



Osmotic and activity coefficients for the CsF + methanol or ethanol + water ternary systems determined by potentiometric measurements

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ABSTRACT

The thermodynamic properties of CsF in the ROH (R = methyl or ethyl) + water mixtures were determined using potentiometric measurements at 298.15 K with the mass fraction of ROH varying from 0.00 to 0.30. The Pitzer, extended Debye–Hückel and Pitzer–Simonson–Clegg equations were successfully utilized to fit the experimental data based on the molality and mole-fraction-composition scale. Except for the standard cell potentials and Pitzer parameters, the mean activity coefficients, osmotic coefficients and standard Gibbs energies of transference of CsF from water to the methanol + water or ethanol + water mixtures have also been discussed herein.

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1. Introduction

It is well-known that the thermodynamic properties of electrolyte in aqueous or mixed solvents, such as activity coefficients, osmotic coefficients, Gibbs excess energies and heat capacities are important for various industrial and environmental processes. Especially, alkali metals in aqueous or aqueous-organic mixed solvent are often selected as part of the research system. For example, Hernández-Luis et al. have reported the experimental data for NaCl [1], NaClO₄ [2] and NaBF₄ [3] in water or poly (ethylene glycol) 4000 + H₂O at temperatures of 288.15, 298.15, and 308.15 K by potentiometric measurements. The activity coefficients of KCl in proline + water [4] and formamide + water [5] systems have been investigated by Ghalami-Chooabar and co-workers. Vera and co-workers have studied the individual ion activity coefficients of 1:1 electrolytes, such as KCl [6], NaNO₃ + KNO₃, NaCl + KCl, and NaCl + NaBr [7], using potentiometric measurements at 298.15 K. The ternary systems NaCl + CH₃OH + H₂O [8] and NH₄Br + NaBr + H₂O [9] was also performed by Deyhimi and co-workers.

Up to now, although the thermodynamic properties for a wide variety of alkali metal salts in organic-water mixtures have been explored, limited reports can be found for the rare-alkali metal salts. As an extension of our work on the thermodynamics of rubidium chloride and cesium chloride in mixed solvents (RbCl/CsCl + methanol/ethanol + water [10], RbCl/CsCl + ethylene

glycol/propylene glycol/glycerol [11,12]), we present herein the thermodynamic properties of CsF in mixed solvents with the mass fraction of methanol or ethanol 0.10, 0.20, and 0.30 at 298.15 K. The experimental data were well fitted to the Pitzer, the extended Debye–Hückel, and Pitzer–Simonson–Clegg equations.

2. Equations

The experimental mean activity coefficients of CsF in the aqueous-organic mixtures were calculated from the following Nernstian equation

$$E = E^0 + 2k \ln(m\gamma_{\pm}) \quad (1)$$

where E and m are the experimental values, which represent the potential of the cell and the molality of CsF, respectively. γ_{\pm} is the mean activity coefficient of CsF; $k = RT/F$ is the theoretical Nernstian slope in which the symbols (R , T , and F) have their usual meanings. E^0 is the standard potential of the cell.

Pitzer equations were used to describe the mean activity coefficient in our calculation. For a 1–1 type electrolyte, the Pitzer equations for the mean activity coefficient (γ_{\pm}) and osmotic coefficient (Φ) can be written as follows [13]:

$$\ln \gamma_{\pm} = f^{\gamma} + mB^{\gamma} + m^2C^{\gamma} \quad (2)$$

$$\Phi - 1 = f^{\phi} + mB^{\phi} + m^2C^{\phi} \quad (3)$$

where

$$f^{\gamma} = -A_{\phi} \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \left(\frac{2}{b} \right) \ln(1 + bI^{1/2}) \right] \quad (2a)$$

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$$B^{\gamma} = 2\beta^{(0)} + 2\beta^{(1)} \left\{ \frac{[1 - \exp(-\alpha I^{1/2})(1 + \alpha I^{1/2} - 1/2\alpha^2 I)]}{\alpha^2 I} \right\} \quad (2b)$$

$$C^{\gamma} = 1.5C^{\varphi} \quad (2c)$$

$$f^{\varphi} = -A_{\varphi}(I^{1/2}/(1 + bI^{1/2})) \quad (3a)$$

$$B^{\varphi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \quad (3b)$$

$\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} are the parameters of the Pitzer equation. I is the ionic strength, $I = 1/2 \sum (mZ^2)$, where Z is the charge number of Cs^+ and F^- . B^{γ} and C^{γ} represent the second and the third virial coefficients, respectively. The term f^{φ} accounts for the long-range (or Debye–Hückel) forces, while the B^{γ} and C^{γ} comprise the short-range forces. The variation of B^{γ} with the ionic strength is given by Eq. (2b) with the parameters $\beta^{(0)}$ and $\beta^{(1)}$. The parameters b and α are equal to 1.2 and 2.0 $\text{kg mol}^{-1/2}$, respectively. A_{φ} is the Debye–Hückel constant for the osmotic coefficient defined by

$$A_{\varphi} = \left(\frac{1}{3}\right) \left[\frac{2\pi N_0 \rho}{1000} \right]^{1/2} \times \left[\frac{e^2}{\varepsilon K T} \right]^{3/2} \quad (4)$$

where N_0 , ρ , e , ε , K , and T are Avogadro’s number, the density of mixed solvent, electronic charge, the dielectric constant, Boltzmann’s constant, and the temperature. Eq. (4) can be simplified as:

$$A_{\varphi} = 1.4006 \times 10^6 \rho^{1/2} (\varepsilon T)^{-3/2} \quad (5)$$

The value of A_{φ} in pure water is 0.3915 [13] at 298.15 K. The A_{φ} value for the investigated ROH–water mixtures is obtained from the bibliography [10].

For 1–1 type electrolyte CsF, the extended Debye–Hückel equation for the mean activity coefficient (γ_{\pm}) is written as [14,15]:

$$\log \gamma_{\pm} = -\frac{Am^{1/2}}{1 + Bam^{1/2}} + cm + dm^2 - \log(1 + 0.002mM) + Ext \quad (6)$$

where a is the ion size parameter, c and d are the ion–interaction parameters, M is the average molecular mass of mixed solvent and Ext is the contribution of the extended terms and obtained from Roy’s experience formula [16]. A and B are the Debye–Hückel constants appropriate to the solvent given by:

$$A = \frac{1.8247 \times 10^6 \times \rho^{1/2}}{(\varepsilon T)^{3/2}} \text{ kg}^{1/2} \text{ mol}^{-1/2} \quad (6a)$$

$$B = \frac{50.2901 \times \rho^{1/2}}{(\varepsilon T)^{1/2}} \text{ kg}^{1/2} \text{ mol}^{-1/2} \text{ \AA}^{-1} \quad (6b)$$

where ρ , ε and T have their usual meaning [14,15].

In this work, we also use the Pitzer–Simonson–Clegg equation to correlate the experiment data, and obtain the parameters of the model. This equation for electrolyte activity coefficients was proposed by Pitzer, Simonson and Clegg [17,18].

The Pitzer–Simonson–Clegg model for a mixture of two neutral species, 1 and 2, and a 1–1 type electrolyte has been discussed in great details in Ref. [19]. For a MX (electrolyte) + alcohol (1) + water (2) system, the mean activity coefficient $\gamma_{\pm MX}$ can be written as

$$\begin{aligned} \ln \gamma_{\pm}^S = & \frac{x_1 x_2}{f^2} \times \left\{ (1 - f^2)W_{12} + \frac{1 - f^3}{f} \times 2(x_1 - x_2)U_{12} \right. \\ & \left. + [f^2(1 - 2x_S) - 1]Z_{12MX} \right\} + \frac{f^2 - 1}{f} (x_1 W_{1MX} + x_2 W_{2MX}) \\ & + \frac{x_1}{3f^2} \times [f^3(2 - 2x_1 + x_S) + x_S f^2(3x_1 + x_2) - 2x_2]U_{1MX} + \frac{x_2}{3f^2} \\ & \times [f^3(2 - 2x_2 + x_S) + x_S f^2(3x_2 + x_1) - 2x_1]U_{2MX} \end{aligned} \quad (7)$$

and

$$\begin{aligned} \ln \gamma_{\pm}^{DH} = & -A_X \left[\left(\frac{2}{\rho}\right) \ln(1 + \rho I_X^{1/2}) + \frac{I_X^{1/2}(1 - 2I_X)}{1 + \rho I_X^{1/2}} \right] \\ & + x_X B_{MX} g(\alpha I_X^{1/2}) - x_X x_M B_{MX} \left[\frac{g(\alpha I_X^{1/2})}{2I_X} + \left(1 - \frac{1}{2I_X}\right) \exp(-\alpha I_X^{1/2}) \right] \end{aligned} \quad (8)$$

By combining Eqs. (6) and (7), the mean activity coefficient of the MX in mixed solvents is:

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{DH} + \ln \gamma_{\pm}^S \quad (9)$$

where W_{12} and U_{12} are the parameters for the alcohol (1) + water (2) binary system; for methanol + water and ethanol + water mixtures, the parameters are $W_{12} = 0.4926$, $U_{12} = 0.0032$ and $W_{12} = 1.2051$, $U_{12} = 0.2583$ [20]. W_{iMX} and U_{iMX} are parameters for the solvent i + MX binary system ($i = 1$ or 2); Z_{12MX} and B_{MX} are the parameters of Pitzer–Simonson–Clegg equation. α is given as a fixed value of 13 [18].

In the above equations

$$g(x) = \frac{2[1 - (1 + x)\exp(-x)]}{x^2} \quad (7-1)$$

$$I_X = \frac{1}{2}(x_M + x_X) \quad (7-2)$$

$$f = 1 - x_S \quad (7-3)$$

$$\rho = 2150 \left(\frac{\rho_S}{\varepsilon T}\right)^{1/2} \quad (7-4)$$

$$A_X = \left(\frac{1000}{M_{sol}}\right)^{1/2} A_{\varphi} \quad (7-5)$$

I_X means the ionic rational strength; x_S is the mole fraction of the total ions in the solution; ρ_S and ε are the density of solvent as well as dielectric constant of the solvent; and M_{sol} is the mean molecular mass of the solvent.

Herein, the following Eq. (10) [19] is applied to the $\text{CsF} + \text{H}_2\text{O}$ binary mixture to obtain the parameters B_{MX} , W_{2MX} and U_{2MX} . In this process, the concentration of CsF in aqueous solutions should be the mole fraction:

$$\begin{aligned} \ln \gamma_{\pm} = & -A_X \left[\left(\frac{2}{\rho}\right) \times \ln(1 + \rho I_X^{1/2}) + \frac{I_X^{1/2}(1 - 2I_X)}{1 + \rho I_X^{1/2}} \right] \\ & + x_X B_{MX} g(\alpha I_X^{1/2}) - x_X x_M B_{MX} \times \left[\frac{g(\alpha I_X^{1/2})}{2I_X} + \left(1 - \frac{1}{2I_X}\right) \exp(-\alpha I_X^{1/2}) \right] \\ & + (x_2^2 - 1)W_{2MX} + 2x_2^2(1 - x_2)U_{2MX} \end{aligned} \quad (10)$$

The mean ionic rational activity coefficient ($\gamma_{\pm X}$) can be related to the mean ionic molal activity coefficient (γ_{\pm}) by:

$$\gamma_{\pm X} = \gamma_{\pm} (1 + 0.002M_{sol}m) \quad (11)$$

where m is the molality of the solution.

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