

## Excess Volumes of Mixing in Liquid Binary Alkali Halide Mixtures

JAN LÜTZOW HOLM

*Institute of Inorganic Chemistry, The Technical University of Norway,  
N-7034 Trondheim-NTH, Norway*

Densities of liquid binary mixtures of the type  $(A^+ - B^+)X^-$ , common anion, and some mixtures of the type  $A^+(X^- - Y^-)$ , common cation, have been measured. Excess volumes

$$V^E = V_{\text{exp}} - (X_1 V_1^\circ + X_2 V_2^\circ)$$

where  $V^\circ$  is the molar volume and  $X_1$  and  $X_2$  the mol fractions, have been calculated from the density data. The calculated excess volumes are all *positive*.

If  $V^E/X_1 X_2$  is plotted *versus* the square of the conformational solution parameter  $\delta_{12}^2 = [(d_1 - d_2)/d_1 d_2]^2$ , the points will not fit a simple straight line, but will instead be gathered in a separate group for each of the mixtures  $(Li^+ - M^+)F^-$ ,  $(Li^+ - M^+)Cl^-$ ,  $(Li^+ - M^+)Br^-$ ,  $(Na^+ - M^+)F^-$ ,  $(Na^+ - M^+)Cl^-$ ,  $(Na^+ - M^+)Br^-$  and so forth, with the common component as a reference salt.

It is assumed that the excess volumes are due to contributions from dispersion interactions as considered by Davis and Rice in the so-called DR theory for mixtures of simple molten salts.

Of the various excess thermodynamic functions,  $G^E$ ,  $H^E$ ,  $S^E$  and  $V^E$  for the mixing process in molten salts, the excess volume  $V^E$  is the most neglected and therefore the least understood. For example, while extensive investigations of the enthalpies of mixing of binary mixtures formed by the alkali nitrates<sup>1</sup> and alkali halides<sup>2-4</sup> have been carried out, only few have been dealing with the volume of mixing. Here the work has only been devoted to mixtures of nitrates.<sup>5,6</sup> Volumes of mixing of the alkali halides have not been measured before.

Powers *et al.*,<sup>5</sup> in their analysis of the excess volumes in fused mixtures of the alkali nitrates  $(Na^+ - Li^+)NO_3^-$ ,  $(Na^+ - K^+)NO_3^-$ ,  $(Na^+ - Rb^+)NO_3^-$  and  $(Na^+ - Cs^+)NO_3^-$ , found that their data varied with the fourth power of the difference in diameter. According to the theory as shown by Davis and McDonald,<sup>7</sup> the excess volume should vary with the *square* of the difference in the ionic diameters of the component salts. The main goal of the present investigation was to clarify some of the rather contradictory results mentioned above.

As mentioned in an earlier publication by Grjotheim *et al.*<sup>8</sup> a number of methods have been suggested for determination of densities in molten salts. The method used in the present investigation, the hydrostatic weighing method, is a very simple one, but is quite reliable, giving densities with an accuracy of 0.2–0.4 % or better in the temperature range 750–1000°C.

### THEORETICAL CONSIDERATIONS

The Gibbs free energy of an ideal solution is given by the eqn.

$$G^M = RT X_1 \ln X_1 + RT X_2 \ln X_2 \quad (1)$$

where  $X_1$  and  $X_2$  are the mol fractions of the two components in the mixture. The enthalpy of mixing is zero, since

$$-\frac{H^M}{T^2} = \frac{\delta(G^M/T)}{\delta T} = 0 \quad (2)$$

Furthermore, if we consider the volume of mixing,  $V^M$ , *i.e.* the change in the volume of the system upon mixing, we find that this is zero for ideal solutions. This follows from

$$V^M = \delta G^M / \delta P = 0 \quad (3)$$

The volume of an ideal solution is equal to the volume occupied by  $n_1$  mol of component 1 and  $n_2$  mol of component 2 taken separately at temperature  $T$  and pressure  $P$ . Hence the process of mixing is accompanied by neither an expansion nor a contraction, according to

$$V_{id} = X_1 V_1^\circ + X_2 V_2^\circ \quad (4)$$

The excess volume is then given by the difference between the observed volume  $V$  and the ideal volume

$$V^E = V - (X_1 V_1^\circ + X_2 V_2^\circ) \quad (5)$$

where  $V_1^\circ$  and  $V_2^\circ$  are the molar volumes of the pure liquids at the same temperature and pressure.

### EXPERIMENTAL

#### 1. Method

The thermo-balance used for the density experiments has been described in a previous paper.<sup>8</sup> The experiments were carried out in an atmosphere of dry nitrogen gas, after the system had been evacuated to about  $10^{-4}$  torr for some time. The temperature gradients around the crucible were less than 0.1°C/cm. Corrections were applied for buoyancy in air or nitrogen and for the surface tension effect on the suspension wire of the sinker.<sup>9</sup> After each experiment the suspension wire was inspected and weighed, to eliminate possible errors due to condensation of vapours on the wire. The volume of the sinker was determined by immersing it in distilled water at room temperature. The volume of the sinker in the temperature range 600°C to 900°C was calculated from the thermal expansion data of Pt–Rh alloys given by Barter and Darling.<sup>10</sup>

## 2. Chemicals

LiF	Baker & Adamson, USA, <i>p.a.</i>
NaF	Merck, Germany, <i>p.a.</i>
KF	Merck, Germany, <i>p.a.</i> 99 %
RbF	» » E.L. quality
LiCl	Baker analyzed, Noury-Baker, Deventer, Holland, 99.8 %
NaCl	» » » » 99.6 %
KCl	Merck, Germany, <i>p.a.</i> 99.5 %
RbCl	» » » 99.5 %
CsCl	» » » 99.5 %
LiBr	Anhydr. Matheson, Coleman & Bell, USA, 99.0 %
NaBr	Baker analyzed, Noury-Baker, Deventer, Holland, 99.4 %
KBr	Merck, Germany, <i>p.a.</i>
RbBr	» » suprapur
CsBr	» » »

The chemicals were dried at about 400–500°C under moderate vacuum (0.1–0.01 torr) and then melted in a platinum crucible in an atmosphere of purified N<sub>2</sub>. Only clear crystals were selected from the samples. It has been shown that by this treatment one obtains very pure crystals even from highly hygroscopic materials. The method was used by Holm and Kleppa<sup>3</sup> to purify fluorides. They obtained fluorides of the following purities: 99.12 ± 0.10 % KF, 99.74 ± 0.10 % RbF and 99.7 ± 0.1 % CsF. The lithium chloride was in addition purified by dehydration at about 400°C in a hydrogen chloride atmosphere.

Table 1. Molar volumes  $V^E$  in cm<sup>3</sup>/mol for molten alkali halides.

Compounds	Temp. °C	This work	Literature <sup>8</sup>
LiF	900	14.48	
LiCl	800	29.75	29.64
LiBr	800	36.41	
NaF	900	20.72	
NaCl	800		37.46
NaBr	800	44.91	
KF	900	30.87	
KCl	800		49.21
KBr	800	57.38	
RbF	900	36.48	
RbCl	800		55.57
RbBr	800	63.90	
CsCl	800	64.15	
CsBr	800	72.41	

## RESULTS

The molar volumes of the pure fused alkali halides as they have been determined in this work are given in Table 1.

Some typical  $V^E$ -composition diagrams for cation mixtures are shown in Figs. 1–6.

The estimated uncertainties in  $V^E$  are of the order ± 0.05 cm<sup>3</sup>. Excess volumes for some anion mixtures are given in Table 2.

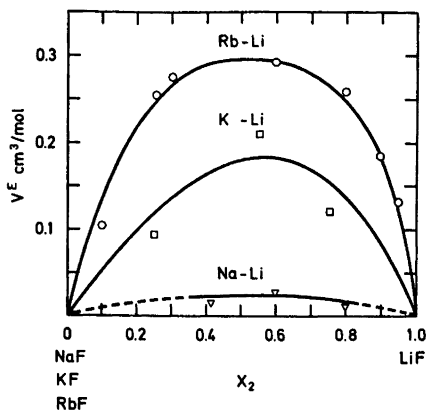


Fig. 1. Excess molar volumes of mixing ( $V^E$ ) at 900°C in some liquid mixtures of lithium fluoride with alkali fluorides.

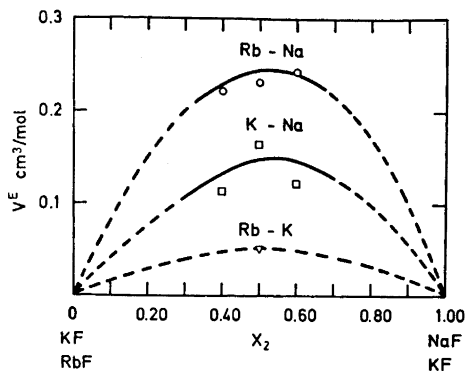


Fig. 2. Excess molar volumes of mixing ( $V^E$ ) at 900°C in some liquid mixtures of alkali fluorides.

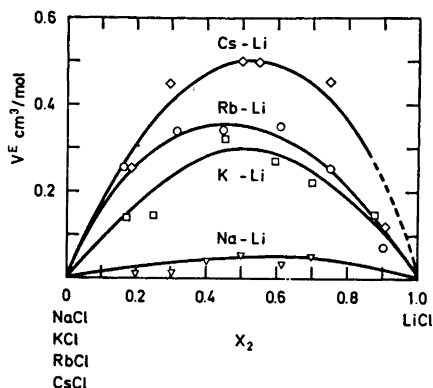


Fig. 3. Excess molar volumes of mixing ( $V^E$ ) at 800°C in some liquid mixtures of lithium chloride with alkali chlorides.

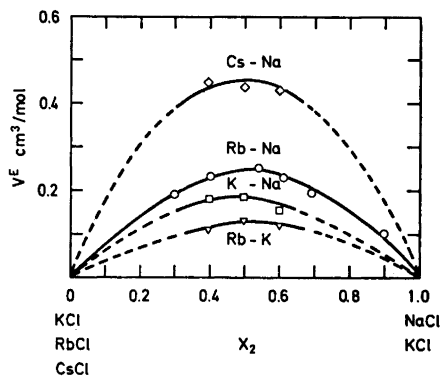


Fig. 4. Excess molar volumes of mixing ( $V^E$ ) at 800°C in some liquid mixtures of alkali chlorides.

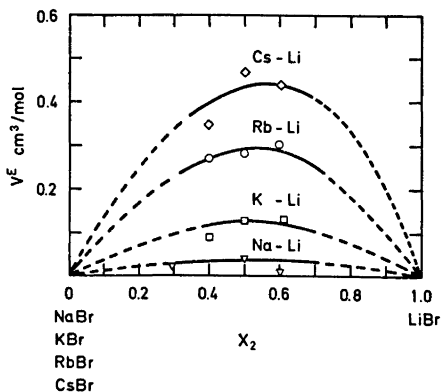


Fig. 5. Excess molar volumes of mixing ( $V^E$ ) at 800°C in some liquid mixtures of lithium bromide with alkali bromides.

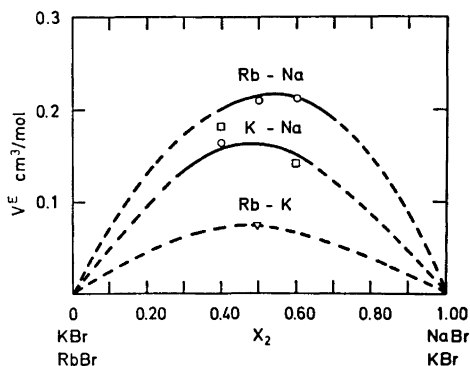


Fig. 6. Excess molar volumes of mixing ( $V^E$ ) at 800°C in some liquid mixtures of alkali bromides.

Table 2. Excess volumes in cm<sup>3</sup> for equimolar common cation mixtures at 800°C.

Anion system	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>
F <sup>-</sup> - Cl <sup>-</sup>	0.31	0.48	0.58	0.30
Cl <sup>-</sup> - Br <sup>-</sup>	0.10	0.06	0.11	

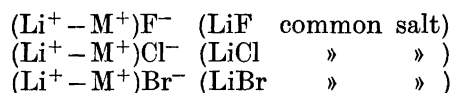
## DISCUSSION

In Fig. 7 is presented a plot of  $V^E/X(1-X)$  at the 50:50 composition *versus* the square of the conformal solution parameter for ionic mixtures,  $\delta_{12}^2$ , where  $\delta_{12}$  is given by

$$\delta_{12} = \frac{d_1 - d_2}{d_1 d_2}$$

and  $d_1$  and  $d_2$  are the sums of cation and anion radii in the pure salts.

As can be seen the mixtures are divided into groups of the type



and so forth.

An explanation of this important observation will be given in the following.

In the perturbation theory for the thermodynamic properties of molten salts by Davis and Rice,<sup>12</sup> the so-called DR theory, the following expression for the enthalpy of mixing is valid for AX - BX mixtures of the type considered

$$\Delta H^M = X_1 X_2 (U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2) \quad (6)$$

with  $U_2 = U_2' + U_2''$

The unevaluated coefficients  $U_0$ ,  $U_1$ , *etc.*, can be described qualitatively in terms of the interactions on which they depend as follows:

$U_0$ . This quantity is determined largely by the change in the dispersion interaction between next-nearest-neighbour cations when the mixture is formed.

$U_1$ ,  $U_2'$ ,  $U_2''$ . These coefficients all include a term which arises from the difference in cation-anion dispersion interaction in the two pure components and in the mixture. In addition  $U_1$  depends on the interaction between next-nearest neighbour cations in the mixture and in the pure components. The term  $U_2''$  is largely of Coulombic origin. It is principally represented by the coefficient  $\Omega(T, P)$  of the Reiss, Katz and Kleppa (RKK) theory,<sup>11</sup> but includes also contributions from nearest-neighbour anion-cation dispersion interactions. These terms also contribute to the  $U_2'$  term.

It was emphasized by Davis and Rice<sup>12</sup> that eqn. (6) can be used for *the comparison of a set of binary systems with a common component, which is then considered as the reference salt*. For ions without dispersion interactions (induced dipole-ion, induced dipole-induced dipole, *etc.*) eqn. (6) reduces to the simple expression given by the RKK-theory<sup>11</sup>

$$\Delta H^M = X_1 X_2 \delta_{12} \Omega(T, P) \quad (7)$$

Here  $\Omega(T, P)$  is an unevaluated integral which is a negative function of temperature and pressure.

This term, which is a sum of complicated integrals and is independent of the perturbation potential, takes into consideration the Coulomb interactions and short range repulsions between the ions only. The term is independent of the choice of reference salt and has been used to compare charge-symmetrical binaries with completely ionized components like the alkali nitrates<sup>1</sup> at a given temperature and pressure.

(a) *Common cation mixtures, AX - AY.* These mixtures are the most simple of all ionic mixtures. Generally very small positive excess Gibbs free energies or enthalpies of mixing are found in these systems.<sup>15,16</sup> Since both the excess enthalpy and the excess volume are positive, one may attribute the observed positive enthalpy of mixing in these systems to the observed expansion in volume of mixing. Such volume or packing effects were indeed anticipated several years ago by Flood.<sup>13</sup>

If for instance there is a lengthening ( $\Delta_1$ ) of one of the cation-anion distances ( $d_1$ ) due to the difference in the cation-anion dispersion interaction in the two pure components and in the mixture, one easily sees<sup>14</sup> that the excess volume,  $V^E$ , will be positive and proportional to

$$V^E \sim \Delta_1^3 + 3d_1 \Delta_1 (d_1 + \Delta_1) \quad (8)$$

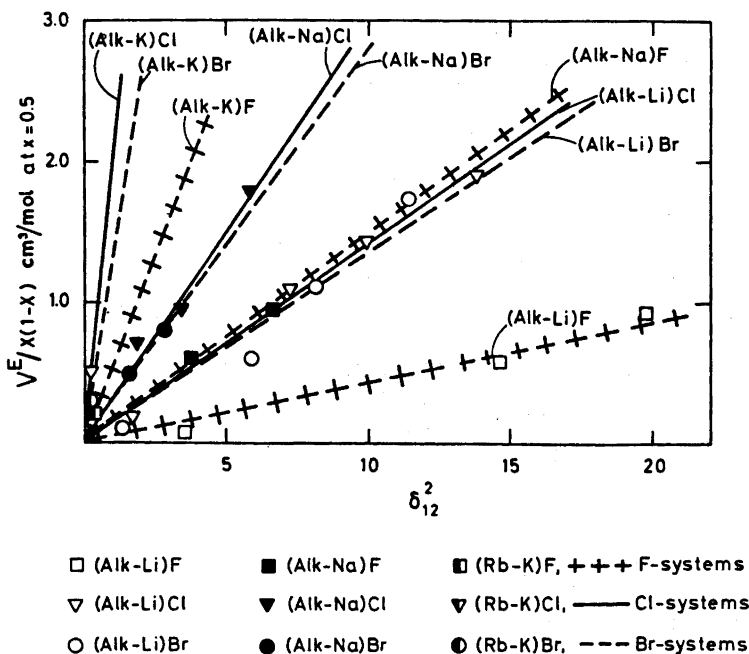


Fig. 7. Plots of  $V^E/X(1-X)$  at the 50:50 composition vs.  $\delta_{12}^2$  for binary mixtures of alkali halides.

(b) *Common anion mixtures, AX-BX.* From the observed correlation between  $V^E$  and  $\delta_{12}^2$  (Fig. 7) one may postulate:

For all mixtures of the common anion type considered, an additional term which arises from the difference in cation-anion dispersion interaction in the two pure components and in the mixture has to be taken into consideration. This term which is included in the  $U_2$ -term in the theoretical expression by Davis and Rice<sup>12</sup> (eqn. (6)  $U_2 = U_2' + U_2''$ ), is proportional to  $\delta_{12}^2$  and gives a positive contribution to the total enthalpy of mixing. This effect is similar to the one observed in the common cation mixtures. However, contrary to the AX-AY mixtures, the positive enthalpy contribution which is due to the expansion in volume, will in most cases be overwhelmed by the large negative enthalpy of mixing due to the contribution from the changes in the Coulomb next-nearest neighbour interaction. However, the volume or dispersion interaction effect clearly shows up in mixtures of large cations, like  $(K^+ - Rb^+)X^-$ ,  $(Rb^+ - Cs^+)X^-$  where the negative Coulomb contribution to  $U_2$  is small. Positive enthalpies of mixing are found in some of the fluoride mixtures<sup>3</sup> as well as in some mixtures of alkali chlorides and bromides.<sup>2</sup>

*Acknowledgement.* Thanks are expressed to Mr. Bjørn Berge for carrying out the experimental part of the work and to Professor Kai Grjotheim for laboratory facilities. Financial support from the *Royal Norwegian Council for Scientific Research* and from *Norges Tekniske Høgskoles Fond* is gratefully acknowledged.

#### REFERENCES

1. Kleppa, O. J. and Hersh, L. S. *J. Chem. Phys.* **34** (1961) 351.
2. Kleppa, O. J. and Hersh, L. S. *J. Chem. Phys.* **42** (1965) 1309.
3. Holm, J. L. and Kleppa, O. J. *J. Chem. Phys.* **49** (1968) 2425.
4. Melnichak, M. E. and Kleppa, O. J. *J. Chem. Phys.* **52** (1970) 1970.
5. Powers, B. F., Katz, J. L. and Kleppa, O. J. *J. Phys. Chem.* **66** (1962) 103.
6. Cleaver, B. and Neil, B. C. *J. Trans. Faraday Soc.* **65** (1969) 2861.
7. Davis, H. T. and McDonald, J. *J. Chem. Phys.* **48** (1968) 1644.
8. Grjotheim, K., Holm, J. L., Lillebuen, B. and Øye, H. A. *Trans. Faraday Soc.* **67** (1971) 640.
9. Bloom, H., Boyd, P. W. D., Laver, J. L. and Wong, J. *Australian J. Chem.* **19** (1966) 138.
10. Barter, B. and Darling, A. S. *Platinum Metals Rev.* **4** (1960) 138.
11. Reiss, H., Katz, J. L. and Kleppa, O. J. *J. Chem. Phys.* **36** (1962) 144.
12. Davis, H. T. and Rice, S. A. *J. Chem. Phys.* **41** (1964) 14.
13. Flood, H. *Discussions Faraday Soc.* **32** (1961) 168.
14. Holm, J. L. *Thermodynamic Properties of Molten Cryolite and Other Fluoride Mixtures*, Thesis, Institute of Inorganic Chemistry, The University of Trondheim, NTH, Norway, Nov. 1971.
15. Toguri, J., Flood, H. and Førland, T. *Acta Chem. Scand.* **17** (1963) 1502.
16. Grjotheim, K., Halvorsen, T. and Holm, J. L. *Acta Chem. Scand.* **21** (1967) 2300.

Received February 25, 1971.