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Microcalorimetric studies of electrolyte mixtures: HCl–KCl and HCl–$CaCl_2$. Application of Pitzer's model

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Abstract

Heats of mixing of two concentrated isomolal aqueous electrolyte solutions have been measured using a flow-mix microcalorimetric method to determine the thermodynamic properties of the mixed solutions. Systems HCl–KCl and HCl–$CaCl_2$ have been examined in the 0.001–2.0 molality and 293–333 K temperature range. Experimental heat values obtained have been interpreted by Pitzer's ion interaction model. Pitzer's mixing coefficients have been calculated and used to estimate the nature and intensity of the ion interactions in mixed solutions, as well as the interaction intensity difference caused by different electron configurations of the ions present. Using Pitzer's parameters, the activity coefficients of the mixed solutions components have been calculated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heat of mixing; Microcalorimetry; Electrolytes; Thermodynamics of mixing; Pitzer's model

1. Introduction

It is well known that the measurement of the heats of mixing of electrolyte solutions is an excellent way to study the interactions of ions in an aqueous medium.

Our previous papers [1,2] on the enthalpy of mixing of sodium carbonate and sodium bicarbonate aqueous solutions have shown that our flow-mix microcalorimetric cell is suitable for direct heat of mixing measurements at temperatures not exceeding 353 K.

We continued our investigation on specific ion interactions occurring in electrolyte mixtures by measuring the heat produced upon mixing the HCl–KCl and HCl–$CaCl_2$ concentrated aqueous solutions.

The systems were chosen according to their practical importance and application as well as in order to study the chemistry of the mixtures.

Chlorides of potassium and calcium are important constituents of many natural and industrial water systems containing hydrochloric acid as one of the components. For that reason it seems necessary to complete the present thermodynamic data for these mixed electrolyte solutions.

Electrolyte mixtures studied, containing different cations and a common anion, are of theoretical interest, too.

Experimental results were interpreted using Pitzer's ion interaction model because it provides the simplest, most accurate and convenient procedure for calculation of the thermodynamic properties of binary electrolyte mixtures containing a common ion.

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2. Experimental

Reagent grade KCl and $CaCl_2 \cdot 2H_2O$ (Merck-Alkaloid) were thermally pre-treated at 383 and 343 K, respectively, for 24 h. All the solutions were prepared with freshly boiled, doubly distilled water.

The upper stock-solution concentration limit was determined according to the maximum heat of mixing value measured in the flow-mix cell, while the lower limit was defined by the calorimeter sensitivity.

Molality of the KCl and $CaCl_2$ stock-solutions was checked by the method of inductively coupled plasma (Perkin Elmer, model ICP 6500).

The solution densities were measured by an AP Paar densimeter, model DMA 55.

Mixing experiments were performed in a flow-mix cell of a Thermometric (LKB) isothermal multichannel microcalorimeter (model 2277). The calibration was performed inside the mixing cell by an electrical heater. The solutions were introduced into the flow-mix cell using a pair of microperpex peristaltic pumps (LKB BROMMA, model 2132) previously calibrated with the same solutions. All the solutions mixed were isomolal and the flow rate of each pump was 10 ml h^{-1}, attaining a molal fraction of each component in the mixture of 0.5.

Measurements were performed in the 293–333 K temperature range and were not continued at higher temperatures due to appearance of air bubbles.

3. Results and discussion

The heat of mixing[1] values measured at 298 K, each calculated as a mean value of three experimental runs, are related to the total ionic strength of the HCl–KCl mixture in Fig. 1. The uncertainty interval was calculated as twice the standard deviation of the mean value. The function presented in Fig. 1 retains the similar form at all temperatures.

The mixing of univalent and positive H^+ and K^+ ions is an example of the symmetrical mixing process involving ions of the same sign and charge [3]. Theoretical curve, indicated by a broken line in Fig. 1, is obtained by fitting experimental data to the equation :

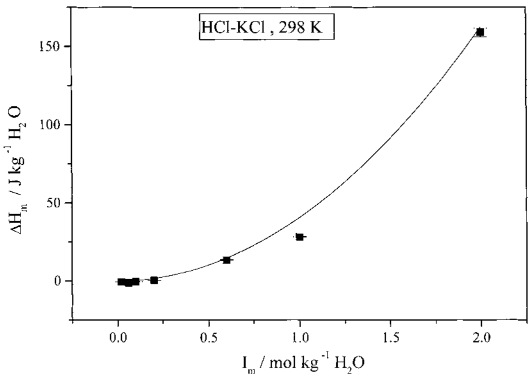

Fig. 1. Heat of mixing of isomolal HCl and KCl solutions as a function of total ionic strength at 298 K; theoretical curve is depicted by a broken line.

$$\Delta H_{\mathrm{mix}} = -\tfrac{1}{2} R T^2 \left[I_{\mathrm{mix}}^2 \theta_{\mathrm{MN}}^L + I_{\mathrm{mix}}^3 \Psi_{\mathrm{MNX}}^L \right], \tag{1}$$

where symbol ΔH_{mix} denotes the heat of mixing, T the experimental temperature and I_{mix} the total ionic strength of the mixture. θ^L represents a mixing coefficient describing M–N pairwise interaction, and Ψ^L is relevant to the M–N–X triplet interactions.

Eq. (1) represents Pitzer's expression for symmetrical mixing of two 1–1 isomolal electrolyte solutions with a common ion [3]. The fitting procedure to Eq. (1) gives the values for temperature derivative of Pitzer's mixing coefficient θ^L, representing the second virial coefficient relevant to the pairwise H^+–K^+ interactions. In order to improve the fit quality, temperature derivative of the third virial coefficient, Ψ^L, representing triplet interactions, was set to zero. Pitzer's mixing parameter, $\theta^{(0)L}$, concerning short-range forces between M and N ions of different signs present in the mixture (H^+ and Cl^-), as well as Ψ^L coefficient, were calculated using the equation [4,5]:

$$\Delta H_{\mathrm{mix}} = -\frac{1}{2} R T^2 I_{\mathrm{mix}}^2 \left\{ \theta_{\mathrm{MN}}^{(0)L} - 2\alpha^2 I_{\mathrm{mix}} \times \left(\frac{\theta_{\mathrm{MN}}^{(0)L} + \frac{\theta A_{\mathrm{H}}}{4RT^2 A_{\Phi}}}{1 + \frac{\alpha}{9z^2 A_{\Phi}}} \right) \left[1 - (1 + \alpha I_{\mathrm{mix}}^{1/2}) \exp(-\alpha I_{\mathrm{mix}}^{1/2}) \right] + \frac{I_{\mathrm{mix}} \Psi_{\mathrm{MNX}}^L}{2} \right\}, \tag{2}$$

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[1] Tables containing experimental heat of mixing and activity coefficient values for HCl–KCl and HCl–$CaCl_2$ mixtures, as well as θ^L, Ψ^L, $\theta^{(0)L}$ and $\theta^{(1)L}$ for HCl–KCl, h_0 for HCl–$CaCl_2$, and ${}^{S}\theta^L$, Ψ^L, ${}^{E}\theta$ and θ values for HCl–$CaCl_2$ system at all temperatures studied, are available upon request.

where z is the valence of ions and α has the value of 2.0 kg$^{-1/2}$ mol$^{-1/2}$, while Debye–Hückel enthalpy, $A_{\rm H}$, and osmotic coefficient, A_Φ, parameters, necessary for calculation of Pitzer's parameters according to the model for symmetrical mixing, are tabulated for different temperatures in Ref. [6]. Symbol θ represents limiting value at zero ionic strength.

The second virial coefficient component, $\theta^{(1)L}$, referring to the pairwise H$^+$–K$^+$ interactions only, was calculated using the equation [4]:

$$\Delta H_{\rm mix} = -\tfrac{1}{2}RT^2\left\{\theta^{(0)L}_{\rm MN}I^2_{\rm mix} + (2\theta^{(1)L}_{\rm MN}I_{\rm mix}/\alpha^2) \times \left[1-(1+\alpha I^{1/2}_{\rm mix})\exp(-\alpha I^{1/2}_{\rm mix})\right] + I^3_{\rm mix}\Psi^L_{\rm MNX}/2\right\}. \quad (3)$$

The mixing coefficients θ^L, Ψ^L and $\theta^{(0)L}$ versus temperature for the HCl–KCl system are represented in Figs. 2–4, respectively. The $\theta^{(1)L}$ temperature dependence is not presented because, disregarding the good fit quality, this parameter was calculated with a great error.

The temperature functions presented in Figs. 2–4 were integrated in the 293–333 K temperature range and the values of θ, Ψ and $\theta^{(0)}$ were obtained and are tabulated in Table 1.

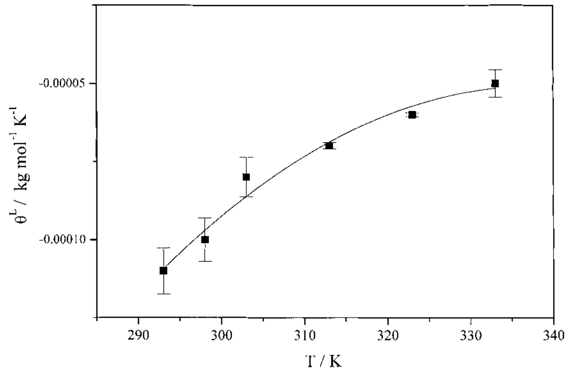

Fig. 2. Mixing coefficient θ^L as a function of temperature for the system HCl–KCl; solid line represents the second-power polynomial.

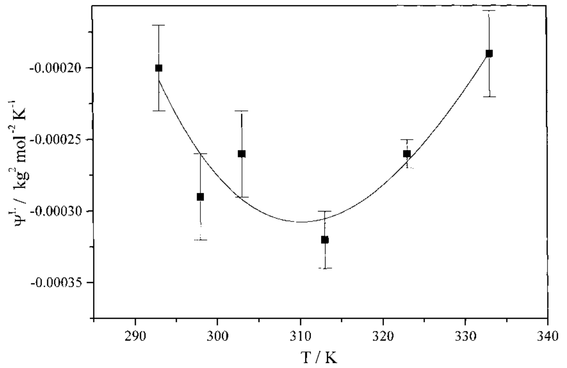

Fig. 3. Mixing coefficient Ψ^L versus temperature for the system HCl–KCl; solid line represents the third-power polynomial.

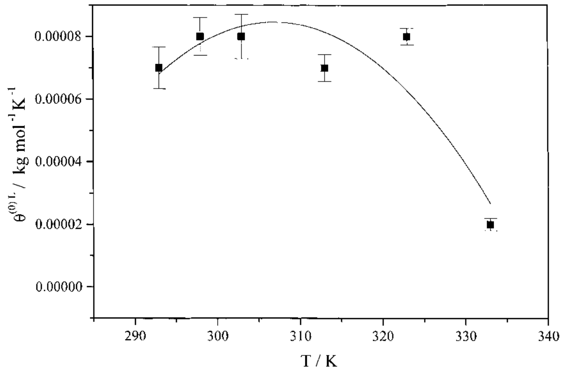

Fig. 4. Mixing coefficient $\theta^{(0)L}$ versus temperature for the system HCl–KCl; solid line represents the second-power polynomial.

The θ value for the HCl–KCl system at 298 K and ionic strength ranging from 1 to 3 mol kg^{-1} as calculated by Phutela and Pitzer [5] is 0.5×10^{-2} kg mol^{-1}, while the Ψ value was not reported. As the mixing parameters tabulated in Table 1 refer to the 293–333 K temperature range, with the ionic strength of the mixture varying from 0.02 to 2 mol kg^{-1}, we can find out that there is an agreement between our experimental and the literature θ values.

According to Fig. 2 we can conclude that the θ^L mixing parameter increases with increasing temperature, which is opposite to the literature examination

Table 1
Pitzer's mixing parameters for the system HCl–KCl in the 293–333 K temperature range (values in brackets stand for standard deviation obtained by fitting the experimental dependence to the polynomial)

θ (kg mol^{-1})	Ψ (kg^2 mol^{-2})	$\theta^{(0)}$ (kg mol^{-1})
0.0024 (4.4×10^{-6})	0.0064 (3.0×10^{-5})	−0.0033 (1.0×10^{-5})

[5] concerning the HCl–KCl system. In the case of simple symmetrical process it appears to be a good approximation to assume that both θ^L and Ψ^L decrease slowly with increasing temperature [5]. The θ coefficient growth with increasing temperature has been noticed for many unsymmetrical mixtures [7–13], while for the system HCl–$MgCl_2$ the temperature dependence minimum has been observed at 298 K [14]. Since the θ^L coefficient refers to the H^+–K^+ short-range forces, we can assume its increase with temperature to be a consequence of increased probability for positive ions to approach each other and interact.

An unusual shape of the Ψ^L temperature dependence (Fig. 3), obtained as a result of poor fit quality, can be caused by a low probability for the H^+–K^+–Cl^- ternary interactions to happen in the concentration range investigated.

The $\theta^{(0)L}$ mixing coefficient, describing the short-range forces acting between the H^+ and Cl^- ion, as a function of temperature is presented in Fig. 4. Since thermal energy of the ions in the mixture increases with increasing temperature, reducing so the probability of their mutual contact, the $\theta^{(0)L}$ drop at temperatures higher than 303 K seems quite acceptable.

Activity coefficient, γ, of the MX component of a symmetrical mixture, containing two 1–1 electrolytes with a common ion X, is given, according to Pitzer's model, by the equation [15]:

$$\ln\gamma_{\mathrm{MX}} = \ln\gamma^*_{\mathrm{MX}} + y\Delta\Phi^* + y\left(\frac{m}{m^0}\right) \times \left\{\theta_{\mathrm{MN}} + \left(\frac{m}{m^0}\right)(1-y/2)\Psi_{\mathrm{MNX}}\right\}, \quad (4)$$

where superscript * denotes pure components of the same molality m as the total molality of the mixture, y is the mole fraction of NX, m^0 has the value of 1 mol kg^{-1}, and an expression for osmotic coefficients difference, $\Delta\Phi^*$, is given in Ref. [15].

An expression for the second component, NX, has the form:

$$\ln\gamma_{\mathrm{NX}} = \ln\gamma^*_{\mathrm{NX}} + (1-y)\Delta\Phi^* + (1-y)(m/m^0) \times \left\{\theta_{\mathrm{MN}} + (m/m^0)(1+y)\Psi_{\mathrm{MNX}}/2\right\}. \quad (5)$$

Activity coefficients for the HCl and KCl components of the mixture were calculated according to Eqs. (4) and (5) and the γ_{KCl} values at all experimental temperatures are related to the total ionic strength of the mixture in Fig. 5. The HCl activity coefficient dependences are of the similar shape.

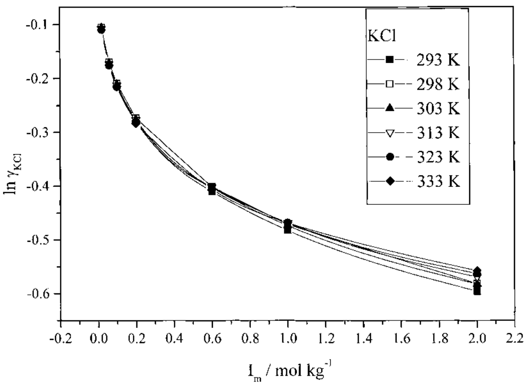

Fig. 5. Activity coefficient of KCl component of the HCl–KCl mixture versus total ionic strength in the 293–333 K temperature interval.

It is obvious from Fig. 5 that the activity coefficient dependence on total ionic strength of the HCl–KCl mixture has the pattern well known in literature [15–19]. It can also be concluded that the γ_{KCl}, as well as the γ_{HCl} values, do not vary significantly with temperature.

Heat of mixing values of isomolal HCl and $CaCl_2$ solutions at 298 K are related to the total ionic strength of the mixture in Fig. 6. In contrast to the HCl–KCl mixing process, representing an example of endothermic reaction, unsymmetrical mixing of H^+ and Cl^-

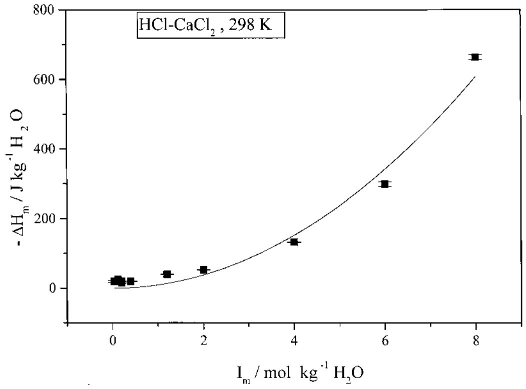

Fig. 6. Heat of mixing of isomolal HCl and $CaCl_2$ solutions as a function of total ionic strength at 298 K; theoretical curve is depicted by a broken line.

cations is characterised by a negative heat effect. A function presented in Fig. 6 retains the similar form at all experimental temperatures. Theoretical curve is obtained by fitting the experimental heat of mixing data to the equation [2]:

$$\frac{\Delta H_{\mathrm{mix}}}{n_{\mathrm{w}} R T I_{mix}^{2}} = y(1-y)[h_0 + (1-2y)h_1 + \cdots], \quad (6)$$

where n_{w} is the number of kilograms of solvent, h_0 is the parameter which refers to the magnitude of ion interaction during the mixing, and h_1 coefficient is the measure of asymmetry from the quadratic relation with respect to the ionic strength fraction. The fitting procedure resulted in the values of mixing coefficient h_0, while the h_1 parameter value was close to zero at all temperatures.

It is well known [3] that the second virial coefficient θ of the unsymmetrical mixture is composed of two components: ${}^{\mathrm{S}}\theta$ and ${}^{\mathrm{E}}\theta$. The first refers to the short-range forces between the cations in the mixture, while the second is a function describing the higher-order electrostatic effects . More exactly, the ${}^{\mathrm{E}}\theta$ coefficient includes the electrostatic contribution to the interaction of cations in the mixed solution of final concentration [3].

Mixing parameters ${}^{\mathrm{S}}\theta^{L}$ and Ψ^{L}, referring to the short-range H^+–Ca^{2+} and triplet H^+–Ca^{2+}–Cl^- interactions, respectively, are calculated, as suggested by Pitzer [3], using the following equations:

$$h_0 = Q_1 + Q_2 - 2T\,{}^{\mathrm{E}}\theta_{\mathrm{MN}}^{L}/3, \quad (7)$$

$$Q_1 = T\left(\frac{2B_{\mathrm{MX}}^{L}}{3} + \frac{11 I_{\mathrm{mix}} C_{\mathrm{MX}}^{L}}{9} - \frac{2B_{\mathrm{NX}}^{L}}{9} - I_{\mathrm{mix}} C_{\mathrm{NX}}^{L}\right), \quad (8)$$

$$Q_2 = -T\left(\frac{2\,{}^{\mathrm{S}}\theta_{\mathrm{MN}}^{L}}{3} + \frac{5 I_{\mathrm{mix}} \Psi_{\mathrm{MNX}}^{L}}{18}\right). \quad (9)$$

Here Q_1 is an array of pure-electrolyte terms available from the heat of dilution measurements, while Q_2 is the combination of cation mixing terms arising from the short-range forces. Parameters B and C, relevant to pure electrolytes, are tabulated in Ref. [20]. Temperature dependences of the ${}^{\mathrm{S}}\theta^{L}$ and Ψ^{L} mixing coefficients are illustrated in Figs. 7 and 8, respectively. Disregarding the higher error values obtained, especially for the Ψ^{L} parameter, the functions presented have a form already known in literature [7–13].

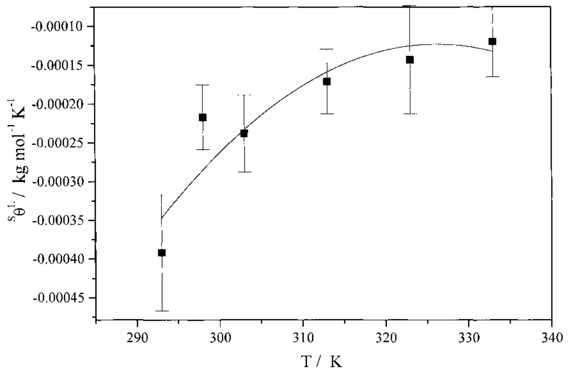

Fig. 7. Mixing coefficient ${}^{\mathrm{S}}\theta^{L}$ versus temperature for the system HCl–$CaCl_2$; solid line represents the second-power polynomial.

Kinetic energy of the H^+ and Ca^{2+} cations rises by increasing the temperature of the mixture, making possible an overcome of repulsive forces and intereaction of mutual ion, which can be an explanation for the ${}^{\mathrm{S}}\theta^{L}$ growth (Fig. 7). The Ψ^{L} drop with increase in temperature (Fig. 8) points out a lower probability for triplet H^+–Ca^{2+}–Cl^- interaction to be attained at higher temperatures.

Integrating the functions presented in Figs. 7 and 8 in the 293–333 K temperature interval, the following values were obtained: ${}^{\mathrm{S}}\theta = 0.00725\ \mathrm{kg\ mol^{-1}}$ (standard deviation of the fit: 0.00005) and $\Psi = 0.00104\ \mathrm{kg^2\ mol^{-2}}$ (standard deviation of the fit: 0.0002). Literature values [21] for the HCl–$CaCl_2$ system at 298 K, obtained by emf measurements, are: ${}^{\mathrm{S}}\theta = 0.0739$ and $0.0612\ \mathrm{kg\ mol^{-1}}$, and $\Psi = 0.0030$

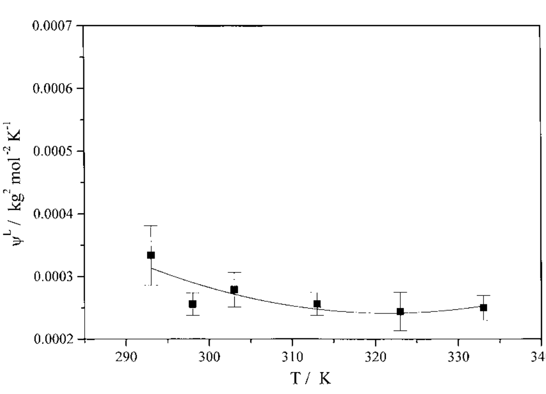

Fig. 8. Mixing coefficient Ψ^{L} versus temperature for the system HCl–$CaCl_2$; solid line represents the second-power polynomial.

and 0.0008 $kg^2\ mol^{-2}$ for maximal total ionic strength of 3 and 5 $mol\ kg^{-1}$, respectively. Disagreement noticed, particularly that concerning the $^S\theta$ coefficient, can be partly explained by the fact that the values we calculated do not refer only to 298 K, but to the whole 293–333 K temperature range. Additionally, the total ionic strength fraction of the HCl–$CaCl_2$ mixture in our case reached even the value of 8 $mol\ kg^{-1}$.

However, to express precisely the intensity of ion interactions during the unsymmetrical mixing process, it is necessary to include the $^E\theta$ second virial coefficient relevant to higher-order electrostatic effects. The higher-order electrostatic term can be computed from the cluster-integral theory for electrolytes introduced by Mayer and applied as generality by Friedman and Pitzer. The $^E\theta$ values for the HCl–$CaCl_2$ system are, for different total ionic strengths of the mixture and in the 293–333 K temperature range, calculated using the equation [22]:

$$^E\theta_{MN} = (z_M z_N / 4I_{mix}) \times \left[J(x_{MN}) - \tfrac{1}{2}J(x_{MM}) - \tfrac{1}{2}J(x_{NN})\right], \quad (10)$$

where x_{MN} is given as:

$$x_{MN} = 6 z_i z_j A_\Phi I_{mix}^{1/2}. \quad (11)$$

An approximate J function value is calculated using both equations [22]:

$$J = -\tfrac{1}{6}x^2(\ln x)e^{-10x^2} + \left(\textstyle\sum_{k=1}^{6} C_k x^{-k}\right)^{-1}, \quad (12)$$

$$J = x\left[4 + C_1 x^{-C_2}\exp(-C_3 x^{C_4})\right]^{-1}. \quad (13)$$

The constant values C are tabulated in Ref. [20]. The $^E\theta^L$ parameter, representing temperature derivative of $^E\theta$ function, was calculated as well and the values are presented in Table 2. Symbols $^E\theta^L_{12}$ and $^E\theta^L_{13}$ refer to the $^E\theta$ values obtained when the J function was computed using Eqs. (12) and (13), respectively.

Table 2
Mixing coefficients $^E\theta^L_{12}$ and $^E\theta^L_{13}$ versus total ionic strength of the HCl–$CaCl_2$ mixture

I_{mix} (mol kg^{-1})	$^E\theta^L_{12}$ (kg mol^{-1} K^{-1})	$^E\theta^L_{13}$ (kg mol^{-1} K^{-1})
0.02	$-(3.31 \pm 0.58)10^{-4}$	$-(3.82 \pm 0.06)10^{-4}$
0.04	$-(1.82 \pm 0.05)10^{-4}$	$-(2.30 \pm 0.04)10^{-4}$
0.12	$-(2.64 \pm 0.07)10^{-4}$	$-(1.02 \pm 0.02)10^{-4}$
0.2	$-(1.50 \pm 0.02)10^{-4}$	$-(6.11 \pm 0.82)10^{-5}$
0.4	$-(5.11 \pm 0.05)10^{-5}$	$-(3.00 \pm 0.48)10^{-5}$
1.2	$(2.23 \pm 0.24)10^{-6}$	$-(4.06 \pm 1.16)10^{-6}$
2	$(6.74 \pm 0.25)10^{-6}$	$-(2.56 \pm 1.10)10^{-7}$
4	$(6.99 \pm 0.16)10^{-6}$	$(1.68 \pm 0.08)10^{-6}$
6	$(6.10 \pm 0.28)10^{-6}$	$(2.12 \pm 0.06)10^{-6}$

The Q_2 value, calculated according to Eq. (9), is related to the total ionic strength of the mixture at 293 K in Fig. 9. Deviation from linearity, observed in the low ionic strength region, is caused by the higher-order electrostatic effect. It is obvious from Fig. 9 that departure from linearity can be corrected introducing the $^E\theta^L_{13}$ higher-order electrostatic function. Hence, it is apparent that the inclusion of the additional $^E\theta$ and $^E\theta^L$ terms is essential in order to treat the H^+–Ca^{2+} unsymmetrical mixing satisfactorily. Higher-order electrostatic component of the second virial coefficient, $^E\theta^L_{13}$, and total Pitzer's mixing coefficient θ, obtained as the sum of $^E\theta^L_{13}$ and the short-range term $^S\theta$, are related to the total ionic strength at 298 K in Fig. 10. The function presented is well known [21] and retains the same pattern at all temperatures. It is obvious that the second virial coefficient component, relevant to the higher-order electrostatic interaction between H^+ and Ca^{2+} ions, changes considerably in the low-concentration range, reaching constant value with increasing ionic strength. Since the $^E\theta$ parameter obviously determines the form of θ function, relevant to the total interaction effect between two ions, the results shown in Fig. 10 clearly confirm the correctness of the higher-order contribution to the H^+–Ca^{2+} unsymmetrical mixing.

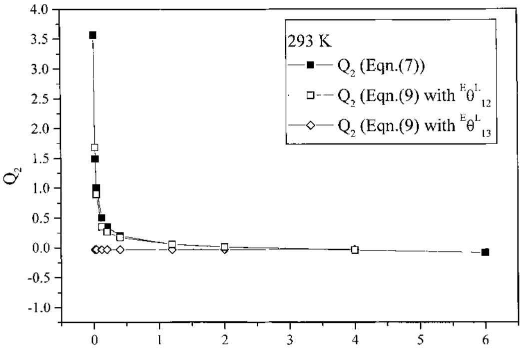

Fig. 9. Q_2 versus total ionic strength of the HCl–$CaCl_2$ mixture at 293 K.

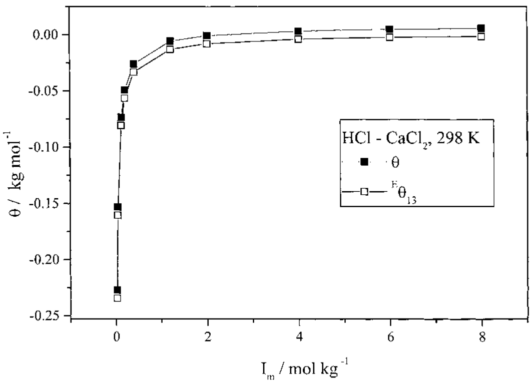

Fig. 10. Pitzer's mixing coefficients ${}^{E}\theta_{13}$ and θ as a function of total ionic strength of the HCl–CaCl$_2$ mixture at 298 K.

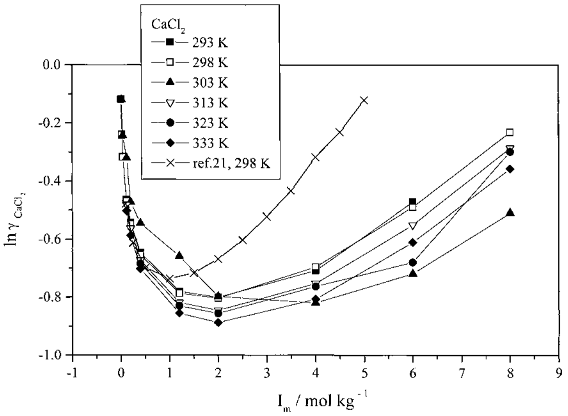

Fig. 11. Activity coefficient of CaCl$_2$ component of the HCl–CaCl$_2$ mixture versus total ionic strength in the 293–333 K temperature interval.

Activity coefficient values for the HCl and CaCl$_2$ components were calculated using Pitzer's expressions [21–23] for unsymmetrical mixture MX + NX$_2$:

$$\begin{aligned}\ln\gamma_{\mathrm{MX}} = {} & f^{\gamma} + (m_{\mathrm{M}} + m_{\mathrm{X}})(B_{\mathrm{MX}} + m_{\mathrm{X}}C_{\mathrm{MX}}) \\ & + m_{\mathrm{N}}(B_{\mathrm{NX}} + m_{\mathrm{X}}C_{\mathrm{NX}} + {}^{\mathrm{S}}\theta_{\mathrm{MN}} + {}^{\mathrm{E}}\theta_{\mathrm{MN}}) \\ & + m_{\mathrm{N}}m_{\mathrm{X}}(B'_{\mathrm{MX}} + C_{\mathrm{MX}}) + m_{\mathrm{N}}m_{\mathrm{X}}(B'_{\mathrm{NX}} \\ & + C_{\mathrm{NX}} + \tfrac{1}{2}\Psi_{\mathrm{MNX}}) + m_{\mathrm{M}}m_{\mathrm{N}}({}^{\mathrm{E}}\theta'_{\mathrm{MN}} \\ & + \tfrac{1}{2}\Psi_{\mathrm{MNX}}),\end{aligned} \tag{14}$$

$$\begin{aligned}\ln\gamma_{\mathrm{NX}} = {} & \ln\gamma^{*}_{\mathrm{NX}} +]0.14476y_{\mathrm{MX}}I_{\mathrm{mix}}(4B_{\mathrm{MX}} - \tfrac{2}{3}B_{\mathrm{NX}} \\ & + 2\theta_{\mathrm{MN}} + I_{\mathrm{mix}}(4B'_{\mathrm{MX}} - \tfrac{2}{3}B'_{\mathrm{NX}} + 2\theta_{\mathrm{MN}} \\ & + I_{\mathrm{mix}}(4B'_{\mathrm{MX}} - \tfrac{2}{3}B'_{\mathrm{NX}} + 2\theta'_{\mathrm{MN}} + \tfrac{4}{3}(\Psi)_{\mathrm{MNX}} \\ & + \tfrac{8}{3}C^{\Phi}_{\mathrm{MX}})) + 0.14476y^{2}_{\mathrm{MX}}I^{2}_{\mathrm{mix}}(2B'_{\mathrm{MX}} \\ & - \tfrac{2}{3}B'_{\mathrm{NX}} - \tfrac{1}{3}\Psi_{\mathrm{MNX}} + \tfrac{4}{3}C^{\Phi}_{\mathrm{MX}} \\ & - \tfrac{1}{6}(2)^{1/2}C^{\Phi}_{\mathrm{NX}} - 2\theta'_{\mathrm{MN}}),\end{aligned} \tag{15}$$

where the molality of the ion is signed by m and y is the molal fraction of the mixture component. Symbol f^{γ} denotes the Debye–Hückel function for the activity coefficient with A_{Φ} parameter, while superscript ' is used to designate ionic strength derivative. Coefficients B and C from Eqs. (14) and (15), relevant to pure electrolytes, were defined and explained earlier [21–23]. Activity coefficient versus total ionic strength curves for the CaCl$_2$ mixture component are for different temperatures presented in Fig. 11. Functions representing the HCl activity dependence on mixture ionic strength are of the similar form.

It is evident from Fig. 11 that the activity coefficient decreases with increasing total ionic strength of the mixture reaching minimum for ionic strength value between 1 and 2 mol kg^{-1}. In that concentration range the activity coefficient is almost constant at the temperature given, but the curves presented for higher ionic strength values are of a slightly different shape. Literature data obtained by emf measurements [21] at 298 K are presented in Fig. 11, too. An agreement between the calculated and the literature activity coefficient value is obvious for total ionic strength not exceeding 2 mol kg^{-1}, while considerable deviation is noticed at higher concentrations.

Temperature dependences presented in Fig. 12 illustrate different intensities of the short-range forces

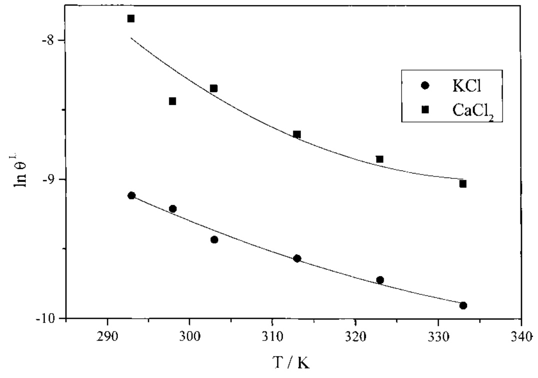

Fig. 12. Temperature dependence of Pitzer's θ^{L} mixing parameter for HCl–KCl and HCl–CaCl$_2$ systems; for unsymmetrical mixture ${}^{S}\theta^{L}$ values are presented.

between cations in the mixed solutions investigated. The θ^L values for the HCl–KCl mixture are presented because the higher-order electrostatic effect does not appear during the symmetrical mixing process. For the unsymmetrical HCl–$CaCl_2$ mixture, ${}^S\theta^L$ parameter, relevant to the short-range ion interaction, is depicted in Fig. 12. A more intensive short-range interaction, compared to the H^+–K^+ symmetrical mixing, is realized between H^+ and Ca^{2+} ions as evident from Fig. 12. In addition, it can be concluded that the θ^L coefficient for both systems studied does not change significantly with temperature.

Acknowledgements

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