Thermodynamic Properties of Solid Systems $AgCl + NaCl$ and $AgBr + NaBr$ from Miscibility Gap Measurements

CESARE SINISTRI, RICCARDO RICCARDI, CHIARA MARGHERITIS, and PAOLO TITTARELLI

Centro di studio per la termodinamica ed elettrochimica dei sistemi salini fusi e solidi
del C.N.R.-Institute of Physical Chemistry, University of Pavia (Italy)

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Miscibility gaps for the solid systems $AgCl+NaCl$ and $AgBr+NaBr$ have been measured by a high temperature X-ray technique.

For the two studied systems the solubility curves are very nearly symmetrical in respect to the compositions $x_{NaCl}=.513$ and $x_{NaBr}=.506$, while the upper critical temperature are 198 °C for $AgCl+NaCl$ and 285 °C for $AgBr+NaBr$.

The thermodynamic properties of the two solid systems have been calculated using only experimental solubility data. Values of activity and of enthalpy of mixing were estimated and compared with those reported in literature.

In 1965 KLEPPA and MESCHEL[1] measured the heats of formation of solid solutions in the systems $AgCl+NaCl$ and $AgBr+NaBr$. On the basis of a previous work[2] reporting for $AgCl+NaCl$ a miscibility gap (MG) with a critical temperature near 175 °C, the authors[1] stated: "since the positive enthalpies of formation of the bromide solutions are about 20% smaller than those for the corresponding chlorides" for the system $AgBr+NaBr$ "a critical temperature somewhat below 175 °C is predicted".

More recently for the solid system $AgBr+NaBr$, Japanese authors[3] found, by study of galvanic cells, a MG confirmed by X-ray diffraction measurements. According to these authors the critical temperature for an equimolar mixture is between 300 °C and 350 °C.

Owing to latter findings that contrast with Kleppa and Meschel's prediction we decided to experimentally reexamine the extension of the MG in the solid phase for both systems $AgCl+NaCl$ and $AgBr+NaBr$. In order to describe as accurately as possible the limits of the MG, high temperature X-ray diffraction measurements were carried out giving particular care to the sample preparation. Through these data, we attempted a description of the general thermodynamic properties of these systems. The results were compared, when possible, with those reported in literature. Finally, for a complete description of the phase diagrams of the two systems, solid-liquid (SL) curves were determined by DTA measurements.

Experimental

a) Apparatus and Materials

The apparatus for DTA measurements has already been described[4]. For X-ray measurements a Philips apparatus, employing Ni-filtered CuKα radiation fitted with a high temperature camera (MRC mod. X-86 N-II), was properly modified[5] to improve temperature homogeneity and control. Thus it was possible to reach temperatures up to 600 °C, controlled within ±1 °C.

NaCl and NaBr were C. Erba RP; AgCl and AgBr were obtained by precipitation from $AgNO_3$ (C. Erba RP). All salts were dried following the usual literature methods.

b) Procedures

The mixtures to be analyzed by X-ray diffraction were prepared by melting the components in a quartz tube and quenching the melt in liquid oxygen in order to obtain a uniform mixture. The finely powdered mixture transferred on the sample holder of the camera was held at 350 °C under N_2 for about 6 hours. After the existence of a solid solution was confirmed, the sample was slowly cooled to the desired temperature and there held for a long time until the equilibrium between the two new solid phases was reached.

It is worth to underline that, while the mixtures $AgBr+NaBr$ reached equilibrium in a relative short time (15 – 20 hours), the mixtures $AgCl+NaCl$ required a much longer time (10 – 20 days) thus showing a large demixing hysteresis. In every case the equilibrium was shown by the constancy of the diffraction patterns taken at different times. The annealing of the samples was carried out in a separate thermostat through periods as long as suggested by preliminary tests.

Results

Figure 1 reports our results for the SL curves in comparison with ZEMCZUZNY's data[6]: for the

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Reprint requests to Prof. CESARE SINISTRI, Istituto di Chimica Fisica, Università di Pavia, *I-27100 Pavia.*

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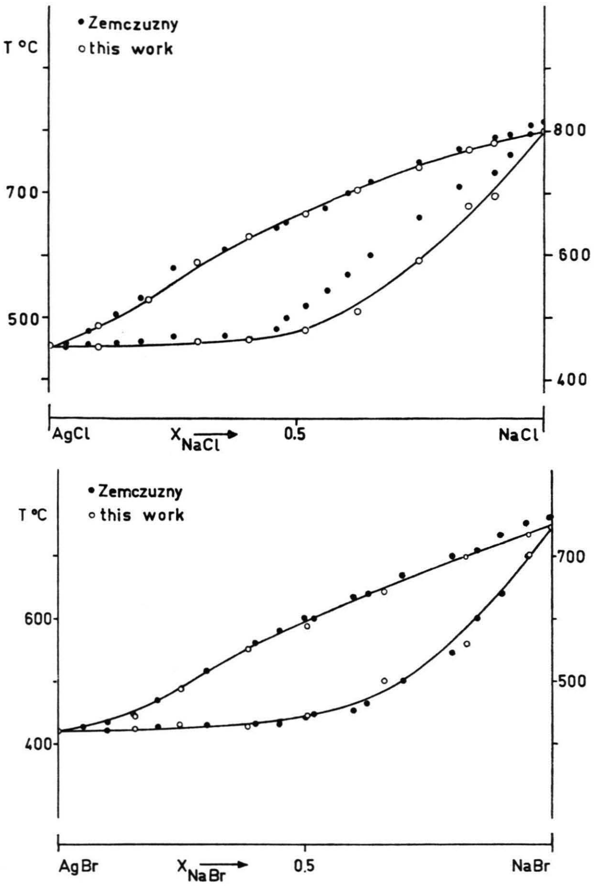

Fig. 1. SL curves for AgCl+NaCl and AgBr+NaBr systems.

AgBr + NaBr system the two sets of data agree fairly well, whilst for the AgCl + NaCl system there are some discrepancies that for $x_{NaCl} > 0.5$ can reach even $60^\circ - 70\ ^\circ C$ in the equilibrium temperature of the solid curve.

Figure 2 shows the lattice constants vs. temperature for the pure salts: as it is well known, all these salts crystallize in the same spatial group of the cubic system (FM3M). It is interesting to observe that up to 370 °C sodium halides show linear expansion whilst silver halides do not. The anomalous increase in the expansion of AgCl and AgBr was interpreted on the basis of the volume requirements of Frenkel defects with mixed Frenkel-Schottky disorder[7]. Before studying the solid phase, the validity of Vegard's law was proved. This law states that the lattice constant a of a substitutional solid solution of substances with the same crystal structure is given by

$$a = a_1 + x(a_2 - a_1) \quad (T = \text{const}) \quad (1)$$

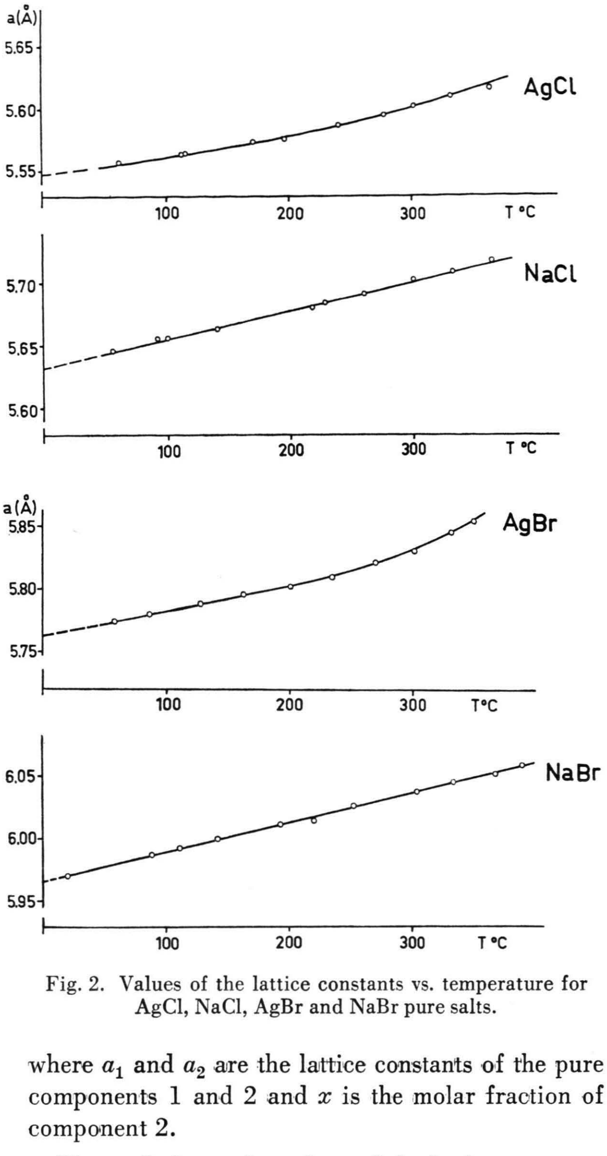

Fig. 2. Values of the lattice constants vs. temperature for AgCl, NaCl, AgBr and NaBr pure salts.

where a_1 and a_2 are the lattice constants of the pure components 1 and 2 and x is the molar fraction of component 2.

Figure 3 shows the values of the lattice constants for the solid solutions at two different temperatures (365° and 248 °C for the system AgCl + NaCl; 351° and 291 °C for the system AgBr + NaBr).

For temperatures below 198 °C for the system AgCl + NaCl and 285 °C for the system AgBr + NaBr, the diffractograms on equimolar mixtures indicate two solid phases in equilibrium. The compositions of the two phases can be deduced from the values of the two lattice constants by Eq. (1).

Table 1 reports the compositions of the two phases along with their "point of symmetry" (PS) at the different temperatures.

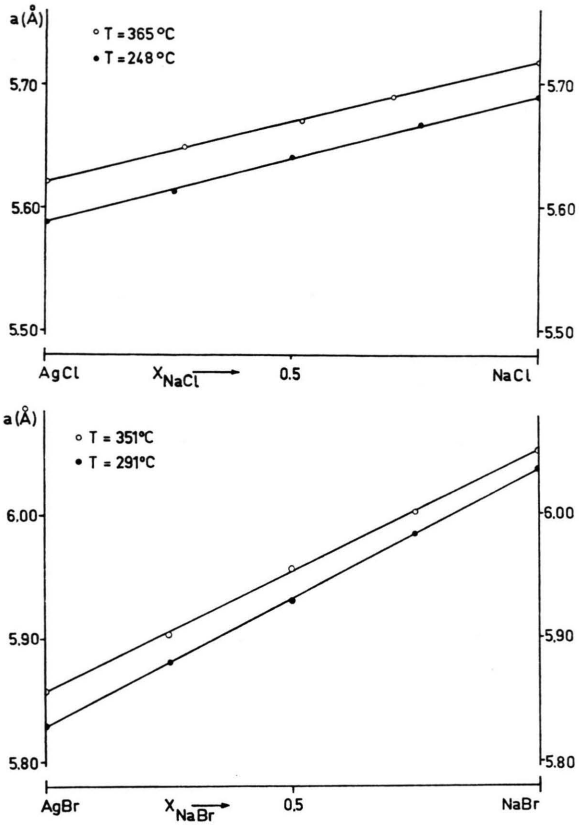

Fig. 3. Test of additivity of lattice constants (Vegard's law) for the solid solutions AgCl+NaCl and AgBr+NaBr.

Figure 4 shows the solid-solid equilibrium curves (SS) obtained from Table 1. These curves are very nearly symmetrical in respect to the compositions $x_{\text{NaCl}} = 0.513$ and $x_{\text{NaBr}} = 0.506$. For the two studied systems the following values of the upper critical point (UCP) were thus deduced:

$$\text{AgCl} + \text{NaCl}: \quad t_c = 198\ ^\circ\text{C}, \quad x_{\text{NaCl, c}} = 0.513\,,$$

$$\text{AgBr} + \text{NaBr}: \quad t_c = 285\ ^\circ\text{C}, \quad x_{\text{NaBr, c}} = 0.506\,.$$

Thermodynamics for the Binary System $C_1 A + C_2 A$

a) General Principles

Let us consider the common anion binary system $C_1 A + C_2 A$, where x is the molar fraction of component $2 (C_2 A)$ and $1 - x$ is that of component $1 (C_1 A)$.

The activities of the two components are[8]:

$$a_1 = f_1 (1 - x)\,; \qquad a_2 = f_2\, x\,. \tag{2}$$

Table 1. Solubility limits of the two solid systems AgCl+NaCl and AgBr+NaBr.

System AgCl $(1-x)$ +NaCl (x)

T °K	The MG extends from	to	PS
337.2	$x = 0.076$	$x = 0.903$	$x = 0.490$
375.2	0.129	0.903	0.516
416.2	0.219	0.815	0.517
424.2	0.266	0.793	0.530
440.2	0.289	0.727	0.508
447.2	0.349	0.680	0.515
460.2	0.407	0.638	0.523
468.2	0.458	0.583	0.521
470.2	0.428	0.559	0.494

mean value $x = 0.513 \pm 0.010$

UCP is at 198 °C (471.2 °K) and $x = 0.513$

System AgBr $(1-x)$ +NaBr (x)

T °K	The MG extends from	to	PS
292.2	$x = 0.054$	$x = 0.969$	$x = 0.512$
330.2	0.077	0.907	0.492
358.2	0.063	0.898	0.481
403.2	0.103	0.900	0.502
439.2	0.131	0.880	0.506
469.2	0.169	0.850	0.510
497.2	0.228	0.803	0.516
522.2	0.280	0.754	0.517
533.2	0.329	0.727	0.528
545.2	0.373	0.638	0.506
554.2	0.411	0.557	0.484
556.2	0.468	0.566	0.517

mean value $x = 0.506 \pm 0.011$

UCP is at 285 °C (558.2 °K) and $x = 0.506$

The excess potentials of components 1 and 2 may be written as:

$$\mu_1^{\text{E}} = R\,T \ln f_1 = A\,x^2 + B\,x^3 + \dots\,, \tag{3}$$

$$\mu_2^{\text{E}} = R\,T \ln f_2 = (A + \tfrac{3}{2}\,B + \dots)\,(1 - x)^2 - B(1 - x)^3 + \dots \tag{4}$$

The dependence on temperature of the parameters $A, B, \dots$ in Eqs. (3), (4) can be assumed, as a first but sufficient approximation, as:

$$A = A_0 + A'\,T\,; \qquad B = B_0 + B'\,T\,. \tag{5}$$

The excess molar Gibbs free energy of mixing can be easily calculated from Eqs. (3) and (4):

$$G^{\text{E}} = x(1 - x)\,(A + \tfrac{1}{2}\,B + \tfrac{1}{2}\,B\,x + \dots)\,. \tag{6}$$

The excess entropies can be calculated from Eqs. (3), (4), (6) with Eq. (5).

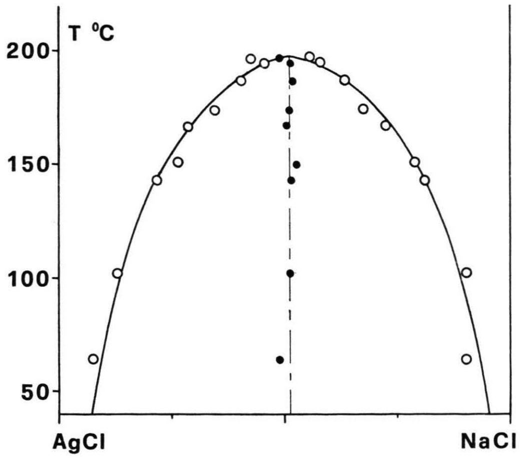

Fig. 4 a. Solid-solid equilibrium curve obtained for AgCl +NaCl system from X-ray measurements (circles). The black dots are the point of symmetry between the two corresponding circles.

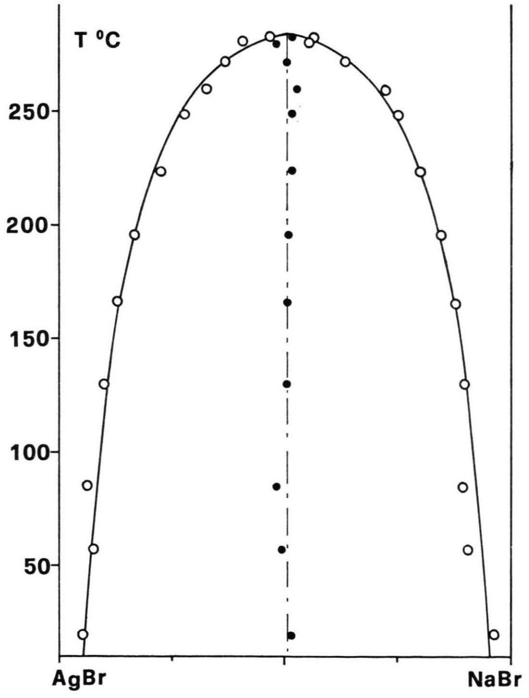

Fig. 4 b. Solid-solid equilibrium curve obtained for AgBr +NaBr system from X-ray measurements (circles). The black dots are the point of symmetry between the two corresponding circles.

Finally the enthalpy of mixing is given by:

$$\Delta H_\mathrm{m} = H^\mathrm{E} = x(1-x)\,[(A-A'T) + \tfrac{1}{2}(B-B'T) + \tfrac{1}{2}(B-B'T)\,x + \ldots] \qquad (7)$$
$$= x(1-x)\,[(A_0 + \tfrac{1}{2}B_0) + \tfrac{1}{2}B_0\,x + \ldots]\,.$$

b) Evaluation of A and B from Miscibility Gap Data

When the binary system $C_1A + C_2A$ can be fully described by the two parameters A and B of Eqs. (3), (4) ("two parameters system"), it is possible, using MG data, to evaluate these parameters by one of the following methods.

The first one, already reported [9], employes the UCP of the MG. At the critical point, both the second and the third derivative of the Gibbs free energy of the mixture $\overline{G}$ must be null, that is:

$$(\partial^2\overline{G}/\partial x^2)_{T,P} = 0; \qquad (\partial^3\overline{G}/\partial x^3)_{T,P} = 0\,. \qquad (8)$$

Using Eqs. (3), (4), (6) with Eq. (8), the following values of A and B are obtained:

$$A = \frac{R\,T_\mathrm{c}}{2\,(1-x_\mathrm{c})^2\,x_\mathrm{c}}\,(2-3\,x_\mathrm{c})\,;$$
$$B = \frac{R\,T_\mathrm{c}}{3\,(1-x_\mathrm{c})^2\,x_\mathrm{c}^2}\,(2\,x_\mathrm{c}-1)\,, \qquad (9)$$

where x_c and T_c are the experimental values of the composition and temperature at the critical point. In this way, values of A and B at the critical temperature only are obtained, besides, the precision of the two parameters is strongly dependent on the precision with which the critical values are measured.

The general conditions of equilibrium between different phases allows one to calculate values of A and B through a second, more complete, procedure. If the two solid phases in equilibrium are indicated with "$'$" and "$''$" at each temperature must be $(x'' > x')$:

$$\mu_1' = \mu_1'', \qquad \mu_2' = \mu_2''. \qquad (10\,\mathrm{a,b})$$

From Eq. (10 a) with Eqs. (2), (3) and using the abbreviation

$$\Delta x^n \equiv (x'')^n - (x')^n$$

it follows:

$$R\,T\ln[(1-x')/(1-x'')] = A\,\Delta x^2 + B\,\Delta x^3 \qquad (11)$$

while from Eq. (10 b) with Eqs. (2), (4) it follows:

$$R\,T\ln x''/x' = -A\,\Delta(1-x)^2 + B[\Delta(1-x)^3 - \tfrac{3}{2}\,\Delta(1-x)^2]. \qquad (12)$$

Equations (11) and (12), at the same temperature, allows one to estimate A and B. If this procedure is applied to all the experimental points of SS equilibrium (or to as many interpolated points as desired), explicit values of A and B vs. T can be obtained. By Eqs. (2) – (7) the thermodynamic properties of the system can thus be described.

Discussion

If the two studied systems can be treated as "two parameters systems" [see f. e. Kleppa's experimental results[1] expressed by a type (7) relation], then it is possible to use the data of Table 1 in connection with Eqs. (2) – (12).

The experimental values of the UCP's applied to Eq. (9) give the following data at the T_c of the two systems (198° and 285 °C respectively)

$$\text{AgCl} + \text{NaCl}: \quad A = 1.77; \quad B = 0.13 \text{ kcal/mole.}$$

$$\text{AgBr} + \text{NaBr}: \quad A = 2.17; \quad B = 0.07 \text{ kcal/mole.}$$

The values of A and B obtained, as functions of temperature, by Eqs. (11), (12) are reported in Fig. 5. It can be observed that in both systems B is independent of temperature, while A shows a small dependence. In the investigated temperature range, the values of A for the AgBr + NaBr system are always larger than those for AgCl + NaCl, while the B values are always rather small. These findings are consistent with the shape of the solubility curves (see Fig. 4).

Assuming each point has the same weight, interpolation of the data through the least square method gives:

$$\begin{aligned} &\text{AgCl} + \text{NaCl}: \\ &\quad A = (2.5 \pm 0.5) + (0.002 \pm 0.001)\, T \text{ kcal/mole}, \\ &\quad B = \ 0.2 \pm 0.2 \qquad \text{kcal/mole}, \end{aligned} \tag{13}$$

$$\begin{aligned} &\text{AgBr} + \text{NaBr}: \\ &\quad \text{A} = (1.8 \pm 0.3) - (0.001 \pm 0.001)\, T \text{ kcal/mole}, \\ &\quad B = \ 0.1 \pm 0.2 \qquad \text{kcal/mole}. \end{aligned} \tag{14}$$

All stated errors are standard deviations[10]. As can be noted, the temperature coefficients of A (directly connected to the excess entropy terms) have opposite signs in the two systems. In particular, for an equimolar mixture, the coefficients A' of Eqs. (13), (14) give an excess entropy of 0.5 ± 0.25 e. u. for AgCl + NaCl and – 0.25 ± 0.25 e. u. for AgBr + NaBr. These values indicate that in the first case the excess entropy is positive, whilst in the second one the excess entropy is either zero or slightly negative.

KLEPPA[1] compared the values of the enthalpy of mixing with those of the excess free energy obtained by PANISH et al.[11] from emf measurements. He found that "solid solutions (AgCl + NaCl) have small positive excess entropies" which amount to about 0.2 e. u. for equimolar mixtures. On the other hand, TSUJI et al.[3], from emf measurements, concluded that for the solid system AgBr + NaBr "the partial molar entropy is the same as it would be in the ideal solution". Our findings are consistent with these statements.

Figure 5 reports (starred points) the values of A and B at T_c as calculated by means of Eq. (9) using the UCP values. As can be observed, these values are in good agreement with those obtained from Eqs. (11) and (12).

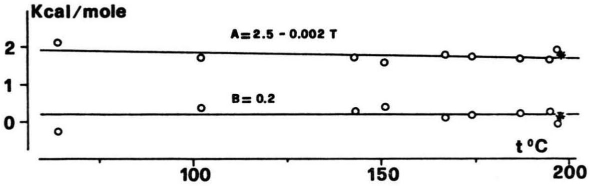

Fig. 5 a. Values of A and B vs. temperature for AgCl+NaCl. The starred points have been obtained from UCP data.

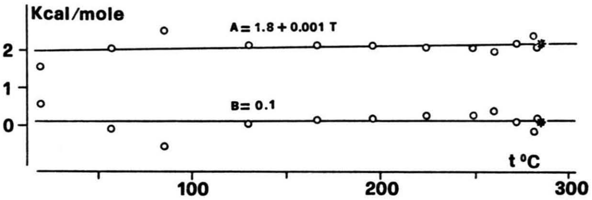

Fig. 5 b. Values of A and B vs. temperature for AgBr+NaBr. The starred points have been obtained from UCP data.

Now, using the explicit values of A and B given by Eqs. (13), (14), it is possible to describe the thermodynamic properties of the two studied systems through Eqs. (2) – (7).

For both systems, activity measurements obtained by galvanic cells[3, 11] have been reported. PANISH's data[11] for solid AgCl + NaCl are very scattered and must be considered merely as indicative. In fact, according to this author, "the upper critical solution temperature for the solid system (AgCl + NaCl) is between 400° and 500 °C". Figure 6 shows Panish's data with their deviations at 300 °C in comparison with the activities of AgCl as calculated on the basis of Eqs. (2), (3), (13). For the solid system AgBr + NaBr, the same figure reports Tsuji's data at 400 °C in comparison with those obtained through Eqs. (2), (3), (14). The agreement in this case is fairly good.

A further comparison can be made referring to the enthalpies of mixing measured by KLEPPA[1].

Kleppa's data can be represented by the following equations valid at 350 °C:

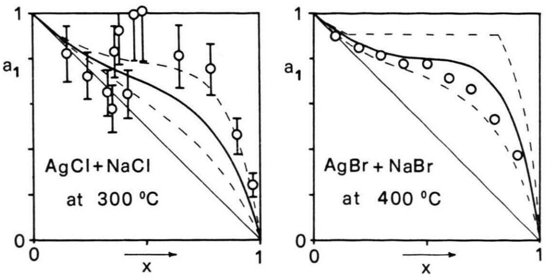

Fig. 6. Comparison between the activity data calculated from our A and B values (continuous line) and the experimental values reported in literature [11, 13] (circles). Dashed lines represent the limits given by the standard deviations of the temperature coefficients in Eqs. (13) and (14).

AgCl + NaCl :

$$\Delta H_\mathrm{m} = x(1-x)\,(2.50 + 0.41\,x)\ \text{kcal/mole},$$

AgBr + NaBr:

$$\Delta H_\mathrm{m} = x(1-x)\,(1.91 + 0.72\,x)\ \text{kcal/mole}.$$

The data derived from Eqs. (7), (13), (14) are:

AgCl + NaCl :

$$\Delta H_\mathrm{m} = x(1-x)\,[(2.6 \pm 0.6) + (0.1 \pm 0.1)\,x]\ \text{kcal/mole}, \tag{15}$$

AgBr + NaBr:

$$\Delta H_\mathrm{m} = x(1-x)\,[(1.85 \pm 0.4) + (0.05 \pm 0.1)\,x]\ \text{kcal/mole}. \tag{16}$$

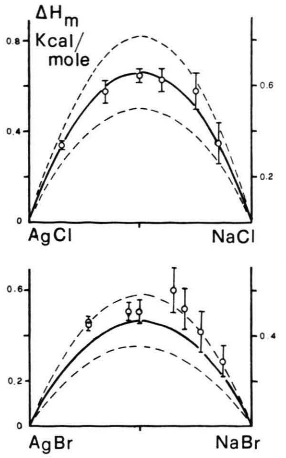

Fig. 7. Comparison between the enthalpy of mixing calculated from our A and B values (continuous line) and KLEPPA's [1] experimental values (circles). Dashed lines represent the limits given by the standard deviations.

Figure 7 compares Kleppa's data (circles with standard deviations) with ours obtained by Eqs. (15), (16). The dotted lines represent the limits provided by the standard deviations of the A_0 and B_0 parameters. It can be noted that in this case the agreement is highly satisfactory.

About Kleppa's prediction that the upper critical temperature should be lower in the AgBr + NaBr than in the AgCl + NaCl system a further comment can now be made. This prevision does not take into account the excess entropy terms, which instead, as it was already pointed out, are positive for AgCl + NaCl system, whilst they are zero or slightly negative for AgBr + NaBr. Thus, even though the enthalpy of mixing is larger in the AgCl + NaCl than in the AgBr + NaBr system, the correspondent upper critical temperatures, related to the free energy values, follow an inverse order.

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