

Theoretical Method for Interconverting Concentrations Scales for Single and Mixed Aqueous Solutions Using Ionic Radii

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A new method for converting molality to concentration and vice versa in electrolyte solutions is proposed. The method utilizes ionic radii to theoretically calculate the solutions' volume instead of depending on the experimentally determined density of the solutions. It produces reliable results in single as well as multiple electrolyte solutions.

Introduction

The need to convert from molality to concentration or vice versa is a common problem in modeling concentrated electrolyte solutions. Most semiempirical models for predicting the electrolyte solutions' activity coefficients define solutions' composition using molality,¹ while in engineering practice concentration is preferred. For concentrated electrolyte solutions (e.g., with molalities higher than 1 mol·kg⁻¹), such conversions requires the knowledge of the solution's density. Density is easy to determine experimentally, but this is not always an option when one is modeling a system theoretically. In this paper a novel method for interconverting molality to concentration is presented that requires no experimental data and is able to produce satisfactory results in single and multiple electrolyte systems.

Theory

The concentration of a solute (c_i) is the number of moles of the solute (n_i) per unit volume of the solution (V), measured in mol·m⁻³ (although the unit mol·dm⁻³ is often used in practice and this quantity is called molarity). The molality of a solute (m_i) is the number of moles of the solute (n_i) per unit mass of the solvent (m_A), measured in mol·kg⁻¹.

To change from molality to concentration, the density of the solution (ρ) is introduced:

$$c_i = m_i \rho / (1 + \sum_j m_j M_j) \quad (1)$$

where c_i , m_i , and M_i are the concentration, molality, and molecular weight of the i solute, respectively, and the summation covers all solutes.

A common assumption used in aqueous analytical chemistry, to avoid any density measurements when converting from one quantity to another, is the use of the density of pure water (ρ_w) instead of the actual solution's density:

$$c_i = m_i \rho_w / (1 + \sum_j m_j M_j) \quad (2)$$

Equation 2 is valid only for solutions with low solute concentrations.

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In many cases, like for example in the derivation of the Debye–Hückel theory,² further simplifications are made, postulating that the total mass of all the solutes is insignificant as compared to the mass of the solvent. Hence, eq 2 becomes

$$c_i = m_i \rho_w \quad (3)$$

Equation 1 converts molality to concentration by accounting for the mass of the solutes and then converting mass to volume through the solution's density. To avoid the use of the solution's density, the authors propose the direct use of the solutes' volume.

Marcus³ shows that the radius of a bare ion in solution (that is of an ion stripped of its hydration sphere) is approximated very well by its Pauling crystal radius. Using the ionic radii provided by Marcus,⁴ the molar volume V_i of a bare i ion is approximated by

$$V_i = \frac{4\pi N_A}{3} (r_i)^3 \quad (4)$$

where $N_A = 6.022 \cdot 10^{23} \cdot \text{mol}^{-1}$ is the Avogadro's constant and r_i is the ionic radius. If the molar volume of the i ion is V_i , then the total volume occupied by all the i ions per unit mass of solvent is $m_i V_i$, and the entire volume occupied by all solutes per unit mass of solvent is $\sum_j m_j V_j$.

Assuming that the volume of the solvent (water) in the solution remains unchanged as compared to the volume of the pure solvent (e.g., ignoring the electrostriction phenomenon in the hydration shells surrounding each ion as well as any alterations in the length of hydrogen bonds between water molecules), the solution's volume per unit mass of solvent can be approximated by

$$V = \left(d_w^{-1} + \frac{4\pi N_A}{3} \sum_j m_j (r_j)^3 \right) \quad (5)$$

The concentration of the i solute is then given by

$$c_i = m_i \left(d_w^{-1} + \frac{4\pi N_A}{3} \sum_j m_j (r_j)^3 \right) \quad (6)$$

Table 1. Ionic Radii (r)^a

ion	r/nm	ion	r/nm	ion	r/nm	ion	r/nm
Ag ⁺	0.1150	ClO ₃ ⁻	0.2559*	I ⁻	0.2200	NH ₄ ⁺	0.1480
Al ³⁺	0.0530	Cu ²⁺	0.0960	K ⁺	0.1380	NO ₃ ⁻	0.2275*
Br ²⁻	0.1960	F ⁻	0.1330	Li ⁻	0.0690	OH ⁻	0.1330
Ca ²⁺	0.1000	Fe ²⁺	0.0780	Mg ²⁻	0.0720	SO ₄ ²⁻	0.2300
Cl ⁻	0.1810	H ⁺	0.0300	Na ⁺	0.1020	Zn ²⁺	0.0750

^a Ionic radii values taken from Marcus⁴ except values marked with an asterisk (*), which were fitted.

With a similar reasoning, if one calculates the volume of the solvent by reducing the volume of the solution with the volume of all solutes, one can derive the conversion from concentration to molality:

$$m_i = c_i/d_w \left(1 - \frac{4\pi N_A}{3} \sum_j c_j (r_j)^3 \right) \quad (7)$$

Results

Using density measurements from Söhnel and Novotný,⁵ a comparison of eqs 1 and 6 for several single electrolyte systems was performed. Ionic radii data used are shown in Table 1, and the density of water was calculated according to the following equation:⁵

$$\rho_w/(\text{kg}\cdot\text{m}^{-3}) = 999.65 + 0.20438(t/^\circ\text{C}) - 0.061744(t/^\circ\text{C})^{3/2} \quad (8)$$

where t is the temperature of the solution.

The results are tabulated in Table 2, where the standard deviations between the two equations are presented for molalities up to (3, 6, and 9) mol·kg⁻¹ or up to saturation molalities, according to data taken from refs 6 and 7. In Figures 1 to 5, the results for some of those systems are presented graphically, along with the predictions of the commonly used assumptions of eqs 2 and 3.

Table 2. Single Electrolyte Systems with Standard Deviations for Different Molality Ranges, up to a Maximum Molality (9.00 mol·kg⁻¹ or Precipitation Molarity) at 0.2 mol·kg⁻¹ Intervals^a

electrolyte	standard deviations/mol·kg ⁻¹				electrolyte	standard deviations/mol·kg ⁻¹			
	0.1 to 3	0.1 to 6	0.1 to m_{max}	m_{max}		0.1 to 3	0.1 to 6	0.1 to m_{max}	m_{max}
AgNO ₃	0.0025	0.0036	0.0152	9.00	LiCl	0.0084	0.0479	0.1290	9.00
AlCl ₃	0.0023		0.0048	3.43	LiI	0.0166	0.0860	0.2160	9.00
Ca(NO ₃) ₂	0.0237	0.0611	0.0779	7.86	LiNO ₃	0.0012	0.0017	0.0081	9.00
CaBr ₂			0.0007	0.72	LiOH	0.0250		0.0715	5.16
CaCl ₂	0.0175	0.0282	0.0284	6.71	Mg(NO ₃) ₂	0.0369		0.0713	4.69
CaI ₂			0.0018	2.30	MgBr ₂	0.0027		0.0250	5.49
Cu(NO ₃) ₂	0.0378	0.1200	0.1300	6.66	MgCl ₂	0.0164		0.0413	5.72
CuCl ₂	0.0254		0.0630	5.43	MgI ₂	0.0014		0.0123	5.03
CuSO ₄			0.0291	2.00	Na ₂ SO ₄			0.0082	1.37
FeCl ₂	0.0286		0.0795	5.40	NaBr	0.0095	0.0559	0.1560	8.82
HBr	0.0116	0.0613	0.1730	9.00	NaCl	0.0045	0.0426	0.0481	6.14
HCl	0.0090	0.0537	0.1600	9.00	NaClO ₃	0.0113	0.0415	0.0726	9.00
HI	0.0172	0.0866	0.2130	9.00	NaF			0.0039	0.97
HNO ₃	0.0013	0.0078	0.0367	9.00	NaI	0.0138	0.0720	0.2020	9.00
KBr	0.0040		0.0397	5.46	NaNO ₃	0.0025	0.0057	0.0329	9.00
KCl	0.0243		0.0746	4.60	NaOH	0.0206	0.0727	0.1240	9.00
KClO ₃			0.0005	0.60	NH ₄ Cl	0.0307	0.1550	0.2820	6.95
KF	0.0026	0.0135	0.0721	9.00	NH ₄ NO ₃			0.0240	2.40
KI	0.0270	0.1230	0.3560	8.69	Zn(NO ₃) ₂	0.0386	0.1170	0.1360	7.29
KNO ₃	0.0151		0.0186	3.13	ZnCl ₂	0.0028	0.0396	0.1430	9.00
KOH	0.0065	0.0098	0.0465	9.00	ZnSO ₄	0.0660		0.0758	3.33
LiBr	0.0139	0.0658	0.1710	9.00					

^a Model results at 25 °C (except for AlCl₃ calculated at 15 °C and FeCl₂ at 15.5 °C). $\sigma = ((1/n)\sum_{i=1}^n (c_i^{\text{exp}} - c_i^{\text{model}})^2)^{1/2}$.

To test the effectiveness of this method on multiple electrolyte systems, density measurements were carried out on the systems H₂O + CuSO₄ + ZnSO₄, H₂O + NaCl + KBr, and H₂O + CuSO₄ + H₂SO₄. Density was measured using the Sartorius YDK 01 Density Determination Kit with a Kern 770 balance. The known concentration of the solutes was compared with the concentration produced from eq 6, where the molality was found through the use of the experimentally measured density (ρ):

$$m_i = c_i/(\rho - \sum_j c_j M_j) \quad (9)$$

(eq 9 is the equivalent of eq 1 for changing from concentration to molality). The results of these comparisons are tabulated in Table 3 and depicted graphically in Figure 6. Each binary system is examined over a range of concentration, under three different ratios of the binary mixtures, which are defined through the use ionic strength fractions. For the i electrolyte, the ionic strength fraction is defined as

$$y_i = \frac{I_{i,c}}{I_c} = \frac{0.5(z_C^2(i)v_C(i) + z_A^2(i)v_A(i))c_i}{\sum_j 0.5(z_C^2(j)v_C(j) + z_A^2(j)v_A(j))c_j} \quad (10)$$

where the summation covers all electrolytes of the solution, $z_C(i)$ and $z_A(i)$ are respectively the cationic and anionic valences, and $v_C(i)$ and $v_A(i)$ are respectively the stoichiometric amount of cations and anions produced per mole of the i electrolyte.

Case Study: Sodium Aluminate Solution. To further test the idea presented in this paper, a simple hydrometallurgical system is examined. The sodium aluminate solution plays an important role in the primary production of alumina using the Bayer process. In Panias et al.,⁸ a theoretical model for the solubility of boehmite in (2 to 4.5) mol·dm⁻³ sodium hydroxide solution for temperatures from (30 to 150) °C is presented. The system is described as mixture of two strong electrolytes (NaAl(OH)₄(aq) and NaOH(aq)) in which solid boehmite

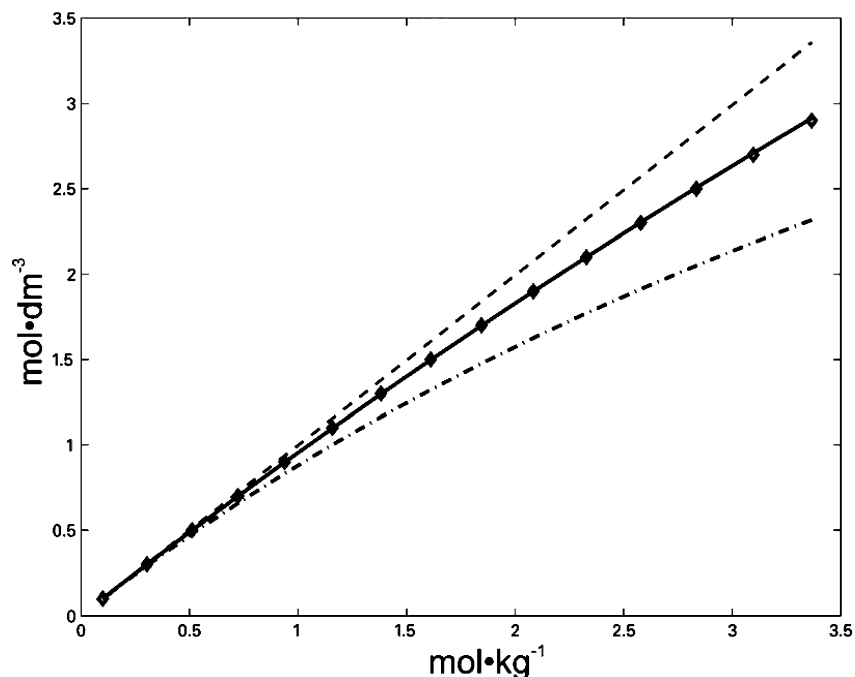


Figure 1. Model results for AlCl_3 aqueous solution at 15 °C. Experimental density data from Söhnel and Novotný⁵ are used in eq 1 to produce the diamonds. Equation 6 is represented with solid lines, eq 2 is represented with dash-dotted lines, and equation 3 is represented with dotted lines

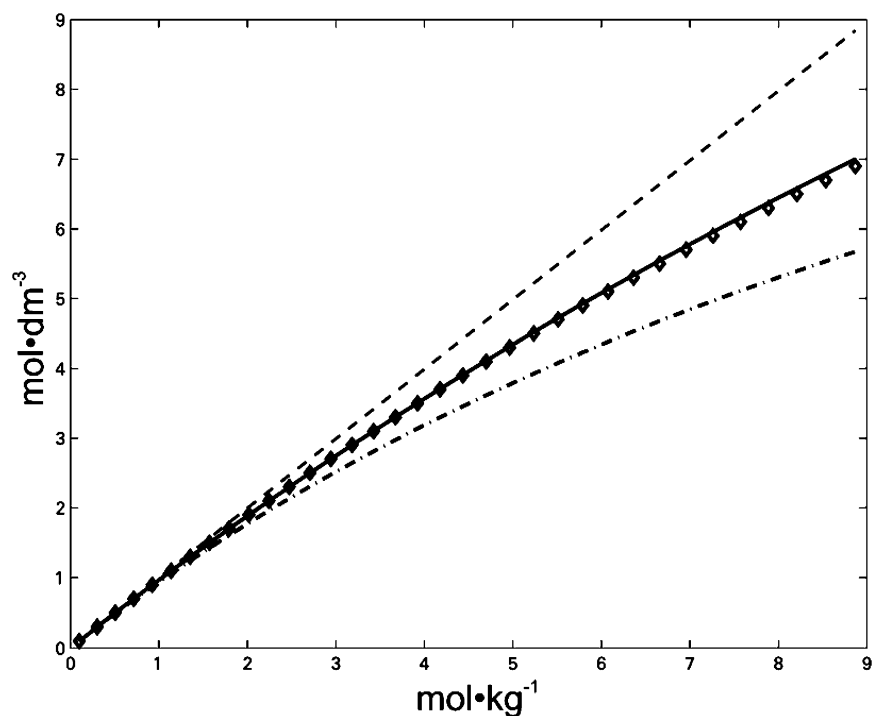
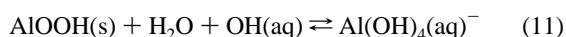


Figure 2. Model results for HNO_3 aqueous solution at 25 °C. Experimental density data from Söhnel and Novotný⁵ are used in eq 1 to produce the diamonds. Equation 6 is represented with solid lines, eq 2 is represented with dash-dotted lines, and eq 3 is represented with dotted lines.

(AlOOH(s)) precipitates, following the chemical reaction



The theoretical model of the system (which is verified by experimental results) leads to the formulation of a correlation, which expresses the equilibrium molar concentration of $\text{NaAl(OH)}_4\text{(aq)}$, (c_1), in relation to the initial molar concentration of NaOH(aq) , ($c_{2,0}$):

$$c_1 = \frac{1}{51.5} (A_1(t/^\circ\text{C})^3 + A_2(t/^\circ\text{C})^2 + A_3(t/^\circ\text{C}) + A_4) \quad (12)$$

where t is the temperature in degrees Celsius and

$$A_1 = (-1.91867c_{2,0} + 1.36953) \cdot 10^{-6}$$

$$A_2 = (0.71331c_{2,0} + 0.17070) \cdot 10^{-3}$$

$$A_3 = (7.44179 \cdot 10^{-2} c_{2,0}^3 - 0.29849 c_{2,0}^2 + 1.69973 c_{2,0} - 1.332) \cdot 10^{-2}$$

$$A_4 = (9.64037 \cdot 10^{-2} c_{2,0}^3 - 0.75794 c_{2,0}^2 + 4.91040 c_{2,0} - 2.518)$$

The molar concentration of $\text{Al(OH)}_4\text{(aq)}^-$ at equilibrium is equal

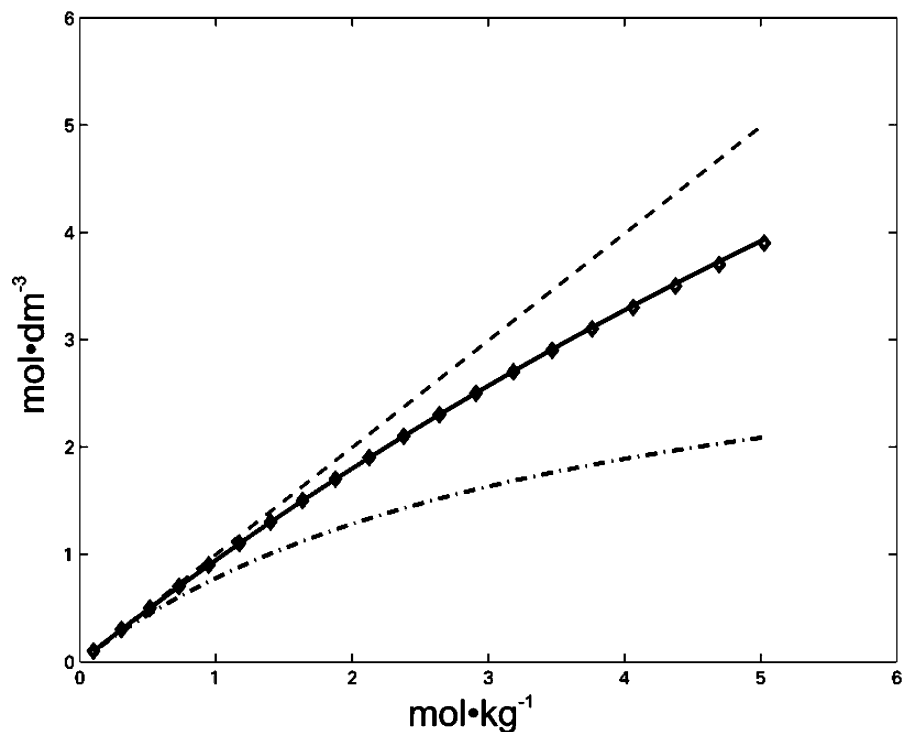


Figure 3. Model results for MgI_2 aqueous solution at 25 °C. Experimental density data from Söhnel and Novotný⁵ are used in eq 1 to produce the diamonds. Equation 6 is represented with solid lines, eq 2 is represented with dash-dotted lines, and eq 3 is represented with dotted lines.

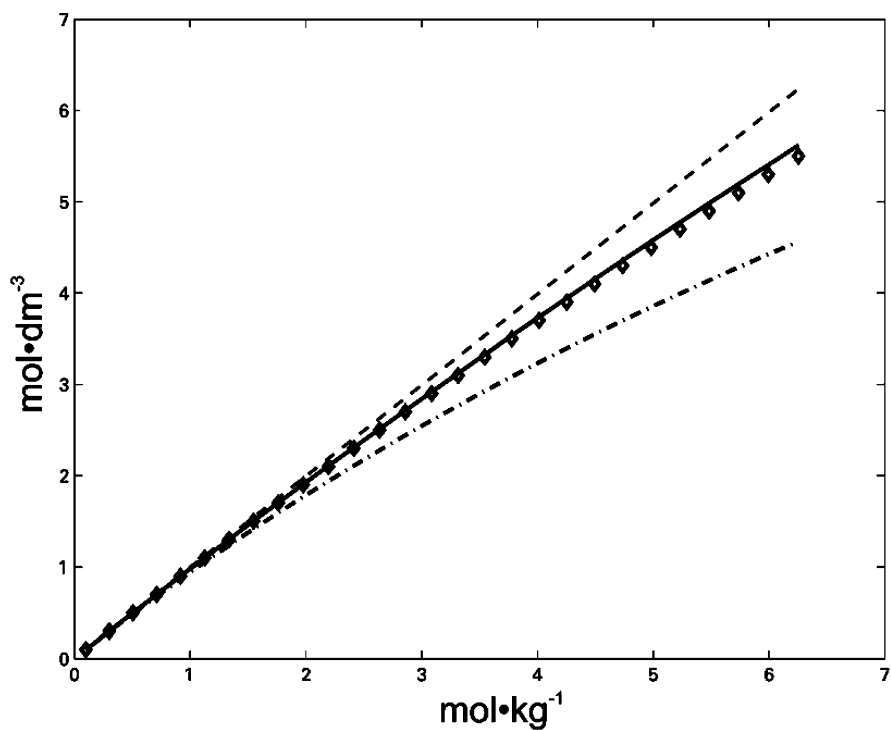


Figure 4. Model results for NaCl aqueous solution at 25 °C. Experimental density data from Söhnel and Novotný⁵ are used in eq 1 to produce the diamonds. Equation 6 is represented with solid lines, eq 2 is represented with dash-dotted lines, and eq 3 is represented with dotted lines.

to the concentration c_1 of eq 12. The molar concentration of $\text{OH}(\text{aq})^-$ at equilibrium can then be calculated through the electroneutrality principle, which in this system takes the form

$$c_{\text{Na}(\text{aq})^+} = c_{\text{OH}(\text{aq})^-} + c_{\text{Al}(\text{OH})_4(\text{aq})^-} \quad (13)$$

The total molar concentration of $\text{Na}(\text{aq})^+$ is obviously equal to the initial $\text{NaOH}(\text{aq})$ concentration ($c_{2,0}$), and so through eqs

12 and 13 the system's molar speciation (c_1 and c_2) at equilibrium is defined in relation to ($c_{2,0}$).

In Panias et al.,⁸ an empirical correlation for the density of this system for temperatures up to 250 °C is also given (and used in the theoretical model that derives eq 12), in relation to $c_{2,0}$ and c_1 :

$$\{\rho\}/\{(\text{kg}\cdot\text{m}^{-3})\} = 998.2(D + F) \quad (14)$$

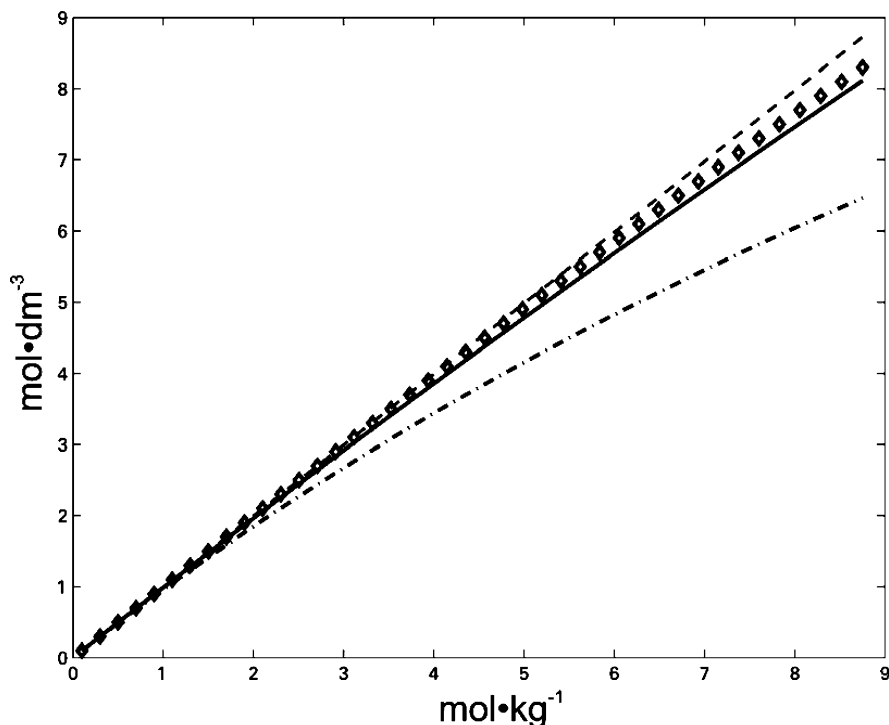


Figure 5. Model results for NaOH aqueous solution at 25 °C. Experimental density data from Söhnel and Novotný⁵ are used in eq 1 to produce the diamonds. Equation 6 is represented with solid lines, eq 2 is represented with dash-dotted lines, and eq 3 is represented with dotted lines.

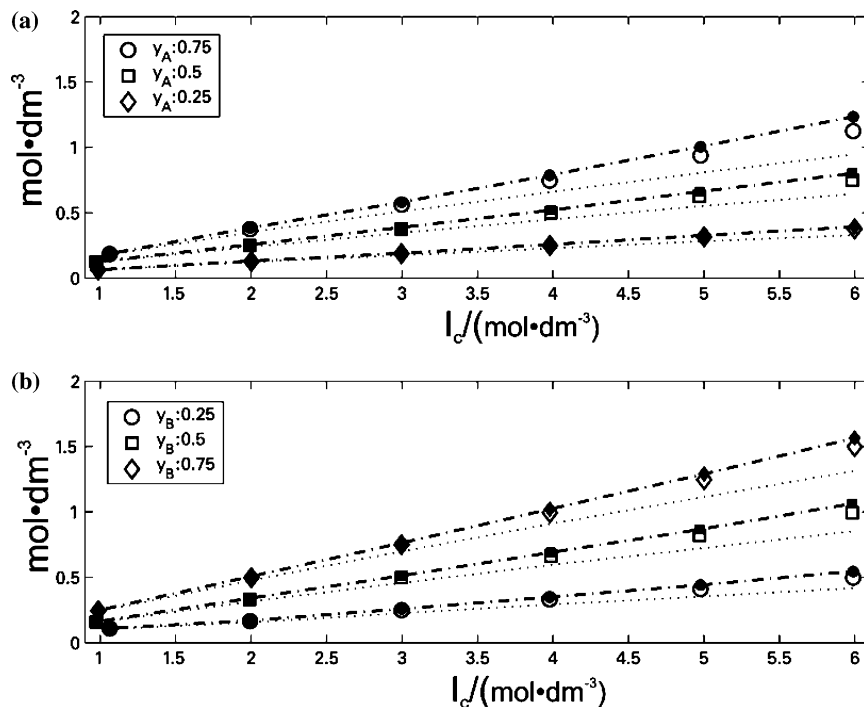


Figure 6. Model results for the system $\text{H}_2\text{O} + \text{CuSO}_4 + \text{H}_2\text{SO}_4$. Experimental concentrations (measured in $\text{mol}\cdot\text{dm}^{-3}$) at different ionic strength fractions (y_A , CuSO_4 ; y_B , H_2SO_4) are presented with hollow points. Concentrations from eq 6 are presented with dash-dotted lines, and smaller solid points and molar concentrations from eq 2 are represented with dotted lines.

where

$$D = 0.5(1 - 9.52832 \cdot 10^{-4}(t/^\circ\text{C} - 20) - 2.64664 \cdot 10^{-6}(t/^\circ\text{C} - 20)^2)$$

$F =$

$$5 \cdot 10^{-4} \sqrt{10^6 + 4 \cdot 10^3(44.2391c_{2,0} + (1.43689 \cdot 10^{-2} + 4.32233 \cdot 10^{-4}c_{2,0})c_1)}$$

Using the system speciation and the density provided through

eq 14, electrolyte concentration at equilibrium is converted to molality using eq 9, and this molality is used in eq 6. The deviations between the concentrations of eqs 12 and 13 and concentrations produced in eq 6, for temperatures between (30 to 150) °C, are presented in Table 4 and in Figures 7 and 8. The ionic radii for the $\text{Al}(\text{OH})_4(\text{aq})^-$ ion is assumed to be equal to the radius of aluminum ion plus the diameter of the hydroxyl complex (see Table 1), since the $\text{Al}(\text{OH})_4(\text{aq})^-$ ion has tetrahedral structure.

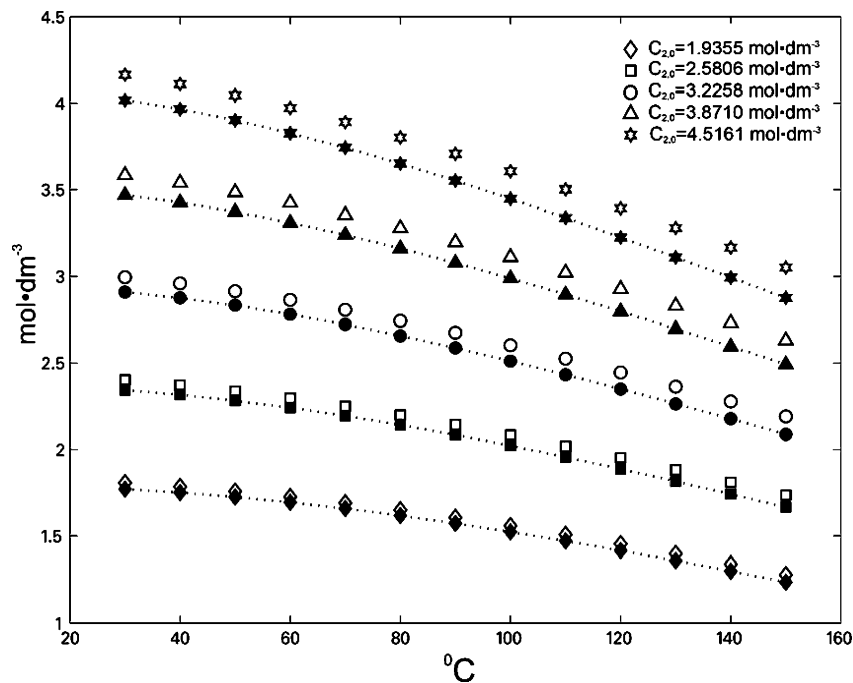


Figure 7. Model results for the system sodium aluminate system. Experimental concentrations (measured in mol·dm⁻³) for NaOH at different temperatures and different initial NaOH concentrations ($c_{2,0}$) are presented with hollow points. Model results are presented with dash-dotted lines and smaller solid points.

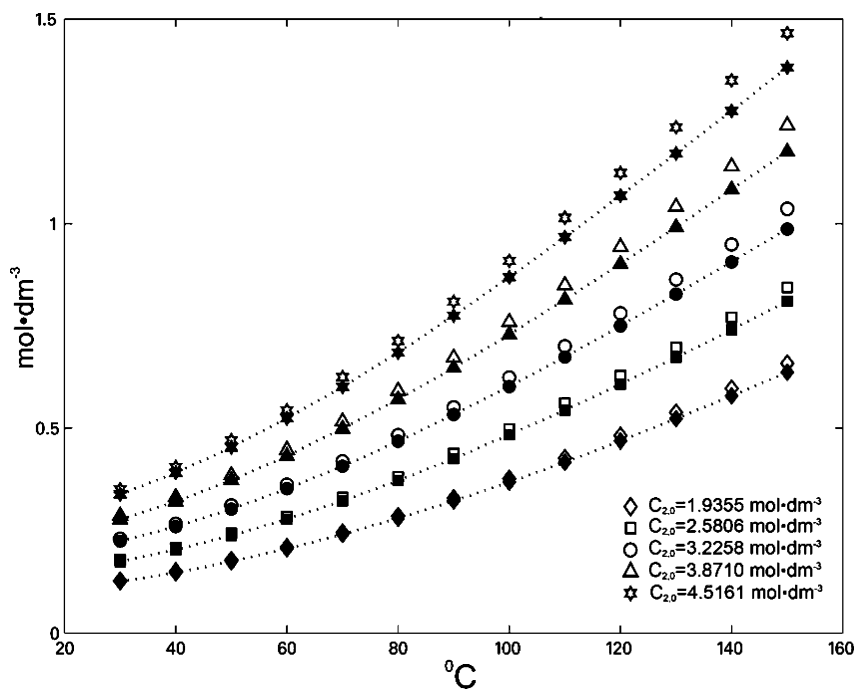


Figure 8. Model results for the system sodium aluminate system. Experimental concentrations (measured in mol·dm⁻³) for NaAl(OH)₄ at different temperatures and different initial NaOH concentrations ($c_{2,0}$) are presented with hollow points. Model results are presented with dash-dotted lines and smaller solid points.

Discussion

The results of the transformation proposed prove to be quite satisfactory in both single and multiple electrolyte systems, especially so for systems of medium molalities (up to 6 mol·kg⁻¹). At higher molalities (up to 9 mol·kg⁻¹) the model begins to diverge. This is to be expected since in the derivation of eqs 5 and 6 it was assumed that the molar volume of the solvent remains unaffected from the addition of the ions. This assumption will become less and less valid

as the ionic concentration increases and the total amount of free (not bound in hydrarion spheres) water molecules decreases.⁴

The shape of the ions was assumed to be spherical, an assumption less accurate when used to describe ionic complexes. In fact the largest deviations were originally encountered in the salts of NO₃⁻ and ClO₃⁻, whose ionic radii were fitted in the results presented here to compensate for this geometrical error. In both cases, the fitting of only one system gave an

Table 3. Multiple Electrolyte Systems with Standard Deviations for Different Ionic Strength Composition Fractions at 20 °C^a

Solution Ionic Strength Range: 0.5 to 3.0 I_c		
ionic strength fractions $y_A - y_B$	standard deviations	
	CuSO ₄	ZnSO ₄
0.75–0.25	0.0167	0.0056
0.50–0.50	0.0115	0.0115
0.25–0.75	0.0069	0.0207
Solution Ionic Strength Range: 1.0 to 4.0 I_c		
ionic strength fractions $y_A - y_B$	standard deviations	
	NaCl	KBr
0.75–0.25	0.0350	0.0117
0.50–0.50	0.0349	0.0350
0.25–0.75	0.0277	0.0833
Solution Ionic Strength Range: 1.0 to 6.0 I_c		
ionic strength fractions $y_A - y_B$	standard deviations	
	CuSO ₄	H ₂ SO ₄
0.75–0.25	0.0350	0.0117
0.50–0.50	0.0349	0.0350
0.25–0.75	0.0277	0.0833

^a The composition column denotes the ionic strengths fractions (y_i) of the first and second component, respectively. The ionic strength range of the experiments, at 0.5 mol·dm⁻³ intervals, is given at the top of each section. $\sigma = ((1/n)\sum_{i=1}^n (c_i^{\text{exp}} - c_i^{\text{model}})^2)^{1/2}$.

Table 4. Sodium Aluminate Solution at Temperatures from (30 to 150) °C at 10 °C Increments^a

$c_{2,0}/\text{mol} \cdot \text{dm}^{-3}$	standard deviations	
	NaOH	NaAl(OH) ₄
1.9355	0.0359	0.0108
2.5806	0.0613	0.0176
3.2258	0.0907	0.0255
3.8710	0.123	0.0348
4.5161	0.158	0.0457

^a $\sigma = ((1/n)\sum_{i=1}^n (c_i^{\text{exp}} - c_i^{\text{model}})^2)^{1/2}$.

ionic radius that could be used with success in all the other systems.

The boemite solubility case study proves that this transformation can be used in real hydrometallurgical systems. It also shows that temperature variations do not affect the results in a significant extent. While the volume of the solutes is assumed to remain unchanged, the density of the pure solvent depends on temperature, thus making this method applicable in higher temperatures.

In closing, this transformation may not be exact due to its theoretical simplifications, but it proves to be a simple and valid way of providing good estimations for converting molality to concentration and vice versa when modeling systems where no density measurements are available. It is hence, a useful “modeling tool” capable of replacing the assumptions of eqs 2 and 3 in concentrated electrolyte solutions.

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