

Notes

Application of Mean Spherical Approximation in Estimating Activity Coefficients of Aqueous Mixed Electrolyte Solutions

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The mean spherical approximation theory is applied to estimate the activity coefficients in aqueous mixed electrolyte solutions. The contribution due to hard-sphere term in the excess free energy is considered. The only adjustable parameter is the ionic diameter. The equations tested for aq. HCl-CoCl₂ at 25°C and aq. HBr-CaBr₂ from 5 to 45°C show excellent agreement with experimental data.

Recently there has been growing interest in developing methods for predicting thermodynamic properties of aqueous mixed electrolyte solutions. Of various methods, the mean spherical approximation (MSA) has frequently been employed¹⁻⁴ to predict thermodynamic properties of single electrolyte solutions. Humffray⁵ included hard-sphere (non-electrostatic) terms into the MSA treatment of mixtures reported by Vericat and Grigera⁶ and predicted the activity coefficients in aq. NaCl-CaCl₂ differing from the experimental values by 13%. Corti⁷ applied the MSA theory to simple electrolyte mixtures like NaCl-HCl upto the ionic strength of 1 mol kg⁻¹ of water.

In this note, an attempt is made to explore the possibility of using MSA theory to relatively complicated systems like HCl-CoCl₂-H₂O⁸ at 25°C and HBr-CaBr₂-H₂O^{9,10} from 5 to 45°C in the region of moderately concentrated electrolyte solutions. Temperature dependence of the adjustable parameter is also discussed.

Theoretical equation for estimating the free energy in a mixture of hard-spheres as applied to the systems undertaken here may be written as^{11,12}

$$\ln \gamma_i^{hs} = \ln \Delta \left(\gamma_i - 1 - \frac{2\eta_i}{\eta} y_3 \right) + \frac{\eta}{\Delta^2} \left\{ 3(1 - \alpha_i) + \gamma_i + \frac{3\eta}{2} (\alpha_i - \beta_i - \gamma_i - 1) \right\} + \frac{\eta}{\Delta^3} \left\{ \eta \left[5y_3 - \frac{9}{2}y_1 - 2 + \eta \left(\frac{3}{2}y_1 - 3y_2 - 4y_3 + 1 \right) \right] - 2y_3 + 4 \right\} \dots (1)$$

Equation (1) is consistent with Baxter equation¹³, which is applicable for the calculation of activity coefficient in low concentration range.

According to unrestricted MSA model^{14,15}, the electrostatic contribution towards excess free energy of an electrolyte mixture, as applicable to present systems containing ionic species with charge Z_i and diameter σ_i, is given by Eq. (2)

$$\ln \gamma_i^e = \frac{\beta e^2 Z_i M_i}{\epsilon_0} - \frac{P_n}{4\Delta} \left(\Gamma a_i + \frac{\pi}{12\Delta} \alpha^2 P_n \sigma_i^2 \right) \dots (2)$$

The physical significance of various terms involved in Eqs (1) and (2) is discussed elsewhere^{11,12,14,15}.

The total excess free energy for an electrolyte mixture is given by Eq. (3), which is a combination of Eqs (1) and (2)

$$\ln \gamma_i = \ln \gamma_i^e + \ln \gamma_i^{hs} \dots (3)$$

The values of σ for H⁺, Co²⁺, Ca²⁺, Cl⁻ and Br⁻ were obtained by fitting the experimental activity coefficient data taken from literature¹⁶. Table 1 lists the σ-values at different temperatures. In this study, it is assumed that σ-values remain constant over the full range of concentration and composition. The ionic activity coefficients in a mixture obtained using σ-values given in Table 1 were converted into practical molal activity coefficients using densities of the mixtures. These densities were obtained from the virial coefficient approach of Pitzer¹⁷. The compressibility effects at atmospheric pressure were neglected.

In Fig. 1 are plotted the calculated results along with the experimental points as a function of Y_{CoCl₂}, the ionic strength fraction of CoCl₂ for aq. HCl-CoCl₂ at different ionic strengths. The results for aq. HBr-CaBr₂ at Y_{CaBr₂} = 0.5 at various temperatures are also shown in Fig. 1. The experimental mixture data fit the MSA theory with ex-

Table 1—Estimated Ionic Diameters (σ, Å) in MSA Theory at Different Temperatures

Ions	σ (Å) at temp				
	5°	15°	25°	35°	45°
H ⁺	5.20	4.70	4.45	4.21	4.10
Ca ²⁺	5.80	5.62	5.52	5.30	5.19
Co ²⁺	—	—	5.10	—	—
Cl ⁻	—	—	3.60	—	—
Br ⁻	4.00	4.00	3.90	3.82	3.78

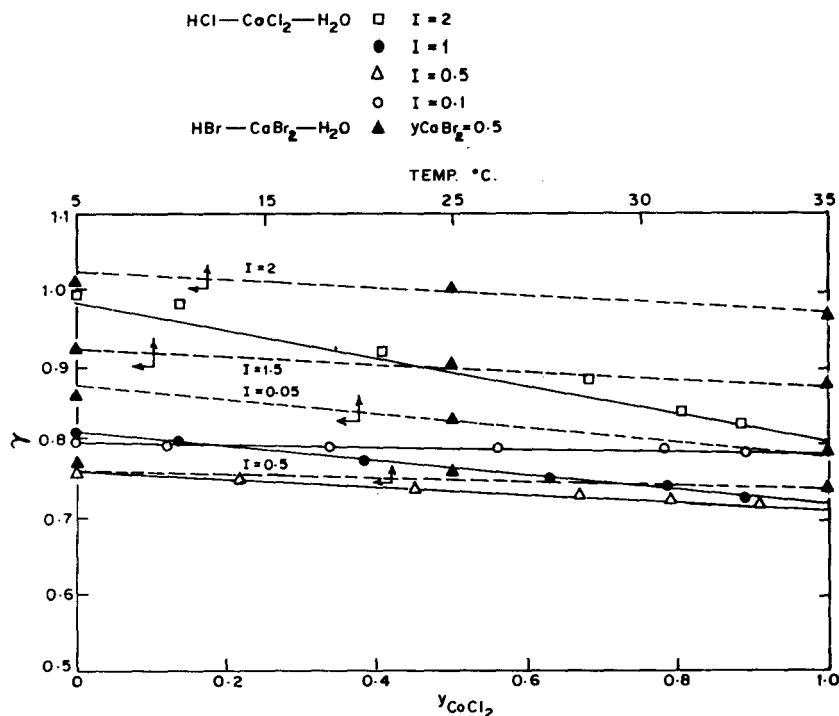


Fig. 1—Comparison of experimental and calculated activity coefficients for aq. HCl—CoCl₂ (—) and aq. HBr—CaBr₂ (---) systems (Temperature dependence is at $y=0.5$)

cellent accuracy upto ionic strength of 1 mol kg^{-1} , but a systematic deviation starts to occur beyond ionic strength of 2 mol kg^{-1} . The estimation for aq. HBr—CaBr₂ are fairly good even at ionic strength of 1.5. The poor fit in the range of high concentrations is due to the fact that the hydration around ions changes and thus the ionic diameters might be varying in the high concentration region. A consideration of concentration—dependent σ , however, will further complicate the system of equations. It was noted that σ_{H^+} values for both aq. HCl—CoCl₂ and aq. HBr—CaBr₂ at 25°C were approximately the same and thus an average value at this temperature is given in Table 1. The values of σ decrease with increase in temperature; however, the temperature dependence of for H^+ is very strong.

In summary, the MSA theory with an adjustable parameter, acts as a powerful tool for predicting the activity coefficients.

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