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Semi-emperical dependance of the excess functions of asymmetrical molten salt systems

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Abstract

The enthalpies of mixing of more than 70 A_pB-AC molten salt systems, containing ions with different valences, have been found in literature. (B = rare earth or alkaline earth metal; C = alkali metal; A = halide.)

Experimental heat of mixing data were fitted against composition to an analytical equation deduced from the Surrounded Ion Model (SIM).

The limiting molar partial enthalpy of mixing of A_pB in AC ($H^{\infty}(A_pB)$) or of AC in A_pB ($H^{\infty}(AC)$), were thus calculated.

The evaluation of these limiting molar partial enthalpies for a series of systems, for example: the rare earth chlorides – alkali chlorides mixtures, is related to the charge and to the radius of the involved ions.

This work made it possible to propose for these limiting partial enthalpies the following analytical expressions:

$$H^{\infty}(A_pB) = \alpha\Delta\mathrm{IP} + \frac{\beta}{r(C_+)} + \gamma \quad or \quad H^{\infty}(AC) = \alpha'\Delta\mathrm{IP} + \frac{\beta'}{r(B_{p+})} + \gamma'$$

where ΔIP is the difference of the ionic potentials of the B_{p+} and C_+ ions: $\Delta\mathrm{IP} = (p/r_B - 1/r_C)$ and α, β, γ, α', β', γ' constants deduced from our calculations.

Keywords: Molten salts; Excess functions; Modeling

1. Introduction

During the last few years a great deal of new information relating to thermodynamic properties of binary mixtures of molten salts has become available. These thermodynamic properties are aimed at understanding the macroscopic behaviour of these molten salts and often are correlated through theory with microscopic properties [1–11], thus enabling conclusions about the bonding and structure of the melt to be drawn. The most commonly employed thermodynamic methods are thermal analysis, cryoscopy, calorimetry, e.m.f. determination from galvanic cells and equilibrium vapor pressure measurements. Other important contributions to the understanding of the structure and constitution of ionic melts have also been made by spectroscopic (IR, Visible, UV, Raman, NMR, Neutronic diffraction, etc.) or computer simulations of pure molten salts and/or their mixtures.

The contributions and importance of the coulombic energy, polarization energy and Van der Waals dispersion energy to the excess thermodynamic functions

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of mixing, were evidenced, semi-qualitatively, by studies of the common anion symmetrical or asymmetrical binary systems.

This paper is a contribution to a better knowledge of the chemical bonding in the asymmetrical binary molten salt systems. Many of these systems have been studied by calorimetry in our group [12–17], and its aim is to correlate the excess functions of mixing of several mixtures to the charge and radius of the cations.

A lot of experimental data used in this study has been published in this review.

2. Modeling

Many years ago we developed in the group the 'Surrounded Ion Model' (SIM) [11,18,19]. This model allows the calculations of the thermodynamic functions for the binary or multicomponent common ion molten salt systems containing ions with different charges as for example: A_pB_q-A_rC_s. In this model a lattice description of the melt implies that the substitution to the B cation of the C cation creates some vacancies on the corresponding sublattice. If the number of vacancies is substantial and if no particular association exists between the cations and the vacancies, Førland [2] found the following relationship for the ideal entropy:

$$\Delta_{\text{mix}} S = -R\{pq(1-x)\ln(1-x') + rsx\ln x'\}$$

where x' the equivalent ionic fraction is given by:

$$x' = \frac{xrs}{[(1-x)pq + xrs]} \quad \text{and} \quad x = x(A_rC_s)$$

The SIM provides, from different theoretical grounds, a relationship for the ideal entropy which is identical to the one found by Førland.

From the model it has been possible to propose for the heat of mixing an analytical relation taking into account the charge of the ions:

$$\Delta_{\text{mix}}H = [(1-x)pq + xrs]x'(1-x')(a + bx') \tag{1}$$

The theoretical development of this model has evidenced the importance of the limiting thermodynamic excess functions in terms of energy perturbations when a foreign ion is introduced into the matrix of the pure salt.

From Eq. (1) it is very easy to obtain the two limiting partial enthalpies by derivation: $H^{\infty}(A_pB_q)$ and $H^{\infty}(A_rC_s)$. The variation of these limiting molar partial enthalpies for a serie of systems, for example: the rare earth chlorides – alkali chlorides mixtures, can be related to the charge and to the radius of the involved ions.

Indeed during the last few decades there have been important advances in our understanding of the solution chemistry of fused salts. Many of these advances have been related to the successful application of theories of fused salt mixtures such as those of Reiss, Katz and Kleppa [4], of Davis and Rice [5] and of Davis [6].These theories are based on the concept of corresponding states as developed for fused salts by Reiss, Mayer and Katz [3]. In these theories the observable thermodynamic quantities for the mixtures, (enthalpy of mixing for example), are related to the properties of the individual salts mainly through various powers of a parameter size δ_{12}. This parameter size is equal to: $\delta_{12} = (d_1 - d_2)/d_1d_2$ where d_1 and d_2 are the characteristic interionic distances of the two molten salts.

Several charge-asymmetrical binary molten salt systems have been investigated. As a first approximation the Davis's theory predicts a linear relationship between the interaction parameter: $\lambda = \Delta_{\text{mix}}H/x(1-x)$ and the size parameter, δ_{12}, at constant temperature, volume and composition [20,21].

More recently Kleppa and co-wokers [22,23], have correlated the interaction parameter, λ, to the difference between the ionic potentials of the cations involved in the melts: $\Delta IP = (p/r_B - 1/r_C)$ for the systems studied in this paper. This correlation applies within a same melt family.

In this work we have fitted the limiting partial molar enthalpy of mixing of A_pB in AC ($H^{\infty}(A_pB)$) or AC in A_pB ($H^{\infty}(AC)$), (i.e. the interaction parameter at $x = 0$ or 1), by using the following analytical expressions:

$$H^{\infty}(A_pB_q) = \alpha\Delta IP + \frac{\beta}{r(C_{s+})} + \gamma \text{ or } H^{\infty}(A_rC_s) = \alpha'\Delta IP + \frac{\beta'}{r(B_{p+})} + \gamma' \tag{2}$$

where α, β, γ, α', β', γ' are constants deduced by least square analysis from the limiting partial molar enthalpy of mixing obtained as described above-mentioned and the radius and charge of the cations involved in the melt.

In this study, we have therefore collected the experimental data of heat of mixing available in the literature for some asymmetrical systems.

3. Results

Eq. (1) has been used for fitting the experimental data points of heat of mixing of more than 70 asymmetrical A_pB-AC molten salts systems, B = rare earth or alkaline earth metal; C = alkali metal; A = halide; therefore $p = 3$ or 2 and $q = r = s = 1$.

The following binary systems has been studied:

Serie I:

NaF-AlF_3, KF-AlF_3 [22], NaF-LaF_3, KF-LaF_3, NaF-YF_3, KF-YF_3, NaF-YbF_3, KF-YbF_3 [17–24], NaF-NdF_3, KF-NdF_3 [25],

Serie II:

NaCl-$NdCl_3$, KCl-$NdCl_3$, RbCl-$NdCl_3$, CsCl-$NdCl_3$ [12], NaCl-$PrCl_3$, KCl-$PrCl_3$ [13], NaCl-$DyCl_3$, KCl-$DyCl_3$[14], NaCl-YCl_3, KCl-YCl_3, RbCl-YCl_3, CsCl-YCl_3 [26], KCl-$CeCl_3$, RbCl-$CeCl_3$, CsCl-$CeCl_3$ [27], NaCl-$LaCl_3$, KCl-$LaCl_3$, RbCl-$LaCl_3$, CsCl-$LaCl_3$-[28], NaCl-$GdCl_3$, KCl-$GdCl_3$, RbCl-$GdCl_3$, CsCl-$GdCl_3$ [29], NaCl-$SmCl_3$, NaCl-$YbCl_3$, NaCl-$ErCl_3$.

Serie III:

NaBr-$NdBr_3$, KBr-$NdBr_3$, RbBr-$NdBr_3$, CsBr-$NdBr_3$ [15], NaBr-$LaBr_3$, KBr-$LaBr_3$, CsBr-$LaBr_3$ [16],

Serie IV:

NaCl-$MgCl_2$, KCl-$MgCl_2$, RbCl-$MgCl_2$, CsCl-$MgCl_2$ [30], NaCl-$CaCl_2$, KCl-$CaCl_2$, RbCl-$CaCl_2$, CsCl-$CaCl_2$, NaCl-$SrCl_2$, KCl-$SrCl_2$, RbCl-$SrCl_2$, CSCl-$SrCl_2$ [20]

Serie V:

NaBr-$MgBr_2$, KBr-$MgBr_2$, RbBr-$MgBr_2$, CsBr-$MgBr_2$, NaBr-$CaBr_2$, KBr-$CaBr_2$, RbBr-$CaBr_2$, CsBr-$CaBr_2$, NaBr-$SrBr_2$, KBr-$SrBr_2$, RbBr-$SrBr_2$, CsBr-$SrBr_2$, NaBr-$BaBr_2$, KBr-$BaBr_2$, RbBr-$BaBr_2$, CsBr-$BaBr_2$ [20].

For these systems the experimental values of heat of mixing versus the composition of the melt were given by the authors in their papers.

For the series I, II, III, the coefficient p is equal to 3 and for the series IV and V $p = 2$; for all series $q = r = s = 1$.

The a and b parameters were obtained from a least-square analysis of Eq. (1). The values obtained for each system are given in Tables 1 and 2 together with the corresponding correlation coefficients.

For all systems Eq. (1) gives a good representation of experimental data.

From the values of a and b, calculated in this way, it is possible to deduce the limiting partial molar enthalpies: A_pB in AC ($H^{\infty}(A_pX_q)$) or AC in A_pB (H^{∞}(AC)), for all these systems.

The values are presented in Tables 1 and 2.

The values of the constants, α, β, γ, α', β', γ' were obtained for each family by least-square analysis. These values are presented in Table 3 together the correlation coefficients. In Figs. 1 and 2, we plotted the calculated limiting partial molar enthalpies versus the experimental limiting partial molar enthalpies. The agreement is not too bad.

In order to check the validity of these analytical relations we tested them on the systems:

$PbCl_2$-CCl (C = Na, K, Rb, Cs): the limiting partial molar enthalpies of CCl in $PbCl_2$ have been measured Kleppa and co-workers [31]. Table hereunder shows that the agreement between the calculated and experimental values is correct, except for the NaCl-$PbCl_2$ system.

	H^{∞}(MCl) (kJ mol^{-1})	
	Calculated	Experimental
NaCl-$PbCl_2$	6.33	−2.09
KCl-$PbCl_2$	−14.52	−17.57
RbCl-$PbCl_2$	−19.88	−24.26
CsCl-$PbCl_2$	−26.50	−29.71

$BiCl_3$-KCl: experimental determinations of the integral enthalpy of mixing have been carried out [32,33]. Fig. 3 reports the comparison between these results and those obtained from modeling. As we can see in the Figure, the calculated values are not too far from the experimental values.

4. Conclusion

The present work shows how it was possible to link several modeling of the thermodynamics of melts. The concept of corresponding states developed earlier indicated the influence of physicochemical parameters

Table 1
Least-square coefficients of $\Delta_{\mathrm{mix}}H$ dependence on composition for A_3B-AC binary molten salt systems, and calculated limiting partial enthalpies

Systems	a (kJ mol^{-1})	b (kJ mol^{-1})	Correlation	$\Delta H(\infty)$AC (kJ mol^{-1})	$\Delta H(\infty)A_3B$ (kJ mol^{-1})
NaF-AlF_3	−110.46	38.96	0.987	−110.46	−214.49
KF-AlF_3	−159.32	100.2	0.994	−159.32	−177.39
NaF-LaF_3	−29.8	17.01	0.999	−29.8	−38.36
KF-LaF_3	−51.76	33.26	0.999	−51.76	−55.48
NaF-YF_3	−50.66	27.8	0.993	−50.66	−68.6
KF-YF_3	−96.35	66.84	0.998	−96.35	−88.54
NaF-YbF_3	−59.9	36.28	0.995	−59.9	−70.86
KF-YbF_3	−98.6	60.34	0.996	−98.6	−114.77
NaF-NdF_3	−28.84	22.69	0.802	−28.84	−18.43
KF-NdF_3	−65.41	48	0.97	−65.41	−52.23
NaCl-NdCl_3	−20	9.04	0.979	−20	−32.9
KCl-NdCl_3	−49.19	25.83	0.966	−49.19	−70.08
RbCl-NdCl_3	−56.28	20.71	0.982	−56.28	−106.69
CsCl-NdCl_3	−65.51	23.39	0.989	−65.51	−126.37
NaCl-PrCl_3	−20.99	9.26	0.995	−20.99	−35.21
KCl-PrCl_3	−39.71	4.34	0.96	−39.71	−106.1
NaCl-DyCl_3	−14.58	−9.52	0.949	−14.58	−72.29
KCl-DyCl_3	−39	−18.08	0.928	−39	−171.21
NaCl-YCl_3	−22.99	−8.85	0.955	−22.99	−95.5
KCl-YCl_3	−50.79	−5.28	0.969	−50.79	−168.23
RbCl-YCl_3	−64.14	−0.81	0.968	−64.14	−194.87
CsCl-YCl_3	−77.39	5.72	0.961	−77.39	−215
KCl-CeCl_3	−46.3	20.54	0.982	−46.3	−77.28
RbCl-CeCl_3	−58.05	26.83	0.994	−58.05	−93.65
CsCl-CeCl_3	−66.48	26.74	0.99	−66.48	−119.22
NaCl-LaCl_3	−24.73	12.8	0.996	−24.73	−35.77
KCl-LaCl_3	−48.69	27.69	0.997	−48.69	−63
RbCl-LaCl_3	−57.02	26.87	0.997	−57.02	−90.46
CsCl-LaCl_3	−71.35	32.14	0.998	−71.35	−117.65
NaCl-GdCl_3	−24.13	7.88	0.96	−24.13	−48.76
KCl-GdCl_3	−50.89	21.45	0.977	−50.89	−88.3
RbCl-GdCl_3	−56.04	19.83	0.985	−56.04	−108.63
CsCl-GdCl_3	−67	25.19	0.931	−67	−125.43
NaCl-SmCl_3	−23.65	10.4	0.994	−23.65	−39.75
NaCl-YbCl_3	−22.13	−15.26	0.956	−22.13	−112.17
NaCl-ErCl_3	−23.81	−2.9	0.93	−23.81	−80.16
NaBr-NdBr_3	−13.59	1.48	0.98	−13.59	−36.32
KBr-NdBr_3	−33.75	8.75	0.982	−33.75	−75
RbBr-NdBr_3	−39.17	−6.5	0.955	−39.17	−136.99
CsBr-NdBr_3	−55.94	14.39	0.98	−55.94	−124.67
NaBr-LaBr_3	−13.42	3.88	0.992	−13.42	−28.63
KBr-LaBr_3	−35.78	14.18	0.98	−35.78	−64.8
RbBr-LaBr_3	−45.43	10.94	0.955	−45.43	−103.47
CsBr-LaBr_3	−54.39	18.85	0.986	−54.39	−106.64

(ionic size and charge) on the interaction forces in these liquids. On the other hand, the SIM revealed suitable to account for the specific composition dependence in asymmetrical molten salt mixtures. These two approaches used in conjunction made it possible to address this dual aspect.

The empirical equations obtained have been tested on an extensive number of asymmetrical melts. The

Table 2
Least-square coefficients of $\Delta_{\mathrm{mix}}H$ dependence on composition for A_2B-AC binary molten salt systems, and calculated limiting partial enthalpies

Systems	a (kJ mol^{-1})	b (kJ mol^{-1})	Correlation	$\Delta H(\infty)$AC (kJ mol^{-1})	$\Delta H(\infty)A_2B$ (kJ mol^{-1})
NaCl-$MgCl_2$	−24.46	5.75	0.99	−24.46	−37.41
KCl-$MgCl_2$	−52.39	19.82	0.98	−52.39	−65.13
RbCl-$MgCl_2$	−65.53	28.1	0.98	−65.53	−74.87
CsCl-$MgCl_2$	−74.85	32.29	0.98	−74.85	−85.13
NaCl-$CaCl_2$	−12.12	2.31	0.99	−12.12	−19.63
KCl-$CaCl_2$	−31.57	10.54	0.95	−31.57	−42.07
RbCl-$CaCl_2$	−37.61	14.74	0.99	−37.61	−45.74
CsCl-$CaCl_2$	−43.86	19.84	1	−43.86	−48.04
NaCl-$SrCl_2$	−2.8	−0.38	1	−2.8	−6.37
KCl-$SrCl_2$	−11.88	−0.25	1	−11.88	−24.24
RbCl-$SrCl_2$	−15.89	0.9	1	−15.89	−29.99
CsCl-$SrCl_2$	−19.12	2.5	1	−19.12	−33.25
NaBr-$MgBr_2$	−12.75	−4.73	0.95	−12.75	−34.96
KBr-$MgBr_2$	−38.32	4.06	0.95	−38.32	−68.52
RbBr-$MgBr_2$	−48.54	8.04	0.95	−48.54	−81.01
CsBr-$MgBr_2$	−58.94	11.73	0.97	−58.94	−94.43
NaBr-$CaBr_2$	−12.77	3.12	1	−12.77	−19.31
KBr-$CaBr_2$	−30.68	12.43	1	−30.68	−36.5
RbBr-$CaBr_2$	−36.43	14.72	0.98	−36.43	−43.41
CsBr-$CaBr_2$	−45.8	25.27	1	−45.8	−41.06
NaBr-$SrBr_2$	−3.4	0.15	1	−3.4	−6.51
KBr-$SrBr_2$	−13.72	1.65	0.99	−13.72	−24.13
RbBr-$SrBr_2$	−18.24	2.31	1	−18.24	−31.86
CsBr-$SrBr_2$	−23.22	4.9	0.99	−23.22	−36.63
NaBr-$BaBr_2$	0.64	−0.29	0.91	0.64	0.69
KBr-$BaBr_2$	−3.9	−0.12	0.99	−3.9	−8.02
RbBr-$BaBr_2$	−6	−0.77	1	−6	−13.53
CsBr-$BaBr_2$	−7.99	−0.54	1	−7.99	−17.05

Table 3
Least-square coefficients of the limiting partial enthalpies

	α (kJ mol^{-1} Å^{-1})	β (kJ mol^{-1} Å^{-1})	γ (kJ mol^{-1})	Correlation
AF in BF_3	−1 37.46	304.54	−68.17	0.96
ACl in BCl_3	−105.75	305.93	−117.94	0.94
ABr in BBr_3	−90.84	301.6	−134.06	0.97
ACl in BCl_2	−74.77	88.73	−20.48	0.89
ABr in BBr_2	−60.03	77.1	−23.62	0.89
	α' (kJ mol^{-1} Å^{-1})	β' (kJ mol^{-1} Å^{-1})	γ' (kJ mol^{-1})	Correlation
BF_3 in AF	−61.8	−6.13	83.05	0.92
BCl_3 in ACl	−158.21	66.83	210.44	0.93
BBr_3 in ABr	−102.22	101.95	57.48	0.89
BCl_2 in ACl	−31.68	47.87	−31.22	0.95
BBr_2 in ABr	−38.11	36.52	−12.41	0.94

representation of all these existing enthalpy-of-mixing data are fairly satisfactory It can be thus concluded that these rather simple considerations can provide a useful tool in subsequent estimation especially when direct experimental investigation may be impossible, for instance in nuclear fuel pyrochemical reprocessing

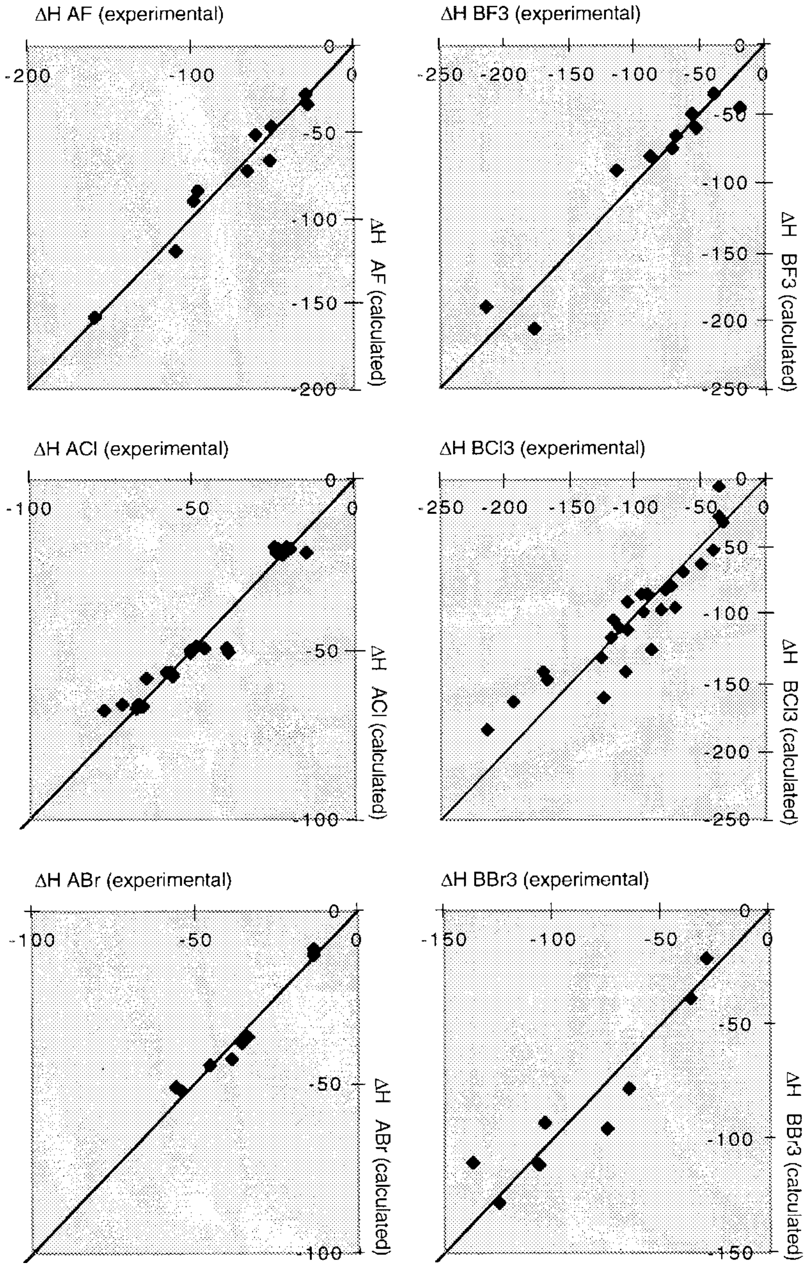

Fig. 1. Experimental and calculated limiting partial molar enthalpies (kJ mol^{-1}) for the A_3B-AC binary molten salt systems.

which requires data on lanthanide and actinide compounds.

It would be thus possible to predict thermochemical functions from the basic properties (charge and ionic radius) of the cations involved in the melt. This result is interesting because it is possible, now, to obtain the order of magnitude of the heat of mixing versus the composition of the melts even if no experimental data

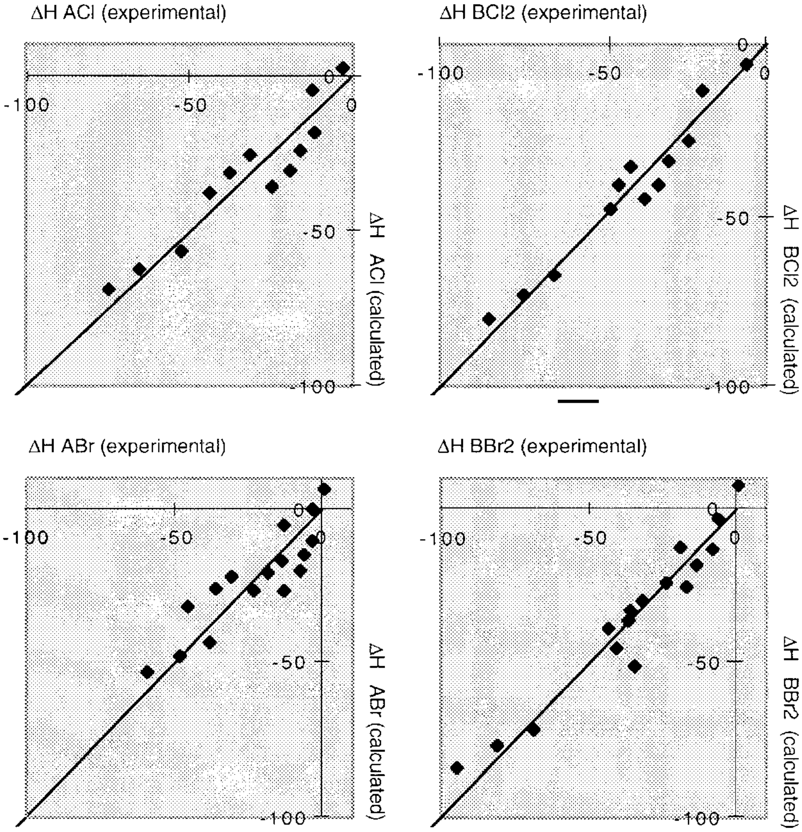

Fig. 2. Experimental and calculated limiting partial molar enthalpies (kJ mol^{-1}) for the A_2B-AC binary molten salt systems.

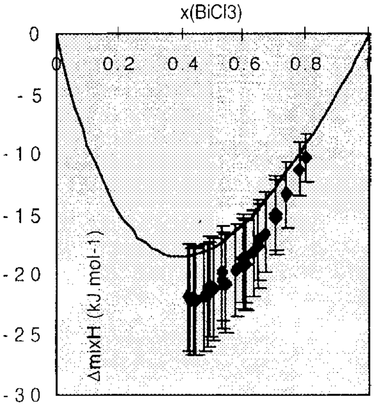

Fig. 3. Experimental and calculated heat of mixing of the $BiCl_3$-KCl molten salt system.

are enable. These values can be used in thermodynamic calculations, for example, to calculate roughly the phase diagram of the system.

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