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Journal

The journal of physical chemistry. A, 119(13)

ISSN

1089-5639

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Publication Date

2015-04-01

DOI

10.1021/jp512646k

Peer reviewed

Isotherm-Based Thermodynamic Model for Electrolyte and Nonelectrolyte Solutions Incorporating Long- and Short-Range Electrostatic Interactions

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ABSTRACT: The activities of solutes and solvents in solutions govern numerous physical phenomena in a wide range of practical applications. In prior work, we used statistical mechanics and multilayer adsorption isotherms to develop a transformative model for capturing thermodynamic properties of multicomponent aqueous solutions over the entire concentration range (Dutcher et al. *J. Phys. Chem.* **2011**, **2012**, **2013**). That model needed only a few adsorption energy values to represent the solution thermodynamics of each solute. In the current work, we posit that the adsorption energies are due to dipole–dipole electrostatic forces in solute–solvent and solvent–solvent interactions. This hypothesis was tested in aqueous solutions on (a) 37 1:1 electrolytes, over a range of cation sizes, from H^+ to tetrabutylammonium, for common anions including Cl^- , Br^- , I^- , NO_3^- , OH^- , ClO_4^- , and (b) 20 water-soluble organic molecules including alcohols and polyols. For both electrolytes and organic solutions, the energies of adsorption can be calculated with the dipole moments of the solvent, molecular size of the solvent and solute, and the solvent–solvent and solvent–solute intermolecular bond lengths. Many of these physical properties are available in the literature, with the exception of the solute–solvent intermolecular bond lengths. For those, predictive correlations developed here enable estimation of solute and solvent solution activities for which there are little or no activity data.

INTRODUCTION

Accurate calculation of gas/liquid/solid equilibrium is crucially important to environmental and industrial processes. In atmospheric chemistry, for example, the water uptake of aerosol particles as a function of temperature and relative humidity is central to new particle formation, the behavior of cloud condensation nuclei, cloud formation, visibility, air quality, and climate. Atmospheric aerosol particles, like most real-world chemical environments, are composed of highly complex chemical mixtures that confound accurate thermodynamic modeling, especially at low relative humidity (i.e., high solute concentration). Recently, a unified thermodynamic treatment valid over the entire concentration range was derived and shown to work for a wide range of solutes by combining the advantages of adsorption isotherm models with traditional solution chemistry models.^{1–3}

Models based on adsorption isotherms (which may loosely be regarded as a form of hydration model) have been used successfully to represent solvent activities of very concentrated solutions and gels (Stokes and Robinson, 1948),⁴ and activity coefficients and volumetric properties of concentrated salt–water systems that are liquid up to the pure salt melt (Abraham and Abraham, 1997, 2002; Ally and Braunstein, 1996).^{5–7} The analogy is between the adsorption of gases on solids in systems at low vapor density and the sorption of solvent molecules on solutes in systems at low solvent activity. The validity of these

isotherm-based models was extended to high water activity values, then extended further to infinite dilution by adding a “Debye–Hückel” term to represent long-range electrostatic interactions by allowing for multiple monolayer adsorption between solvent and solute.^{1–3} The resulting model accurately predicts solute and solvent activities in both single solute (binary) solutions and multicomponent mixtures over the full concentration range. While employing no mixing parameters, the model reduces to the commonly used Zdanovskii–Stokes–Robinson (ZSR)^{8,9} empirical mixing equation at high concentration but predicts mixture osmotic coefficients better at low concentrations.⁹

Ultimately, however, the need in chemical equilibrium modeling is for fully predictive models. In fields where the chemical composition is highly complex, such as in atmospheric aerosols that contain many electrolytes and organics, data are not available for many of the relevant compounds. Prior models required fit parameters for each dissolved species and often also ternary species–species interaction parameters, leading to an intractable number of adjustable parameters in complex mixtures. For example, the widely used Pitzer model is known to have limitations due to the number of parameters

Received: December 18, 2014

Revised: February 11, 2015

Published: February 16, 2015

necessary and the parameters' dependence on the accuracy of experimental data.¹⁰ In our prior work, a power law expression that related the energies to each other was employed to substantially reduce the number of required parameters (Dutcher et al., 2012, 2013).^{1,3} Here we test the hypothesis that these energies are due to shorter-range dipole–dipole electrostatic forces at the molecular level, thereby reducing the number of fit parameters even further.

2. THEORETICAL DEVELOPMENT

Consider an aqueous solution of solvent (water) activity a_w^o containing a single solute j , where j can be either an electrolyte or a nonelectrolyte. Previously,^{1–3} using statistical mechanics of lattice adsorption isotherms in combination with long-range electrostatic interactions, equations for the solution molality, m_j^o , and solute activity, a_j^o , as a function of solvent activity, a_w^o , were derived and shown to be valid over the entire concentration range

$$m_j^o = \left[\left(\frac{1 - \bar{a}_w^o}{M_w \nu_j \bar{a}_w^o} \right) \left(1 - \sum_{i=1}^{n_j-1} ((\bar{a}_w^o)^i (1 - C_{j,i}) \prod_{k=1}^{i-1} C_{j,k}) \right) \right] / \left[(1 - \bar{a}_w^o)^2 \sum_{p=1}^{n_j-2} (p (\bar{a}_w^o)^{p-1} \prod_{k=1}^p C_{j,k}) + ((n_j - 1) - (n_j - 2) \bar{a}_w^o) (\bar{a}_w^o)^{n_j-2} \prod_{k=1}^{n_j-1} C_{j,k} \right] \quad (1)$$

$$\bar{a}_j^o = \left((1 - \bar{a}_w^o) / \left(1 - \sum_{i=1}^{n_j-1} ((\bar{a}_w^o)^i (1 - C_{j,i}) \prod_{k=1}^{i-1} C_{j,k}) \right) \right)^{\nu_j} \quad (2)$$

where M_w (kg mol^{−1}) is the molecular weight of the solvent (water), ν_j is the stoichiometric coefficient of solute j , n_j is the number of sorption layers surrounding solute j , and superscript o indicates that the quantities are those of single solute (binary) aqueous solutions. The variables $\bar{a}_w^o$ or $\bar{a}_j^o$ are the solvent and solute activities normalized by the long-range Debye–Hückel terms, $K_w^{\text{DH},o}$ and $K_j^{\text{DH},o}$, respectively. For a nonelectrolyte j , $K_w^{\text{DH},o}$ and $K_j^{\text{DH},o} = 1$. For an electrolyte j , $K_w^{\text{DH},o}$ and $K_j^{\text{DH},o}$ are given by

$$K_w^{\text{DH},o} = \exp \left(\frac{2A_x (I_x^o)^{3/2}}{1 + \rho_j (I_x^o)^{1/2}} \right) \quad (3)$$

$$K_j^{\text{DH},o} = \left[\exp \left[-z_{j+} |z_{j-}| A_x \left\{ (I_x^o)^{1/2} \left[1 - \frac{2I_x^o}{z_{j+} |z_{j-}|} \right] / (1 + \rho_j (I_x^o)^{1/2}) \right\} \right] + \frac{2}{\rho_j} \ln \left(\frac{1 + \rho_j (I_x^o)^{1/2}}{1 + \rho_j (I_{x,j}^{\text{ref}})^{1/2}} \right) \right]^{\nu_j} \quad (4)$$

where I_x^o is the ionic strength of the solution, $I_{x,j}^{\text{ref}}$ is the ionic strength of a pure aqueous solution of j at the chosen reference state (pure liquid solute), z_i is the charge on ion i (cation, j_+ or anion, j_- , of solute j), and A_x is the Debye–Hückel coefficient on a mole fraction basis (equal to 2.917 at 298.15 K).¹¹ The parameter ρ_j has been related to the hard-core collision diameter of solute ions¹² but in practice is treated either as a

constant for all solutes,^{11,13,14} or as an adjustable parameter.¹ Here the parameter ρ_j is treated as an adjustable parameter that in this work will be related to properties of the ions in solution.

For multicomponent systems, the binary expressions for solute molality and activity coefficients (eqs 1–4) can be used directly in the isotherm-based, zero-parameter mixing models developed previously (eqs 25 and 26 of Dutcher et al. 2013).¹ The solute concentrations in mixtures conform to a modified Zdanovskii–Stokes–Robinson mixing rule, and solute activity coefficients conform to a modified McKay–Perring relation, when the effects of the long-range terms (eqs 3 and 4) for each binary component are included. No additional mixing parameters are used, and the results for the mixtures show satisfactory accuracy over the entire concentration range. Ionic strength for a multicomponent system is given by

$$I_x = \frac{1}{2} \frac{\sum_j N_j |z_{j-}| |z_{j+}| \nu_j}{\sum_j \nu_j N_j + N_w} = \frac{1}{2} \frac{\sum_j m_j |z_{j-}| |z_{j+}| \nu_j}{\sum_j \nu_j m_j + M_w^{-1}} \quad (5)$$

where N_w is the number of water molecules and N_j is the number of molecules of solute j . Finally, the short-range sorption energy parameter, $C_{j,i}$ in eqs 1 and 2 for the lattice sorption of a solvent molecule to a site in layer i of solute j is given by

$$C_{j,i} = \exp(\Delta \varepsilon_{j,i} / kT) \quad (6)$$

where k is Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J K^{−1}, T is temperature, and $\Delta \varepsilon_{j,i}$ is the energy change accompanying adsorption of solvent to monolayer i of solute j . The energy change is expressed as

$$\Delta \varepsilon_{j,i} = E_{j,i} - E_L \quad (7)$$

where E_L is the energy of the free solvent in the bulk and $E_{j,i}$ is the energy of the bound solvent in layer i . Prior to the inclusion of the long-range electrostatics, $C_{j,i}$ was a fit parameter with values that appeared independent of layer number (cf., table 5 in ref 1). After the inclusion of long-range electrostatics, an empirical relationship between the $C_{j,i}$ values as a function of layer emerged, where the value in layers 2 to $n - 1$ monotonically approached unity. An empirical model was then used: n and $C_{j,1}$ (the energy parameter for layer 1) were fit directly, and $C_{j,i}$ values were obtained by fitting P_j in the equation: $C_{j,i} = (n_j/i)^{P_j}$ in layers 2 to $n - 1$ (cf., table 4 in ref 1).

Here we estimate the values of $\Delta \varepsilon_{j,i}$ by assuming that electrostatics characterize solute–solvent and solvent–solvent interactions in solution. That is, all solute and solvent molecules are modeled as dipoles, or ‘apparent’ dipoles, including electrolytes. Solute ion parameters cannot simultaneously be adjusted to predict the aqueous electrolyte solution properties for all of the complementary pairs. In other words, the behavior of an ion in solution depends on the nature of its counterion. This is, in part, due to ion association effects such as contact ion pairing at high concentrations and solvent-separated ion pairing at low and moderate concentrations, which have been observed experimentally^{15–17} (e.g., see figure 6 of ref 12 for a H⁺–Cl[−] water ternary cluster). Thus, for electrolytes, extensive literature has established that activities in solution relate to electrolytes as the fundamental solute unit, not to ions.

The dipole–dipole interaction energy is

$$E = \mu_1 \mu_2 D^2 / 4\pi \epsilon_0 r^3 \quad (8)$$

Table 1. Two-Parameter Fit for Aqueous Organics at 298.15 K^a

species	<i>n</i>	μ_j	r_{jw} (Å)	MSE ^b	min a_w	min m [mol kg ⁻¹]	max m [mol kg ⁻¹]	n_p	ref
1,2-butanediol ^c	8	1.669	2.39	1.14×10^{-2}	1.85×10^{-2}	0.230	6.79×10^2	52	33, 34
1,3-butanediol ^c	9	2.304	2.65	3.64×10^{-3}	9.80×10^{-3}	0.229	6.79×10^2	48	33, 34, 46
1,4-butanediol ^c	8	1.798	2.43	4.86×10^{-3}	1.54×10^{-2}	0.117	6.79×10^2	54	33, 34, 46
2,3-butanediol ^c	3	1.818	2.44	3.62×10^{-4}	1.28×10^{-2}	0.128	5.87×10^2	42	33, 34
1,2,3,4-butanetetrol	9	442.8 ^d	22.57	2.15×10^{-5}	9.60×10^{-1}	0.051	1.11×10^0	19	46, 47
1,2,4-butanetriol	3	5.716	3.50	3.04×10^{-3}	1.43×10^{-2}	0.753	3.11×10^2	22	33, 46
ethanediol	3	4.324	3.21	2.52×10^{-3}	2.30×10^{-3}	0.119	9.41×10^2	23	33, 47
ethanol	2	2.939	3.03	3.45×10^{-3}	7.76×10^{-2}	0.056	3.97×10^2	31	30
glycerol	12	3.804	3.04	1.35×10^{-4}	3.11×10^{-3}	0.185	5.39×10^2	106	28, 29, 33, 48
isopropyl alcohol	2	0.6580	1.86	1.65×10^{-1}	4.80×10^{-2}	0.431	8.81×10^2	15	31
methanol	4	2.192	2.60	3.95×10^{-3}	2.18×10^{-2}	0.100	4.97×10^2	10	31
1,2-pentanediol	3	5.5×10^{-4d}	0.17	3.87×10^{-1}	3.96×10^{-2}	0.834	3.79×10^2	14	33
1,4-pentanediol	11	0.7989	1.85	5.70×10^{-3}	4.16×10^{-2}	1.058	3.07×10^2	14	33
1,5-pentanediol	4	2.0×10^{-4d}	0.12	6.06×10^{-3}	1.88×10^{-2}	1.225	5.28×10^2	14	33
2,4-pentanediol	7	0.5386	1.62	4.29×10^{-3}	3.57×10^{-2}	1.035	3.56×10^2	14	33
1,2-propanediol	6	3.044	2.88	1.20×10^{-3}	6.89×10^{-3}	2.482	6.42×10^2	13	33
1,3-propanediol	5	2.278	2.59	2.99×10^{-3}	5.18×10^{-3}	2.561	6.98×10^2	13	33
sorbitol	9	10.05	4.44	5.26×10^{-3}	2.49×10^{-3}	0.200	1.89×10^3	133	29, 49, 50
sucrose	15	14.09	4.58	1.38×10^{-3}	1.30×10^{-1}	0.100	2.62×10^1	52	28, 32
urea	10	0.9652	1.88	2.76×10^{-6}	5.68×10^{-1}	0.100	2.00×10^1	41	28

^aValues for r_{jw} and μ_j were fit. The number of sorption layers n was also fit but separately from r_{jw} and μ_j . ^bMSE is a normalized mean-square error, equal to $1/n_p \sum_{i=1}^{n_p} ((m_{\text{model},i} - m_{\text{data},i})/(m_{\text{model},i}))^2$, where n_p is the number of data points. ^cFit with nonrobust weighting (e.g., unweighted fit). ^dUnrealistic value.

Table 2. Single-Parameter Fit for Aqueous Organics at 298.15 K^a

species	<i>n</i>	μ_j^b	r_{jw} (Å)	MSE ^c	ref
1,2-butanediol ^d	8	1.912	2.51	1.15×10^{-2}	33, 34
1,3-butanediol ^d	6	2.807	2.85	4.46×10^{-3}	33, 34, 46
1,4-butanediol ^d	8	2.566	2.77	6.70×10^{-3}	33, 34, 46
2,3-butanediol ^d	3	3.162	2.97	1.47×10^{-3}	33, 34
1,2,3,4-butanetetrol	12	5.942	3.66	2.39×10^{-5}	46, 47
1,2,4-butanetriol	3	16.90	5.19	6.45×10^{-3}	33, 46
ethanediol	3	12.00	4.63	7.52×10^{-3}	33, 47
ethanol	3	0.2653	1.30	5.80×10^{-3}	30
glycerol	3	15.28	5.02	2.38×10^{-3}	28, 29, 33, 48
isopropyl alcohol	3	0.0140	0.49	2.00×10^{-1}	31
methanol	3	3.462	3.06	3.83×10^{-3}	31
1,2-pentanediol	10	4.69×10^{-13e}	1.57×10^{-4e}	4.68×10^{-2}	33
1,4-pentanediol	8	1.427	2.28	1.36×10^{-2}	33
1,5-pentanediol	10	0.7127	1.81	2.17×10^{-2}	33
2,4-pentanediol	12	1.215	2.16	8.67×10^{-3}	33
1,2-propanediol	3	7.082	3.88	5.23×10^{-3}	33
1,3-propanediol	3	6.706	3.81	1.40×10^{-2}	33
sorbitol	12	7.260	3.92	7.89×10^{-3}	29, 49, 50
sucrose	7	26.70	6.05	4.19×10^{-3}	28, 32
urea	3	3.046	2.93	8.24×10^{-3}	28

^aNumber of sorption shell layers n was also fit but separately from the intermolecular distance, r_{jw} . ^bDipole moment was calculated using eq 12 and was not a fit parameter. ^cMSE is a normalized mean-square error, equal to $(1/n_p) \sum_{i=1}^{n_p} ((m_{\text{model},i} - m_{\text{data},i})/(m_{\text{model},i}))^2$, where n_p is the number of data points. ^dFit with nonrobust weighting. ^eUnrealistic value.

where ϵ_0 is the permittivity of space and $4\pi\epsilon_0 = 1.113 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$, D is a unit of conversion (Debye), $D = 3.33564 \times 10^{-30} \text{ C} \cdot \text{m}$, and μ_j is the dipole moment of species j . We assume that induced dipole moments are negligible, and we include further discussion about this in the Appendix.

2.1. Nonelectrolytes. Consider a single solute solution, where the solute j and solvent w (i.e., water) are modeled as dipoles. Three kinds of dipole–dipole interactions are present: solute–solute, solute–solvent, and solvent–solvent. In what follows, we will neglect secondary effects such as induced dipole

moments from multibody effects, for example, (solute with bound solvent) – (solvent). (See the Appendix for more discussion.) For nonelectrolytes, the unknowns in eqs 1–7 are n_j and $\Delta\epsilon_{ji} = E_{ji} - E_L$, where $\Delta\epsilon_{ji}$ is the change of energy between two states A and B, where A represents the presence of solute in the lattice and B represents the absence of solute. In other words, A represents solvent sorption to *solute* while B represents sorption of solvent to *solvent*. These solvent–solute and solvent–solvent interactions depend on the dipole of each species and the distance between these dipoles, which is related

Table 3. Two-Parameter Fit for Aqueous 1:1 Electrolyte Solutions at 298.15 K^a

species	<i>n</i>	ρ	r_{ji} (Å) ^b	cation <i>r</i> (Å) ^c	anion <i>r</i> (Å) ^c	MSE ^d	min <i>a_w</i>	max <i>m</i> [mol kg ⁻¹]	η_p	ref
HNO ₃	3	37.287	2.27	0.21	1.65	1.57×10^{-2}	0.072	5.65×10^1	150	36
HCl	7	28.172	1.47	0.21	1.81	2.63×10^{-4}	0.174	1.60×10^1	39	35, 36
HBr	13	22.852	2.22	0.21	1.96	2.13×10^{-4}	0.639	6.00×10^0	40	51, 52
LiOH	3	8.4789	2.76	0.76	1.53	3.41×10^{-5}	0.879	4.00×10^0	25	36
LiNO ₃ ^e	4	22.925	2.28	0.76	1.65	2.40×10^{-3}	0.271	2.00×10^1	43	36
LiCl	6	27.275	1.25	0.76	1.81	3.95×10^{-4}	0.119	1.92×10^1	43	35, 36
NaF	2	15.188	2.46	1.01	1.33	3.56×10^{-7}	0.969	1.00×10^0	17	36
NaOH	4	11.706	1.50	1.01	1.53	1.00×10^{-3}	0.063	2.90×10^1	52	36
NaNO ₃	2	9.7517	2.26	1.01	1.65	4.93×10^{-4}	0.152	1.60×10^2	162	41
NaCl	4	8.5709	2.24	1.01	1.81	5.63×10^{-4}	0.391	1.67×10^1	179	37–40
NaBr	4	18.011	2.11	1.01	1.96	7.38×10^{-6}	0.592	9.00×10^0	32	36
NaI	4	30.924	1.59	1.01	2.20	2.73×10^{-4}	0.392	1.20×10^1	35	36
NaClO ₄ ^e	3	15.566	2.24	1.01	2.22	1.29×10^{-5}	0.795	6.00×10^0	29	36
KF ^e	3	20.921	1.82	1.38	1.33	4.03×10^{-4}	0.292	1.75×10^1	41	36
KNO ₃	2	6.2577	2.55	1.38	1.65	3.78×10^{-4}	0.843	1.03×10^1	37	36, 42
KCl	3	13.497	2.32	1.38	1.81	9.67×10^{-6}	0.836	5.00×10^0	28	36
KBr	3	14.802	2.21	1.38	1.96	3.59×10^{-6}	0.816	5.50×10^0	28	36
KI	3	18.712	2.05	1.38	2.20	2.53×10^{-6}	0.846	4.50×10^0	26	36
RbF	6	18.959	3.25	1.52	1.33	9.37×10^{-6}	0.873	3.50×10^0	24	36
RbNO ₃	4	11.265	3.74	1.52	1.65	1.17×10^{-6}	0.919	4.50×10^0	26	36
RbCl	3	11.654	2.26	1.52	1.81	1.25×10^{-5}	0.752	7.80×10^0	32	36
RbBr	2	13.501	1.36	1.52	1.96	1.41×10^{-4}	0.845	5.00×10^0	27	36
RbI	2	12.926	1.05	1.52	2.20	2.51×10^{-7}	0.844	5.00×10^0	27	36
CsNO ₃	2	10.516	2.71	1.67	1.65	2.46×10^{-6}	0.963	1.50×10^0	19	36
CsCl	3	8.2649	2.15	1.67	1.81	4.97×10^{-5}	0.668	1.10×10^1	34	36
NH ₄ NO ₃	2	8.0672	2.16	1.78	1.65	2.70×10^{-4}	0.320	1.11×10^2	94	43–45
NH ₄ Cl	3	14.586	2.23	1.78	1.81	2.21×10^{-4}	0.527	2.18×10^1	132	35
DMANO ₃	2	11.292	1.66	2.42	1.65	9.60×10^{-6}	0.845	6.00×10^0	23	53
DMACl	3	10.967	1.71	2.42	1.81	8.84×10^{-5}	0.503	1.70×10^1	58	54
(CH ₃) ₄ NBr	3	4.3046	1.62	2.51	1.96	1.86×10^{-5}	0.846	5.50×10^0	36	55, 56
(CH ₃) ₄ NCl	3	8.9861	1.29	2.51	1.81	9.26×10^{-4}	0.331	1.90×10^1	36	55
(C ₂ H ₅) ₄ NCl	5	5.6277	0.94	3.08	1.81	2.87×10^{-5}	0.555	9.00×10^0	26	55
(C ₂ H ₅) ₄ NBr	4	1.3976	0.96	3.08	1.96	1.80×10^{-3}	0.552	1.20×10^1	29	55
(C ₂ H ₅) ₄ NI	2	7.8866	2.17	3.08	2.20	2.32×10^{-4}	0.966	1.90×10^0	19	55
TMANO ₃	2	6.8027	0.91	3.47	1.65	2.21×10^{-5}	0.784	8.50×10^0	28	53
(C ₃ H ₇) ₄ NBr	5	1.7025	1.26	3.49	1.96	7.54×10^{-4}	0.707	9.00×10^0	26	55
(C ₄ H ₉) ₄ NBr	2	1.1356	0.45	3.81	1.96	6.23×10^{-4}	0.520	2.70×10^1	54	55, 56

^aValues for r_{ji} and ρ were fit. The number of sorption layers, n , was also fit, but separately from r_{ji} and ρ . ^b r_{ji} is related to r_{jw} through eq 11. ^cMost ionic radii are from Shannon;⁵⁷ (CH₃)₄N⁺, (C₂H₅)₄N⁺, (C₃H₇)₄N⁺, and (C₄H₉)₄N⁺ were from Masterton et al.;⁵⁸ OH⁻, NO₃⁻, and NH₄⁺ were from Marcus.⁵⁹ ^dMSE is the mean-square error, equal to $(1/n_p) \sum_{i=1}^{n_p} ((m_{\text{model},i} - m_{\text{data},i})/(m_{\text{model},i}))^2$, where n_p is the number of data points. ^eFit with nonrobust weighting (e.g., unweighted fit).

to the size of the solute and solvent molecules. Thus, eqs 7 and 8 can be combined to obtain an expression for the change in energy between states A and B:

$$\Delta\epsilon_{j,i} = \frac{\mu_j \mu_w D^2}{4\pi\epsilon_0(r_{jw} + (i-1)r_{ww})^3} - \frac{\mu_w \mu_w D^2}{4\pi\epsilon_0(i \cdot r_{ww})^3} \quad (9)$$

where $r_{ww} = 2.83 \times 10^{-10}$ m and $\mu_w = 2.9$.¹⁸ (See the Appendix for the derivation of eq 9.) Thus, for nonelectrolytes, the remaining unknowns to the model (eqs 1–4, 9) are the number of layers, n_j , the solute dipole moment, μ_j , and the intermolecular distance between solute j and solvent w , r_{jw} . Further parameter reduction is possible by relating μ_j to the interspatial distance, discussed later.

2.2. Electrolytes. In the isotherm model in Dutcher et al. 2013, it was shown that the leading contributions to the thermodynamic model predictions could be broken down into a Debye–Hückel contribution that dominates at low

concentrations and an adsorption contribution that dominates at moderate to high concentrations (cf. part c in figures 2–7 in Dutcher et al. 2013).¹ Here we assume that the screening of individual ions is accounted for by the Debye–Hückel term and that the sorbing species in the isotherm portion of the model is a solvent-separated ion pair state, a ternary cation–water–anion cluster. So, a 1:1 electrolyte j is cast as a single compound with an apparent dipole moment, μ_j , calculated by

$$\mu_j = qe((r_{j+} + r_{j-})/2 + r_{ji})/D \quad (10)$$

where q is the charge, which in the case of 1:1 electrolytes has a value of 1, e is the elementary charge, $e = 1.60218 \times 10^{-19}$ C, r_{j+} and r_{j-} are the effective radii of the cation and anion, respectively, and r_{ji} is an interspatial distance that includes the additional distance due to the solvent separation in the adsorbent structure. We assume that this interspatial distance is related to the intermolecular distance r_{jw} through the following relationship

$$r_{jw} = r_{jj} + \frac{r_{j+} + r_{j-}}{2} + \frac{r_{ww}}{2} \quad (11)$$

With these assumptions, effective dipoles can be calculated for electrolytes (eq 10), and eqs 10 and 11 yield a relationship for the energy change that is identical to eq 9 for organics. Thus, for electrolytes, the remaining unknowns in the model (eqs 1–4 and 9) are the number of layers, n_j , the intermolecular distance, r_{jw} , and the Debye–Hückel parameter, ρ . Further parameter reduction is possible by relating ρ to the interspatial distance, discussed later.

3. MODEL APPLICATIONS AND PARAMETERIZATION

Employing eqs 1–4 and 9, the initial model parameters are n_j , r_{jw} , and μ_j for nonelectrolytes and n_j , r_{jw} , and ρ for electrolytes. These sets will be reduced further in later sections of this work. These parameter values were fit using MATLAB's built-in nonlinear regression model, `nlinfit`, and molality activity data from the literature. For robust fitting, the `nlinfit` function uses an iterative reweighting least-squares algorithm.^{19,20} At each iteration, the robust weights are recalculated and outlying points are down-weighted. Because robust weighting was used (except when noted in Tables 1–3), no weights were explicitly assigned. The maximum number of `nlinfit` iterations used was set to 1000, and the termination tolerance on the residual sum of squares as well as on the estimated coefficients was set to 1×10^{-300} which is on the order of the smallest nonzero number for MATLAB. A script looped through sorption layers ranging from $n_j = 1$ to 10. Because of the implicit nature of eq 1, a minimization algorithm was run to obtain molalities. The “goodness of fit” was calculated using a normalized mean square error, defined by $(1/n_p) \sum_{i=1}^{n_p} ((m_{\text{model},i} - m_{\text{data},i})/m_{\text{model},i})^2$, where n_p is the number of data points. Tables 1–3 provide the data sources, number of data points, and concentration ranges for each solute.

3.1. Nonelectrolytes. Model predictions for osmotic coefficients of glycerol, ethanol, methanol, sucrose, and 1,4-butanediol are given in Figure 1. Figure 1a shows the model predictions from fitting both μ_j and r_{jw} simultaneously; Table 1 shows the corresponding parameter values. Figure 1b shows the relationship between these two parameters, which is well described by the cubic polynomial given in eq 12, where r_{jw} is given in Angstroms. The fit for eq 12 has an R -squared value of 0.9745. Figure 1c shows the model predictions from fitting r_{jw} and using eq 12 to estimate μ_j ; Table 2 provides the corresponding fit parameter values.

$$\mu_j = (r_{jw}/2 \text{ \AA})^3 \quad (12)$$

3.2. Electrolytes. Model predictions for osmotic coefficients for families of chlorides, nitrates, and sodium electrolytes are given in Figures 2–4, respectively. The model predictions result from fitting ρ and r_{jw} simultaneously and using eqs 10 and 11 to calculate μ_j . The parameter ρ is from the Debye–Hückel treatment of the aqueous solvent and nominally relates to the hard core collision radius of the solute. The parameter ρ first appears in Pitzer's modification of the Debye–Hückel model as a fit parameter,^{21,22} which was later related to the distance of closest approach, a^{12} or the Stokes radii^{23,24} of the corresponding anion and cation. However, due to the lack of an accurate model for a , in practice, ρ is treated empirically, as it is here. As with nonelectrolyte solutes, the parameter r_{jw} represents the average center to center distance of

Figure 1. (a) Measured and calculated osmotic coefficients, ϕ , of aqueous organic solutes plotted versus the square root of the solute mole fraction. Solute mole fraction is defined as $x_s = m/(m + 1/M_w)$, where m is molality of the organic solute and M_w is the molar mass of water in kg/mol. (a) Solid lines show current model with both μ_j and r_{jw} fit as parameters. Symbols: blue triangles, glycerol, Scatchard et al.,²⁸ Ninni et al.,²⁹ red circles, ethanol, Strey et al.,³⁰ green diamonds, methanol, Zhu et al.,³¹ light-blue crosses, sucrose, Scatchard et al.,²⁸ Bubnik et al. (data from Baeza et al. 2010);³² black squares, 1,4-butanediol, Marcolli and Peter,³³ Paez et al.,³⁴ (b) Relation between the r_{jw} and μ_j fit parameters for all organic species fit in this paper (eq 12). (c) Current model with μ_j constrained to the relation shown in panel b.

a solute j and a nearest neighboring water molecule. Table 3 shows the fit parameters ρ and r_{jw} for all electrolyte species.

Figure 2. Measured and calculated osmotic coefficients, ϕ , for aqueous chloride solutions plotted versus the square root of the solute mole fraction. Solute mole fraction is defined as $x_s = m/(m + 1/M_w)$, where m is molality of the electrolyte and M_w is the molar mass of water in kilograms per mole. Solid lines show the current model. Symbols: red circles, HCl, Guendouzi et al. and Hamer and Wu;^{35,36} blue diamonds, LiCl, Guendouzi et al. and Hamer and Wu;^{35,36} light blue crosses, NaCl, Archer, Tang et al., Cohen et al., and Chan et al.;^{37–40} green triangles, KCl, Hamer and Wu;³⁶ gold asterisk, RbCl, Hamer and Wu;³⁶ black squares, CsCl, Hamer and Wu;³⁶ and magenta $\times$, NH_4Cl , Guendouzi et al. and Hamer and Wu.

There is excellent agreement between the model predictions and the available data for all solutes except LiNO_3 and HNO_3 (Figure 3a). The model is able to capture the low concentration characteristics of HNO_3 and LiNO_3 but is unable to predict the behavior at higher concentrations. However, LiNO_3 and HNO_3 can both be accurately modeled using the power law fit for the C parameters employed in prior work,¹ as shown in Figure 3b. The poor fit for HNO_3 and LiNO_3 may be due to the planar structure of the nitrate ion, which may allow for a closer approach for small cations than an equivalently sized elemental anion. Another source of the anomalous nature may be that electrolyte solutions containing lithium are known to form clusters,²⁵ which are not being adequately captured by the current model approach.

The two fit parameters used here for the electrolyte solutions are correlated, although to a lesser extent than observed with the nonelectrolyte solutions. Figure 5 shows a plot of ρ versus $r_{j+} + r_{j-}$, given in Angstroms, which follows the relationship

$$\rho = [11.04 \text{ \AA} / (r_{j+} + r_{j-})]^2 \quad (13)$$

Although the fit is not nearly as good as that for nonelectrolytes (see Figure 1b), the Debye–Hückel term only plays a role for dilute solutions, so errors in its value do not substantially alter the overall fit to the data. For example, for NH_4NO_3 solutions, the MSE is 8.0×10^{-3} and 2.7×10^{-4} for the ρ -constrained and unconstrained fits, respectively.

4. SUMMARY AND CONCLUDING REMARKS

In prior work, we used statistical mechanics to develop a solution thermodynamic model valid over the full range of concentrations. That model required at least three parameters for each solute. In this work we used a model of electrostatic interactions between solute and solvent molecules in solution to reduce the number of parameters required in the model and to relate the value of these parameters to properties of the

Figure 3. (a) Measured and calculated osmotic coefficients, ϕ , of aqueous nitrate solutions plotted versus the square root of the solute mole fraction. Solute mole fraction is defined as in Figure 2. Solid lines show the current model. Symbols: green triangles, HNO_3 , Hamer and Wu;³⁶ blue diamonds, LiNO_3 , Hamer and Wu;³⁶ light-blue crosses, NaNO_3 , data sources in Clegg et al. (1997);⁴¹ red circles, KNO_3 , Hamer and Wu and Kelly et al.;^{36,42} gold asterisk, RbNO_3 , Hamer and Wu;³⁶ black squares, CsNO_3 , Hamer and Wu;³⁶ and magenta $\times$, NH_4NO_3 , Wishaw and Stokes, Chan et al., and Kirgintsev and Lukyanov.^{43–45} (b) Species for which the power law fit is capable of providing a much better fit than the Coulombic fit.

solute and solvent molecules. The improved treatment and reduction of the parameters in the isotherm model yield accurate predictions of activity and osmotic coefficients for a wide range of electrolytes and nonelectrolytes in water, including 37 binary electrolyte systems, over a range of cation sizes from H^+ to tetrabutylammonium for all of the common anions including Cl^- , Br^- , I^- , NO_3^- , OH^- , and ClO_4^- and 20 water-soluble nonelectrolytes of mostly alcohol and polyol systems.

The parametrization itself can also be used to estimate unknown physicochemical properties, such as intermolecular spacing, although we emphasize that caution should be used to not overinterpret the parametrization. For example, for both electrolyte and nonelectrolyte solutions, there are instances of high “ n ” values, nominally indicating a large number of solvation layers; however, what is more likely is that larger “ n ” values are simply compensating for solute–solute association effects (e.g., dimerization for nonelectrolytes, associations for electrolytes). Despite this caveat, large n values may still be within the realm of possibility. For instance,

Figure 4. Measured and calculated osmotic coefficients, ϕ , of aqueous sodium electrolyte solutions plotted versus the square root of the solute mole fraction. Solute mole fraction is defined as in Figure 2. Solid line shows the current model. Symbols: blue diamonds, NaF, Hamer and Wu;³⁶ gold asterisk, NaOH, calculated values using the equation of Hamer and Wu;³⁶ Magenta $\times$, NaNO₃, Clegg et al. (1997);⁴¹ red circles, NaCl, Archer, Tang et al., Cohen et al., and Chan et al.;^{37–40} black squares, NaBr, Hamer and Wu;³⁶ light-blue crosses, NaI, Hamer and Wu;³⁶ and green triangles, NaClO₄, Hamer and Wu.³⁶

Figure 5. Fit parameter ρ plotted against the sum of the anion and cation radii for the electrolytes listed in Table 3. Solid line is eq 13

measurements have shown some very long-range effects from sulfate ions on water well outside the first solvation ring.²⁶ Regardless, it was generally found that different n values could be used with little change in MSE, and the resultant values of the fitted parameters are still well represented by the results shown in Figures 1b (eq 12) and 5 (eq 13). Future work is needed to better understand the role of the ‘ n ’ parameter.

To take steps toward connecting the lattice adsorption construct seen here to molecular modeling, in the future we must further consider the interpretation of the traditional gas-adsorption isotherm construct applied to solutions, where ‘ r ’ is the number of adsorption sites (here $r = \nu$), n is the number of layers of adsorption, and X_{ij} is the number of water molecules in layer i surrounding solute j . Instead, in solution, the parameter may be more along the lines of r being the number of sources or point charges (or induced charges) that induce a local non-Gaussian distribution of solvent molecules in some

structural, dynamic, or electric manner,²⁷ ‘ n ’ may be recast in terms of some radial distance from the source, and X_{ij} (which is also a fractional number between $0 < X_{ij} < \nu$) is a relative fractional number of solvent molecules effects by the point source at a given distance.

In conclusion, this work represents a significant advancement toward a fully predictive quantitative structure property relationship for activity coefficient modeling. For the non-electrolytes, the physical properties necessary to calculate the energies of adsorption are the dipole moments of the solvent and the solute and the intermolecular solute–solvent and solvent–solvent bond lengths. For electrolyte solutions, the ion charge types, ion–solvent bond lengths, and solvent–solvent bond lengths are the parameters necessary for calculating the energy of adsorption. The majority of these physical properties, with the exception of intermolecular distances for many solutes, are available in the literature. For the remaining properties, predictive correlations developed here for electrolytes (eq 13) and nonelectrolytes (eq 12) allow for a remarkable reduction in the number of adjustable parameters. In fact, for systems where estimates for intermolecular spacing for a solute and solvent molecular are known, the model is fully predictive. For solute concentration and activity predictions of multicomponent systems, the reduced parameter binary model predictions found here can be applied directly to the zero-parameter mixing model previously developed.¹

APPENDIX

Here we consider the effects of induced dipoles on the change in energy, $\Delta\epsilon_{ij,p}$ due to the sorption of a solvent molecule to a hydration layer, i , of a solute, j . An induced dipole moment, μ^* , is equal to the electric field, E , times the polarizability of a molecule, a ($\mu^* = Ea$). The parallel in this work is found when considering the presence of local non-neutrality (local electric field) near a point charge ($E = q/r$) or dipole (field = μ^*D/r^2). The resultant induced dipole of molecule 2 is then described by either $\mu_2^* = q_1Ca/r_{1,2}^2$ (point charge, 1) or $\mu_2^* = \mu_1Ca/r_{1,2}^2$ (dipole, 1). The Coulombic energy for a third induced dipole molecule, 3, near the point charge–dipole or dipole–dipole is given by $\mu_2^*\mu_3D^2/4\pi\epsilon_0r_{2,3}^3$, yielding

$$E = q_1Ca\mu_3D^2/4\pi\epsilon_0r_{1,2}^2r_{2,3}^3 \text{ (point charge)} \quad (\text{A1})$$

$$E = \mu_1Ca\mu_3D^2/4\pi\epsilon_0r_{1,2}^3r_{2,3}^3 \text{ (dipole)} \quad (\text{A2})$$

In the same manner, additional relationships can be found for all molecules present.

To calculate $\Delta\epsilon_{ij,p}$ we look at the energy difference between two states A and B, where A represents the presence of solute in the lattice while B represents the absence of solute. Consider an example of a nonelectrolyte species with a solvent molecule, w3, in a third monolayer. In state A, there are interactions between the solute molecule j and the solvent molecule w3, as well as the interactions between w3 and the two intervening solvent molecules, w1 and w2, in monolayers 1 and 2, respectively. In State B, the solute is replaced with a solvent molecule w0 and all the interactions between it, and the solvent molecules w1, w2, and w3 are as a result altered. Allowing for all absolute (no superscript) and induced (* superscript) dipole interactions and intermolecular differences, the Coulombic electrostatic difference of state B from state A is

$$\begin{aligned} \Delta\epsilon_{j,3} = & \mu_j(\mu_w + \mu_{w3}^*)D^2 \\ & / 4\pi\epsilon_0(r_{jw} + 2r_{ww} + r_{jw1}^* + r_{w1w2}^* + r_{w2w3}^*)^3 \\ & + (\mu_w + \mu_{w1}^*)(\mu_w + \mu_{w3}^*)D^2 / 4\pi\epsilon_0(2r_{ww} + r_{w1w2}^* + r_{w2w3}^*)^3 \\ & + (\mu_w + \mu_{w2}^*)(\mu_w + \mu_{w3}^*)D^2 / 4\pi\epsilon_0(r_{ww} + r_{w2w3}^*)^3 \\ & - \mu_w^2 D^2 / 4\pi\epsilon_0(3r_{ww})^3 - \mu_w^2 D^2 / 4\pi\epsilon_0(2r_{ww})^3 \\ & - \mu_w^2 D^2 / 4\pi\epsilon_0(r_{ww})^3 \end{aligned} \quad (A3)$$

where $D_w = 2.28 \times 10^{-10} \text{ m} = D_{\text{covalent}} + L_{\text{Hbond}} = (0.6498 + 2.1711) \times 10^{-10} \text{ m}$, $\mu_w = 2.9$,¹⁸ $\mu_{w1}^* = \mu_j D C \alpha / (r_{jw} + r_{jw1}^*)^3$, and $\mu_{w2}^* = \mu_j D C \alpha / (r_{jw} + r_{jw1}^*)^3$.

Note that we allow each water molecule to have an absolute dipole and induced dipole due to the presence of the other dipoles, and the intermolecular distance to the first monolayer varies for each species according to the size of the sorbent species and the strength of the intermolecular attraction. However, because $r_{xy} \gg r_{xy}^*$ and $\mu_{xy} \gg \mu_{xy}^*$, to leading order, the induced moments can be neglected and the change of energy reduces to

$$\Delta\epsilon_{j,3} = \mu_j \mu_w D^2 / 4\pi\epsilon_0(r_{jw} - 2r_{ww})^3 - \mu_w^2 D^2 / 4\pi\epsilon_0(3r_{ww})^3 \quad (A4)$$

For an arbitrary layer, the leading order energy of sorption parameter in an isotherm model in layer i of solute j , as defined in eq 6, is

$$C_{j,i} = \exp \left[\left(\frac{\mu_j \mu_w D^2}{4\pi\epsilon_0(r_{jw} + (i-1)r_{ww})^3} - \frac{\mu_w \mu_w D^2}{4\pi\epsilon_0(i \cdot r_{ww})^3} \right) / (k_B T) \right] \quad (A5)$$

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the National Oceanic and Atmospheric Administration (grant NA07OAR4310191) and the Department of Energy (grant DE-FG02-08ER64530). C.S.D was supported by a National Science Foundation Atmospheric and Geospace Sciences Postdoctoral Research Fellowship during a portion of this work. We thank Simon Clegg for his helpful critiques of the manuscript.

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