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Mean Activity Coefficient of a Simple Electrolyte, Dissolved in the Presence of an Arbitrary Number of Cosolute Components[†]

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An extension of the Gibbs−Duhem equation appropriate for a multicomponent fluid containing a solvent, a simple electrolyte, and an arbitrary number of cosolute components is proposed. The general formula is applied to two different systems: (i) a primitive model +1:−1 electrolyte in mixture with a neutral cosolute component and (ii) a mixture of primitive model +1:−1 and +2:−1 electrolytes (cosolute) with a common anion. The mean spherical and hypernetted chain integral equation approximations are used to calculate thermodynamic quantities such as the osmotic coefficient of the solution and the activity coefficients of various species. The mean activity coefficient of the principal solute, which is in this study the +1:−1 electrolyte, is calculated directly using the mean spherical and hypernetted chain integral equation theories or via the extended version of the Gibbs−Duhem equation. The calculations utilizing the two different routes are in agreement, providing a numerical check on the analytical derivations.

I. Introduction

Understanding the thermodynamic properties of electrolyte solutions is essential for the design and/or simulation of a variety of important chemical processes in industry and the biological sciences (see for example, refs 1 to 9). Thermodynamic properties of such solutions can be expressed either via the properties of solvent or, alternatively, by properties of solute(s). Two relevant quantities, essential to characterizing the thermodynamics of charged fluids, are the osmotic coefficient, ϕ, which describes the solvent, and the mean activity coefficient of the dissolved electrolyte. In a solution containing a single electrolyte and solvent, the two quantities are connected via the well-known two-component Gibbs−Duhem equation[1]

$$\ln \gamma_{\pm} = \phi - 1 + \int_{m=0}^{m} (\phi - 1) d \ln m \qquad (1)$$

where m is the molality of solute and $\gamma_{\pm}$ is its activity coefficient. Thus, knowing the osmotic coefficient, which is a property of the solvent, as a function of the electrolyte concentration, enables us to calculate the mean activity coefficient of the dissolved salt, which is a property of the solute component.

A great majority of theoretical and experimental studies are devoted to solutions of a single electrolyte, while studies related to mixed electrolytes[1,2] are less frequent (see also ref 10 and the references therein). This is in contrast to the real life situation; the electrolyte mixtures are far more common than pure electrolytes. There is thus often the need to calculate the properties of one electrolyte in a mixture with another electrolyte or perhaps with a neutral component.

For binary solutions, the determination of the chemical potential of the solute requires knowledge of the chemical potential (osmotic coefficient) of solvent as a function of the solute concentration. One may therefore expect that for a ternary system more information is needed. Several procedures have been suggested in the literature to treat mixtures.[1,2] One method has been proposed by Darken.[11] This approach and further developments by Gocken[12] use the properties of exact differentials

$$\left[\frac{\partial \mu_j}{\partial n_i}\right]_{n_{k\neq i}} = \left[\frac{\partial \mu_i}{\partial n_j}\right]_{n_{k\neq j}} \qquad (2)$$

If the chemical potential of the component j is known at all compositions of the s-component system, than each of the $s - 1$ partial derivatives of μ_j can be obtained. Other chemical potentials can then be obtained by integration of each of the $s - 1$ thermodynamic equations of the type of eq 2. For electrolyte mixtures with the solute components 2, 3, ..., it is convenient to express concentration on the molality scale, because by this means the number of moles of solvent (component 1) remains constant, and rewrite the relevant equations in the form[1]

$$\nu_2\left[\frac{\partial \ln \gamma_2}{\partial m_3}\right]_{m_2,...} = \nu_3\left[\frac{\partial \ln \gamma_3}{\partial m_2}\right]_{m_3,...} \qquad (3)$$

Thus, it is, in principle, possible to calculate the activity coefficients of all other components in the multicomponent system from the experimental determination of the activity coefficient of a single component at all compositions.

In this contribution, we present another approach to thermodynamics of multicomponent systems based on a straightforward generalization of the two-component Gibbs−Duhem equation, eq 1. The equation allows, in ternary systems, for example, calculation of the activity coefficient of the first solute, if the osmotic coefficient of the solution and the activity coefficients

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of the other solutes present are known as functions of the concentration of the first solute. We will apply the new expression to two different systems: (i) calculation of the mean activity coefficient of a +1:−1 electrolyte in the presence of hard-sphere particles (treated as cosolute) and (ii) the mean activity coefficient of a +1:−1 electrolyte in the presence of a +2:−1 electrolyte, which is now the cosolute. To obtain numerical results, two different integral equation theories, the mean spherical approximation (MSA) and hypernetted chain (HNC) approximation, are utilized. These results will later be used to numerically confirm the derived extension of the Gibbs−Duhem equation.

II. Generalization of the Gibbs−Duhem Equation

A. Binary System: Electrolyte in Solvent. For a two-component system (1, solvent; 2, solute), the solute and solvent activities are related as[2]

$$0 = n_1 d \ln a_1 + n_2 d \ln a_2 \tag{4}$$

where n_i ($i = 1{,}2$) is the number of moles of component i and a_i the corresponding activity. According to the definition of the osmotic coefficient ϕ, we also have[1,2]

$$\phi = -\frac{n_1}{n_2} \ln a_1 \tag{5}$$

or for a solute being an electrolyte, which dissociates onto ν ions

$$\ln a_1 = -\nu m M_1 \phi \tag{6}$$

Here $m \equiv m_2$ is the molality of the electrolyte defined as

$$m = \frac{n_2}{n_1 M_1} \tag{7}$$

and M_1 is the molar mass of solvent. From these equations, the Gibbs−Duhem equation for the mean activity coefficient, $\gamma_\pm$, of the electrolyte in solvent, viz., eq 1, follows immediately. In the derivation, the following conditions are invoked: for $m = 0$, $\gamma_\pm = \phi = 1$.

B. Ternary System. For a ternary system (1, solvent; 2, electrolyte; 3, cosolute), eq 4 contains another term

$$0 = n_1 d \ln a_1 + n_2 d \ln a_2 + n_3 d \ln a_3 \tag{8}$$

Here n_3 is the number of moles of component 3, which for the moment is assumed to be a neutral molecule. The additional component will be treated as a cosolute; that is, it does not cross the semipermeable membrane. The definition of the osmotic coefficient for a binary system, eq 5, now changes to

$$\phi = -\frac{n_1}{n_2 + n_3} \ln a_1 \tag{9}$$

If we denote the molality of component 3 by m_3

$$m_3 = \frac{n_3}{n_1 M_1} \tag{10}$$

and the activity coefficient of the extra solute by γ_3, we can obtain an extension of eq 1 now valid for three components, viz.

$$\ln \frac{\gamma_\pm(m, m_3)}{\gamma_\pm(0, m_3)} = \phi(m, m_3) - \phi(0, m_3) + \int_0^m [\phi(m, m_3) - 1] \times \frac{dm}{m} - \frac{m_3}{\nu} \int_0^m \left[\left(\frac{d \ln \gamma_3}{dm} \right)_{m_3} - \left(\frac{d\phi}{dm} \right)_{m_3} \right] \frac{dm}{m} \tag{11}$$

For $m_3 = 0$, we have $\gamma_\pm(0, 0) = \phi(0, 0) = 1$, and eq 11 reduces to eq 1. For a given $m_3 > 0$, this expression specifies how the logarithm of the mean activity coefficient, $\ln \gamma_\pm(m, m_3)$, in the presence of component 3 varies with an increase of the electrolyte molality, m.

The derivation of eq 11 proceeds as for the earlier simpler two-component case. From eqs 8 and 9, we obtain

$$\frac{n_2}{n_1} d \ln a_2 = d\left[\phi \left(\frac{n_2 + n_3}{n_1} \right) \right] - \frac{n_3}{n_1} d \ln a_3 \tag{12}$$

We rewrite this expression as

$$\nu m d \ln a_\pm = d[\nu m \phi + m_3 \phi] - m_3 d \ln a_3 \tag{13}$$

and thus

$$d \ln a_\pm = \frac{d(m\phi)}{m} + \frac{d(m_3 \phi)}{\nu m} - \frac{m_3}{\nu m} d \ln a_3 \tag{14}$$

Notice that m_3 is the parameter and m the integration variable as in the two-component situation shown before. This suggests all integrals should be evaluated at a fixed m_3 so that

$$\frac{dm_3}{dm} = 0 \tag{15}$$

Equation 14 now becomes

$$d \ln \gamma_\pm + d \ln m = [\phi d \ln m + d\phi] - \frac{m_3}{\nu m}[d \ln a_3 - d\phi] \tag{16}$$

and hence

$$d \ln \gamma_\pm = (\phi - 1) d \ln m + d\phi - \frac{m_3}{\nu m}[d \ln a_3 - d\phi] \tag{17}$$

The a_3 term in eq 17 simplifies to

$$-\frac{m_3}{\nu m} d \ln(\gamma_3 m_3) = -\frac{m_3}{\nu m} d \ln \gamma_3 \tag{18}$$

which eventually yields eq 11.

The derivation shown above has been performed for an added neutral cosolute, but the result can straightforwardly be extended to the case where the third component is an electrolyte. In the latter case, m_3 in eq 11 has to be replaced by $\nu_3 m_3$, and γ_3 by $\gamma_{\pm,3}$. The accuracy of the expression can be verified numerically by the mean-spherical or hypernetted-chain calculations for the same model. These theories can estimate all the individual activities and the osmotic coefficient directly without recourse to the Gibbs−Duhem equation.

C. Solvent, Solute, and Arbitrary Number of Cosolutes. We will now outline a general derivation of the Gibbs−Duhem equation for a system consisting of solvent (component 1), a principal solute (component 2), and arbitrary number (3, 4, ..., s) of the cosolute components. For this, we write eq 4 in a more general form

$$0 = n_1 d \ln a_1 + n_2 d \ln a_2 + \sum_{j=3}^{s} n_j d \ln a_j \tag{19}$$

where n_1 denotes the number of moles of solvent, n_2 the number of moles of principal solute, and n_j ($j = 3, 4, ..., s$) is the number of moles of cosolute component j. Accordingly, a_j, is the activity of the cosolute component j.

Derivation of eq 11 can easily be generalized. We start with eq 19 and a general form of the definition of the osmotic coefficient, ϕ, where n_3 is replaced by the sum over all cosolute components present.

$$\phi = -\frac{n_1}{n_2 + \sum_{j=3}^{s} n_j} \ln a_1 \qquad (20)$$

As before, we have denoted by m_j the molality of solute component j.

$$m_j = \frac{n_j}{n_1 M_1}$$

The rest of the derivation follows that for the ternary system in the previous section with the final expression being of the form

$$\ln \frac{\gamma_\pm(m, m_3, ..., m_s)}{\gamma_\pm(0, m_3, ..., m_s)} = \phi(m, m_3, ..., m_s) - \phi(0, m_3, ..., m_s) + \int_0^m [\phi(m, m_3, ..., m_s) - 1]\frac{dm}{m} - \frac{1}{\nu}\int_0^m \sum_{j=3}^{s} m_j\nu_j\left[\left(\frac{d \ln \gamma_{\pm,j}}{dm}\right)_{m_3,...,m_s} - \left(\frac{d\phi}{dm}\right)_{m_3,...,m_s}\right]\frac{dm}{m} \qquad (21)$$

Note that by substituting $s = 3$, $\nu_3 = 1$, and $\ln \gamma_{\pm,3} = \ln \gamma_3$, that is, for one neutral cosolute component only, we recover eq 11.

III. Results and Discussion

Equation 11 has been tested numerically for two different systems: (i) through calculation of the mean activity coefficient, $\ln \gamma_\pm$, of the $+1{:}-1$ electrolyte in the presence of hard-sphere particles (a neutral cosolute component of diameter $d_3 = 3.25$, 4.25, and 5.25 Å, respectively) and (ii) through calculation of the mean activity coefficient of a $+1{:}-1$ electrolyte in the presence of a $+2{:}-1$ electrolyte. In the latter case, the cosolute component is the $+2{:}-1$ electrolyte. In keeping with such values used in theoretical studies of charged fluids in the literature, we chose the diameters of all ionic species to be 4.25 Å. In all cases, we have utilized the MSA and HNC integral equations to obtain numerical results. The $\ln \gamma_\pm$ of the principal $+1{:}-1$ electrolyte was calculated at a number of concentrations (a) directly from the individual activity coefficients and (b) from the extended Gibbs−Duhem equation, eq 11 or eq 21.

A. HNC and MSA Integral Equation Theories. The HNC and MSA integral equations for primitive model electrolyte solutions are widely used techniques in the statistical mechanics of charged fluids.[13−15] We will therefore restrict ourselves here to giving a brief outline of these equations. The theories are based on the Ornstein−Zernike integral equation (see for example, ref 13)

$$h_{\rm st}(r_{\rm st}) = c_{\rm st}(r_{\rm st}) + \sum_k \rho_k \int c_{sk}(r_{sk})h_{kt}(r_{kt}){\rm d}r_k \qquad (22)$$

where the summation is performed over all the components. This equation is merely a definition of the direct correlation function $c_{\rm st}$ and another relation by, namely, a closure relation between the total correlation function $h_{\rm st} = g_{\rm st} - 1$ and $c_{\rm st}$. The second relation reads

$$\ln[h_{\rm st}(r_{\rm st}) + 1] = -\beta u_{\rm st}(r_{\rm st}) + h_{\rm st}(r_{\rm st}) + B_{\rm st}(r_{\rm st}) - c_{\rm st}(r_{\rm st}) \qquad (23)$$

Here, $u_{\rm st}(r_{\rm st})$ is the pair potential of species s and t and $\beta = (k_{\rm B}T)^{-1}$, where $k_{\rm B}$ is Boltzmann's constant and T the absolute temperature. The problem with this expression is that the term $B_{\rm st}(r)$, known in the literature as the bridge graph term, cannot be written as a closed form. In the absence of a better approximation, the bridge graph term is set to zero. Thus, $B_{\rm st}(r_{\rm st}) = 0$ defines the HNC approximation, and it has been quite successful in describing the properties of charged fluids (see for example, the reviews[14,15]). Due to the long-range nature of Coulomb interactions, the set of integral equations given above is not suitable for numerical work and has to be renormalized before it can be solved numerically.[16] The renormalized form of the integral equations was solved by direct iteration using fast Fourier transform routine on a linear grid. For dilute solutions, a large number of division points ($N = 2^{17}$) was needed to obtain acceptable accuracy in the calculations.

The logarithm of the individual activity coefficient γ_s of ionic species s for the HNC approximation was calculated via[17]

$$\ln \gamma_s = -\sum_{t=+,-} \rho_t c_{\rm st}^{(s)}(0) + 0.5 \sum_{t=+,-} \rho_t \int {\rm d}r[h_{\rm st}(h_{\rm st} - c_{\rm st})] \qquad (24)$$

The activity coefficient calculated in this manner has earlier been found to be in very good agreement with computer simulations[18] for the limited cases treated. Notice that the expression above is valid only within the HNC approximation and not generally. The same expression was used for the calculation of the logarithm of the activity coefficient, $\ln \gamma_s$, of a neutral species s, taking into account that all the interactions with neutral species are short-ranged.

The MSA is obtained simply by linearizing the HNC approximation. For example, further to the approximation $B_{\rm st}(r_{\rm st}) = 0$, if the left-hand side of eq 23 is linearized, one obtains

$$c_{\rm st}(r_{\rm st}) = -\beta u_{\rm st}(r_{\rm st}) \qquad (25)$$

which is the well-known MSA closure. The advantage of the MSA is that it affords analytic solution[19] and yields all thermodynamic quantities in closed form.[20−23]

B. Numerical Solution. Numerical problems in solving the two-component Gibbs−Duhem equation, eq 1, are well-known. The problem may be severe for the nonanalytical approaches such as the HNC. In fact, to minimize numerical errors one needs to use analytical continuation, for example, DHLL + B2, for very low electrolyte concentrations.[24] There is, however, no such problem with the MSA theory, which is fully analytical.

Unfortunately, there is no exact analytical continuation available when an extra component is added to the system. Equation 11 cannot be treated in an analogous way within the HNC theory, since only numerical results are available. The derivatives in eq 11 were calculated numerically from the concentration dependence of the quantities as obtained from the HNC equation. In the actual calculation the molalities (m, m_3) were replaced by molarities (c, c_3). Note that the left- and right-hand sides of eq 11 (or eq 21) are dimensionless with cancellation of units occurring in the terms involving the integrals on the right-hand side. This makes the evaluation of these terms independent of any units used. Due to numerical errors, the integration was only reliable above a low concentration ~0.001 mol·dm^{-3}. The absolute values for $\ln[\gamma_\pm(c, c_3)]$ were then obtained by adding the value of $\ln[\gamma_\pm(c = 0.001$ M, $c_3]$ obtained directly by solving the HNC using eq 24.

The results are given in tabular form in Tables 1 to 3. Tables 1 and 2 correspond to case (i) (mixture of $+1{:}-1$ electrolyte and neutral hard spheres), while Table 3 corresponds to case (ii) (mixture of $+1{:}-1$ and $+2{:}-1$ electrolytes). The calculations have been done at room temperature (~298 K) for a solvent modeled as continuum with relative permittivity ~78.5. All MSA results have been obtained using the energy route, while

Table 1. ln $\gamma_\pm$ as Obtained Using Different Methods for $z_3 = 0$ (Addition of a Neutral Component) and $d_3 = 4.25$ Å[a]

		HNC		MSA	
c_3	c	eq 24	eq 11	MSA^e	eq 11
0.1 M	0.005 M	−0.0550	−0.0560	−0.0543	−0.0543
	0.01 M	−0.0811	−0.0820	−0.0801	−0.0801
	0.05 M	−0.166	−0.167	−0.164	−0.164
	0.1 M	−0.207	−0.208	−0.205	−0.205
	0.5 M	−0.228	−0.230	−0.223	−0.223
	1.0 M	−0.102	−0.103	−0.0917	−0.0917
0.5 M	0.005 M	+0.0244	+0.0240	−0.0254	−0.0254
	0.01 M	−0.00160	−0.00200	−0.000310	−0.000266
	0.05 M	−0.0859	−0.0860	−0.0835	−0.0836
	0.1 M	−0.127	−0.127	−0.124	−0.124
	0.5 M	−0.142	−0.143	−0.136	−0.136
	1.0 M	−0.00590	−0.00700	+0.00436	+0.00447

[a] The diameters of all ionic species are 4.25 Å. The column MSA^e corresponds to the ln $\gamma_\pm$ calculated directly from the individual activity coefficients in the MSA via the energy route.

Table 2. ln $\gamma_\pm$ as Obtained Using Different Methods for $z_3 = 0$ (Addition of a Neutral Component) and $c_3 = 0.1$ M[a]

		HNC		MSA	
d_3	c	eq 24	eq 11	MSA^e	eq 11
3.25 Å	0.005 M	−0.0611	−0.0620	−0.0617	−0.0617
	0.01 M	−0.0872	−0.0880	−0.0875	−0.0875
	0.05 M	−0.172	−0.173	−0.171	−0.171
	0.1 M	−0.213	−0.214	−0.213	−0.213
	0.5 M	−0.235	−0.236	−0.231	−0.231
	1.0 M	−0.109	−0.111	−0.101	−0.101
4.25 Å	0.005 M	−0.0550	−0.0560	−0.0543	−0.0543
	0.01 M	−0.0811	−0.0820	−0.0801	−0.0801
	0.05 M	−0.166	−0.167	−0.164	−0.164
	0.1 M	−0.207	−0.208	−0.205	−0.205
	0.5 M	−0.228	−0.230	−0.223	−0.223
	1.0 M	−0.102	−0.103	−0.0917	−0.0917
5.25 Å	0.005 M	−0.0472	−0.0480	−0.0465	−0.0465
	0.01 M	−0.0733	−0.0740	−0.0722	−0.0722
	0.05 M	−0.158	−0.159	−0.156	−0.156
	0.1 M	−0.199	−0.200	−0.197	−0.197
	0.5 M	−0.219	−0.221	−0.214	−0.214
	1.0 M	−0.0918	−0.0930	−0.0817	−0.0817

[a] The diameters of all ionic species are 4.25 Å. The column MSA^e corresponds to the ln $\gamma_\pm$ calculated directly from the individual activity coefficients in the MSA via the energy route.

Table 3. ln $\gamma_\pm$ as Obtained Using Different Methods for Addition of a +2:−1 Electrolyte[a]

		HNC		MSA	
c_3	c	eq 24	eq 21	MSA^e	eq 21
0.1 M	0.005 M	−0.334	−0.333	−0.324	−0.324
	0.01 M	−0.333	−0.333	−0.324	−0.324
	0.05 M	−0.331	−0.330	−0.323	−0.323
	0.1 M	−0.326	−0.325	−0.320	−0.320
	0.5 M	−0.250	−0.249	−0.242	−0.242
	1.0 M	−0.0933	−0.0920	−0.0809	−0.0807
0.5 M	0.005 M	−0.304	−0.303	−0.284	−0.284
	0.01 M	−0.302	−0.301	−0.283	−0.283
	0.05 M	−0.288	−0.287	−0.268	−0.268
	0.1 M	−0.270	−0.269	−0.250	−0.250
	0.5 M	−0.115	−0.113	−0.0937	−0.0937
	1.0 M	+0.108	+0.110	+0.131	+0.131

[a] The diameters of all ionic species are 4.25 Å. The column MSA^e corresponds to the ln $\gamma_\pm$ calculated directly from the individual activity coefficients in the MSA via the energy route.

the HNC results are from the virial route (osmotic coefficient) and from eq 24 (activity coefficient). For the MSA, the energy route is recognized to be the most accurate and for which the analytic expressions for the individual activity coefficients are available.[20,22,23]

It is clear from the tables that both the HNC and the MSA results for ln $\gamma_\pm$, obtained via the extended Gibbs−Duhem equation, are consistent with those calculated directly from the individual activity coefficients. For the MSA, the associated numerical errors are minimal. This is not surprising since the MSA is analytical and the only numerical uncertainties come from the numerical differentiation and integration in eq 11. With the HNC, however, one has to contend with additional uncertainty emanating from the numerical solution of the (HNC) integral equation itself. Such numerics notwithstanding, our results for the range of physical states studied do seem to validate the purported extension of the Gibbs−Duhem equation.

It is of interest to note from the three tables that the predicted thermodynamics from the HNC (virial route for the osmotic and eq 24 for the activity coefficient) and the MSA energy route show a reasonably good consistency overall. This is in keeping with the generally accepted notion that these routes for the respective theories are the most accurate.

IV. Conclusions

The achievement of this paper has been the formulation of an extension of the Gibbs−Duhem equation to multicomponent mixtures. The application of the HNC and MSA integral equations to some primitive model mixtures and the ensuing consistency of the predicted thermodynamics with that from the extended equation have provided the needed numerical support to establish the equation.

The extended Gibbs−Duhem equation may prove useful in thermodynamic analysis of electrolyte mixtures in cases where in addition to the osmotic coefficient the activity coefficient of the cosolute is known. In such a case, the new expression readily provides a mechanism to evaluate the activity coefficient of the principal solute. The extended Gibbs−Duhem equation needs different input information vis-a-vis the previously known equations. The two numerical approaches, one based on the cross-differentiation equations (eq 3) and the version of the Gibbs−Duhem equation presented here, are complementary. While eq 3 only needs the chemical potential of the second component as an input, and consequently looks more efficient to use, it has to be evaluated at considerably more state points than the alternative expressions (eqs 11 or 21), presented in this study. The choice of using one or another approach therefore depends on the system under study.

The extended equation may be of some use in computer simulations too since it is well-known that osmotic coefficients can be calculated more accurately than activity coefficients. For example, in recent years simulation studies of structure and thermodynamics of multicomponent electrolyte mixtures have begun to be available (see, for example, the review[25] and the references therein). Very recently, Lamperski and Płuciennnik[26] have published simulation results for the activity coefficient of a solvent primitive model electrolyte at high densities for the neutral component. Such a system is an ideal candidate for a theoretical thermodynamic analysis where the extended Gibbs−Duhem equation could be very useful. We are presently engaged in such a study which will be reported in a future publication.

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