.9	
barium bromide	$BaBr_2$	2.3	2.3	0.33	−308	36.9	
barium chloride	$BaCl_2$	1.8	1.8	0.56	−300	23.1	
barium iodide	BaI_2	2.0	2.0	2.4	−288	59.9	
barium nitrate	$Ba(NO_3)_2$	0.4	0.4	0.11	−190	45.5	
barium perchlorate	$Ba(ClO_4)_2$	5.5	3.6	0.61	−96	75.7	
beryllium sulfate	$BeSO_4$	4.0	4.0	0.31	−196	2.0	
cadmium nitrate	$Cd(NO_3)_2$	3.0	3.0	0.44	−152	38.0	$V^o = 43$
cadmium nitrite	$Cd(NO_2)_2$	7.8	5.0	4.3	−184	32.4	
cadmium perchlorate	$Cd(ClO_4)_2$	1.9	1.9	0.41	−58	68.2	
cadmium sulfate	$CdSO_4$	3.5	3.5	0.12	−288	−6.0	
cesium acetate	$Cs(C_2H_3O_2)$	3.5	3.5	0.08	3	62.0	
cesium bromide	$CsBr$	5.0	5.0	0.40	−154	46.0	
cesium chloride	$CsCl$	11.0	11.0	0.66	−150	39.1	
cesium fluoride	CsF	9.0	3.5	1.0	−139	20.1	*c*
cesium hydroxide	$CsOH$	5.0	5.0	0.48	−163	17.3	
cesium iodide	CsI	3.0	3.0	0.58	−144	57.5	
cesium nitrate	$CsNO_3$	1.5	1.5	1.3	−95	50.3	*d*; $V^o = 35$
cesium nitrite	$CsNO_2$	7.0	7.0	0.14	−111	47.5	
cesium sulfate	Cs_2SO_4	4.0	4.0	2.8	−326	56.6	*d*; $V^o = 40$
calcium bromide	$CaBr_2$	9.2	6.0	2.3	−289	31.5	
calcium chloride	$CaCl_2$	11.0	5.0	1.3	−281	17.7	$V^o = 20$
calcium iodide	CaI_2	2.0	2.0	0.11	−269	54.5	
calcium nitrate	$Ca(NO_3)_2$	6.0	6.0	2.2	−171	40.1	
calcium perchlorate	$Ca(ClO_4)_2$	6.0	6.0	2.8	−77	70.3	
cerium(III) chloride	$CeCl_3$	2.0	2.0	5.8	−483	13.6	
chromium(III) chloride	$CrCl_3$	1.2	1.2	0.63	−364	13.9	
chromium(III) nitrate	$Cr(NO_3)_3$	1.4	1.4	1.2	−199	47.5	
chromium(III) sulfate	$Cr_2(SO_4)_3$						*b*
cobalt(II) bromide	$CoBr_2$	5.0	5.0	4.7	−289	25.4	
cobalt(II) chloride	$CoCl_2$	4.0	4.0	1.2	−281	11.6	
cobalt(II) iodide	CoI_2	6.0	4.0	3.5	−269	48.4	
cobalt(II) nitrate	$Co(NO_3)_2$	5.0	5.0	0.17	−171	34.0	
copper(II) chloride	$CuCl_2$	6.0	3.7	3.4	−274	7.8	$V^o = 10$
copper(II) nitrate	$Cu(NO_3)_2$	7.8	7.8	2.9	−164	30.2	
copper(II) sulfate	$CuSO_4$	1.4	1.4	18	−300	−13.8	$V^o = -6$
europium chloride	$EuCl_3$	3.6	3.6	7.3	−519	9.7	
europium nitrate	$Eu(NO_3)_3$	6.4	2.0	3.3	−354	43.3	
gadolinium chloride	$GdCl_3$	3.6	3.6	5.2	−499	13.5	
hydriodic acid	HI	10.0	7.5	0.53	−121	36.2	
hydrobromic acid	HBr	11.0	11.0	0.29	−131	24.7	
hydrochloric acid	HCl	16.0	10.6	0.83	−127	17.8	
hydrofluoric acid	HF	20.0	20.0	7760	−116	−1.0	*e*
iron(II) chloride	$FeCl_2$	2.0	2.0	3.2	−300	12.2	

Table 1. Continued

solute name	electrolyte formula	upper conc.	optim. conc.	OF	C_p^o	V^o	comments/footnotes
iron(III) chloride	$FeCl_3$	7.0	2.3	2.1	−372	9.7	$V^o = 25$
lanthanum chloride	$LaCl_3$	3.9	3.9	3.8	−507	14.3	
lanthanum nitrate	$La(NO_3)_3$	6.5	1.6	3.4	−342	47.9	
lead chloride	$PbCl_2$						*b*
lead nitrate	$Pb(NO_3)_2$	2.0	2.0	15	−197	42.5	*d*
lead perchlorate	$Pb(ClO_4)_2$	12.6	12.6	1.4	−103	72.7	
lithium acetate	$Li(C_2H_3O_2)$	4.0	4.0	0.62	88	39.8	
lithium bromide	$LiBr$	20.0	11.0	5.0	−69	23.8	
lithium chloride	$LiCl$	20.0	8.5	3.8	−65	16.9	
lithium hydroxide	$LiOH$	5.0	5.0	1.4	−78	−4.9	
lithium iodide	LiI	3.0	3.0	1.1	−59	35.3	
lithium nitrate	$LiNO_3$	20.0	14.3	2.6	−10	28.1	
lithium nitrite	$LiNO_2$	9.0	9.0	0.38	−26	25.3	
lithium perchlorate	$LiClO_4$	4.5	4.5	0.16	37	43.2	
lithium sulfate	Li_2SO_4	3.2	3.2	3.1	−156	12.2	
magnesium acetate	$Mg(C_2H_3O_2)_2$	4.0	4.0	0.78	36	60.2	
magnesium bromide	$MgBr_2$	5.6	5.6	4.8	−278	28.2	
magnesium chloride	$MgCl_2$	5.9	5.9	4.4	−270	14.4	
magnesium iodide	MgI_2	5.0	5.0	5.1	−258	51.2	
magnesium nitrate	$Mg(NO_3)_2$	5.5	4.1	3.5	−160	36.8	
magnesium perchlorate	$Mg(ClO_4)_2$	4.0	4.0	2.6	−66	67.0	
magnesium sulfate	$MgSO_4$	3.6	3.6	3.9	−296	−7.2	
manganese chloride	$MnCl_2$	7.7	5.1	2.1	−266	17.9	
manganese sulfate	$MnSO_4$	5.0	5.0	3.0	−292	−3.7	
neodymium chloride	$NdCl_3$	3.9	2.4	6.2	−535	10.1	scattered $\gamma_\pm$ data
neodymium nitrate	$Nd(NO_3)_3$	6.3	2.6	32	−370	43.7	
nickel chloride	$NiCl_2$	6.1	4.0	3.4	−296	11.6	
nickel nitrate	$Ni(NO_3)_2$	5.5	5.5	3.6	−186	34.0	
nickel sulfate	$NiSO_4$	2.5	2.5	0.90	−322	−10.0	
nitric acid	HNO_3	28.0	11.3	0.64	−72	29.0	
perchloric acid	$HClO_4$	16.0	8.0	0.77	−25	44.1	
phosphoric acid	H_3PO_4	30.0	1.5	34	−496	−30.6	*e*
potassium acetate	$K(C_2H_3O_2)$	3.5	3.5	0.06	39	49.7	
potassium bicarbonate	$KHCO_3$	1.0	1.0	0.06	−40	32.4	
potassium bisulfate	$KHSO_4$	4.0	4.0	372	35	44.7	*e*
potassium bromate	$KBrO_3$	0.5	0.5	0.02	−79	44.3	
potassium bromide	KBr	5.5	5.5	0.13	−118	33.7	
potassium carbonate	K_2CO_3	8.1	8.1	3.3	−275	13.7	
potassium chlorate	$KClO_3$	0.7	0.7	0.01	−45	45.7	
potassium chloride	KCl	8.0	5.0	0.29	−114	26.8	
potassium chromate	K_2CrO_4	3.5	3.5	0.51	−225	37.7	
potassium dichromate	$K_2Cr_2O_7$						*b*
potassium dihydrogen phosphate	KH_2PO_4	1.8	1.8	0.60	−21	38.1	
potassium ferricyanide	$K_3Fe(CN)_6$	1.4	1.4	0.91	−413	147.8	
potassium ferrocyanide	$K_4Fe(CN)_6$	0.9	0.9	4.6	−271	110.0	
potassium fluoride	KF	17.5	10.1	1.1	−103	7.8	
potassium hydrogen phosphate	K_2HPO_4	9.0	7.1	1.2	−218	25.7	
potassium hydroxide	KOH	20.0	14.3	2.6	−127	5.0	
potassium iodide	KI	9.0	9.0	0.43	−108	45.2	
potassium nitrate	KNO_3	3.8	3.8	0.49	−59	38.0	
potassium nitrite	KNO_2	5.0	5.0	3.9	−75	35.2	
potassium perchlorate	$KClO_4$						*b*
potassium phosphate	K_3PO_4	0.7	0.7	4.1	−457	−3.6	
potassium sulfate	K_2SO_4	2.0	2.0	1.7	−254	32.0	

Table 1. Continued

solute name	electrolyte formula	upper conc.	optim. conc.	OF	C_p^o	V^o	comments/footnotes
potassium thiocyanate	KSCN	10.0	5.0	1.9	−16	44.7	
praseodymium chloride	$PrCl_3$	3.9	3.9	6.3	−546	10.9	
praseodymium nitrate	$Pr(NO_3)_3$	6.3	2.1	31	−381	44.5	*e*
rubidium acetate	$Rb(C_2H_3O_2)$	3.5	3.5	0.05	17	54.8	
rubidium bromide	RbBr	5.0	5.0	0.02	−140	38.8	
rubidium chloride	RbCl	7.8	7.8	0.27	−136	31.9	
rubidium fluoride	RbF	3.5	3.5	1.2	−125	12.9	
rubidium hydroxide	RbOH	6.0	6.0	0.00	−149	10.1	
rubidium iodide	RbI	5.0	5.0	0.18	−130	50.3	
rubidium nitrate	$RbNO_3$	4.5	4.5	0.43	−81	43.1	
rubidium nitrite	$RbNO_2$	7.0	7.0	0.14	−97	40.0	
rubidium sulfate	Rb_2SO_4	1.8	1.8	3.8	−298	42.2	
samarium chloride	$SmCl_3$	3.6	3.6	6.7	−530	11.1	
scandium chloride	$ScCl_3$	1.9	1.9	1.1	−387	11.5	
silver nitrate	$AgNO_3$	15.0	9.0	1.7	−46	28.3	
sodium acetate	$Na(C_2H_3O_2)$	3.5	3.5	0.33	69	39.5	
sodium bicarbonate	$NaHCO_3$	1.3	1.3	0.15	−10	22.2	
sodium bisulfate	$NaHSO_4$	6.0	6.0	1026	65	34.5	*e*
sodium bromate	$NaBrO_3$	2.6	2.6	0.03	−49	34.1	
sodium bromide	NaBr	9.0	9.0	1.4	−88	23.5	
sodium carbonate	Na_2CO_3	3.1	3.1	4.0	−215	−6.7	
sodium chlorate	$NaClO_3$	3.5	3.5	0.05	−15	35.5	
sodium chloride	NaCl	6.1	6.1	0.10	−84	16.6	
sodium chromate	Na_2CrO_4	4.3	4.3	1.8	−165	17.3	
sodium dihydrogen phosphate	NaH_2PO_4	6.5	6.5	1.5	9	27.9	
sodium fluoride	NaF	1.0	1.0	0.24	−73	−2.4	
sodium formate	$Na(CHO_2)$	3.5	3.5	0.22	−42	24.9	
sodium hydrogen phosphate	Na_2HPO_4	2.1	2.1	0.06	−158	5.3	
sodium hydroxide	NaOH	29.0	11.6	2.3	−97	−5.2	
sodium iodide	NaI	12.0	9.0	1.4	−78	35.0	
sodium nitrate	$NaNO_3$	10.8	10.8	0.29	−29	27.8	
sodium nitrite	$NaNO_2$	12.3	8.4	2.5	−45	25.0	
sodium perchlorate	$NaClO_4$	6.0	6.0	1.0	18	42.9	
sodium phosphate	Na_3PO_4	0.8	0.8	4.4	−367	−34.2	*d*; $V^o = -25$
sodium propanoate	$Na(C_3H_5O_2)$	3.0	3.0	0.91	156	52.8	
sodium sulfate	Na_2SO_4	5.0	5.0	2.0	−194	11.6	
sodium thiocyanate	NaSCN	18.0	12.0	3.4	14	34.5	
sodium thiosulfate	$Na_2S_2O_3$	4.0	4.0	0.59	−126	31.5	
strontium bromide	$SrBr_2$	2.1	2.1	1.7	−297	31.2	
strontium chloride	$SrCl_2$	4.0	4.0	4.3	−289	17.4	
strontium iodide	SrI_2	2.0	2.0	0.88	−277	54.2	
strontium nitrate	$Sr(NO_3)_2$	4.0	4.0	1.8	−179	39.8	
strontium perchlorate	$Sr(ClO_4)_2$	6.0	6.0	6.7	−85	70.0	
sulfuric acid	H_2SO_4	76.	30.0	419	−280	14.0	*e*
tetra-*n*-butylammonium bromide	Bu_4NBr	4.0	4.0	0.43	1208	300.4	
tetra-*n*-butylammonium chloride	Bu_4NCl	15.0	3.0	5.5	1212	293.5	
tetra-*n*-butylammonium fluoride	Bu_4NF	1.6	1.6	0.96	1223	274.5	
tetraethylammonium chloride	Et_4NCl	9.0	6.0	0.70	387	166.9	
tetraethylammonium fluoride	Et_4NF	5.5	4.1	1.9	398	147.9	
tetraethylammonium nitrate	Et_4NNO_3	8.0	8.0	2.9	442	178.1	
tetramethylammonium chloride	Me_4NCl	19.0	6.7	0.78	110	107.4	
tetramethylammonium fluoride	Me_4NF	7.0	7.0	0.79	121	88.4	
tetramethylammonium nitrate	Me_4NNO_3	7.0	7.0	0.66	165	118.6	
tetra-*n*-propylammonium bromide	Pr_4NBr	4.0	4.0	1.2	792	239.1	

Table 1. Continued

solute name	electrolyte formula	upper conc.	optim. conc.	OF	C_p°	V°	comments/footnotes
tetra-*n*-propylammonium chloride	Pr_4NCl	18.0	4.0	3.3	796	232.2	
tetra-*n*-propylammonium fluoride	Pr_4NF	5.0	3.0	1.1	807	213.2	
thallium acetate	$Tl(C_2H_3O_2)$	6.0	6.0	0.31	8	51.3	
thallium chloride	TlCl						*b*
thallium nitrate	$TlNO_3$	0.4	0.4	0.00	−90	39.6	
thallium nitrite	$TlNO_2$	1.4	1.4	0.01	−106	36.8	
thallium perchlorate	$TlClO_4$	0.5	0.5	0.00	−43	54.7	
thorium nitrate	$Th(NO_3)_4$	5.0	1.5	2.5	−364	62.5	*c*
uranyl chloride	UO_2Cl_2	3.2	3.1	2.2	−249	41.5	
uranyl nitrate	$UO_2(NO_3)_2$	5.5	2.7	0.70	−139	63.9	
uranyl perchlorate	$UO_2(ClO_4)_2$	5.5	4.1	13.6	−45	94.1	
uranyl sulfate	UO_2SO_4	6.0	6.0	1.7	−275	19.9	
yttrium chloride	YCl_3	4.1	4.1	5.4	−388	12.6	
yttrium nitrate	$Y(NO_3)_3$	7.2	1.2	1.0	−223	46.2	
zinc bromide	$ZnBr_2$	20.1	2.1	1.6	−284	27.8	V° = 20
zinc chloride	$ZnCl_2$	23.2	3.2	6.2	−276	14.0	V° = 2
zinc fluoride	ZnF_2						*b*
zinc iodide	ZnI_2	11.9	2.9	10	−264	50.8	
zinc nitrate	$Zn(NO_3)_2$	7.1	7.1	0.81	−166	36.4	
zinc perchlorate	$Zn(ClO_4)_2$	4.3	4.3	2.2	−72	66.6	V° = 63
zinc sulfate	$ZnSO_4$	3.5	3.5	5.5	−302	−7.6	see ref 17, Appendix H

[a] Units: upper concentration of data/mol·kg^{-1}; optimized concentration limit/mol·kg^{-1}; C_p°/J·K^{-1}·mol^{-1}; V°/cm^3·mol^{-1}. [b] Insufficient data for parametrization (see text); often due to limited solubility. [c] $\gamma_\pm$ at high concentrations have been estimated. [d] Limited or contradictory data. [e] Pitzer function failure possibly due to speciation (see text).

For a similar numerical advantage, C_p° and V° have been divided by a factor of 100, and $\beta_{MX}^{(0)V}$, $\beta_{MX}^{(1)V}$, $\beta_{MX}^{(2)V}$, and $C_{MX}^{\phi V}$ have been multiplied by a factor of 100. These differences do not have any significant effect on calculated properties once the appropriate factors are applied. The standard Pitzer approach has been followed in all other respects.

■ METHODS

The data available in the chemical literature were examined for a total of 183 electrolytes in water. Thermodynamic property values from 207 separate literature sources were evaluated, noting that many of these sources provide critically assessed data for multiple systems (e.g., refs 24 and 25). A least-squares regression analysis was performed using the JESS (Joint Expert Speciation System) software package (see http://jess.murdoch.edu.au).[12,15,26−28] The overall strategy adopted for data processing and critical selection was similar to that used for thermodynamic data for chemical reaction equilibria in solution.[27,28] Since the Pitzer equations are *linear* in the adjustable parameters, all required equation coefficients can be readily determined by singular value decomposition.[12] This computational technique avoids numerical ill-conditioning and minimizes the impacts of correlation.[29] Typically, values from the literature were rejected (i.e., given zero weight) when they were judged to be inconsistent with the body of other data. Nonzero weights for the remaining data were based (this work) on an assigned quality for each data set and property. Regressions were performed by minimizing a normalized (χ^2) objective function, OF, comprising a weighted sum of residuals between the experimental and calculated data for activity coefficients, osmotic coefficients, apparent relative molar enthalpies, apparent molar heat capacities, and apparent molar volumes. Other equivalent properties were included if this could be done by simple numerical conversion; for example, the residuals in molar volumes include transformed values of solution densities and of solution densities relative to water. The ranges of concentration for the fitting of each target property were determined by an iterative process in which the concentration range was expanded systematically until the normalized objective function exceeded a certain, fairly tight, threshold value. For each system investigated and each target property, the agreement between observed and calculated values was represented graphically and compared by visual inspection. In addition, the worst-fitting points in each case were identified numerically and examined individually to assess possible reasons for their deviation. In this way, all significant outliers were rejected systematically, and an assessment was then made of the ability of the Pitzer equations to represent the accepted physicochemical property data.

To improve control over systematic errors in the optimized Pitzer parameters, the regressed coefficients obtained in this work were based concurrently on multiple sources of data available in the literature for various properties. This contrasts with previous studies where parameters (at least for osmotic and activity coefficients) were typically derived from smoothed experimental data taken from only one source per property and electrolyte. For example, Pitzer and Mayorga[30] used mainly osmotic coefficient data from Robinson and Stokes[24] to evaluate their parameters; Kim and Frederick[19] obtained Pitzer parameters from smoothed osmotic coefficient data evaluated by Hamer and Wu[25] and other authorities. As Meinrath[31] has pointed out, non-normal distributions of residuals arise when preprocessed and smoothed experimental data are used to fit Pitzer equations. Moreover, the largest deviations from a normal distribution are found[31] in $\beta^{(1)}$, probably because this parameter depends

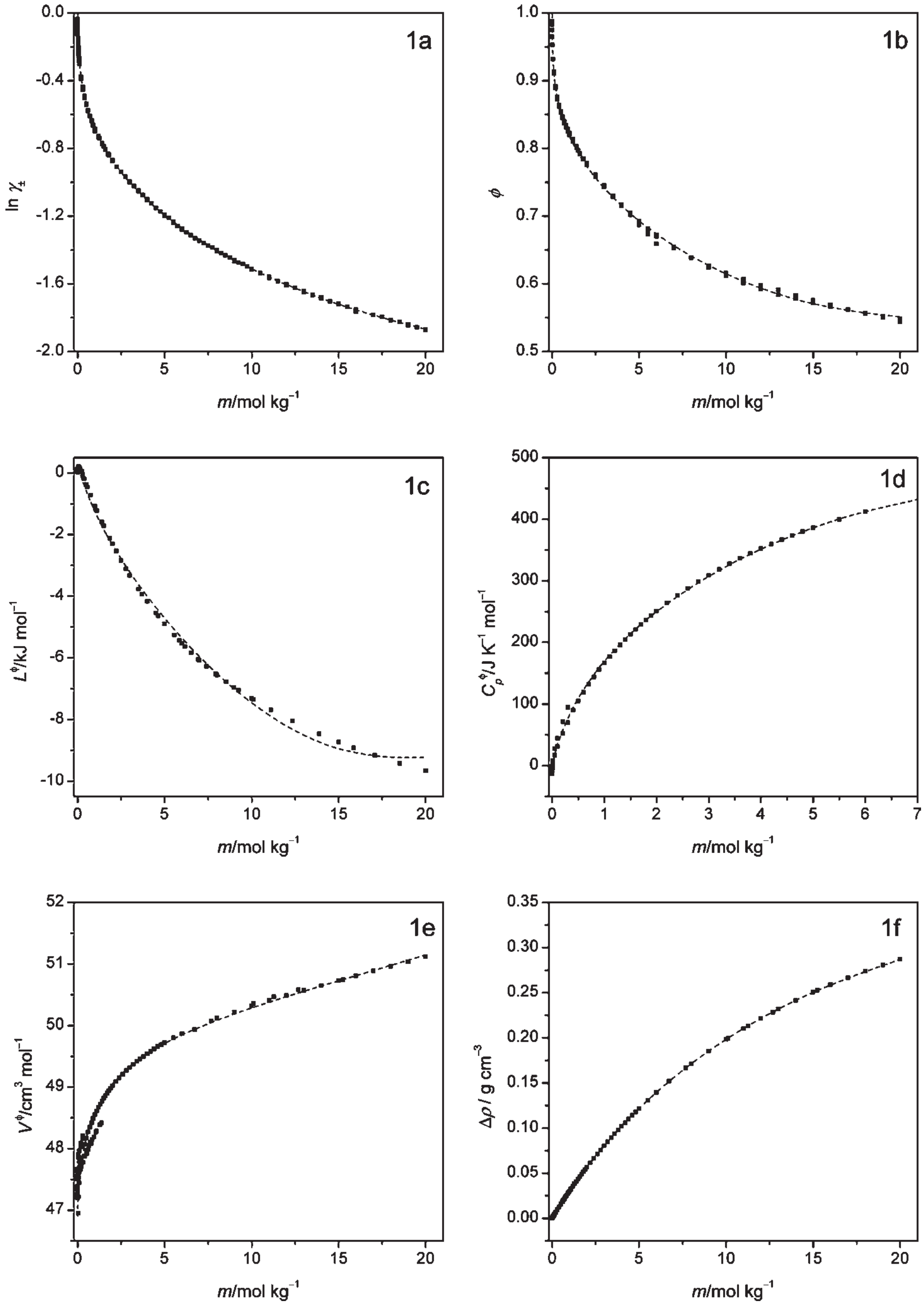

Figure 1. Pitzer fits of the activity coefficient (a), osmotic coefficient (b), apparent molar relative enthalpy (c), apparent molar heat capacity (d), apparent molar volume (e), and relative density difference values (f) for ammonium nitrate, NH_4NO_3(aq), at 25 °C to high concentration. Main data sources are refs 24, 25, and 38 to 42.

strongly on osmotic coefficient data at low concentrations where the experimental uncertainty is usually largest. It is reasonable to expect that the systematic bias arising in such cases will be reduced when the regressed data are obtained from diverse sources.

■ RESULTS

The results of the general regression performed on the accepted literature data for the aqueous solutions investigated are summarized in Table 1. This table also gives, for each electrolyte, infinite dilution values of the isobaric molar heat capacity, C_p°, and volume, V°, taken from Marcus.[32] These values were generally accepted and held constant during the regression calculations. However, as noted in the final column of Table 1, alternative values for C_p° or V° were occasionally used when those from Marcus were found to be incompatible with the present database. (There are many possible reasons for such discrepancies including complexation/ion pairing, experimental error, and absence of reliable data at low concentrations. However, with no significant impact on the predicted bulk solution properties at finite concentrations, this issue is not considered in detail here. Our fitted values are not intended to replace those of Marcus.)

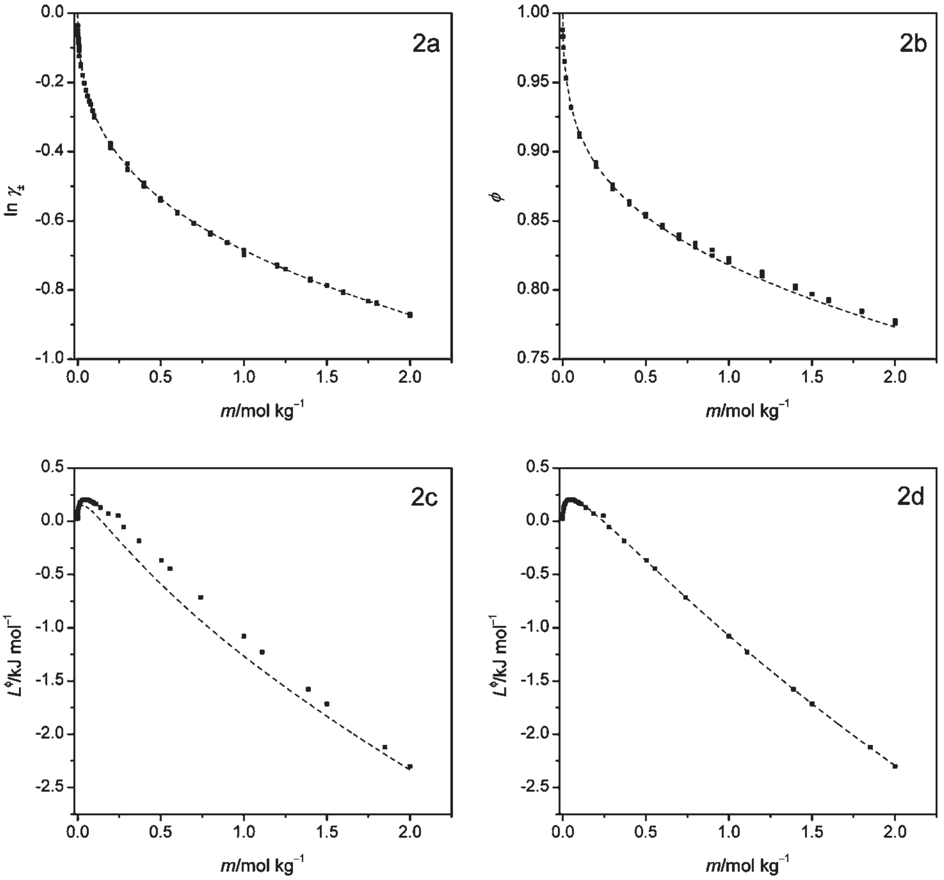

Figure 2. Pitzer fits of the activity coefficient (a), osmotic coefficient (b), and apparent molar relative enthalpy (c, d) for ammonium nitrate, NH_4NO_3(aq), at 25 °C and lower concentration. Data sources are the same as in Figure 1; the source for apparent molar relative enthalpy is ref 39.

As can be seen from the objective function OF (Table 1) and from the examples given below, the description of thermodynamic properties achieved by the Pitzer equations at 25 °C is mostly very good. This is consistent with the findings of previous investigators.[1,6,17−23] Of the 183 solutes studied, 8 could not be analyzed meaningfully, either because of their limited solubilities or because the available database is inadequate (see Comments column in Table 1.) Of the remaining 175 solutes, more than two-thirds (122) gave satisfactory fits to the upper concentration limit of the available data. A significant number (19) gave acceptable fits to concentrations up to m = 6 mol·kg^{-1}, while most of the rest (28) could only be described accurately over a more restricted concentration range, which varied from salt to salt. Just 6 systems—HF, H_2SO_4, H_3PO_4, $KHSO_4$, $NaHSO_4$, $Pr(NO_3)_3$—were found to be completely intractable. These systems are known to undergo changes in chemical speciation at relatively low concentrations, causing behavior inconsistent with the Debye−Hückel slope and which therefore cannot be described satisfactorily without explicitly involving speciation equilibria.[33] Other electrolytes exhibiting signs that they too may belong in this category include certain trivalent nitrates and the zinc halides. Note, however, that ion pair-complex formation per se does not preclude a good Pitzer fit. It is well-known, for example, that $CuSO_4$ (where the fit is satisfactory, as discussed below) forms a complex with an equilibrium constant ($\log K_A{}^\circ \approx$ 2.3 at 25 °C)[34] implying[35] ∼40 % association at m = 0.5 mol·kg^{-1}. Indeed, under the Pitzer framework all 2:2 and higher valence electrolytes are implicitly assumed to exhibit some association (since there is a close relationship[17] between $\beta^{(2)}$ and $K_A{}^\circ$). In its effect, the association between a cation and an anion is approximately linear with respect to the solute concentration,[12] and so it is highly correlated with other linear solution phenomena influencing the activity coefficient (in logarithmic form).

Representative Systems. Perhaps the "best-behaved" solute of all those analyzed was ammonium nitrate, where the fit was excellent up to concentrations approaching 20 mol·kg^{-1} (Figure 1), without noticeable distortion at low concentrations in either the activity coefficient or osmotic coefficient data (Figure 2). When displayed on a larger scale, a small but systematic deviation in the fit to the apparent molar relative enthalpy is clearly evident (Figure 2c), but the significance of this is difficult to assess since the data come from a single source and are well-fitted by the same Pitzer function over a reduced concentration range (Figure 2d).

By way of comparison, with OF = 18 as the limit of what was considered to be satisfactory, one of the least well-fitted solutes in Table 1 was copper(II) sulfate. Nevertheless, as can be seen in Figure 3, the model still describes the data for this salt adequately. The decrease in $^\phi V$ of $CuSO_4$(aq) as it approaches infinite dilution (Figure 3c) is sharper than occurs with most other 2:2 electrolytes, but this is probably just a manifestation of the usual problems, both experimental and numerical, typical of $^\phi V$ values at low concentration.[36] In this regard it is instructive to note the (good) corresponding plot (Figure 3d) for the relative density difference, $(\rho - \rho_o)/\rho_o$, the quantity often measured

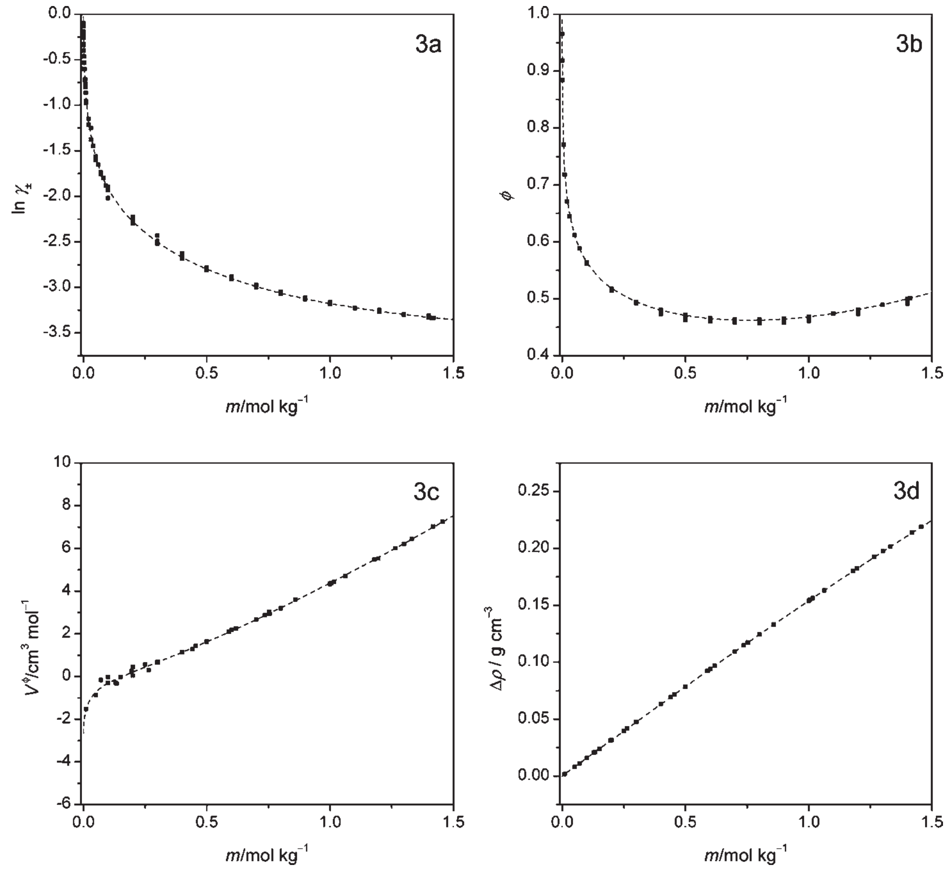

Figure 3. Pitzer fits of activity coefficient (a), osmotic coefficient (b), apparent molar volume (c), and relative solution density difference (d) for copper(II) sulfate, $CuSO_4(aq)$, as one of the worst-fitting but still acceptable solutes in Table 1. Main data sources are refs 24, 40, and 42 to 44.

experimentally and one which avoids the extreme sensitivity of ϕ_V during extrapolations to infinite dilution.[36] This is consistent with a lack of information content in property data at very low concentrations, which has been frequently observed during this investigation.

For comparison, Figure 4 illustrates a system, $H_2SO_4(aq)$, that could **not** be well-described by the standard Pitzer framework used in this work (for the reasons described above). Even though the activity coefficients (Figure 4a) are represented reasonably well, the deviations while small are systematic and significant. More problematic is the osmotic coefficient (Figure 4b), reflecting the effects of speciation change at concentrations below 0.1 $\text{mol}\cdot\text{kg}^{-1}$ on the determination of this property. Large deviations can also be seen in the fits for apparent molar heat capacity (Figure 4c) and apparent molar volume (Figure 4d). Evidently, the fits shown in Figures 4c and 4d could be improved by adjusting the values for C_p° or V°, but we have confirmed that a good match to the experimental profiles can still not be achieved. On the other hand, it is noteworthy that even in this difficult case the standard Pitzer equations have sufficient flexibility to reproduce many of the broad features of the system.

Tables of the fitted Pitzer coefficients for all of the systems (and properties) deemed to have been fitted satisfactorily are given in the Supporting Information, as are plots of differences between observed and calculated property values versus concentration for some selected systems, generally those found to be among the least well-fitted. The systematic effects identified by Meinrath[31] (see above) are clearly evident in many of the difference plots. Such effects could, of course, be reduced by fitting functions with more empirical parameters. In our view, however, the advantages of doing so would be outweighed by the disadvantages.

■ DISCUSSION

Numerous judgments must be made whenever scientific data are used to inform predictions of observable behavior. In general, however, few of these decisions receive detailed attention—inevitably there are too many issues, often *apparently* trivial or self-evident, to be considered. This tends to leave modeling results dependent on implicit choices to a much greater extent than is commonly recognized. For instance, Krumgalz et al.[20,21] created a volumetric database for binary electrolyte solutions, discarding almost all previbrating-tube densimeter data. The "best (most reliable) data" were then selected by fitting a power series to the remaining data and rejecting all data points that deviated from the fitted curve by two or more standard deviations. No information about weighting of the data selected for fitting to the volumetric Pitzer equation was given. Similarly, Criss and Millero[22,23] employed data measured with Picker flow calorimeters at low concentrations together with values from the tabulation of Parker,[37] mostly determined by static calorimetry at higher molalities, but they left the relative importance of these different inputs unclear.

As the present work demonstrates, new ways of processing physicochemical property data for modeling aqueous solution

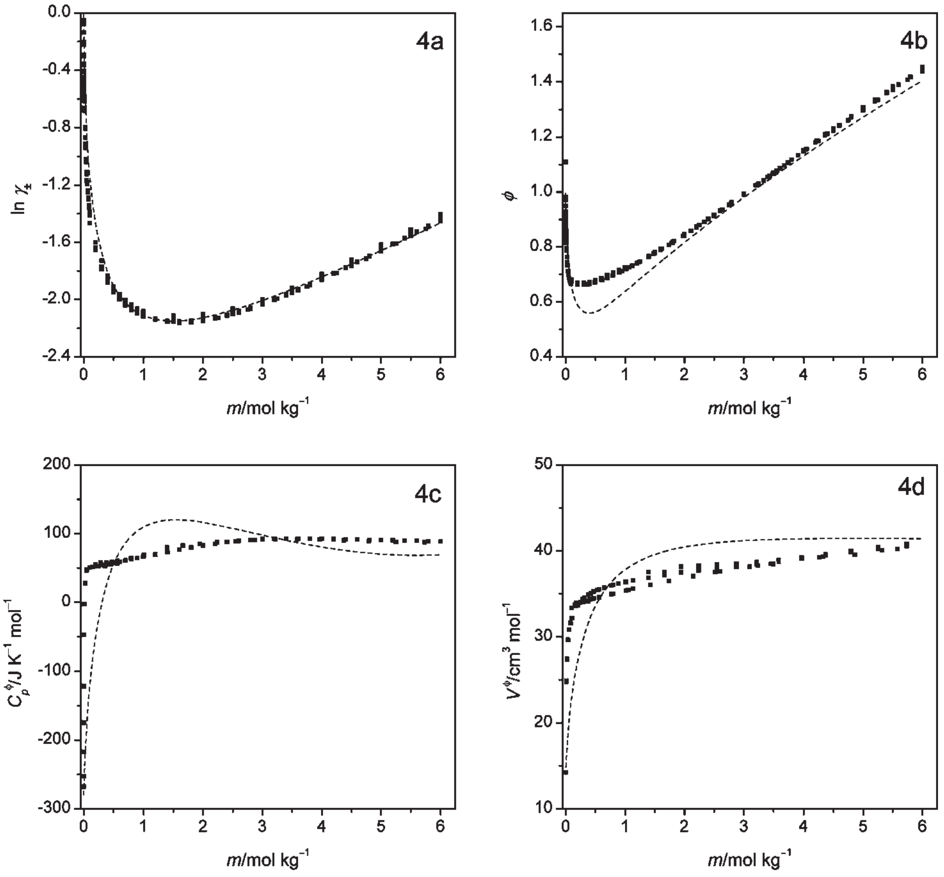

Figure 4. Pitzer fits of activity coefficient (a), osmotic coefficient (b), apparent molar heat capacity (c), and apparent molar volume (d) for sulfuric acid, H_2SO_4(aq), as one of the intractable solutes in Table 1. Main data sources are refs 6, 24, 40, 42, and 45 to 51.

thermodynamics are evolving. It is now technically possible to store in computer databases as many physicochemical property values as are reported in the literature so that a very large body of information about each property can be assembled progressively. Newly published data can be included rapidly and without undue effort. The current literature base is more comprehensive and more accessible (for details see http://jess.murdoch.edu.au) than ever before. Furthermore, thermodynamic consistency can be achieved by automatic procedures, such as the mechanism[12] for data selection and subsequent Pitzer regression analysis used here. Such improvements in the way data are handled should, in turn, lead to more robust modeling processes as well as to models that are much easier to keep up-to-date. At the same time, the present study underlines the sensitivity of the modeling process to data assessment (i.e., "expert" opinion by which poor quality data are rejected and the relative merit of the remaining sources assigned). As noted above, these subjective judgments have always been necessary, but now through advancing computer technology, they can become more explicit and open, and they can also be continuously refined. Minimizing the effort needed to re-establish thermodynamic consistency whenever additional data are introduced, or existing data modified, is the key.[28]

A constantly enlarging physicochemical property database implies that sets of modeling coefficients, such as the Pitzer parameters reported in this work, will change over time. These coefficient data sets are thus likely to decline in importance; rather, it will be the underlying assemblage of (critically assessed, increasingly stable) data that counts. Parameterized representations of the data—previously used to encapsulate and communicate the results of critical evaluation and analysis—cannot do the job as well the data themselves, particularly when it comes to specifying individual weights and defining the detailed ranges of conditions spanned by complicated data sets. Consequently, it seems that the process of determining thermodynamic parameters for models of aqueous solution chemistry will likely become more dynamic (i.e., performed "on-the-fly"), implying that the parameter sets used to make thermodynamic predictions will come to exist only transiently.

■ CONCLUDING REMARKS

Among the many approaches currently available for modeling the thermodynamics of aqueous electrolyte solutions, the Pitzer equations are, with good reason, pre-eminent. As demonstrated by many authors and confirmed here, they provide an accurate and thermodynamically consistent description of the relevant physicochemical properties for the great majority of binary aqueous electrolyte solutions at 1 bar and 25 °C. Using the well-established mixing rules of Young and Zdanovskii, various bulk solution properties (density, heat capacity, and water activities) can accordingly be calculated for multicomponent systems without the need for any additional fitting parameters. Harned's rule (ref 24, p 438) can likewise be used to calculate activity coefficients in certain electrolyte mixtures. The robust nature of this approach to aqueous solution thermodynamics of multicomponent systems makes it a potentially valuable tool for detecting and correcting errors in other, more commonly used, modeling frameworks (such as Pitzer models with ternary interaction parameters). Due mainly to the poor predictive capability of empirical functions, such errors currently plague efforts to characterize the properties of real multicomponent aqueous solutions like seawater, which are needed in topical modeling applications such as ocean acidification[9] and desalination.[10]

On the other hand, several serious outstanding issues still limit progress in this area. Most importantly, these include difficulties with error propagation in: (a) Pitzer models for systems at superambient conditions and (b) all calculations that rely on the Gibbs−Duhem equation to determine the thermodynamic characteristics of minor system components. These considerations are currently being investigated.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Tables of fitted Pitzer constants and plots of differences between observed and calculated property values versus concentration for selected systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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