Thermodynamic Properties of Aqueous Solutions of Mixed Electrolytes: A New Mixing Rule

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The prediction of several thermodynamic properties of mixed aqueous electrolyte solutions has been considered earlier (Patwardhan and Kumar, 1986a,b). A unified set of predictive equations for several properties was presented by them and was tested against experimental data. These predictive equations require knowledge of properties of corresponding single electrolyte solutions. No further system-specific empirical constants are involved. The experimental data used for testing these equations involved mixed systems having a common ion in most cases, with only a few exceptions. It is thus clear that the equations developed earlier can be used with confidence for common ion systems. We consider here the application of these equations to mixed systems having no common ion, as well as several properties for which reliable data are available for different systems involving four ions.

Process of Mixing

Let us consider the mixing of single electrolyte solutions of equal ionic strength which do not have any common ion, for example, mixing of NaCl solution and KBr solution. In the final solution, interactions of sodium ions with both chloride and bromide ions are present and may be important. A similar statement can be made about the potassium ions. If an equation involving only these two electrolytes were used for predicting the vapor pressure of the final mixture, then it would account for only the Na-Cl and K-Br interactions, leaving out the other two interactions, namely Na-Br and K-Cl. Therefore, even though the final mixed electrolyte solution has been actually prepared by mixing NaCl solution with KBr solution, it should be considered as obtained by conceptually mixing four single electrolyte solutions: NaCl, KCl, NaBr, and KBr. The amounts of these solutions have to be so selected that each mixing process involves a common ion or a common ionic atmosphere (cationic or anionic). These amounts can be calculated in the following manner. Consider a mixed electrolyte solution containing several species of cations and anions. Let i refer to cations and j refer to anions. The total anionic charge, (CH), which is also equal to the total cationic charge, is given by:

$$(CH)=\sum_i m_i z_i=\sum_j m_j z_j \tag{1}$$

The cationic strength is:

$$I_c=0.5\sum_i m_i z_i^2 \tag{2}$$

and the anionic strength is:

$$I_a=0.5\sum_j m_j z_j^2 \tag{3}$$

The total ionic strength is given by:

$$I=I_c+I_a \tag{4}$$

Let the cationic strength fraction and the anionic strength fractions be defined as:

$$X_i=0.5m_i z_i^2/I_c \tag{5}$$

and

$$Y_j=0.5m_j z_j^2/I_a \tag{6}$$

Let us consider a quantity of the mixed electrolyte solution which contains 1,000 g of water. Consider a process whereby cation i in the solution is conceptually separated from other cations into a region containing $(1{,}000\,y_i)$ g water, keeping the anions well mixed where y_i is unknown at present. The cationic strength in this region is $X_i I_c/Y_i$ and the anionic strength in the same region is $[m_i z_i/(CH)]I_a/y_i$. We now select y_i such that the total ionic strength in this region is equal to I.

$$I=X_i I_c/y_i+[m_i z_i/(CH)]I_a/y_i \tag{7}$$

Therefore,

$$y_i=X_i I_c/I+[m_i z_i/(CH)]I_a/I \tag{8}$$

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We now have a region within the mixed electrolyte solution which has cations of type i only, anions having the same composition as the mixed solution, 1,000 y_i g water, and an ionic strength of I. We now further subdivide this region into several subregions, each containing a different species of anions. Let anion j be separated into a subregion containing 1,000 y_{ij} g water and a quantity of cation i needed for electrical neutrality where y_{ij} is not known at this stage. The total moles of anions in this subregion are $m_j(m_i z_i)/(CH)$. The total moles of cations is therefore $m_j z_j m_i/(CH)$. y_{ij} is now selected such that the total ionic strength in this subregion is equal to I. Therefore,

$$I = m_i m_j z_j z_i (z_i + z_j)/[2y_{ij}(CH)] \qquad (9)$$

This gives, after algebraic manipulations:

$$y_{ij} = (ISF)_i (CF)_j + (ISF)_j (CF)_i \qquad (10)$$

where $(ISF)_i$, the ionic strength fraction and $(CF)_i$, the charge fraction of ionic species i are defined as $[m_i z_i^2/(2I)]$ and $m_i z_i/(\Sigma m_i z_i)$, respectively. If the mixed electrolyte solution is considered to be made up by mixing single electrolyte solutions (of equal ionic strengths) of all cation-anion combinations, then y_{ij} represents the fractional contribution of the single electrolyte solutions i-j toward the total ionic strength.

It can be shown that $\Sigma_j y_{ij} = y_i$ and $\Sigma_i y_i = 1$. At this stage we have several subregions, each having a single electrolyte solution of ionic strength I. All possible combinations of cations and anions are covered. If the subregions having the same cations are now mixed together, we get several regions, each having a different cationic species, but identical composition of anions. Subsequent mixing of these regions, which involves a common anionic atmosphere, gives the final mixed electrolyte solution. Thus, Eq. 10 enables us to visualize the final mixed electrolyte solution, as if it is made up by mixing all possible single electrolyte solutions (under conditions of a common ion or common ionic atmosphere and a constant ionic strength), irrespective of how it is actually prepared in practice.

Thermodynamic properties of mixed solutions

Let us now see how the concept developed above can be applied for predicting several different thermodynamic properties of mixed electrolyte solutions.

Vapor pressure

For a common ion system, the vapor pressure of a mixed electrolyte solution can be predicted by (Patwardhan and Kumar, 1986a):

$$\ln a_w = \sum_J y_J \ln a^o_{w,J} \qquad (11)$$

where index J refers to the electrolytes actually used for preparing the solution. For a four-ion system, however, the equations stated in the previous section can be applied, by calculating the ionic composition of the final solution, calculating all y_{ij} with Eq. 10 and using the following equation:

$$\ln a_w = \sum_i \sum_j y_{ij} \ln a^o_{w,ij} \qquad (12$$

where $a^o_{w,ij}$ is the water activity in a single electrolyte solutio of cation i and anion j, at the same ionic strength as that o the final solution.

Ten four-ion systems for which vapor pressure data ar available in literature are listed Table 1. The vapor pressure for these systems were predicted using Eq. 12 and compare with experimental values. The average deviations obtained fo each system is also listed in the table. It is also of interest t see how well Eq. 11 itself can predict vapor pressures of mixe solution. The average deviations for this case is also presente in Table 1. It is seen that for all these systems Eq. 12 is mor accurate than Eq. 11 in vapor pressure prediction. The re duction in σ is quite substantial for some system such as LiCl Na_2SO_4 and KCl-$MgSO_4$. For all the systems considered to gether, Eq. 12 gives an average σ (0.62%) which is almost hal of that (1.16%) obtained from Eq. 11.

Density

The predictive equation for the density of a common io system as given by Patwardhan and Kumar (1986b) is:

$$d = \sum_J \psi_J / \sum_J (\psi_J / d^o_J) \qquad (13$$

where

$$\psi_J = (1{,}000 y_J + m_J M_J) \qquad (14$$

where the sum is over the constituent electrolytes in a mixture Using the above mixing scheme for a four-ion system, th density can be predicted by the following expression:

$$d = \sum_i \sum_j \psi_{ij} / \sum_i \sum_j (\psi_{ij}/d^o_{ij}) \qquad (15$$

with

$$\psi_{ij} = (1{,}000 y_{ij} + m_{ij} M_{ij}) \qquad (16$$

Compressibility and expansibility

The equations for estimating compressibility, β, and expansibility, ϕ_E, for common ion systems are given as:

$$\beta = \sum_J (\psi_J \beta^o_J / d^o_J) / \sum_J (\psi_J / d^o_J) \qquad (17$$

and

$$\phi_E = \sum_J (m_J \phi^o_{EJ}) / \sum_J m_J \qquad (18$$

Both the above expressions can be rewritten in terms of new mixing scheme as:

$$\beta = \sum_i \sum_j (\psi_{ij} \beta^o_{ij} / d^o_{ij}) / \sum_i \sum_j (\psi_{ij} / d^o_{ij}) \qquad (19$$

Table 1. Results Obtained from the Present and Earlier Mixing Rules for Four-Ion Systems

System	I_{max} mol·kg^{-1}	Comp. Range, % Second Electro.	σ (%)		Source of Data
			Present Mixing Rule	Earlier Mixing Rule	
Vapor Pressure					
Na_2SO_4-$MgCl_2$	8.22	24-77	0.11	0.24	Wu et al. (1968)
NaCl-$MgSO_4$	7.77	25-75	0.10	0.15	Wu et al. (1968)
KCl-$NaNO_3$	5.80	22-82	0.38	0.56	Bezboruah et al. (1970)
NaCl-KNO_3	3.21	22-86	0.04	0.10	Bezboruah et al. (1970)
KCl-NaBr	4.16	17-78	0.14	0.27	Covington et al. (1968)
NaCl-KBr	4.48	19-79	1.11	1.37	Covington et al. (1968)
LiCl-Na_2SO_4	4.49	24-75	0.19	1.06	Robinson (1972)
$MgCl_2$-$Ca(NO_3)_2$	20.25	11-84	2.09	4.25	Platford (1971)
$Mg(NO_3)_2$-$CaCl_2$	16.68	11-84	1.95	2.74	Platford (1971)
KCl-$MgSO_4$	11.69	5-75	0.11	0.84	Seidel et al. (1985)
Density					
$MgCl_2$-Na_2SO_4	3	9-90	0.21	0.31	Millero et al. (1985)
NaCl-$MgSO_4$	3	9-90	0.01	0.18	Millero et al. (1985)
NaCl-K_2SO_4	1.5	10-90	0.01	0.01	Millero & Sotolongo (1986)
KCl-Na_2SO_4	1.5	10-90	0.02	0.02	Millero & Sotolongo (1986)
NaCl-KBr	4	8-96	0.07	0.08	Kumar (1985)
KCl-NaBr	4	12-90	0.01	0.03	Kumar (1989)
Compressibility					
$MgSO_4$-NaCl	3	9-90	0.07	0.28	Millero & Lampreia (1985)
$MgCl_2$-Na_2SO_4	3	10-90	0.05	0.37	Millero & Lampreia (1985)
Expansibility					
$MgCl_2$-Na_2SO_4	3	20-80	1.39	1.93	Connaughton et al. (1987)
NaCl-$MgSO_4$	3	20-80	5.49	7.87	Millero et al. (1985)

and

$$\phi_E = \sum_i \sum_j (m_{ij}\phi^o_{Eij}) / \sum_i \sum_j m_{ij} \tag{20}$$

The above equation for estimating the volumetric properties, that is, density, compressibility, and expansibility, was tested against the experimental data in Table 1. The results based on the present mixing rule and the earlier one are also summarized in the table. The table shows that an improvement in the prediction capability for density, compressibility, and expansibility is noticed for ten systems investigated.

Conclusions

The analysis of experimental data on vapor pressure, density, compressibility, and expansibility shows that the newly proposed mixing rule can be employed to predict with good accuracy the thermodynamic properties of aqueous systems with no common ions.

In this study the equations developed have been applied to strong electrolyte solutions, including those containing nitrate and sulfate ions (which are known to associate in solutions). The results indicate that for systems involving associating ions, the standard deviation is somewhat higher. The predictions, however, are still quite accurate, as the associating characteristics of these ions appear to have been adequately accounted for in terms of the single electrolyte solutions, which are mixed to get the final solution. The present method could not be tested on systems containing ions such as zinc and cadmium, due to lack of adequate experimental data.

Notation

a = water activity = p/p_w
(CF) = charge fraction = $mz/(CH)$
(CH) = total charge $\Sigma_i m_i z_i$
d = density
I = ionic strength
(ISF) = ionic strength fraction, $mz^2/(2I)$
m = molality
p = vapor pressure of aqueous electrolyte solution
p_w = vapor pressure of water
X_i = defined by Eq. 5
y_i = defined by Eq. 8
y_{ij} = defined by Eq. 10
Y_j = defined by Eq. 6
Y_j = ionic strength fraction of electrolyte J
z = ionic charge

Subscripts

a = anionic
c = cationic
i = cations
j = anions
J = electrolyte
w = water

Superscript

o = single electrolyte solution of the same ionic strength as the mixed solution

Greek letters

β = adiabatic compressibility = $(1/d)(\partial d/\partial P)_T$
σ = standard deviation
ϕ = osmotic coefficient, $-1{,}000 \ln a_w/[M_w(\Sigma m_i + \Sigma m_j)]$

ϕ_E = apparent molal expansibility
ψ_{ij} = defined by Eq. 16
ψ_J = defined by Eq. 14

Literature Cited

Bezboruah, C. P., A. K. Covington, and R. A. Robinson, "Excess Gibbs Energies of Aqueous Mixture of Alkali Metal Chloride and Nitrates," *J. Chem. Thermodyn.*, **2**, 431 (1970).

Connaugton, L. M., and F. J. Millero, "The PVT Properties of Concentrated Aqueous Electrolytes: VIII. The Volume Changes for Mixing the Major Sea Salts of an Ionic Strength of 3.0 from 5-95°C," *J. Solution Chem.*, **16**, 491 (1987).

Covington, A. K., T. H. Lilley, and R. A. Robinson, "Excess Free Energies of Aqueous Mixtures of Some Alkali Metal Halide Salt Pair," *J. Phys. Chem.*, **72**, 2759 (1968).

Kumar, A., "Densities and Apparent Molar Volumes of Aqueous NaCl-KBr Mixtures at 298.15 K," *Can. J. Chem.*, **63**, 3200 (1985).

Kumar, A., "Densities and Excess Volumes of Aqueous KCl-NaBr Up to Ionic Strength of 4 mol·kg^{-1}," *J. Chem. Eng. Data*, **34**, 446 (1989).

Millero, F. J., and M. I. Lampreia, "The PVT Properties of Concentrated Aqueous Electrolytes: IV. Changes in the Compressibilities of Mixing the Major Sea Salts at 25°C," *J. Solution Chem.*, **14**, 853 (1985).

Millero, F. J., and S. Sotolongo, "The PVT Properties of Concentrated Aqueous Electrolytes: I. The Volume of Mixing of the Reciprocal Salt Pairs $KCl-K_2SO_4$, $NaCl-Na_2SO_4$ at 25°C and I = 1.5m," *J. Chem. Eng. Data*, **31**, 470 (1986).

Millero, F. J., L. M. Connaughton, F. Vinokurova, and P. Chetirkin, "PVT Properties of Concentrated Aqueous Electrolytes: III. Volume Changes for Mixing the Major Sea Salts at I = 1.0 and 3.0 at 25°C," *J. Solution Chem.*, **14**, 837 (1985).

Patwardhan, V. S., and A. Kumar, "A Unified Approach for Prediction of Thermodynamic Properties of Aqueous Mixed Electrolyte Solutions: Vapor Pressure and Heat of Vaporisation," *AIChE J.*, **32**, 1419 (1986a).

Patwardhan, V. S., and A. Kumar, "A Unified Approach for Prediction of Thermodynamic Properties of Aqueous Mixed Electrolyte Solutions: II. Volume, Thermal and Other Properties," *AIChE J.*, **32**, 1429 (1986b).

Platford, R. F., "Thermodynamics of Mixed Salt Solutions: Excess Energies of Mixing for the Six Ternary Systems Formed from Aqueous $MgCl_2$, $Mg(NO3)_2$, $CaCl_2$ and $Ca(NO3)_2$ at 25°C," *J. Chem. Thermodyn.*, **3**, 319 (1971).

Robinson, R. A., "Excess Gibbs Free Energy of Mixing of the Systems Water-Lithium Chloride-Sodium Sulphate and Water-Cesium Chloride-Sodium Sulphate at 25°C," *J. Solution Chem.*, **1**, 71 (1972).

Seidel, J., K. Rossner, and F. Kuschel, "Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of Potassium Chloride and Magnesium Sulfate up to High Concentration at 25°C," *J. Chem. Eng. Data*, **30**, 289 (1985).

Wu, Y. C., R. M. Rush, and G. Scatchard, "Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulphate, Magnesium Sulphate and Magnesium Chloride in Water at 25°C: II. Isopiestic and Electromotive Forces Measurements on the Two Systems Without Common Ions," *J. Phys. Chem.*, **73**, 2047 (1969).

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Errata

◆ In the note titled "Free Rising Spheres Do Not Obey Newton's Law for Free Settling" by D. G. Karamanev and L. N. Nikolov (November 1992, p. 1846), the "Conclusions" should read: 2) C_D of free-rising light particle can be described by the laws of free settling, only when $Re_t < 130$ and/or ρ_p is greater than approximately 900 kg/m^3; 3) C_D of free-rising light particle depends on both Re_t and ρ_p when $300 < \rho_p < 900$ kg/m^3 and $Re_t > 130$.

◆ In the article titled "Circulation and Scale-Up in Bubble Columns" by Geary and Rice (January 1992, p. 76), the section titled "Scale-Up Predictions" uses derived velocity profile to forecast mixing time. The mixing time is, of course, inversely proportional to velocity. Thus, the lefthand-side of Eq. 21 should read τ_{mix}^{-1}, and the items in Table 1 are proportional to τ_{mix}^{-1}.