

Surface Tension in Alkali Halide Mixtures

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The surface tension in binary molten mixtures of NaF—NaCl, NaF—NaBr, and NaCl—NaBr was measured by the pin detachment method.

The surface tension isotherm of each system at 900 °C was compared to isotherms calculated by applying an equation derived by Guggenheim for ideal mixtures and two modified forms of this equation as well as a model proposed by Eberhart. The observed values were represented within 1 % by the Eberhart model, while the values predicted by the other equations were found to be as much as 27 and 10 % too high, respectively.

As part of a general study of the physico-chemical properties of molten binary alkali halide systems, surface tension measurements were carried out in NaF—NaCl, NaF—NaBr, and NaCl—NaBr.

The pin detachment method, which has been shown to be an absolute method¹ was combined with density measurements² using a Pt-10 % Rh sinker. The sinker was attached to a thermobalance³ at the top of the furnace by means of a thin Pt-wire (diameter 0.2 mm).

Equating the detachment force of the pin, ΔW , to the weight of the liquid being lifted above the surface plane by the pin prior to its detachment from the melt surface, the surface tension was calculated by expressing ΔW as a function of the surface tension, the pin radius and the density of the bulk liquid, using a general Laplace equation for a liquid surface around a vertical rod.¹

EXPERIMENTAL

The furnace and thermobalance together with the vacuum system of the apparatus applied have been described in detail elsewhere.^{3,4}

The salts used (Baker Anal. 99.3 % NaF, 99.8 % NaCl, and 99.8 % NaBr, J. T. Baker, Holland) were dried under vacuum and recrystallized from the molten state in a nitrogen atmosphere. To ensure homogeneous mixtures, the weighed portion of the salts were melted in a closed Pt-crucible and were then finely crushed prior to each experiment.

Having inserted the salt to be investigated in a Pt- or vitreous carbon crucible in the furnace, the furnace was evacuated to $\sim 10^{-4}$ Torr and N₂-gas fed in to give a small overpressure (the N₂-gas rate being 0.2 l/h).

The crucible was raised or lowered relative to the sinker by means of a reversible DC-motor connected to a gear box from which an extended shaft drove the furnace up or down at a continuously adjustable speed of 0–1 cm/min.

On lifting the furnace until contact between the pin and the melt surface, a sudden increase of the recorded weight of the sinker was observed. By slowly lowering the furnace from this position, the recorded weight passed through a well-defined maximum before a reproducible minimum corresponding to the weight of the sinker in nitrogen atmosphere was attained. Weight changes were read to ± 0.1 mg. The recorded detachment weight, ΔW , ranged between 60 and 100 mg depending on the surface tension of the system investigated. The measurement of ΔW was repeated four times at each temperature. With few exceptions the values obtained corresponded within the accuracy of the recorder.

RESULTS

The surface tensions measured at different temperatures were fitted to the linear function

$$\gamma = \gamma_0 - \beta(t - t_0) \quad (1)$$

where γ and γ_0 are the surface tensions at temperature t and t_0 , respectively, and β the temperature coefficient (Table 1). The experimental standard deviation in γ is denoted σ_γ .

Table 1. Surface tension α in alkali halide systems. $\gamma = \gamma_0 - \beta(t - t_0)$ (N m^{-1}).

System	Mol fraction	t_0	$\gamma_0 \times 10^3$ N m^{-1}	$\beta \times 10^6$ $\text{N m}^{-1} \text{ degree}^{-1}$	σ_γ %	Temp. range $^\circ\text{C}$
NaCl - NaF	X_{NaF}					
	0.00	800	115.7	69	0.3	839 - 912
	0.25	800	123.4	94	0.9	719 - 857
	0.50	800	132.8	78	0.1	806 - 896
	0.75	900	141.1	81	0.1	918 - 943
	1.00	1000	187.6	100	0.1	996 - 1052
NaBr - NaF	0.00	800	99.9	71	0.1	753 - 828
	0.25	800	106.2	64	0.1	701 - 849
	0.50	800	116.4	89	0.3	814 - 893
	0.75	900	128.4	54	0.1	915 - 949
NaBr - NaCl	X_{NaCl}					
	0.25	800	101.5	67	0.3	770 - 857
	0.35	800	102.5	66	0.3	747 - 812
	0.50	800	105.6	71	0.2	771 - 891
	0.60	800	107.4	72	0.1	715 - 805
	0.75	800	109.8	68	0.1	807 - 889
	0.85	800	113.2	85	0.2	783 - 839

α The isothermal surface tension is plotted *versus* the bulk mol fraction for each system in Fig. 1.

DISCUSSION

According to Guggenheim,⁵ the following expression applies to the surface tension, γ , of an ideal solution of two components 1 and 2, with molar fractions X_1 and X_2 and a surface area per mol a :

$$\exp(-\gamma a/RT) = X_1 \exp(-\gamma_1 a/RT) + X_2 \exp(-\gamma_2 a/RT) \quad (2)$$

Usually the value of a is calculated by assuming equal packing density in the surface and the bulk phase. But this approach may seem somewhat crude in terms of ionic interactions. However, in binary and ternary alkali earth chloride mixtures,⁶ and in binary alkali halide systems⁷ the equation has been found to give reasonable estimates when mol fractions are replaced by volume fractions, ϕ :

$$\exp(-\gamma A/RT) = \phi_1 \exp(-\gamma_1 A/RT) + \phi_2 \exp(-\gamma_2 A/RT) \quad (3)$$

$$\phi_1 = \frac{V_1 X_1}{V_1 X_1 + V_2 X_2}$$

$$\phi_2 = 1 - \phi_1$$

$$A = [\phi_1 V_1 + \phi_2 V_2]^{2/3}$$

where A is taken to be the surface area per mol anion-cation pair, and V is the molar volume.

Assuming the molar surface area, A_i , for each component in a mixture to be the same as for the pure state:

$$A_i = \left[\frac{M_i}{\rho_i} \right]^{2/3}$$

where M_i is the molar weight and ρ_i the density of the component i , a second modification of eqn. (2) may be written:

$$\exp(-\gamma A/RT) = \phi_1 \exp(-\gamma_1 A_1/RT) + \phi_2 \exp(-\gamma_2 A_2/RT) \quad (4)$$

In a different approach Eberhart⁸ assumed the surface tension to be a linear function of the surface mol fraction, X_1^s , defined in terms of experimental parameters by the equations:

$$\gamma = X_1^s \gamma_1 + X_2^s \gamma_2 \quad (5a)$$

$$X_1^s + X_2^s = 1 \quad (5b)$$

Assuming equilibrium between the bulk and surface phase, a concentration independent enrichment factor, S_{12} , is defined by

$$S_{12} = (f_1^s X_1^s / f_1^b X_1^b) / (f_2^s X_2^s / f_2^b X_2^b) \quad (6)$$

where f is the activity coefficient and the superscript τ , as before, denotes the surface phase.

Setting the activity coefficient ratios in eqn. (6) equal to unity

$$S_{12} = (X_1^\tau/X_2^\tau)(X_1X_2) \quad (7)$$

Combining eqns. (5) and (7)

$$\gamma = \frac{S_{12}X_1\gamma_1 + X_2\gamma_2}{S_{12}X_1 + X_2} \quad (8a)$$

or rearranged:

$$S_{12} = (X_2/X_1)[(\gamma_2 - \gamma)/(\gamma - \gamma_1)] \quad (8b)$$

The assumed temperature independent factor, S_{12} , can be determined from eqn. (8a) by a least squares fitting procedure or by testing the linearity of the rearranged eqn. (8b):³

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = -S_{12} \frac{X_1}{X_2} \left[\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} \right] + 1 \quad (9)$$

Another consequence of the model is that if we have determined this enrichment factor experimentally for a mixture of components 1 and 2, S_{12} , and of components 2 and 3, S_{23} , then according to eqn. (7):

$$S_{13} = S_{12}S_{23} \quad (10)$$

Fig. 1 gives the experimental surface tension compared with the Guggenheim model, eqn. (2), the modified Guggenheim model, eqn. (3), and the Eberhart model, eqn. (8a). The model corresponding to eqn. (4) gives essentially the same results as eqn. (3). The enrichment factors, S_{ij} , are calculated from a least square fit of eqn. (8a) and are given in the second column of Table 2.

Eqns. (2) and (3) which in principle contain no adjustable parameters do predict the direction of the deviation from additivity, but tend

Table 2. Enrichment factor and standard deviation in fit of γ at 900 °C.

System	S_{ij}	σ_γ , %	S_{ij}
i j	Eqn. (8b)		Eqn. (10)
NaCl-NaF	5.05 ± 0.25	0.97	3.14
NaBr-NaF	5.84 ± 0.17	1.03	9.39
NaBr-NaCl	1.86 ± 0.60	0.36	1.16

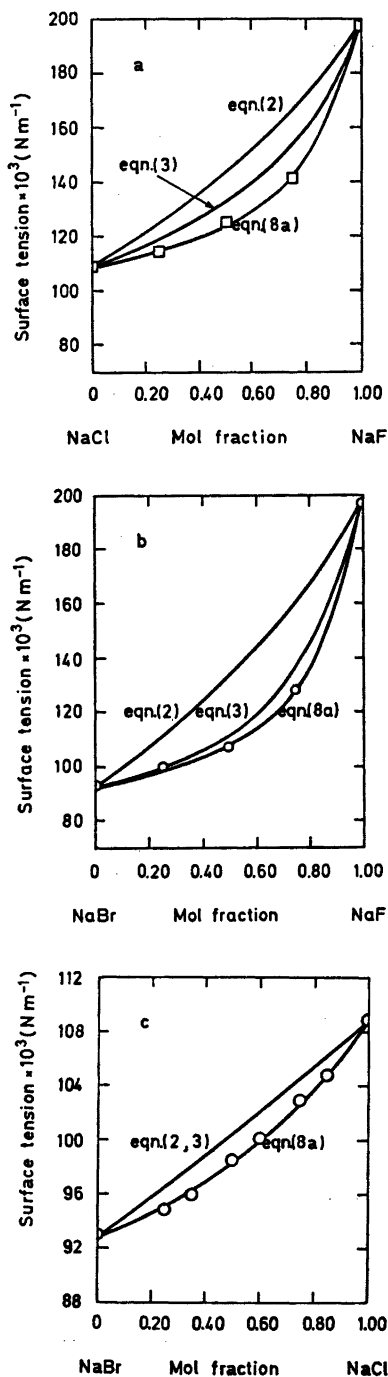


Fig. 1. Surface tension of sodium halide mixtures at 900 °C, compared with models according to eqn. (2), eqn. (3) and eqn. (8a). (a) NaCl-NaF; (b) NaBr-NaF; (c) NaBr-NaCl.

to underestimate it, although eqn. (3) gives a significant improvement over eqn. (2). This is probably because the volume fractions are more directly related to the packing efficiency of each species than the molar fractions.

The Eberhart model which introduces the parameter S_{ij} is seen to give a very satisfactory fit of the experimental surface tension values, the standard deviation being 0.4–1 % (Table 2) and hence of the same order of magnitude as the experimental standard deviation (Table 1).

The test of consistency according to eqn. (10) is, however, not satisfactory (Table 2, last column) but it should be stressed that S_{ij} is very sensitive towards small errors in the measured surface tension, especially in systems like NaBr–NaCl where differences between almost equal numbers enter the calculation of S_{ij} according to eqn. (8b).

In conclusion the Eberhart model seems to be acceptable for representing the surface tension of the investigated binary molten mixtures, and is able to accommodate larger deviations from additivity than the Guggenheim models. The neglect of the activity coefficients, however, limits the Eberhart model to systems with medium chemical interactions and it may not be suitable for such strongly interacting systems as, for instance the $MgCl_2$ –AlkCl systems.⁶ The reported good fit⁶ to eqn. (10) is not found, but a larger quantity of material is needed to draw possible chemical conclusions from these deviations.⁶

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REFERENCES

1. Lillebuen, B. *Acta Chem. Scand.* 24 (1970) 3287.
2. Grjotheim, K., Naterstad, T. and Øye, H. A. *To be published.*
3. Bratland, D., Grjotheim, K., Krohn, C. and Motzfeldt, K. *Acta Chem. Scand.* 20 (1966) 1811.
4. Grjotheim, K., Lillebuen, B. and Øye, H. A. *Trans. Faraday Soc.* 67 (1971) 640.
5. Guggenheim, E. A. *Mixtures*, Oxford at the Clarendon Press, London 1952, p. 181.
6. Grjotheim, K., Holm, J. L., Lillebuen, B. and Øye, H. A. *Acta Chem. Scand.* 26 (1972) 2050.
7. Berge, B. and Holm, J. L. *Rapport til Norges Tekniske Høgskoles Fond*, NTH, Trondheim 1970.
8. Eberhart, J. G. *J. Phys. Chem.* 70 (1966) 1183.
9. Guggenheim, E. A. *Thermodynamics*, 5th Ed., North-Holland, Amsterdam 1967, p. 207–213.

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