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Binary common-ion alkali halide mixtures; a uniform description of the liquid and solid state

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Abstract

Empirical relations for the thermodynamic excess behaviour of binary common-ion alkali halide mixtures were derived. For the liquid state this gave rise to $G^{E(l)}(x, T_g) = 0.68H^{E(l)}(x, T_g)$ and $S^{E(l)}(x, T_g) = 0.32H^{E(l)}(x, T_g)/T_g$, and for the solid state $G^{E(s)}(x, T) = A(1 - T/(2565\ \mathrm{K}))x(1-x)(1+B(1-2x))$, in which the A parameter can be calculated from relative differences in unit cell volumes of the pure solid components A_{calc} (kJ mol^{-1}) $= 11.53(\Delta V/V_s) + 89.40(\Delta V/V_s)^2$ and the B parameter which is a measure for the asymmetry can be calculated from the A parameter using $B = 1.04 \times 10^{-2}(A_{\mathrm{calc}}/\mathrm{kJ\ mol^{-1}})$. The phase diagrams were calculated and compared with experimental phase diagram data for twenty binary common-ion alkali halide systems that show complete sub-solidus miscibility.

INTRODUCTION

The alkali halides form a chemically coherent group of substances. The alkali metals are all strongly electropositive and the halogens all strongly electronegative; therefore the alkali halides are model systems of ionic bonding. Except for cesium chloride, bromide and iodide, all alkali halides crystallize in the sodium chloride structure, space group P_{m3m}, at ambient conditions. Cesium chloride, bromide and iodide crystallize in the cesium chloride structure space group F_{m3m}. The 20 alkali halides form 70 binary common-ion systems: 40 common-anion and 30 common-cation systems. In the liquid state all systems show complete miscibility; in the solid state this is not the case, depending on the difference in ionic radii of the non-common ions.

In previous work, Oonk et al. [1] and van Ekeren [2] developed a model for the description of the excess behaviour in binary common-anion alkali halide mixtures. For the liquid state this gave rise to

$$G^{E(l)}(x, T_g) = 0.66H^{E(l)}(x, T_g) \tag{1a}$$

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which leads to

$$S^{E(l)}(x, T_g) = 0.34 H^{E(l)}(x, T_g)/T_g \tag{1b}$$

where T_g is the reference temperature for which the calculated excess Gibbs energy is valid. For the solid state

$$G^{E(s)}(x, T) = A(1 - T/\Theta)x(1 - x)(1 + B(1 - 2x)) \tag{2}$$

where Θ is a temperature characteristic for the whole group, A is a function of the relative difference in size of the unit cells of the pure components (each member of the group has its own A value) and B is a measure of asymmetry of $G^{E(s)}$ with respect to x.

For the binary common-anion alkali halides, $\Theta = 2.6$ kK and $B = 0.15$. The same behaviour was found for the *p*-dihalobenzene family where $\Theta = 0.5$ kK and $B = 0.2$ [3].

In this paper, the model is extended to the binary common-cation alkali halide mixtures and a uniform description of the liquid and solid state of the complete family of binary common-ion alkali halide systems will be given. In the next sections, thermodynamic excess functions will be frequently used in the Redlich–Kister [4,5] form, i.e.

$$Z^E(x) = x(1 - x)\sum_{i=1}^{n} Z_i(1 - 2x)^{i-1} \tag{3}$$

with Z_i being the *i*th Redlich–Kister coefficient.

THE LIQUID STATE

The most important sources from which thermodynamic excess properties of the liquid state can be obtained are calorimetry and T–x phase diagrams of systems with no or negligible solid solubility. The enthalpies of mixing for most of the binary common-ion alkali halide systems have been measured by Kleppa and coworkers [6–11]. For the common-anion alkali halide systems, an approximation of the enthalpy of mixing can be represented by

$$H^{E(l)}(x)(\text{kJ mol}^{-1}) = -1600x(1 - x)\delta_{12}^2 \tag{4}$$

This relation was derived from the work of Hersh and Kleppa [6] (Fig. 13), where $\delta_{12} = (d_2 - d_1)/d_1 d_2$ and d_1 and d_2 are the nearest neighbour distances for the two pure salts in the liquid state. The enthalpies of mixing for the common-cation alkali halide systems (except for the mixtures containing fluoride) can be represented by the relation

$$H^{E(l)}(x) = x(1 - x)C\delta_{12}^2 \tag{5}$$

which was proposed by Melnichak and Kleppa [9] where $C = 1050$ Å^{-2} kJ mol^{-1} for mixtures containing Na, K, Rb and Cs ions, and $C = 525$ Å^{-2} kJ mol^{-1} for mixtures containing Li ions. For the systems with no or negligible solid solubility, we calculated the excess Gibbs energy of the liquid state by means of the EXTXD [12–15] method. The calculated first coefficients of the Redlich–Kister expressions for the excess Gibbs energy ($G_1^{(l)}$) and for the enthalpies of mixing ($H_1^{(l)}$) obtained from literature are summarized in Table 1. The last column of Table 1 gives the enthalpy of mixing at the temperature T_g for which the excess Gibbs energy is valid. These values were calculated with the assumption that for all binary common-ion alkali halide systems the linear extrapolated enthalpy of mixing becomes zero at a temperature of approximately $T = 2.2$ kK [1]. Figure 1 gives a plot of $G_1^{(l)}(T_g)$ versus $H_1^{(l)}(T_g)$. The open circles represent the common-anion systems and the solid circles the common-cation systems. A linear least-squares fit of the data leads to

$$G_1^{(l)}(T_g) = 0.68 H_1^{(l)}(T_g) \tag{6a}$$

from which it follows that

$$S_1^{(l)}(T_g) = \left[0.32 H_1^{(l)}(T_g)\right] / T_g \tag{6b}$$

which is only slightly different from the equation that was calculated for the common-anion systems for which the coefficient of eqn. (6a) was 0.66 [1]. The heat of mixing for the common-anion systems is a function of the common anion and for the common-cation systems it is a function of the non-common anions. Using eqns. (4)–(6), it is possible to calculate an approximation of the excess Gibbs energy of the liquid state for binary common-ion alkali halide systems based exclusively on ionic radii. Equation (6a) can be used to calculate the phase diagrams [20] for the systems Rb(F,I) and (Li,Cs)I, for which only enthalpy of mixing data are available, and to calculate $G^{E(s)}$ from $\Delta_s^l G^E$ values obtained from solid–liquid equilibria.

THE SOLID STATE

For the solid state of binary common-ion alkali halide mixtures with solid solubility, information on the excess Gibbs energy can be obtained from heats of mixing, regions of demixing, solid–liquid equilibria, and other experimental data, for example mass spectrometry, solubility diagrams etc.

Experimental heats of mixing

If excess heat capacities are neglected, then the enthalpy of mixing can be considered as equal to the excess Gibbs energy at $T = 0$ K. Table 2 gives a summary of the available enthalpies of mixing for the various systems.

TABLE 1

First Redlich–Kister coefficient of the excess Gibbs energy and enthalpy of mixing for the liquid state of some binary common-ion alkali systems at temperature T_g

System	$G_1^{(1)}(T_g)$ (kJ mol^{-1})	T_g (K)	Ref.	$H_1^{(1)}(T_g)$ (kJ mol^{-1})	Ref.
(Li,Na)F	-6.1	985	16	-10.7	7
				-10.7	11
(Li,K)F	-15.4	860	17	-25.5	18
				-25.3	7
				-24.4	11
				-25.7	11
(Li,K)Cl	-14.6	725	17	-22.1	6
(Li,K)Br	-12.3	685	17	-18.7	6
(Li,K)I	-14.2	580	17	-17.5	8
(Li,Rb)F	-15.3	850	2	-26.6	7
(Li,Rb)Cl	-18.7	660	17	-27.6	6
				-24.9	19
(Li,Rb)Br	-15.4	600	17	-25.1	6
(Li,Rb)I	-17.2	550	2	-24.4	8
(Li,Cs)F	-13.3	800	16	-19.2	7
(Li,Cs)Cl	-21.3	720	16	-30.0	6
(Li,Cs)Br	-20.1	750	16	-28.9	6
(Na,K)F	0.5	1040	16	-0.5	7
				-0.5	11
(Na,Rb)F	1.0	975	17	0.5	7
(Na,Rb)Cl	-2.9	880	16	-4.0	6
				-4.9	19
(Na,Cs)Cl	-3.5	820	16	-5.1	6
(Na,Cs)Br	-4.4	810	16	-5.8	6
(Na,Cs)I	-6.0	760	16	-9.3	6
				-6.9	8
Li(F,Cl)	-1.5	890	17	-1.7	10
Na(F,Cl)	1.5	1060	17	1.1	10
K(F,Cl)	0.4	980	17	0.0	10
Rb(F,Cl)	-3.8	875	2	-0.4	10
Cs(F,Cl)	-2.9	750	2	-3.5	10
Li(F,Br)	-2.4	770	2	-1.5	10
Na(F,Br)	-0.1	1030	17	2.3	10
K(F,Br)	-0.6	900	2	-0.1	10
Rb(F,Br)	-5.7	850	2	-1.2	10
Cs(F,Br)	-6.0	750	2	-4.3	10
Li(F,I)	0.7	770	2	-0.2	10
Na(F,I)	4.7	990	17	5.5	10
K(F,I)	-0.3	930	17	0.2	10
Cs(F,I)	-8.3	750	2	-4.8	10
Li(Cl,I)	1.4	675	2	2.0	10
Na(Cl,I)	-0.4	900	2	2.3	10
				-4.1	10

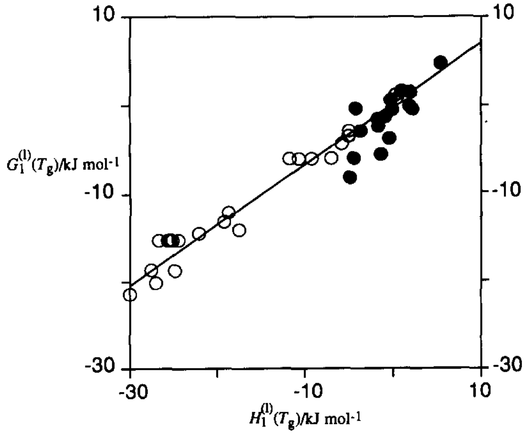

Fig. 1. First Redlich–Kister coefficient for the excess Gibbs energy as a function of the first Redlich–Kister coefficient for the enthalpy of mixing for liquid binary common-ion alkali halide mixtures. Open circles, common-anion systems; filled circles, common-cation systems.

Regions of demixing

Using the EXTXD method, the excess Gibbs energies of the solid state were calculated from region-of-demixing data. The results are shown in Table 3.

TABLE 2

First Redlich–Kister coefficient for the enthalpies of mixing in the solid state for binary common-ion alkali halide systems

System	$H_1^{(s)}$ (kJ mol^{-1})	Ref.	System	$H_1^{(s)}$ (kJ mol^{-1})	Ref.
(Li,Na)Br	12.3	21	Na(Cl,Br)	5.5	22, 26
(Na,K)Cl	17.7	22–24	K(Cl,Br)	3.8	27–32
(Na,K)Br	14.3	22	Na(Br,I)	10.0	22
(Na,K)I	10.5	22	K(Br,I)	7.4	22
(K,Rb)I	2.6	25	Rb(Br,I)	5.5	33

TABLE 3

First and second Redlich–Kister coefficients of the excess Gibbs energy for the solid state calculated from region-of-demixing data

System	$G_1^{(s)}$ (kJ mol^{-1})	$G_2^{(s)}$ (kJ mol^{-1})	T_g (K)	Ref.
(Li,Na)Br	8.79	0.83	455	34
(Na,K)Cl	13.83	2.77	678	23, 24, 35–37
(Na,K)Br	11.98	1.56	599	35
(Na,K)I	9.09	1.09	444	35
K(Br,I)	7.18	0.86	390	37
Rb(Br,I)	5.15	0.57	280	38

TABLE 4

First Redlich–Kister coefficients for the excess Gibbs energy of the solid state (last column) for some binary common-ion alkali halide mixtures derived from solid–liquid equilibria

System	$\Delta_s^l G_1(T_g)$ (kJ mol^{-1})	T_g (K)	Ref.	$H_1^{(l)}(T_{exp})$ (kJ mol^{-1})	T_{exp} (K)	Ref.	$G_1^{(l)}(T_g)$ (kJ mol^{-1})	$G_1^{(s)}(T_g)$ (kJ mol^{-1})
(Li,Na)Br	−9.6	860	21	−3.3	963	6	−2.3	7.3
	−8.7	840	41				−2.4	6.3
(Na,K)Cl	−13.0	1000	42	−2.2	1083	6	−1.6	11.4
(Na,K)Br	−10.2	965	43	−2.3	1043	6	−1.6	8.6
				−2.3	1133	49	−1.8	8.4
(Na,K)I	−8.8	905	44	−2.2	973	6	−1.5	7.3
				−2.3	1013	8	−1.7	7.1
(K,Rb)Cl	−3.1	1005	55	0.1	1083	6	0.1	3.2
(K,Rb)Br	−2.4	965	56	0.0	1043	6	0.0	2.7
(K,Rb)I	−1.5	935	25	−0.3	973	6	−0.2	1.3
				−0.1	1013	8	−0.1	1.4
Na(Cl,Br)	−2.29	1030	45	0.3	1084	9	0.3	2.5
K(Cl,Br)	−2.05	1015	46	0.2	1084	9	0.2	2.2
Na(Br,I)	−5.23	950	47	0.6	1085	9	0.5	5.7
K(Br,I)	−4.25	960	42	0.4	1085	9	0.3	4.6
Rb(Cl,Br)	−2.14	965	57	0.1	1004	9	0.1	2.3
Rb(Br,I)	−4.07	910	48	0.4	1013	9	0.3	4.4

Solid–liquid equilibria

Using the LIQFIT method [39,40], the difference in excess Gibbs energies between the solid and the liquid state of the various binary common-ion alkali halide systems were calculated from experimental data on the solid–liquid equilibria. The excess Gibbs energies of the solid state were calculated using eqn. (6) and the enthalpies of mixing of the liquid state. The results are summarized in Table 4.

Other experimental data

For a few systems there is some additional information available on the excess Gibbs energy of the solid state (see Table 5).

THE MODEL

For each system, the first Redlich–Kister coefficient for the excess Gibbs energy of the solid state (Tables 2–5) is plotted against temperature (Fig. 2). The common-anion systems are represented by the circles and the common-cation systems by the squares. The points plotted on the vertical axis are enthalpies of mixing in the solid state determined by means of solution calorimetry. In the middle region, most of the points are from

TABLE 5

First Redlich–Kister coefficients for the excess Gibbs energy of the solid state of some binary common-ion alkali halide mixtures obtained from additional experimental techniques

System	$G_1^{(s)}$ (kJ mol^{-1})	T (K)	Method	Ref.
(K,Rb)Cl	3.35	298	Solubility diagram	58
(K,Rb)Br	2.71	298	Solubility diagram	58
Na(Cl,Br)	3.01	840	Mass spectrometry	50
K(Cl,Br)	3.30	298	Activity measurements	51
	3.46	298	Solubility diagram	58
	1.94	820	Mass spectrometry	52
Rb(Cl,Br)	2.92	298	Solubility diagram	58
K(Br,I)	5.15	298	Isopiestic measurements	53
	6.10	298	Solubility diagram	58

region-of-demixing data and solubility diagrams; at the highest temperatures, the points are from solid–liquid equilibria. For all systems the excess Gibbs energy is positive and decreases with temperature. The drawn lines are linear least-squares fits of the data for each system through the characteristic temperature $T = 2565$ K. The fits and the characteristic temperature are calculated by means of an iterative procedure

$$G_1^{(s)}(T) = A(1 - T/\Theta) \tag{7}$$

in which A is a parameter depending on the system and Θ is a temperature characteristic for all binary common-ion alkali halide systems. The results of this procedure are summarized in Table 6.

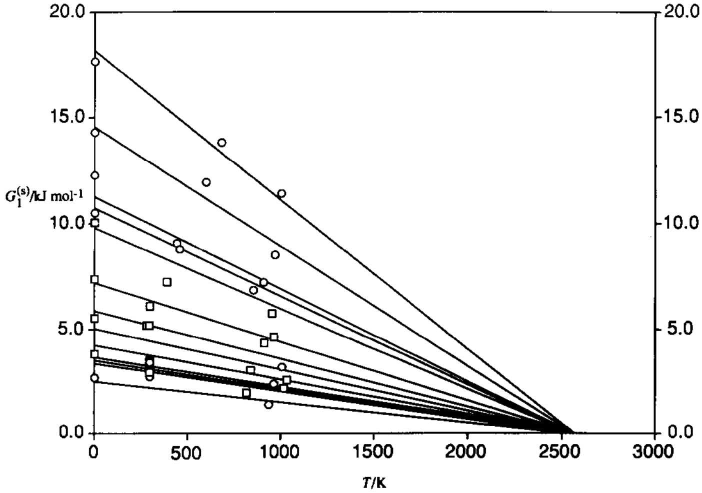

Fig. 2. First Redlich–Kister coefficient for the excess Gibbs energy of solid binary common-ion alkali halide mixtures as a function of temperature. Circles, common-anion systems; squares, common-cation systems.

TABLE 6

Values of A (eqn. (7)) for binary common-ion alkali halide mixtures; the characteristic temperature was calculated to be $\Theta = 2565$ K

System	A (kJ mol^{-1})	System	A (kJ mol^{-1})
(Li,Na)Br	11.3	Na(Cl,Br)	5.0
(Na,K)Cl	18.2	K(Cl,Br)	3.7
(Na,K)Br	14.6	Na(Br,I)	9.8
(Na,K)I	10.8	K(Br,I)	7.1
(K,Rb)Cl	4.3	Rb(Cl,Br)	3.4
(K,Rb)Br	3.3	Rb(Br,I)	5.8
(K,Rb)I	2.5		

The A parameter as a function of cell parameters

In Fig. 3, the A parameters for the different systems calculated by means of the iterative fitting procedure are plotted against the difference in cell volume of the two components divided by the smallest cell volume. A least-squares fit through zero leads to the following equation

$$A_{\text{calc}}\ (\text{kJ mol}^{-1}) = 11.53(\Delta V/V_s) + 89.40(\Delta V/V_s)^2 \qquad (8)$$

The systems that show the largest deviation from the least-squares fit are lithium–sodium bromide and rubidium bromide–iodide. Equation (7) leads to the excess entropy of the solid state for the different mixtures using the characteristic temperature $\Theta = 2565$ K

$$S_1^{(s)} = A/2565\ \text{K} \qquad (9)$$

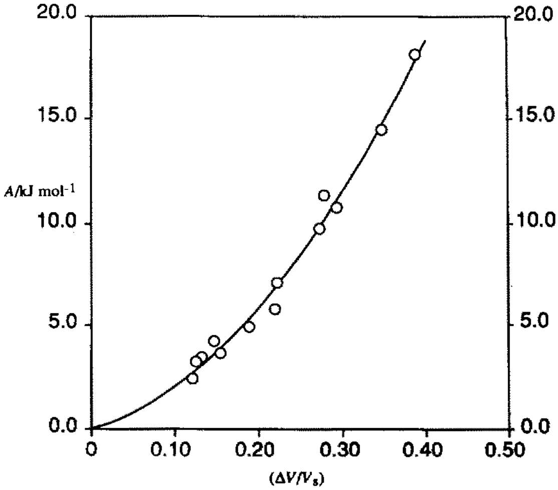

Fig. 3. The A parameter as a function of $\Delta V/V_s$. Cell parameters from ref. 54.

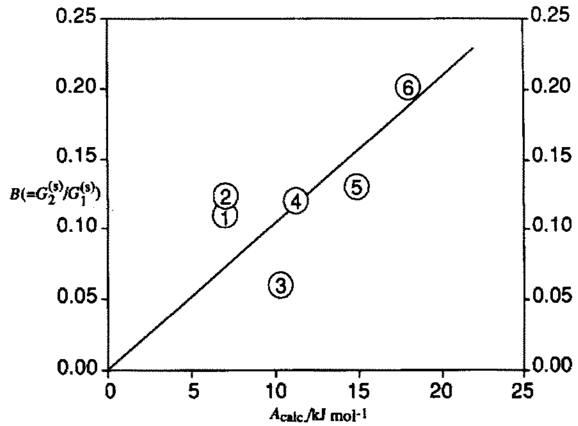

Fig. 4. *B* parameter versus calculated *A* parameter, eqn. (8); 1, Rb(Br,I); 2, K(Br,I); 3, (Li,Na)Br; 4, (Na,K)I; 5, (Na,K)Br; 6, (Na,K)Cl.

Correction for asymmetry

In Fig. 4, the ratio $(G_2^{(s)}/G_1^{(s)} = B$ derived from region-of-demixing data is plotted against the calculated *A* parameter, eqn. (8). The correlation is not striking but there tends to be a linear relation between *B* and the *A* parameter. A linear least-squares fit through zero leads to

$$B = 1.04 \times 10^{-2} A_{\text{calc}} \qquad (10)$$

CALCULATION OF PHASE DIAGRAMS WITH THE MODEL

For the twenty binary common-ion alkali halide mixtures that show continuous sub-solidus miscibility, the phase diagrams are calculated according to the model; the excess enthalpies for liquid and solid state are calculated from the interionic distances of the liquid pure components and the relative difference in cell volume of the pure solid components, respectively. The excess entropies are calculated from the excess enthalpies using eqns. (6b) and (9). A correction for asymmetry is made using eqn. (10). The results are compared with experimental phase diagram data in Tables 7 and 8. Figures 5–9 give two examples of phase diagram and heat of mixing calculations using the presented model. For the system (Na,K)Cl, Figs. 5 and 6 give the heat of mixing and the phase diagram respectively. The calculated diagrams match very well with the experimental data.

For the system R(Br,I), Figs. 7–9 give the heat of mixing, the region of demixing and the solid–liquid loop, respectively. The calculated heat of mixing is larger than the experimental one. The absolute error in the experimentally determined heat of mixing is approximately 0.5 kJ mol^{-1};

TABLE 7

Critical point of solid state region of demixing

System	Calculated		Experimental		
	x_c	T_c (K)	x_c	T_c (K)	Ref.
(Li,Na)Cl	0.41	614	0.35–0.42	544–587, ≈ 673	59, 60, 61
(Li,Na)Br	0.43	507		513	34
(Li,Na)I	0.44	429			
(Na,K)Cl	0.38	798	0.30–0.50	763–775	23, 24, 35, 62
(Na,K)Br	0.40	687	0.35–0.50	668	35, 63
(Na,K)I	0.42	543	0.33–0.38	513–693	35, 63
(K,Rb)F	0.46	260			
(K,Rb)Cl	0.47	204			
(K,Rb)Br	0.48	165			
(K,Rb)I	0.48	153			
Li(Cl,Br)	0.45	373			
Li(Br,I)	0.42	572			
Na(Cl,Br)	0.46	286			
Na(Br,I)	0.43	491			
K(Cl,Br)	0.47	214			
K(Cl,I)	0.37	872	0.30	823–878	63
K(Br,I)	0.45	365	0.34	478	37
Rb(Cl,Br)	0.48	173			
Rb(Cl,I)	0.39	778			
Rb(Br,I)	0.45	361	0.35	349–422	38, 64, 65

TABLE 8

Minimum of solid–liquid loop

System	Calculated		Experimental		
	x_m	T_m (K)	x_m	T_m (K)	Ref.
(Li,Na)Cl	0.29	826	0.25–0.29	801–828	59, 60, 61, 72
(Li,Na)Br	0.25	788	0.20–0.24	783–797	21, 41, 70, 71
(Li, Na)I	0.22	717	0.1	703	66
(Na,K)Cl	0.49	925	0.5	918–931	67,68
(Na,K)Br	0.48	900	0.46–0.54	899–917	43, 44, 69
(Na,K)I	0.45	855	0.38–0.42	856–857	44, 73, 74
(K,Rb)F	0.72	1058	0.72	1043	75
(K,Rb)Cl	0.74	989	0.60–0.75	988–989	55
(K,Rb)Br	0.76	961	0.60–0.95	946–959	76, 77, 78
(K,Rb)I	0.67	921	≈ 0.70	≈ 899	79
Li(Cl,Br)	0.63	796	0.60–0.64	795	80, 81
Li(Br,I)	0.58	681	≈ 0.60	690–691	82, 83
Na(Cl,Br)	0.73	1013	0.60–0.84	1011–1017	47, 43, 45
Na(Br,I)	0.67	911	0.65–0.76	908–923	47, 84, 85
K(Cl,Br)	0.69	998	0.68–0.70	993–1007	46, 43, 78
K(Cl,I)	0.54	875	0.50–0.55	853–863	86, 87, 88
K(Br,I)	0.65	936	0.65–0.68	936–937	46, 42
Rb(Cl,Br)	0.70	959	0.50–0.77	959–963	57, 89
Rb(Cl,I)	0.53	847	0.54–0.55	833–843	90, 91, 92
Rb(Br,I)	0.59	902	0.50	890–891	89, 93

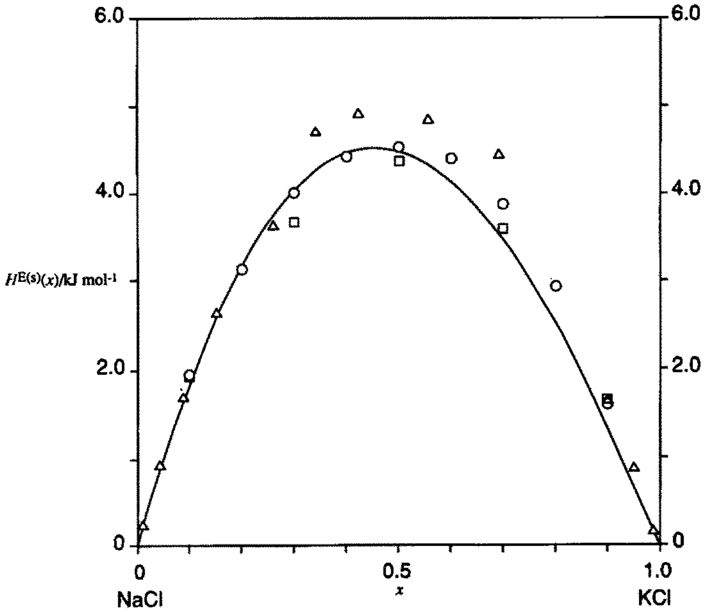

Fig. 5. Heat of mixing as a function of composition for (Na,K)Cl mixtures: △, [22]; ○, [23]; □, [24].

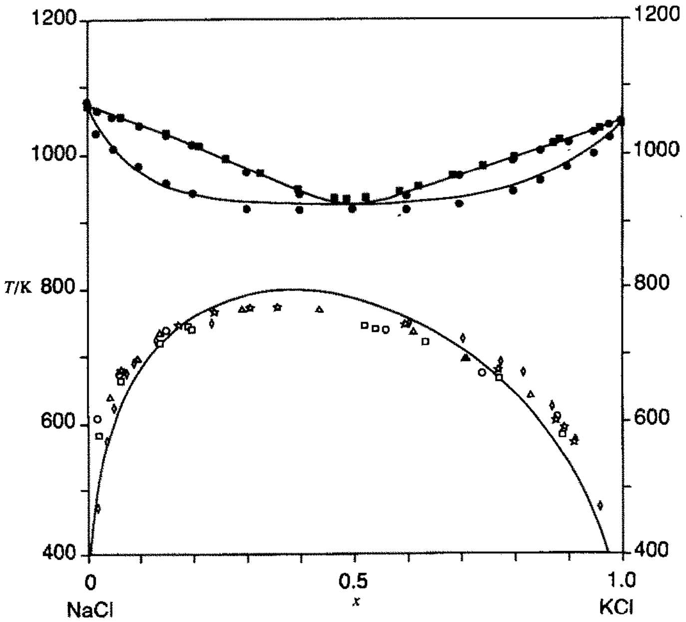

Fig. 6. Phase diagram for the binary common-anion system (Na,K)Cl: □, [23]; △, [24]; ◇, [35]; ○, [36]; ☆, [37]; ■, [67]; ●, [68].

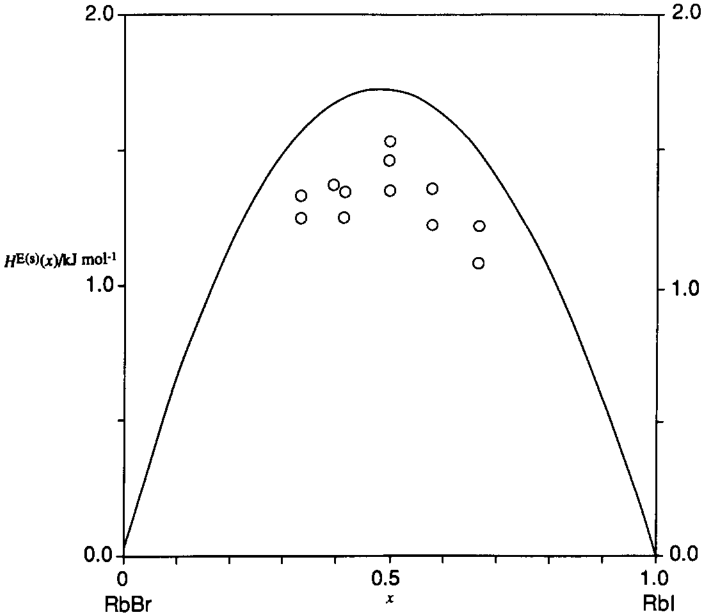

Fig. 7. Heat of mixing as a function of composition for Rb(Br,I) mixtures: ○, [33].

therefore, the calculated heat of mixing falls between the error bounds. The experimental region of demixing (Fig. 8) is not as broad as the calculated one. If one tries to fit the experimental region of demixing with

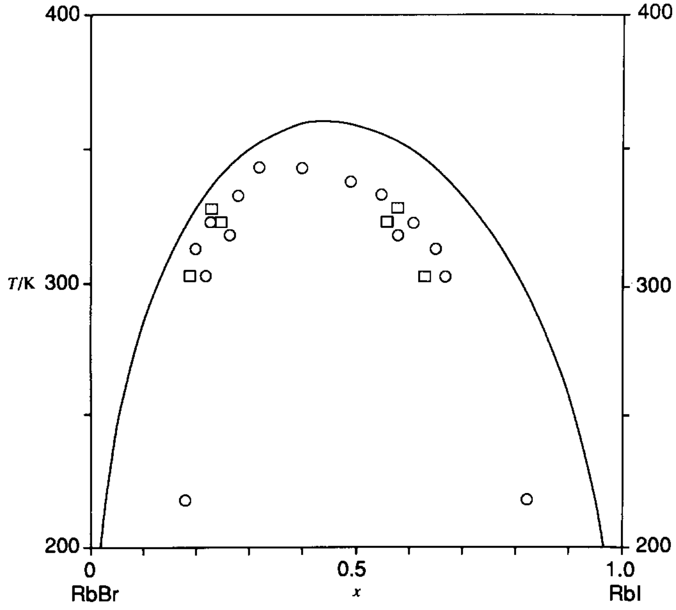

Fig. 8. Region of demixing for the binary common-cation system Rb(Br,I): ○ and □, [38].

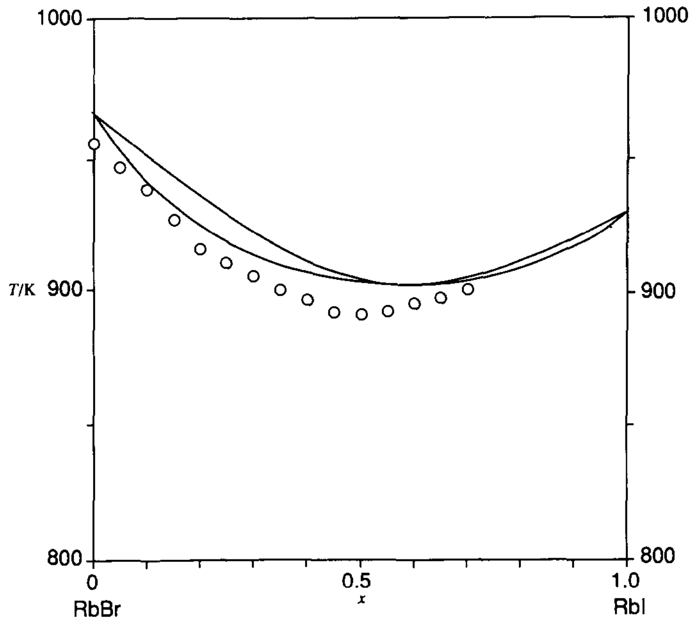

Fig. 9. Solid–liquid loop for the binary common-cation system Rb(Br,I): o, [48].

the EXTXD method, negative excess entropies are obtained, which is very unlikely considering Fig. 2. If one takes into account the low temperatures at which demixing experiments were performed and the low diffusion velocities of large anions such as bromide and iodide, then it becomes likely that the equilibration times were too short. The calculated solid–liquid loop lies about 10 K higher than the experimental one. This is mainly caused by a difference in the melting temperature of the pure rubidium bromide for which we chose the most recent value of Barin et al. [94].

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