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THE BINARY SYSTEM (Li, Na)Br: MEASUREMENT OF THE EXCESS ENTHALPY OF SOLID MIXTURES; MEASUREMENT AND ANALYSIS OF THE SOLID–LIQUID PHASE DIAGRAM

J.C. VAN MILTENBURG, G.D. JONGERT, P.J. VAN EKEREN and H.A.J. OONK

General Chemistry Laboratory, Chemical Thermodynamics Group, University of Utrecht, Padualaan 8, 3584 CH Utrecht (The Netherlands)

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ABSTRACT

Excess enthalpies of solid mixtures of $(1-X)$ LiBr + X NaBr were evaluated from measured enthalpies of solution. The result is represented by

$$H^E(X, T=298\text{ K}) = X(1-X)\{12.33+2.3(1-2X)\}\text{kJ mol}^{-1}$$

DTA was used to redetermine the position of the liquidus curve, from which the solidus was calculated by LIQFIT, together with the excess Gibbs energy difference function

$$\Delta G^E(X, T=860\text{ K}) = G^{E\,\text{liq}}(X, T=860\text{ K}) - G^{E\,\text{sol}}(X, T=860\text{ K})$$
$$= X(1-X)\{-9.63-1.13(1-2X)\}\text{kJ mol}^{-1}$$

The thermochemical and phase-diagram data give rise to the following excess Gibbs energy function for the solid phase

$$4G^{E\,\text{sol}}(X=0.5, T) = (12.1-5.8\times10^{-3}\ T/K)\text{kJ mol}^{-1}$$

INTRODUCTION

In a recent paper [1] we reported on the region of demixing (ROD) in solid LiBr + NaBr. The top of the ROD is at 513 K, which is about 280 K below the minimum of the solid–liquid two-phase region, so there is a considerable range of complete sub-solidus miscibility.

In this paper we report on the determination of the heat of mixing in the solid state and on the redetermination of the solid–liquid equilibrium.

The heat of mixing was determined indirectly by measuring and comparing the heats of solution of mechanical mixtures and of (metastable) homogeneous mixtures. The latter had been prepared by quenching homogeneous mixtures from conditions above the ROD to room temperature.

The solid–liquid relations were studied by means of differential thermal analysis (DTA). Earlier experiments made by Kellner [2] and by Bugaenko et al. [3] indicated complete sub-solidus miscibility. Arabadzhan and Bergman [4], on the other hand, reported compound formation.

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The LiBr + NaBr system is one of the systems used for the correlation of thermochemical and phase-diagram data on common-anion alkali halide mixtures [5].

EXPERIMENTAL

Sample preparation

The starting materials, LiBr and NaBr (Merck, purity > 99%), were dried in vacuo at 470 K. Because of the hygroscopicity of LiBr most operations were carried out in a glove box under argon atmosphere.

Mechanical mixtures were prepared by powdering (in an agate mortar) carefully weighed amounts of the pure components. The metastable solid mixtures were, starting from mechanical mixtures, made as follows. After melting and solidifying, the mixtures were kept for 20 h at 600 K and then quenched to room temperature.

Samples for DTA experiments were enclosed in small platinum capsules which were closed by welding. Samples for heat-of-solution measurements were enclosed in quartz capsules. In the case of the metastable solid mixtures, the heat-of-solution experiments were carried out as quickly as possible after the preparation of the samples.

Excess enthalpy

The excess enthalpy was determined indirectly by measuring the heats of solution in water of mixed crystals and of mechanical mixtures.

An isoperibolic calorimeter was used. This consists of a glass dewar, a 100 kΩ thermistor (Fenwall), a calibrated resistance of 180 Ω and a stirrer with adjustable speed. A small clamp is used for the quartz sample container which can be broken by screwing down a fine stainless steel needle. The calorimeter is immersed in a 50 l thermostat (Tronac) which is stable to within 0.0002 K. The thermistor is part of a Wheatstone bridge; all the other components of the bridge have temperature coefficients of one p.p.m. or less. Rechargeable Nicad batteries are used for the bridge. A change of one microvolt in the bridge output corresponds to a change in temperature of 3×10^{-5} K. A constant current source (0 to 50 mA) is used for the heater. Timing is achieved by reading the clock in the HP 3497 A scanner just after switching the actuator. A HP 3455 A digital voltmeter is used to read the bridge signal and the voltages over the heater and the standard resistance during a heat input. These instruments are connected with an IEEE interface to an Apple II computer. Data collection is automated and the data are corrected for heat leak after measuring the heat-leak constant in a separate measurement.

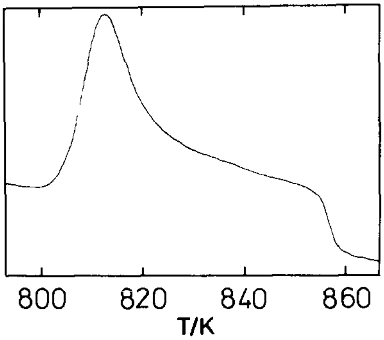

Fig. 1. Heating curve for the sample with mole fraction $X = 0.49$. This plot is a typical example of the measured heating curves.

The instrument was checked by measuring the heat of solution of KCl, the result of 10 measurements being (17.32 ± 0.10) kJ mol^{-1}, which is in good agreement with the value of 17.50 kJ mol^{-1} given by Lange and Mondheim [6] for the same final concentration.

Measurements were made at 298 K. After introducing 100 ml pre-equilibrated water and the capsule, the calorimeter was equilibrated for about 30 min. Specific heat measurements were made before the breaking of the capsules. The heat effect was calculated as the temperature difference times the heat capacity.

Solid–liquid equilibrium

The liquidus temperatures were determined by recording the heating curves on a DTA (Setaram DSC-111), with a heating rate of 2 K min^{-1}. The liquidus points are the points where the melting process ends; from there the heating curve falls exponentially to the base-line (relaxation). A typical heating curve is shown in Fig. 1. We estimate the error ranges for the liquidus temperatures to be about 3 K.

We have also recorded cooling curves; the samples showed a supercooling of about 10 K.

RESULTS

Excess enthalpy

Heats of solution of mechanical mixtures and homogenized solid mixtures were measured; the results, which are corrected for the heat of breaking a capsule (measured in a separate experiment: $Q_b = -(0.23 \pm 0.02)$ J), are

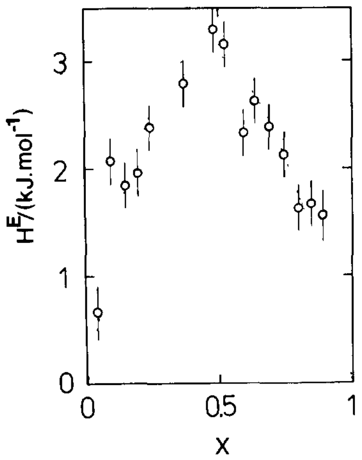

Fig. 2. Experimental excess enthalpies as a function of mole fraction of NaBr; the best fit is represented by the dashed line.

reported in Tables 1 and 2. The molar heat of solution of mechanical mixtures can be described by the following linear equation

$$\Delta_{\mathrm{sol}}H(\mathrm{mm};\ X) = (1 - X)\Delta_{\mathrm{sol}}H_1^* + X\Delta_{\mathrm{sol}}H_2^* \tag{1}$$

where $\Delta_{\mathrm{sol}}H(\mathrm{mm};\ X)$ is the molar heat of solution of a mechanical mixture as a function of the mole fraction X of the second component and $\Delta_{\mathrm{sol}}H_i^*$ is the heat of solution of the pure i-th component. The coefficients of this equation were fitted to the experimental results; the result of the fit is

$$\Delta_{\mathrm{sol}}H^*(\mathrm{LiBr}) = -(48.50 \pm 0.15)\mathrm{kJ\ mol^{-1}}$$

$$\Delta_{\mathrm{sol}}H^*(\mathrm{NaBr}) = -(0.39 \pm 0.15)\mathrm{kJ\ mol^{-1}} \tag{2}$$

TABLE 1

Heats of solution of mechanical mixtures: total amount of substance; mole fraction of sodium bromide; experimental heat of solution; experimental molar heat of solution; molar heat of solution calculated using eqns. (1) and (2)

n (mmol)	X	Q (J)	$\Delta_{\mathrm{sol}}H$(mm) (kJ mol^{-1})	$\Delta_{\mathrm{sol}}H^{\mathrm{CALC}}$(mm) (kJ mol^{-1})
3.6123	0	−175.4	−48.54	−48.50
3.3220	0.1737	−132.9	−40.02	−40.15
4.2276	0.2002	−165.2	−39.07	−38.87
6.0580	0.3663	−186.8	−30.83	−30.88
5.1631	0.4052	−150.0	−29.06	−29.01
4.9276	0.6084	−93.2	−18.92	−19.23
4.7432	0.7115	−68.1	−14.35	−14.27
4.5858	0.7953	−47.0	−10.26	−10.24
4.6427	0.9061	−23.0	−4.96	−4.91
3.3644	1	−1.5	−0.45	−0.39

TABLE 2

Heats of solution of mixed crystals: total amount of substance; mole fraction of sodium bromide; experimental heat of solution; experimental molar heat of solution; molar heat of solution of mechanical mixture calculated using eqns. (1) and (2); experimental excess enthalpy of the mixed crystal; excess enthalpy calculated using eqns. (4) and (5)

n (mmol)	X	Q (J)	$\Delta_{sol}H$(mc) (kJ mol^{-1})	$\Delta_{sol}H$(mm) (kJ mol^{-1})	H^E (kJ mol^{-1})	$H^{E\,CALC}$ (kJ mol^{-1})
2.4682	0.0431	−116.3	−47.11	−46.43	0.68	0.60
2.9510	0.0973	−135.5	−45.91	−43.82	2.09	1.25
3.1308	0.1516	−134.8	−43.07	−41.21	1.86	1.79
2.8031	0.1994	−114.6	−40.88	−38.91	1.97	2.19
4.0475	0.2447	−158.4	−39.13	−36.73	2.40	2.50
3.9588	0.3743	−131.8	−33.30	−30.49	2.81	3.02
3.2368	0.4884	−91.7	−28.32	−25.01	3.31	3.09
3.1036	0.5286	−81.4	−26.24	−23.07	3.17	3.04
2.9466	0.5961	−65.3	−22.16	−19.82	2.34	2.86
2.9641	0.6388	−60.5	−20.41	−17.77	2.64	2.70
3.0360	0.6910	−53.6	−17.66	−15.26	2.40	2.45
3.4045	0.7470	−50.1	−14.77	−12.57	2.14	2.12
3.6974	0.7993	−43.2	−11.69	−10.05	1.64	1.76
3.5785	0.8447	−34.1	−9.54	−7.86	1.68	1.41
2.5859	0.8907	−18.7	−7.22	−5.65	1.57	1.03

These values are in good agreement with literature values (−48.7 and −0.26 kJ mol^{-1}, respectively) [7].

The excess enthalpy of the mixed crystals is the difference between the heat of solution of the mechanical mixtures (mm) and that of the mixed crystals (mc)

$$H^E(X) = \Delta_{sol}H(\text{mm};\ X) - \Delta_{sol}H(\text{mc};\ X). \tag{3}$$

The excess-enthalpy values are given in the sixth column of Table 2; they were fitted to a so-called Redlich–Kister expression [8]

$$H^E(X) = X(1-X)\left\{H_1 + H_2(1-2X) + H_3(1-2X)^2 + \ldots\right\} \tag{4}$$

where the coefficients H_i are the adjustable parameters. Two coefficients could be evaluated; the values that represent the most probable fit (root-mean-square deviation 0.35 kJ mol^{-1}) are

$$H_1 = (12.33 \pm 0.49)\text{kJ mol}^{-1};\ H_2 = (2.3 \pm 1.2)\text{kJ mol}^{-1} \tag{5}$$

In Fig. 2 the experimental excess-enthalpy values are plotted as a function of mole fraction; the dashed line in this Figure represents the best fit.

The solid–liquid equilibrium

The experimental liquidus points are listed in Table 3. These were, together with values for two coefficients of the Redlich–Kister expression

TABLE 3

Experimental liquidus points and phase diagram assessed by LIQFIT: mole fraction of sodium bromide; experimental liquidus temperature; calculated mole fraction of the liquidus and solidus at the stated temperature

Experimental		Calculated	
X	T (K)	X^{liq}	X^{sol}
1.00	1015	–	–
0.89	991	0.909	0.978
0.69	929	0.701	0.906
0.60	896	0.601	0.854
0.49	855	0.484	0.761
0.37	817	0.372	0.598
0.30	796	0.282	0.357
0.24	795	0.273	0.330
0.20	797	0.171	0.127
0.10	808	0.091	0.050
0.00	824	–	–

for the excess Gibbs energy of the liquid phase (estimated from the heat-of-mixing data), used as input values for the LIQFIT computer program. LIQFIT is an iterative procedure, with intermediate phase diagram calculations, in which the calculated liquidus curve is made to run through the experimental liquidus points. The procedure yields a reliable solidus curve and the difference in excess Gibbs energy between the liquid and the solid phase for the mean temperature of the data set [9,10]. The LIQFIT program is written in FORTRAN; the text is given in ref. 11, with two subroutines in ref. 12. The procedure for estimating the excess Gibbs energy of the liquid phase from the heat-of-mixing data is, for the first coefficient, indicated in ref. 5. Here we suppose that the same procedure holds for the second coefficient. In short the procedure reads: extrapolation of the excess enthalpy to the mean temperature of the solid–liquid region and next multiplication by 0.66. According to Hersh and Kleppa [13] the Redlich–Kister coefficients for the excess enthalpy of the liquid mixture are

$$H_1^{\mathrm{liq}}(T=963\ \mathrm{K}) = -3264\ \mathrm{J\ mol^{-1}};\ H_2^{\mathrm{liq}}(T=963\ \mathrm{K}) = -293\ \mathrm{J\ mol^{-1}} \qquad (6)$$

For the excess Gibbs energy coefficients we obtain

$$G_1^{\mathrm{liq}}(T=860\ \mathrm{K}) = -2334\ \mathrm{J\ mol^{-1}};\ G_2^{\mathrm{liq}}(T=860\ \mathrm{K}) = -209\ \mathrm{J\ mol^{-1}} \qquad (7)$$

Two coefficients of the Redlich–Kister expression for the excess Gibbs energy difference function (liquid minus solid) could be evaluated

$$\Delta G_1 = -9.63\ \mathrm{kJ\ mol^{-1}};\ \Delta G_2 = -1.13\ \mathrm{kJ\ mol^{-1}} \qquad (8)$$

Combination of eqns. (7) and (8) yields the coefficients for the excess Gibbs energy of the homogenized solid mixtures

$$G_1^{\mathrm{sol}}(T=860\ \mathrm{K}) = 7300\ \mathrm{J\ mol^{-1}};\ G_2^{\mathrm{sol}}(T=860\ \mathrm{K}) = 921\ \mathrm{J\ mol^{-1}} \qquad (9)$$

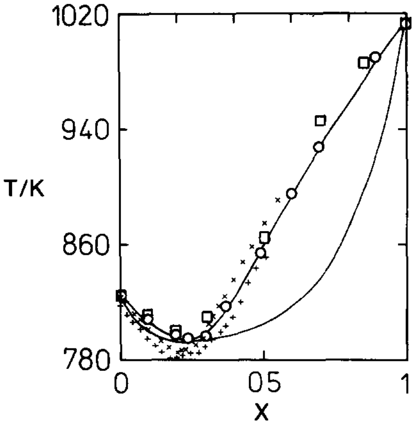

Fig. 3. Experimental liquidus points as a function of mole fraction of NaBr: (○) this work; (□) according to Kellner [2]; (×) according to Bugaenko et al. [3]; (+) according to Arabadzhan and Bergman [4]. The phase diagram assessed by LIQFIT is also drawn in this Figure.

The disagreement between the calculated and the experimental liquidus points is expressed in the Δ_T value, which is defined as

$$\Delta_T = n^{-1} \sum_{i=1}^{n} \mathrm{abs}(T_{\mathrm{EXP},i} - T_{\mathrm{CALC},i});\ X_{\mathrm{EXP},i} = X_{\mathrm{CALC},i} \tag{10}$$

where n is the number of experimental liquidus points. We have found that $\Delta_T = 2$ K. The calculated liquidus and solidus points are also given in Table 3.

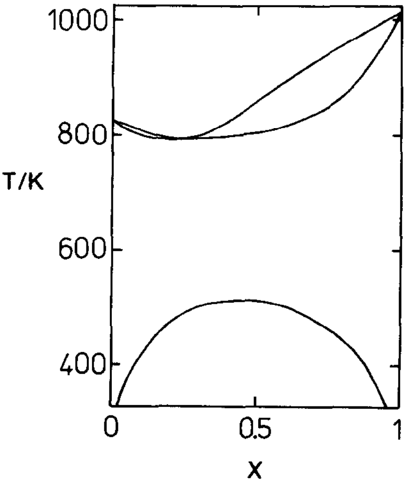

Fig. 4. Complete *TX* phase diagram of the system (Li, Na)Br as determined in this work and in ref. 1.

In Fig. 3 we have plotted the experimental liquidus points and drawn the calculated liquidus and solidus curves. We have also plotted the liquidus points measured by Kellner [2], Arabadzhan and Bergman [4] and Bugaenko et al. [3].

DISCUSSION

In this section we combine, for the system under consideration, the available information. From this work two coefficients of the expression for the excess enthalpy (eqn. (5)) and two coefficients of the expression for the excess Gibbs energy at the mean temperature of the solid–liquid region (eqn. (9)) are available. Doornhof et al. [1] reported the excess Gibbs energy at the mean temperature of the region of demixing.

If excess heat capacities are neglected (there is little information on excess heat capacities of solid alkali halide mixtures, but there is evidence that their influence is small [14]), the experimental heat of mixing is representative for the excess Gibbs energy at zero kelvin, and the temperature dependence of the coefficients G_i is given by

$$G_i(T) = H_i - TS_i \tag{11}$$

where S_t are the coefficients of the expression for the excess entropy. We then have values for the excess Gibbs energy at three different temperatures; these values are listed in Table 4. The first coefficient (i.e. G_1) can be described well by eqn. (11) if we put

$$H_1 = 12.1 \text{ kJ mol}^{-1};\ S_1 = 5.9 \text{ J K}^{-1} \text{ mol}^{-1} \tag{12}$$

For the second coefficient this procedure is not useful, because the relative error ranges are large.

In another paper [5] we correlated thermochemical and phase-diagram data for homogenized solid mixtures of common-anion alkali halide systems and proposed a common-vanishing point at 2631 K for the first coefficient of the expression for the excess Gibbs energy of all common-anion alkali

TABLE 4

Coefficients of the Redlich–Kister expression for the excess Gibbs energy of the homogenized solid mixtures as a function of temperature

T (K)	$G_1(T)$ (kJ mol^{-1})	$G_2(T)$ (kJ mol^{-1})	Ref.
0	12.33	2.3	this work
440	8.93	0.6	17
860	7.30	0.9	this work

halide systems. For the system (Li, Na)Br this resulted in the following values for the coefficients of eqn. (11)

$$H_1 = 11.5\ \text{kJ mol}^{-1};\ S_1 = 4.4\ \text{J K}^{-1}\ \text{mol}^{-1} \qquad (13)$$

which are in reasonable accordance with the values of eqn. (12).

Finally the complete *TX* phase diagram of (Li, Na)Br, as determined in this work and in ref. 1 is depicted in Fig. 4.

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