Calculation of the Density of Electrolyte Solution

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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

\[
V = N_w^* V_w + N_p^* V_p + N_n^* V_n + n_p^* V_{hp} + n_n^* V_{hn} \quad (1)
\]

where \( N_w^* \), \( N_p^* \), \( N_n^* \), \( n_p^* \), \( n_n^* \) 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

\[
\nu_p V_p + \nu_n V_n = \Delta V_p + \Delta V_n \quad (2)
\]

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

\[
h_p = \frac{n_p^*}{\nu_p m} \quad h_n = \frac{n_n^*}{\nu_n m} \quad (3)
\]

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

\[
\nu_p m = n_p^* + n_p^* h_p \quad (4)
\]

\[
\nu_n m = n_n^* + n_n^* h_n \quad (5)
\]

Eq.(1) can be represented in the form

\[
V = wV_w + \nu_p mV_p + \nu_n mV_n + \nu_p^* \Delta V_p + \nu_n^* \Delta V_n \quad (2)
\]
\[ h = \frac{n_i k_i a_i^n w}{1 + n_i k_i a_i^n w}, \quad h = \frac{n_i k_i w_i^{n_i}}{1 + n_i k_i w_i^{n_i}} \quad (4) \]

where \( K_i \) and \( K_{ii} \) is constant of formation of hydrated complex, \( a_i \) is the activity of solvent.

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

\[ V = w V_w + \sum \nu_i m V_i - \sum \nu_i m \Delta V_i \quad (5) \]

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

\[ v_p = \lim_{m \to 0} \frac{\partial V}{\partial m} = \sum \nu_i v_i \frac{h_i - h_i^0}{n_i V_i} \quad (6) \]

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

\[ V = w V_w + \sum \nu_i m V_i - \sum \nu_i m \Delta V_i \quad (7) \]

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

\[ \rho = \frac{M_m m + M_w w}{V} \quad (8) \]

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

\[ z = \frac{M_m m}{M_m + M_w w} \quad (9) \]

hence the equality

\[ m = \frac{M_w z}{M_m} \quad (10) \]

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

\[ \frac{1}{\rho} \left( 1 - z + \sum a_i c_i - \sum \frac{M_m c_i}{M_w + \sum a_i c_i} \frac{z}{M_m} \right) \quad (11) \]

where \( \rho \) 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

\[ \ln a_w = -\varphi \frac{m}{w} = -\varphi \frac{M_w z}{M_m} \quad (12) \]

where \( \varphi \) 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

\[ h_i = h_i^0 + \left( \frac{dh_i}{d \ln a_w} \right) \frac{d \ln a_w}{dz} \]

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

\[ \frac{1}{\rho} = \frac{1}{\rho_w} \left[ 1 - A z + B z^2 \right] \quad (14) \]

where

\[ A = 1 - \frac{\rho_{w0}^0}{\rho_w} \quad B = \frac{\nu_i h_i^0}{M_w} \frac{\sum \nu_i h_i^0 \Delta V_i}{1 + k_v V_m} \]

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

\[ z = \frac{M_w c}{\rho} \quad (15) \]

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

\[ \frac{1}{\rho} = \frac{1}{\rho_w} \left[ 1 - A z + B z^2 \right] \quad (17) \]

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

\[ \rho = \rho_w + A c - \frac{b c^2}{\rho_w + B c} \quad (18) \]

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 \( V_{w0} \), then in structure of pure water \( V_w \). Then \( V_{w0} = V_w + h^0 V_w \) and the volume of solution can be represented as

\[ V = w V_w + m \sum \nu_i V_i - m \sum \nu_i h_i (V_w - V_{w0}) \quad (19) \]

and further partial molar volume as

\[ V_c = \nu_i V_i - \sum \nu_i h_i (V_w - V_{w0}) \quad (20) \]

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

| Electrolyte | \( a, \text{kg/mol} \) | \( b, \text{kg}^2/\text{mol}^2 \) | \( V_c^0, \text{cm}^3/\text{mol} \) | \( \Delta, \% \text{mass} \) | \( \delta, \% \) |
|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 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            | 0.0002            | 36.7              | 1-60              | 0.02              |

\[ \frac{d h_i}{d \ln a_w} = \frac{\nu_i h_i^0}{1 + k_v V_m} M_w z \quad (13) \]
It is obvious that at high values of the difference \( \Delta \), 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 \[2\].

\[
\rho = \rho_v + a c + b c^2 \quad (21)
\]

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

\[
\frac{V}{\rho} = \frac{M_e}{\rho} \left( 1 - \frac{\rho}{\rho_w} \right) \quad (22)
\]

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

\[
v^0 = \frac{M_e}{\rho_w} \left( 1 + \frac{\rho}{\rho_w} \right) \quad (25)
\]

Table 2: The partial molar volume (cm\(^3\)/mol) in aqueous infinite diluted solutions at 293K. The extrapolation error of experimental data [3,4] to the field of infinitely diluted solution is ±1cm\(^3\)/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    |
Table 3: The density of mixed aqueous solutions LiNO$_3$+NaNO$_3$ and Li+KI at 298K.

| c, mol/L | ρ, 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       |

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

References

1. Allakhverdov GR (2008) Thermodynamics of electrolyte solutions. Doklady Physica 53(8): 420-424.
2. Root W (1933) The equation of density of the solutions. J Amer Chem Soc 50: 850-852.
3. Sohnel O, Novotny P (1985) Densities of aqueous solution of inorganic substances. Phys Science Data 22, Amsterdam Elsevier New York, USA.
4. Novotny P, Sohnel O (1988) Densities of binary aqueous solutions of 306 inorganic substances. J Chem Eng Data 33(1): 49-55.
5. Mikulin GI (1968) Current issues in the physical chemistry of electrolyte solutions. In: Mikulin GI (Ed.), Leningrad, Khimiya Russia.