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Thermal Analysis

Microcalorimetric studies of electrolyte mixtures: HCl–$GaCl_3$ Application of Pitzer's model

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Abstract

The heat of mixing of HCl and $GaCl_3$ concentrated isomolal aqueous solutions has been measured, in the 0.0005–0.159 molality and 293–333 K temperature range by a flow-mix microcalorimetric method, to determine the thermodynamic properties of the solutions.

The results obtained have been successfully explained by Pitzer's ion interaction model. Pitzer's mixing coefficients have been calculated and used to study the nature and intensity of ion interactions in the mixed solutions. Using Pitzer's parameters, the activity coefficients of the mixture components have been calculated.

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

1. Introduction

Our previous investigations [1–3] of the Na_2CO_3–$NaHCO_3$, HCl–KCl and HCl–$CaCl_2$ mixtures by a flow-mix microcalorimetric method clearly confirm the fact that the heat of mixing of electrolyte solutions can be successfully used to study the interactions of ions in an aqueous medium. Additionally, Pitzer's ion interaction model as a simple and convenient system of equations has been found to explain the specific ion interactions in binary electrolyte mixtures containing a common ion [3].

Our research continued by measuring the heat produced upon mixing of HCl and $GaCl_3$ concentrated aqueous solutions. The system obtained is interesting because of the complex Ga^{3+} ion interactions as an example of a trivalent cation, as well as for practical applications of gallium and its compounds.

Gallium metal, becoming increasingly important as a raw material for the production of various semiconductor materials, used as a substrate for fast integrated circuits and in laser technology, has been obtained by Bayer liquid extraction using anion exchangers and hydrochloric or sulfuric acid [4]. Although this industrial process has been well developed, many relevant thermodynamic properties remain incomplete or unknown. Since the Ga^{3+}–Cl^- interaction is enhanced at higher temperatures and increasing chloride concentrations, determination of the thermodynamic properties, particularly those related to hydrothermal ore formation or marine geothermal systems examination, is important to understand and to model the Ga^{3+} ion behavior [4].

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2. Experimental

Behaviour of Ga^{3+} ion in aqueous solutions is determined by its strong hydrolytic tendency. It has been shown [4] that the HCl–$GaCl_3$ solution containing 0.1345 m HCl (pH≈0.9) ensures hydrolysis of ≈0.5%, which is very low and as such can be ignored. In order to prevent hydrolysis of Ga^{3+} ion, a $GaCl_3$ stock solution was prepared as follows [5]: 2.776 g of pure gallium metal were dissolved in 380 ml of concentrated hydrochloric acid (although the dissolution process was stimulated by heating, it lasted for three working days). The solution was evaporated to dryness and the residue dissolved in 250 ml of 1% HCl.

All the solutions used in mixing experiments were prepared by diluting the stock solution with freshly boiled, doubly distilled water.

Molality of the $GaCl_3$ stock solution was checked by the method of inductively coupled plasma (Perkin–Elmer, model ICP 6500).

The solutions densities were measured by an AP Paar calculating density meter, model DMA 55.

The mixing experiments, performed in a flow-mix cell of a Thermometric (LKB) isothermal multichannel microcalorimeter (model 2277), have been already described in details [1–3].

The measurements were carried out in the 293–333 K temperature and 0.0005–0.159 molality range.

3. Results and discussion

Exothermic heat of mixing of isomolal HCl and $GaCl_3$ solutions as a function of the total ionic strength at 298 K is presented in Fig. 1, the curves retain the same shape at all temperatures. Each heat of mixing was calculated as a mean value of three experimental runs and the uncertainty interval was calculated as twice the standard deviation of the mean value. Temperature derivatives of Pitzer's mixing coefficients ${}^{S}\theta^{L}$ and ψ^{L}, relevant to the short range H^{+}–Ga^{3+} and triplet H^{+}–Ga^{3+}–Cl^{-} ion interactions, respectively, were obtained by fitting the experimental data to Pitzer's general equation [6], modified for the unsymmetrical HCl–$GaCl_3$ mixture, which relates the heat of mixing, ΔH_{mix} to the total ionic strength of mixture, I_{mix}:

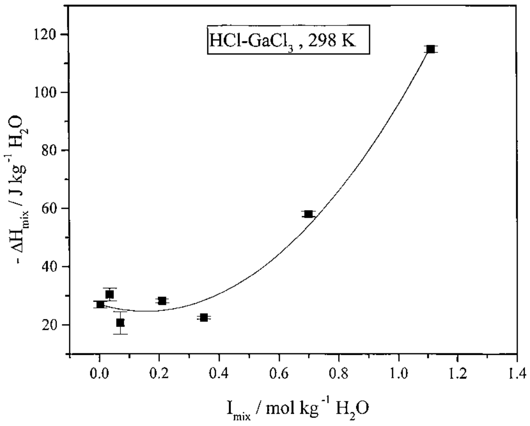

Fig. 1. Heat of mixing of isomolal HCl and $GaCl_3$ solutions versus total ionic strength of the mixture at 298 K; theoretical curve is depicted by a broken line.

$$\begin{aligned}\Delta H_{\mathrm{mix}} = \frac{A_{\mathrm{H}}}{b}&[I_{\mathrm{mix}}\ln(1+bI_{\mathrm{mix}}^{1/2})\\&-I_{\mathrm{MX}}\ln(1+bI_{\mathrm{MX}}^{1/2})\\&-I_{\mathrm{NX}}\ln(1+bI_{\mathrm{NX}}^{1/2})]\\&-2RT^{2}m_{\mathrm{M}}m_{\mathrm{N}}[\theta_{\mathrm{MN}}^{\mathrm{L}}+\tfrac{1}{2}m_{\mathrm{M}}\psi_{\mathrm{MNX}}^{\mathrm{L}}]\end{aligned} \qquad (1)$$

Here, A_{H} is the Debye–Hückel enthalpy parameter, b the value of 1.2 $kg^{1/2}$ $mol^{-1/2}$, I_{MX} and I_{NX} the ionic strength of pure solutions to be mixed, I_{mix} the total ionic strength of the mixture, and m_{M} and m_{N} the molalities of the ionic species M and N. Temperature dependences of the ${}^{S}\theta^{L}$ and ψ^{L} mixing coefficients, computed by the fitting procedure, are illustrated in Figs. 2 and 3, respectively.

Using the results for the HCl–$CaCl_2$ system from earlier paper [3] and comparing the ${}^{S}\theta^{L}$ and ψ^{L} temperature dependences for the HCl–$CaCl_2$ (Figures 7 and 8 in Ref. [3]) and HCl–$GaCl_3$ (Figs. 2 and 3) mixtures, a similar trend can be noticed which indicates the same type of interaction between ions in these unsymmetrical mixtures.

Integrating temperature dependences presented in Figs. 2 and 3, the mixing parameters values obtained for the temperature range investigated are as follows: ${}^{S}\theta$=1.141 kg mol^{-1} (standard deviation of the fit — 0.0017) and ψ=8.495 kg^{2} mol^{-2} (standard deviation

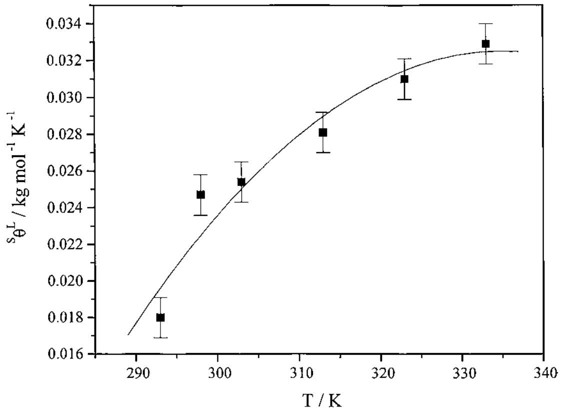

Fig. 2. Mixing coefficient $^S\theta^L$ versus temperature for the system HCl–GaCl$_3$; solid line represents the second-power polynomial.

of the fit — 0.011). The second virial coefficient $^E\theta$, referring to the higher-order electrostatic interaction between H^+ and Ga^{3+} ions, was calculated using the equation [7]:

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

where x_{MN} is given as:

$$x_{MN}=6z_M z_N A_\Phi I_{mix}^{1/2} \tag{3}$$

Symbol z denotes the valence of M and N ions, while A_Φ is the Debye–Hückel osmotic coefficient parameter. Approximate J function values were computed using both the following equations [7]:

$$J=-\tfrac{1}{6}x^2(\ln x)e^{-10x^2}+\left(\textstyle\sum_{k=1}^{6}C_k x^{-k}\right)^{-1} \tag{4}$$

$$J=x[4+C_1x^{-C_2}\ \exp(-C_3x^{C_4})]^{-1} \tag{5}$$

the C constant values tabulated in Ref. [8]. The $^E\theta$ and θ coefficient values given as a function of the total ionic strength of the mixture in the 293–333 K temperature range are illustrated in Fig. 4.

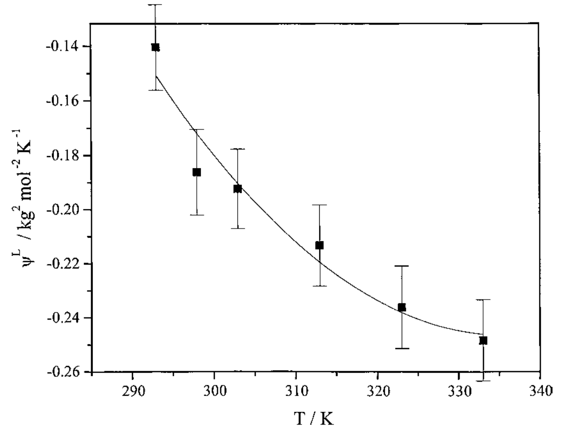

Fig. 3. Mixing coefficient ψ^L versus temperature for the system HCl–GaCl$_3$; solid line represents the second-power polynomial.

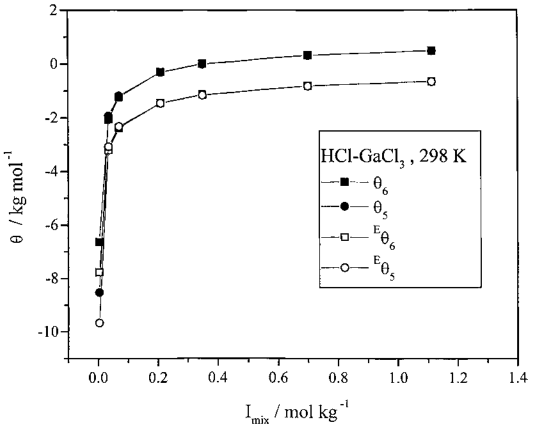

Fig. 4. Pitzer's mixing coefficients $^E\theta$ and θ as a function of total ionic strength of the HCl–GaCl$_3$ mixture at 298 K.

Only a pronounced higher-order electrostatic effect exists at low mixture concentrations as obvious from Fig. 4, disregarding the J function computed using Eq. (4) or Eq. (5). With increasing total ionic strength of the mixture, the short-range forces become dominant type of H^+–Ga^{3+} interaction, with $^S\theta$ parameter value used to estimate its intensity.

Pitzer's mixing parameter values for the HCl–GaCl$_3$ system were not found in the literature. Mixed electrolyte HCl–LaCl$_3$ of the 1–3 type was also studied using the emf measurements [9]. The virial coefficient values thus obtained are $^S\theta_{H\text{–}La}=0.278$ kg mol^{-1} and $\psi_{H\text{–}La\text{–}Cl}=0.009$ kg^2 mol^{-2} (higher-order term included) as well as $\theta_{H\text{–}La}=-0.324$ kg mol^{-1} and $\psi_{H\text{–}La\text{–}Cl}=0.118$ kg^2 mol^{-2} (the higher-order effect not taken into account).

The HCl–GaCl$_3$ and HCl–LaCl$_3$ systems were investigated under different conditions using different experimental techniques. But, as both are of the 1–3 electrolyte type, obviously higher mixing coefficient values obtained for the HCl–$GaCl_3$ system suggest more intensive ion interactions.

Activity coefficients for the HCl and $GaCl_3$ components were calculated using Pitzer's expressions [7]:

$$\begin{aligned}\ln\gamma_{\mathrm{MX}} = {} & f^{\gamma} + (m_{\mathrm{M}} + m_{\mathrm{X}})(B_{\mathrm{MX}} + m_{\mathrm{X}}C_{\mathrm{MX}}) \\ & + m_{\mathrm{N}}(B_{\mathrm{NX}} + m_{\mathrm{X}}C_{\mathrm{NX}} + {}^{\mathrm{S}}\theta_{\mathrm{MN}} + {}^{\mathrm{E}}\theta_{\mathrm{MN}}) \\ & + m_{\mathrm{N}}m_{\mathrm{X}}(B'_{\mathrm{MX}} + C_{\mathrm{MX}}) \\ & + m_{\mathrm{N}}m_{\mathrm{X}}(B'_{\mathrm{NX}} + C_{\mathrm{NX}} + \tfrac{1}{2}\psi_{\mathrm{MNX}}) \\ & + m_{\mathrm{M}}m_{\mathrm{N}}({}^{\mathrm{E}}\theta'_{\mathrm{MN}} + \tfrac{1}{2}\psi_{\mathrm{MNX}}) \end{aligned} \tag{6}$$

$$\begin{aligned}\ln\gamma_{\mathrm{NX}} = {} & \ln\gamma^{0}_{\mathrm{NX}} + 0.14476 y_{\mathrm{MX}} I_{\mathrm{mix}}(4B_{\mathrm{MX}} \\ & - \tfrac{2}{3}B_{\mathrm{NX}} + 2\theta_{\mathrm{MN}} + I_{\mathrm{mix}}(4B'_{\mathrm{MX}} - \tfrac{2}{3}B'_{\mathrm{NX}} \\ & + 2\theta_{\mathrm{MN}} + I_{\mathrm{mix}}(4B'_{\mathrm{MX}} - \tfrac{2}{3}B'_{\mathrm{NX}} + 2\theta'_{\mathrm{MN}} \\ & + \tfrac{4}{3}\psi_{\mathrm{MNX}} + \tfrac{8}{3}C^{\Phi}_{\mathrm{MX}})) \\ & + 0.14476 y^{2}_{\mathrm{MX}} I^{2}_{\mathrm{mix}}(2B'_{\mathrm{MX}} - \tfrac{2}{3}B'_{\mathrm{NX}} \\ & - \tfrac{1}{3}\psi_{\mathrm{MNX}} + \tfrac{4}{3}C^{\Phi}_{\mathrm{MX}} - \tfrac{1}{6}(2)^{1/2}C^{\Phi}_{\mathrm{NX}} \\ & - 2\theta'_{\mathrm{MN}} \end{aligned} \tag{7}$$

valid for the 1–3 electrolyte type as well. The molality of the ion is signed by *m* and the molal fraction of the mixture component by *y*. Symbol f^{γ} denotes the Debye–Hückel function for the activity coefficient with A_{Φ} parameter, while superscript "′" is used to designate the ionic strength derivative. Coefficients *B* and *C* from Eqs. (6) and (7), relevant to pure electrolytes, were defined and explained earlier [7,10,11]. Activity coefficient values for the $GaCl_3$ component as a function of the total ionic strength of the mixture at different temperatures, are presented in Fig. 5. Dependences for the HCl mixture components show similar trend.

As evident from Fig. 5 the curves presented are of the same shape as those obtained for the unsymmetrical HCl–$CaCl_2$ mixture (Fig. 11, Ref. [3]), and the activity coefficients for the HCl–$GaCl_3$ system remain constant with temperature.

Temperature dependences given in Fig. 6 illustrate different intensities of the short-range forces between cations in the HCl–KCl, HCl–$CaCl_2$ and HCl–$GaCl_3$ mixed solutions. Data for the HCl–KCl and HCl–$CaCl_2$ systems were taken from our previous paper [3]. For the HCl–KCl mixture, the θ^{L} values are presented because the higher-order electrostatic effect does not exist in the symmetrical mixing process. For the unsymmetrical mixtures, the ${}^{\mathrm{S}}\theta^{\mathrm{L}}$ parameter, relevant to the short-range ion interaction was depicted in Fig. 6. As can be seen from the figure the most intensive short-range interaction is realized between $H^+$and Ga^{3+} ions. In addition, it can be concluded that the θ^{L} coefficient, for all the systems we studied, does not change significantly with temperature.

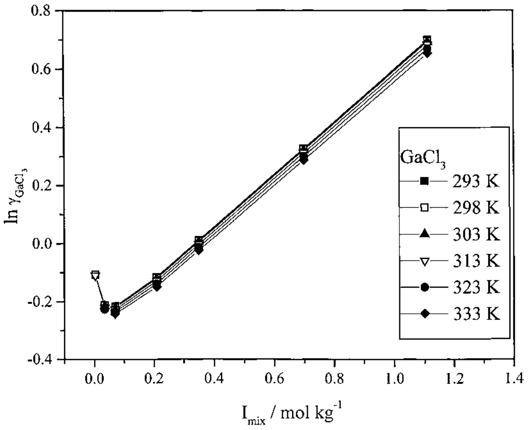

Fig. 5. Activity coefficient of the $GaCl_3$ component of the HCl–$GaCl_3$ mixture versus total ionic strength in the 293–333 K temperature interval.

Higher-order electrostatic effect, characteristic of unsymmetrical mixtures, is depicted in Fig. 7. In the case of very diluted HCl–$GaCl_3$ solution, the ${}^{\mathrm{E}}\theta$ values are extremely negative, pointing out at an intensive higher-order electrostatic H^+–Ga^{3+} interaction. With increasing ionic strength, the effect becomes less

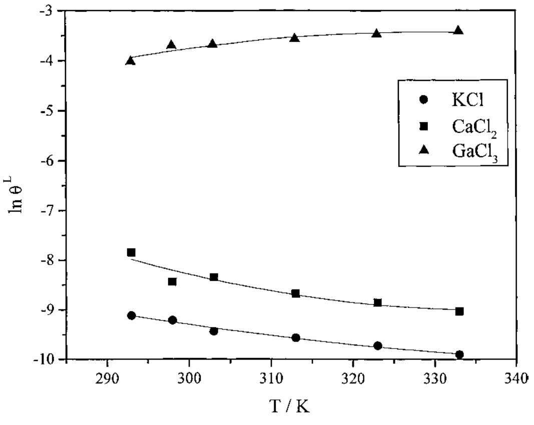

Fig. 6. Temperature dependence of Pitzer's θ^{L} mixing parameter for HCl–KCl, HCl–$CaCl_2$ and HCl–$GaCl_3$ systems; data for HCl–KCl and HCl–$CaCl_2$ mixtures are taken from Ref. [3]; for unsymmetrical mixtures ${}^{S}\theta^{\mathrm{L}}$ values are presented.

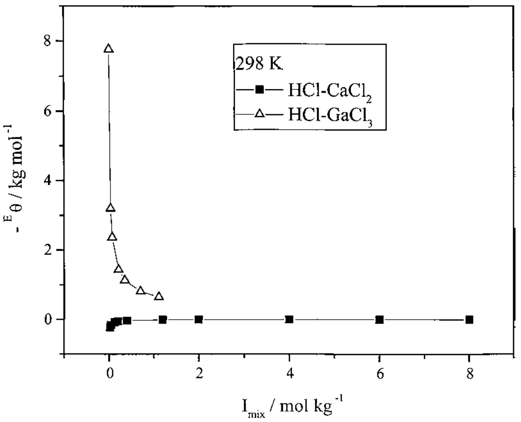

Fig. 7. Pitzer's ${}^{E}\theta$ coefficient versus total ionic strength of the HCl–$CaCl_2$ and HCl–$GaCl_3$ mixtures at 298 K; data for HCl–$CaCl_2$ system are taken from Ref. [3].

pronounced with ${}^{E}\theta$ versus ionic strength function approaching the HCl–$CaCl_2$ curve.

Acknowledgements

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Appendix A. Supplementary material

Tables containing experimental heat of mixing and activity coefficient values, as well as ${}^{S}\theta^{L}$, ψ^{L}, ${}^{E}\theta$ and θ values, for HCl–$GaCl_3$ system at all the experimental temperatures are available upon request.

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