

Calculation of the Density of Electrolyte Solution

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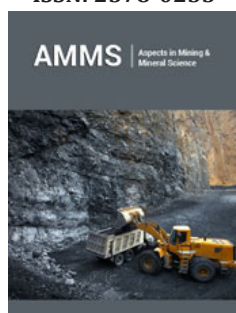
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Abstract

Based on the solvate model of solutions, the relation of density with the thermodynamics functions is established and an equation for the density of binary solutions is obtained. A generalization of this equation to mixed electrolyte solutions is given.

Keywords: Partial molar volume; Activity of solvent; Hydration number

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Introduction

The density of electrolyte solutions plays a large role in the processing mineral raw materials, since in many cases it is the main source of information of the concentration of substances in solutions. The exact equation for the density of solutions is also of great theoretical importance for determining the partial molar volumes of electrolytes and the osmotic pressure of solutions. This article proposes a method for describing the density of binary and mixed solutions on the solvate model of solutions.

Theory

Let us consider a binary solution containing m moles of electrolyte and w mole solvent (e.g. water) in the volume of solution V . If we assume, without loss of generality, that positive and negative ions form hydrated complexes of a fixed composition containing n_p and n_n solvent molecules, respectively. than the volume of such solution can be determine as

$$V = N_w^* V_w + N_p^* V_p + N_n^* V_n + N_{hp}^* V_{hp} + N_{hn}^* V_{hn} \quad (1)$$

where N_w^* , N_p^* , N_n^* , N_{hp}^* , N_{hn}^* are equilibrium amounts of solvent, ions and hydrated complexes, V_w is molar volume of pure solvent, V_p , V_n , V_{hp} , V_{hn} are molar volumes of ions and hydrated complexes, respectively. Taking into account the equations of material balance

$$v_p m = N_p^* + N_{hp}^*$$

$$v_n m = N_n^* + N_{hn}^*$$

$$w = N_w^* + n_p N_{hp}^* + n_n N_{hn}^*$$

Eq.(1) can be represented in the form

$$V = wV_w + v_p mV_p + v_n mV_n + N_{hp}^* \Delta V_p + N_{hn}^* \Delta V_n \quad (2)$$

where v_p and v_n are the stoichiometric coefficients ($v = v_p + v_n$ is stoichiometric coefficient of electrolyte), $\Delta V_p = V_p + h_p V_w - V_{hp}$, $\Delta V_n = V_n + h_n V_w - V_{hn}$. Here the hydration number of corresponding current concentration of each ions h_p , h_n can be defined as

$$h_p = \frac{n_p N_{hp}^*}{v_p m}, \quad h_n = \frac{n_n N_{hn}^*}{v_n m} \quad (3)$$

These values according to Ref.[1] can be expressed in the form

$$h_p = \frac{n_p k_p a_w^{n_p}}{1 + n_p k_p a_w^{n_p}}, \quad h_n = \frac{n_n k_n a_w^{n_n}}{1 + n_n k_n a_w^{n_n}} \quad (4)$$

where K_p and K_n is constant of formation of hydrated complex, a_w is the activity of solvent.

Using Eq. (3), Eq. (2) can be transformed to

$$V = wV_w + \sum v_i m V_i - \sum v_i m \frac{h_i}{n_i} \Delta V_i \quad (5)$$

Differentiating Eq. (5), we can determine the partial molar volume of the electrolyte, which in the infinitely dilute solution takes on the value

$$v_e^0 = \lim_{m \rightarrow 0} \frac{\partial V}{\partial m} = \sum v_i V_i - \sum v_i m \frac{h_i^0}{n_i} \Delta V_i \quad (6)$$

Combining Eq. (5) and Eq. (6), we have

$$V = wV_w \left(1 + \frac{m v_e^0}{w V_w} - \frac{m}{w} \sum v_i \frac{h_i - h_i^0}{n_i} \frac{\Delta V_i}{V_w} \right) \quad (7)$$

where h_i^0 is the hydration number of ions in the infinitely dilute solution, which can be determined from Eq. (4) at $a_w \rightarrow 1$. The density of the solution is determined by the formula

$$\rho = \frac{M_e m + M_w w}{V} \quad (8)$$

where M_e and M_w are molecular weights of the electrolyte and solvent, respectively. Mass fraction of electrolyte in solution z can be defined as

$$z = \frac{M_e m}{M_e m + M_w w} \quad (9)$$

hence the equality

$$\frac{m}{w} = \frac{M_w}{M_e} \frac{z}{1-z} \quad (10)$$

Substituting Eq. (10) into Eq. (7) and then the result obtained into Eq. (8), the latter can be expressed as

$$\frac{1}{\rho} = \frac{1}{\rho_w} \left(1 - z + z \frac{\rho_w v_e^0}{M_e} - z \frac{M_w}{M_e} \sum v_i \frac{h_i - h_i^0}{n_i} \frac{\Delta V_i}{V_w} \right) \quad (11)$$

where ρ_w is the density of pure solvent. Let us further imagine the hydration number of the electrolyte h_i as a function of the concentration z . The activity of the solvent according [1] can be determined using Eq. (10) as

$$\ln a_w = -v\varphi \frac{m}{w} = -v\varphi \frac{M_w}{M_e} \frac{z}{1-z} \quad (12)$$

where φ is the osmotic coefficient of the solution. Using Eq. (4), the value of h_i can be expanded in a Taylor series and limited to a linear term to represent it in the form

$$h_i = h_i^0 + \left(\frac{dh_i}{d \ln a_w} \frac{d \ln a_w}{dz} \right)_0 z = h_i^0 - \frac{v n_i h_i^0}{1 + k_i} \frac{M_w}{M_e} z \quad (13)$$

Substituting Eq. (13) into Eq. (11) we finally have

$$\frac{1}{\rho} = \frac{1}{\rho_w} (1 - Az + Bz^2) \quad (14)$$

$$A = 1 - \frac{\rho_w v_e^0}{M_e}, \quad B = v \frac{M_w^2}{M_e^2} \sum \frac{v_i h_i^0 \Delta V_i}{1 + k_i V_w}$$

where

Next, we use the relationship of dimensionless concentration z with molality c . Combining equality $c = m/V$ and Eq. (8), (9) we have

$$z = \frac{M_e}{\rho} c \quad (15)$$

Substituting Eq. (15) into Eq. (14) and limiting to the quadratic term, we can determine the density of solution in the form

$$\rho = \rho_w + ac - \frac{bc^2}{\rho_w + ac} \quad (16)$$

where $a = M_e A$, $b = M_e^2 B$.

Eq. (14) can be extended to mixed electrolyte solutions. If we neglect the influence of the last term Eq. (14), the density of the mixed solution can be calculated by the principle of additivity and is presented in the form

$$\frac{1}{\rho} = \frac{1}{\rho_w} (1 - \sum A_i z_i + (\sum z_i) \sum B_i z_i) \quad (17)$$

Further, using Eq. (15), (16), the density of the mixed solution can be expressed by molality

$$\rho = \rho_w + \sum a_i c_i - \frac{\sum M_{ei} c_i}{\rho_w + \sum a_i c_i} \sum \frac{b_i c_i}{M_{ei}} \quad (18)$$

Discussion

Table 1 shows the applicability of the model used for electrolytes of various types. And in all cases, the main contribution of the linear term of Eq. (17) from which it is possible to calculate the partial molar volume of the electrolyte. To estimate this value, we present the volume of the hydrated complex as the sum of the volumes of the central ion and the surrounding water molecules where per one molecule of water accounts for a significantly smaller volume V_w^* , then in structure of pure water V_w . Then $V_{hi} = V_i + h_i V_w^*$ and the volume of solution can be represented as

$$V = wV_w + m \sum v_i V_i - m \sum v_i h_i (V_w - V_w^*) \quad (19)$$

and further partial molar volume as

$$v_c = \sum v_i V_i - \sum v_i h_i (V_w - V_w^*) \quad (20)$$

Table 1: The parameters of equation of aqueous solution (16) at 298K. *) at 298K; Δ is interval of concentration; δ is average approximation error; calculation according experimental data Ref. [3, 4].

Electrolyte	a, kg/mol	b, kg ² /mol ²	v_c^0 , cm ³ /mol	Δ , % mass	δ , %
HCl	0,0180	0,0003	18,6	1-40	0,02
LiOH	0,0279	0,0011	-4,0	1-10	0,02
LiNO ₃ ^{*)}	0,0390	0,0002	30,0	1-40	0,02
LiI ^{*)}	0,0972	0	36,7	1-60	0,02

NaCl	0,0409	0,0008	17,5	1-26	0,02
NaNO ₃ ^{*)}	0,0551	0,0009	30,1	1-45	0,02
KBr	0,0846	0,0009	34,5	1-40	0,01
KI ^{*)}	0,1192	0,0007	46,9	1-60	0,02
RbI	0,1620	0,0012	50,4	1-60	0,03
Cs ₂ SO ₄	0,2982	0,0085	63,8	1-26	0,05
MgCl ₂	0,0777	0,0028	17,6	2-32	0,02
MgSO ₄	0,1201	0,0065	0,3	2-26	0,02
Mn(NO ₃) ₂	0,1379	0,0046	41,1	2-55	0,04
CuCl ₂	0,1239	0,0057	10,6	1-26	0,03
CuSO ₄	0,1626	0,0089	-3,0	1-18	0,02
ZnSO ₄	0,1645	0,0089	-3,1	2-30	0,02
CdSO ₄	0,2009	0,0085	7,6	2-40	0,03
FeCl ₃	0,1335	0,0057	28,7	1-50	0,05
LaCl ₃	0,2254	0,0095	19,9	1-40	0,02

It is obvious that at high values of the difference ($V_w - V_w^*$) the partial molar volume can even have negative values. Thus, this volume reflects structural change in the solution. Eq. (16) can be compared with the widely used Root equation [2].

$$\rho = \rho_w + a'c + b'c^2 \quad (21)$$

where the parameter a' completely corresponds to the parameter a: $a' = M_e - \rho_w v_c^0$. Hence, we can for each equation determined partial molar volume and compared these values with the experimental data (Table 2). For this purpose, we use Eq.(8) from where follows

$$v_c = \frac{\partial V}{\partial m} = \frac{M_e}{\rho} - \frac{M_e m + M_w w}{\rho^2} \frac{\partial \rho}{\partial m} = \frac{1}{\rho} \left(M_e - V \frac{\partial \rho}{\partial m} \right) \quad (22)$$

Further, determining the derived function

$$\frac{\partial \rho}{\partial m} = \frac{\partial \rho}{\partial c} \frac{\partial c}{\partial m} = \frac{\partial \rho}{\partial c} \left(\frac{1-c}{V} \frac{\partial V}{\partial m} \right) \quad (23)$$

and substituting it into Eq.(22), we find

$$v_c \left(\rho - \frac{\partial \rho}{\partial c} \right) = M_e - \frac{\partial \rho}{\partial c} \quad (24)$$

Using Eq. (24), we can determine the value of v_c^0 by extrapolation data $\partial \rho / \partial c$ to the field of an infinitely diluted solution at $c \rightarrow 0$

$$v_c^0 = \frac{\left(M_e - \left(\frac{\partial \rho}{\partial c} \right)_0 \right)}{\rho_w} \quad (25)$$

Table 2: The partial molar volume (cm³/mol) in aqueous infinite diluted solutions at 293K. The extrapolation error of experimental data [3,4] to the field of infinitely diluted solution is ±1cm³/mol.

Electrolyte	Eq.(16)	Eq.(21)	Meas.
LiOH	-4	-6.9	-4.6
Li ₂ SO ₄	16.2	11,1	15,5
NaOH	-3.8	-7.5	-4,0
NaCl	17.5	15.8	17.1
NaBr	23.8	22.7	24.3
NaI	34.9	34.1	35.3
NaNO ₃	28.3	26.9	28.4
NaHSO ₄	28.1	24.3	28.1
Na ₂ SO ₄	13.7	7.6	14

Na ₂ CO ₃	-3.1	-7.4	-3.3
KOH	6.7	3.2	6.3
K ₂ SO ₄	33.3	30.1	32.9
MgCl ₂	17.6	13.8	18.1
CaCl ₂	20.5	16.5	20.7
Al ₂ (SO ₄) ₃	-4.6	-22	-3.6

Figure 1 also shows the correspondence of the calculated values according to equations (16) and (24) and experimental data of partial molar volumes. Turning to the calculation of the density on mixed solutions should be noted that the Eq. (17), (18) are approximate because the initial Eq. (14), (16) are not linear. A strict solution can be obtained using as a starting Eq. (11) which turns into a linear one under the condition $a_w = \text{const}$, since the value

of h_i according Eq. (4) depends only on the activity of the solvent. Then using the notation ρ_i^* , z_i^* for binary isopiestic solutions, the inverse density of the mixed solution can be represented as a linear combination and expressed taking into account the boundary conditions as

$$\frac{1}{\rho} = \frac{z_1}{\rho_1^* z_1^*} + \frac{z_2}{\rho_2^* z_2^*} \quad (26)$$

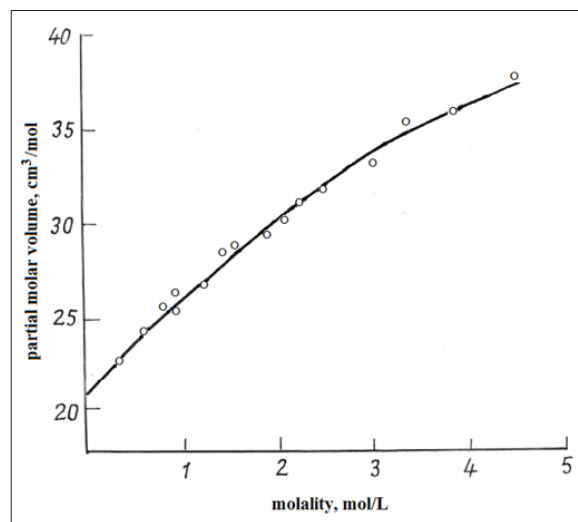


Figure 1: Partial molar volume of calcium chloride in aqueous solution at 298K. Experimental data and calculated curve.

where z_1 and z_2 are the concentration of components in mixed solution. However, the data in Table 3 show that the use of Eq. (17), (18) is a good approximation for calculating the density of mixed

solutions and have significant advantage over Eq. (26), which requires a set of experimental data that is not always available.

Table 3: The density of mixed aqueous solutions LiNO₃+NaNO₃ and LI+KI at 298K.

c, mol/L		$\rho, \text{g/cm}^3$			
		Eq.(14)	Eq.(16)	Eq.(26) Ref.[5]	Meas. Ref.[5]
LiNO ₃	NaNO ₃				
8,986	0,688	1,3694	1,3685	1,3663	1,3656
7,936	2,054	1,3968	1,3963	1,3942	1,3948
5,463	3,102	1,3584	1,3633	1,3565	1,3564

1,467	6,280	1,3680	1,3683	1,3705	1,3669
LiI	KI				
8,123	0,481	1,8398	1,8429	1,8437	1,8444
5,653	1,238	1,6911	1,6910	1,6900	1,6916
3,488	2,768	1,6589	1,6593	1,6573	1,6609
1,603	4,535	1,6822	1,6823	1,6812	1,6828

Conclusion

Solvate model of solution leads to equations allowing to describe the density of electrolyte solutions with an accuracy acceptable for solving not only technological but also science problems [3-5]. The resulting equations using different concentration are convenient for the reverse calculation of the concentration reagents in the solution according to density data, which is of interest in the control of technological processes.

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