Thermodynamic Study of the NaCl + CaCl$_2$ + H$_2$O Mixed System by EMF Measurements at Different Temperatures

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Activity coefficients for NaCl in the NaCl + CaCl$_2$ + H$_2$O ternary system are determined from emf measurements of galvanic cells at 15, 25, 35 and 45 °C. The experimental data were analysed using the Harned, Scatchard and Pitzer treatments.

Several researchers have studied the NaCl + CaCl$_2$ + H$_2$O system at 25 °C by the use of different experimental techniques.[6–8] However there is a lack of information about studies done at temperatures other than 25 °C, and when they are available, unfortunately, the measured concentration range is not as wide as desirable.[9] In this work, activity coefficient values have been measured at 15, 25, 35 and 45 °C for ionic strengths of 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 4 and 6 mol kg^{-1}. The ionic strength fraction for CaCl$_2$, y_B was varied between 0 and 0.8.

The activity coefficients for NaCl in the mixture were obtained from emf measurements of cell (1)

$$\text{ISE-Na}|\text{NaCl}(m_A), \text{CaCl}_2(m_B), \text{AgCl}_{(s)}|\text{Ag} \qquad (1)$$

in which m_i denotes the molality of electrolyte i. The asymmetry potential[16,17] of the ISE-Na glass electrode was cancelled by combining cell (1) with reference cell (2)

$$\text{ISE-Na}|\text{NaCl}(I_{\text{ref}} = m_A + 3m_B), \text{AgCl}_{(s)}|\text{Ag} \qquad (2)$$

The difference in potential ΔE between cells (1) and (2) is given by eqn. (3)

$$\Delta E = E_1 - E_2 = k \log \frac{I_{\text{ref}}^2}{m_A(m_A + 2m_B)} - 2k \log(\gamma_A/\gamma_A^0) \quad (3)$$

where γ_A and γ_A^0 are the mean ionic activity coefficients of NaCl in the mixture and in *pure* water at the same total ionic strength of the mixture ($I_{\text{ref}} = I_A + I_B$) respectively, and $k = (\ln 10)RT/F$ (R, T and F have their usual meaning). Eqn. (3) can be rearranged to obtain eqn. (4).

$$\log \gamma_A = \log \gamma_A^0 + 0.5k \log \frac{I_{\text{ref}}^2}{m_A(m_A + 2m_B)} - (\Delta E/2k) \quad (4)$$

Values of γ_A^0 were calculated from the Pitzer equation for the *pure* electrolyte. With the experimental ΔE values and using eqn. (4), log γ_A values were calculated. The γ_A values were analysed using various models. One of the best known models is the Harned rule given by eqn. (5)

$$\log \gamma_A = \log \gamma_A^0 - \alpha_A y_B I - \beta_A y_B^2 I^2 - \cdots \qquad (5)$$

where α_A and β_A are adjustable parameters. In this work, the results show that it is only necessary to consider the parameter α_A to fit the experimental data within experimental error. Only at 15 °C it is observed that the deviations are greater than experimental error at some ionic strengths. We can thus confirm that NaCl obeys the Harned rule.

Experimental values of log γ_A are also analysed by two ionic interaction models, for which we make use of eqn. (6) proposed by Lim *et al.*[26]

$$\log \gamma_A = \log \gamma_A^0 + \frac{y_B I}{2 \ln 10}\left[g_0 + \left(\frac{I}{2} + \frac{3YI}{2}\right)g_1 + \left(\frac{I}{2} + \frac{YI}{2}\right)g_0 - \Phi\right] \qquad (6)$$

where all the symbols have their usual significance.[27,28]

The approximations used for g_n as function of the ionic strength lead to the different fitting methods. In present work we have utilised Scatchard and Pitzer methods. Below, a summary of these I-dependent methods is given.

Method S (Scatchard)

$$g_0 = b_{01} + \tfrac{1}{2}b_{02}I + \tfrac{1}{3}b_{03}I^2 \qquad (7\text{a})$$

$$g_0' = \tfrac{1}{2}b_{02} + \tfrac{2}{3}b_{03}I \qquad (7\text{b})$$

$$g_1 = b_{12}/2 \qquad (7\text{c})$$

$$g_1' = 0 \qquad (7\text{d})$$

Method P (Pitzer)

$$g_0 = K_1 B_A + K_2 B_B + K_3 \theta + I(K_4 C_A + K_5 C_B + K_6 \psi) \qquad (8\text{a})$$

$$g_0' = K_1 B_A' + K_2 B_B' + K_3 \theta' + K_4 C_A + K_5 C_B + K_6 \psi \qquad (8\text{b})$$

$$g_1 = K_7 C_A + K_8 C_B + K_9 \psi \qquad (8\text{c})$$

$$g_1' = 0 \qquad (8\text{d})$$

In these equations, b_{nk} coefficients (method S) and θ and ψ (method P) are the mixing parameters whose values were obtained by fitting the experimental log γ_A data. In method *P*, K_i are constants that depend on the electrolyte stoichiometric coefficients.[28] The results show that the two methods are adequate for treating the experimental activity coefficients. For both the Scatchard and Pitzer methods it is necessary to use two mixing parameters for the description of the studied system, within the estimated experimental error (0.18 mV). Also, at 15 °C the deviation is slightly larger than the estimated experimental error. In the Pitzer method, the fit to the experimental data is improved when high-order electrostatic terms are considered.

Trace activity coefficients (Fig. 2) and Gibbs excess energy of mixing (Fig. 3) at 25 °C were obtained using the Pitzer equation. Fig. 2 shows that in both electrolytes the log γ^{tr} curve lies above the log γ^0 curve. For NaCl, this behaviour can be explained by the increase of ion–solvent

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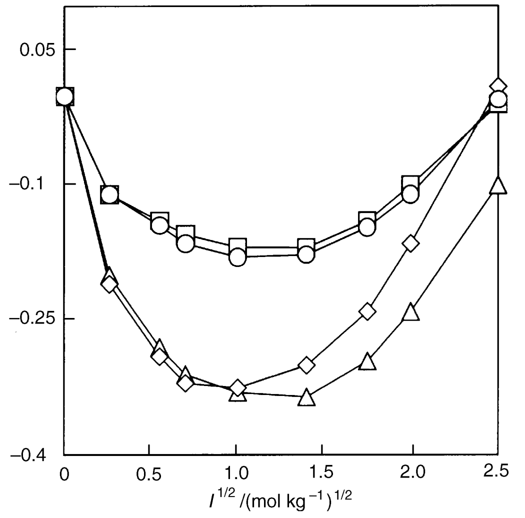

Fig. 2 Plot of log γ *vs.* $I^{1/2}$ for the system $NaCl + CaCl_2 + H_2O$ at 25 °C. (○) log γ^0 (NaCl), (□) log γ^{tr} (NaCl), (△) log γ^0 ($CaCl_2$) and (◇) log γ^{tr} ($CaCl_2$)

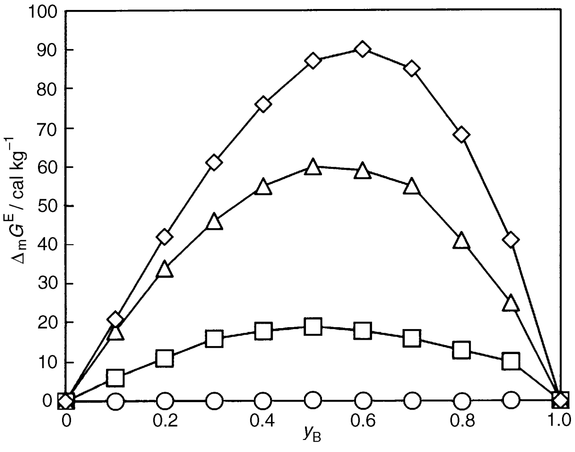

Fig. 3 Plot of $\Delta_m G^E$ *vs.* y_B for the system $NaCl + CaCl_2 + H_2O$ at 25 °C. (○) $I = 0.5$ mol kg^{-1}, (□) $I = 2.0$ mol kg^{-1}, (△) $I = 4.0$ mol kg^{-1} and (◇) $I = 6.0$ mol kg^{-1}.

interactions, produced by replacement of Na^+ ions by Ca^{2+} ions. This might be a consequence of the higher hydration of Ca^{2+} ions in comparison with Na^+ ions. For $CaCl_2$, this result indicates that the substitution of Ca^{2+} ions by Na^+ ions produces a decrease of ion–ion interactions. This is a consequence of: (a) a smaller z/r^2 value for Na^+ ions in comparison with Ca^{2+} ions, and (b) elimination of $(CaCl)^-$ ionic pairs and possible $(ClCaCl)^0$ triple ion associations.

Fig. 3 shows that ΔG_m^{ex} values are always positive for all studied ionic strengths. It can be observed that this system presents parabolic curves with a degree of asymmetry, whose maximum shifts towards the $CaCl_2$ rich zone.

Finally ΔH_m^{ex} values were calculated using the Pitzer equation. Despite the uncertainty in prediction of our ΔH_m^{ex} values, they are similar in magnitude to those reported by Wood and Ghamkhar.[49]

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Technique used: emf measurements of galvanic cells

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Fig. 1: Plot of α_A *vs.* I for the system $NaCl + CaCl_2 + H_2O$ at 25 °C

Fig. 4: Plot of $\Delta_m H^E$ *vs.* y_B for the system $NaCl + CaCl_2 + H_2O$ at 25 °C

Tables: 8 (experimental ΔE values, α_A and mixing parameter values, $\Delta G_m^{ex}(y_B = 0.5)$ values at 25 °C, *etc.*)

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