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Surface Tension in the Ternary System NaF—NaCl—NaBr

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The surface tension in the ternary molten mixture of NaF – NaCl – NaBr has been measured by the pin detachment method. The surface tension isotherms at 900 °C were compared to isotherms calculated by applying an equation derived by Guggenheim for binary mixtures and here extended to ternary systems. Using volume fractions instead of mol fractions as concentration measure in the model equations gave better correlation with the experimental data. An equation derived on the basis of Eberhart model applying enrichment factors obtained from the corresponding binary systems gave satisfactory agreement between observed and calculated data.

The surface tension was measured in the ternary system NaF – NaCl – NaBr. The surface tension of the corresponding binary systems was measured in a previous study.[1] The measurements were carried out by the pin detachment method which, besides being an absolute method, also provides simultaneous determination of the densities of the salts. The measurement of the densities of salts has been reported in a separate publication.[2] The theory of the method has been described previously.[3] It employs measurement of the force required for separation of a pin of known diameter from the surface of the melt. The force is measured as the difference in weight of the pin, and it is related to the density of the liquid and its surface tension through the Laplace equation for describing a liquid surface around a vertical rod.

EXPERIMENTAL

All salts used were reagent grade, additionally purified by vacuum drying and recrystallization in dry nitrogen atmosphere. Materials were premelted in platinum crucibles in nitrogen atmosphere and recrushed prior to the experiment, in order to ensure homogeneity. Handling and storing of the purified salts were done in glove boxes in which moisture content was kept below 5 ppm.

Measurements were made in dry nitrogen atmosphere, using a Pt 10 % Rh alloy sinker, the lower part of which was machined in the form of a pin with a diameter of 1.978 mm at room temperature. The sinker was suspended from the thermobalance by by a thin (0.2 mm) Pt wire. The furnace and the electrical recording thermobalance were described in detail previously.[4] The furnace with crucible could be moved relative to the thermobalance at desired rates by an electromotor. Contact of the pin with the surface of the melt was marked by the sudden increase of the pin weight. By subsequently raising the pin from the liquid a well-defined maximum of its weight could be observed, prior to the return to the same weight as before the contact. The weight changes ranged from 65 to 90 mg, depending on the surface tension of the melts, and individual recordings were reproducible to within 0.2 mg. Calculations of the surface tensions and the least-squares fitting of their temperature dependence were done by a computer program.

The accuracy of the apparatus was checked by measuring the surface tension of pure NaCl, and these results agreed with literature data within ±0.5 %.

RESULTS

The observed surface tensions of all measured mixtures showed linear temperature dependence within the experimental temperature ranges, and they could be represented by the equation:

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Table 1. The surface tension, γ_0, at 900 °C in the ternary system NaF – NaCl – NaBr. β = temperature coefficient of the surface tension. σ_γ = experimental standard deviation in γ.

Mol fraction NaF	NaCl	NaBr	$\gamma_0 \times 10^3$ N m^{-1}	$\times 10^6$ N m^{-1} °C^{-1}	σ_γ %	Temperature range (°C)
0.6	0.2	0.2	119.7	−57.8	0.54	938 – 1045
0.2	0.6	0.2	108.5	−58.9	0.26	751 – 873
0.4	0.4	0.2	110.0	−74.9	0.17	840 – 902
0.2	0.4	0.4	102.2	−68.0	0.10	781 – 885
0.4	0.2	0.4	108.4	−65.0	0.16	775 – 904
0.2	0.2	0.6	99.5	−67.5	0.06	760 – 885

$$\gamma = \gamma_0 + \beta(t - t_0)$$

where γ and γ_0 are surface tensions at temperatures t and t_0, respectively, and β is the temperature coefficient. The results are summarized in Table 1.

In Fig. 1, the data on the relevant binary systems reported previously[1] have been included along with the data from the present work. Curves were not drawn through the points in the system NaF – NaBr, for the sake of clarity of the figure.

DISCUSSION

For all systems in which the surface tension has been measured, negative deviations from additivity have been observed. To predict the surface tension in binary systems, Guggenheim[5] has derived an equation of the form:

$$\exp(\gamma a/kT) = x_1 \exp(\gamma_1 a/kT) + x_2 \exp(\gamma_2 a/kT) \quad (1)$$

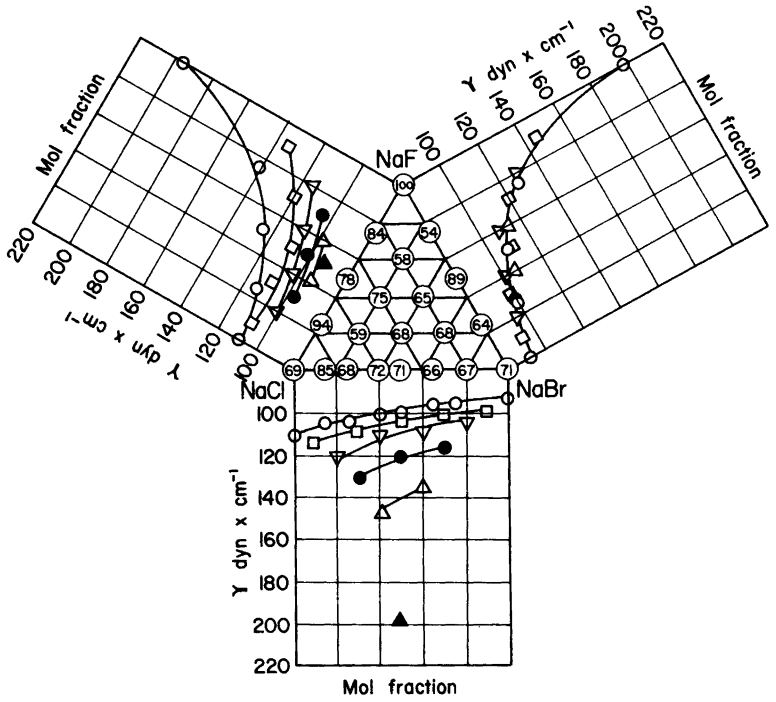

Fig. 1. The changes of the surface tensions with composition in theternary system NaF – NaCl – NaBr at 900 °C. ○, Binary system; One component in the ternary system with constant mol % composition; □, 20 mol %; △, 40 mol %, ●, 60 mol %; ▽, 80 mol %; ▼, pure one component system.

where x_1 and x_2 are the mol fractions, a is the area per molecule defined as: $a=(V/N)^{2/3}$, V is the molar volume and N is Avogardros number. It has been shown[2] that experimental data in ionic melts are better represented by an equation where mol fractions are replaced by the volume fractions

$$\psi_i = \frac{x_i V_i}{\sum x_i V_i}$$

$$\exp(\gamma a/kT) = \psi_i \exp(\gamma_1 a_1/kT) + \psi_2 \exp(\gamma_2 a_2/kT) \quad (2)$$

It has been assumed in this work that the same type of additive relation can be expected in ternary system, and that the surface tension of the ternary compositions can be predicted by equations of the type:

$$\exp(\gamma a/kT) = \sum_{i=1}^{3} x_i \exp(\gamma_i a_i/kT) \quad (3)$$

and

$$\exp(\gamma a/kT) = \sum_{i=1}^{3} \psi_i \exp(\gamma_i a_i/kT) \quad (4)$$

where a_i refers to pure salts, and a refers to an average surface area per molecule in the mixture. This modification was introduced because the original equation was derived for liquid mixture where sizes were not too different. Surface area per molecule refers here to an anion-cation pair. The values of the surface tension predicted by these two formulas (3) and (4) are shown in columns 2 and 3 of Table 2 as $\gamma_{(3)}$ and $\gamma_{(4)}$. The first column of Table 2 gives experimental results, while the others show values calculated by different models. Second last line in this table shows the average of the deviation calculated from experimental results, while the last line gives their standard deviations. Both of the eqns. (3) and (4) give too high results, but it is seen that eqn. (4) gives a much better fit to the experimental results than eqn. (3).

In order to obtain better agreement with the experimental results a correction factor, based on the data of the corresponding binary systems has been introduced[3] to obtain equations of the following form:

$$\gamma = (-kT/a) \ln \sum_{i=1}^{3} x_i \exp(\gamma_i a_i/kT) + \sum_{j=2}^{3} \sum_{i=1}^{j=1} N_i N_i \lambda_{ij}^1 \quad (5)$$

and

$$\gamma = (-kT/a) \ln \sum_{i=1}^{3} x_i \exp(\gamma_i a_i/kT) + \sum_{j=1}^{3} \sum_{i=1}^{j-1} N_i N_j \lambda_{ij}^1 \quad (6)$$

where N_i and N_j are the mol fractions of the components i and j of the ternary mixture and λ_{ij} is the interaction parameter, the other terms having their previous meaning. The interaction parameter is defined as: $\lambda_{ij}^1 = \gamma_{ij}^{E1}/x_i x_j$; γ_{ij}^{E1} is the excess surface tension calculated from eqn. (1), and the terms with subscript 2 refer to eqn. (2). Results obtained by these two equations are shown in columns 4 and 5 of Table 2 as $\gamma(5)$ and $\gamma(6)$. Eqn. (5) tends to over-correct

Table 2. Comparison of the experimentally obtained surface tensions, γ_{exp}, with values calculated from different models. The first four sets of data calculated with mol fractions and volume fractions, respectively. $\gamma(3)$ and $\gamma(4)$ values calculated by use of the extended Guggenheim formula. $\gamma(5)$ and $\gamma(6)$ values calculated by use of the corrected Guggenheim formula. γ_F, γ_{Cl} and γ_{Br} values calculated by use of the extended Eberhart model using the three possible combinations of the reported binary enrichment factors.

γ_{exp}	$\gamma_{(3)}$	$\gamma_{(4)}$	$\gamma_{(5)}$	$\gamma_{(6)}$	γ_F	γ_{Cl}	γ_{Br}
119.8	144.6	126.3	124.1	121.1	121.2	123.2	115.5
108.5	116.0	109.4	112.0	106.7	108.6	108.5	106.4
110.0	129.1	116.4	108.7	112.0	113.5	114.8	110.1
102.2	112.2	105.1	97.7	102.5	104.5	103.6	101.7
108.4	124.6	110.6	103.6	107.2	108.3	108.2	104.0
99.5	108.6	101.4	94.1	99.4	100.7	100.0	98.2
Average deviation	14.45	3.54	−1.37	0.12	1.4	1.65	−2.08
Average abs. deviation	14.45	3.52	3.98	1.15	1.43	1.72	2.12

eqn. (3), while agreement of eqn. (6) and the experimental results are very satisfactory.

In his treatment of surface tensions of binary mixtures Eberhart [5] assumed that the surface tension is a linear function of the surface phase mol fractions, x_i, superscript τ denoting surface phase quantities, giving:

$$\gamma = \gamma_1 x_1^\tau + \gamma_2 x_2^\tau$$

Eberhart defined a surface enrichment factor, S, as:

$$S_{12} = \frac{a_1^\tau / a_2^\tau}{a_1/a_2} = \left(\frac{f_1^\tau / f_2^\tau}{f_1/f_2}\right)\left(\frac{x_1^\tau / x_2^\tau}{x_1/x_2}\right)$$

Here a_i is the chemical activity of component i and f_i is the corresponding activity coefficient.

Using the relation $x_1 + x_2 = 1$, Eberhart derived an equation for the surface tension of the binary mixtures of the form:

$$\gamma = \frac{S_{12}x_{11} + x_{22}}{S_{12}x_1 + x_2} \tag{7}$$

The enrichment factor is seen to be related to the enrichment of the surface phase in one of the components; values higher than 1 indicating enrichment in component 1, and values less than 1 indicating enrichment in component 2. It is determined from the experimental results, hence it is an adjustable parameter in eqn. (7). The physical meaning of this enrichment factor has been discussed before.[1]

The same approach was used in this study to derive an equation for the ternary systems. It was presumed that the surface enrichment (S) factors for the three binary systems were known. It was further assumed that the additivity relation applies to a ternary system, so that:

$$\gamma = \gamma_1 x_1^\tau + \gamma_2 x_2^\tau + \gamma_3 x_3^\tau \tag{8}$$

Using the definitions:

$$S_{12} = \frac{x_1^\tau / x_2^\tau}{x_1/x_2} \text{ and}$$

$$S_{32} = \frac{x_3^\tau / x_2^\tau}{x_3/x_2}$$

and the relation $x_1^\tau + x_2^\tau + x_3^\tau = 1$ to eliminate the x_i^τ terms, eqn. (8) can be rewritten in the form:

$$\gamma = \frac{S_{12}x_1\gamma_1 + x_2\gamma_2 + S_{32}x_3\gamma_3}{S_{12}x_1 + x_2 + S_{32}x_2} \tag{9}$$

All symbols in eqn. (9) have the meanings defined above, S_{12} and S_{32} are the defined enrichment of the surface phase by component 1 in the binary system (1 – 2), and by component 3 in the binary system (3 – 2). By definition, the S_{ij} factors for corresponding binary systems should satisfy the relation

$$S_{ij} \times S_{jk} = S_{ik} \tag{10}$$

Therefore, any two enrichment factors from the three binary systems can be used in eqn. (9).

The enrichment factors previously reported [1] for the three binary systems were: $S_{NaCl-NaF} = 5.05$, $S_{NaBr-NaF} = 5.84$ and $S_{NaBr-NaCl} = 1.86$; and did not satisfy the consistency test according to eqn. (10). Therefore all three possible combinations of the published binary enrichment factors were tried were tried here for these calculations. They are reported in columns 6, 7 and 8 of Table 2, as γ_F, γ_{Cl} and γ_{Br}. The subscript on the surface tension here represents the common anion for the two binary systems combined in the enrichment factor. For example γ_F represents the combination of $S_{NaCl-NaF}$ and $S_{NaBr-NaF}$. The agreement of all three sets of values with the experimental results is satisfactory. The fact that two of the combinations overestimate and the third underestimates the values of the surface tension shows that the experimental results could be fitted better by small adjustments of these parameters.

Rather than adjusting the parameters for the best fit of the results only obtained for the ternary compositions, it is possible also to include the results obtained for the binary compositions. For the binary compositions eqn. (9) reduces to eqn. (7), while the constraint imposed by relation (10) is implied in the treatment. It is expected, therefore, that the values of the S parameters calculated in such a way would be more representative of the system. The form of eqn. (9) makes it not easily treated by the least-squares fitting method, hence the improved values of the enrichment factors were calculated by trial and error. A computer program was used to vary the values of the enrichment factors through a reasonable range of values and as the "best" values, those minimizing the average of the standard deviations of the differences of calculated and experimental results were chosen. The enrichment factors thus obtained were

Table 3. Comparison of the experimental surface tension, γ_{exp}, with calculated results, γ_{calc}, obtained from Eberharts model using refined values of the enrichment factors.

Composition NaBr	NaF	NaCl	γ_{exp}	γ_{calc}	Deviation
0.20	0.60	0.20	119.7	121.2	1.5
0.20	0.20	0.60	108.5	108.5	0.0
0.20	0.40	0.40	110.0	113.4	3.4
0.40	0.20	0.40	102.2	104.4	2.2
0.40	0.40	0.20	108.4	108.3	−0.1
0.60	0.20	0.20	99.5	100.6	1.1
0.00	0.25	0.75	114.0	114.2	0.2
0.00	0.50	0.50	125.0	123.5	−1.5
0.00	0.75	0.25	141.0	141.8	0.8
0.75	0.25	0.00	99.8	98.4	−1.3
0.50	0.50	0.00	107.5	108.0	0.5
0.25	0.75	0.00	128.4	128.3	−0.1
0.75	0.00	0.25	94.8	96.3	1.5
0.65	0.00	0.35	95.9	97.8	1.9
0.50	0.00	0.50	98.5	100.2	1.7
0.40	0.00	0.60	100.2	101.8	1.6
0.25	0.00	0.75	103.2	104.3	1.3
0.15	0.00	0.85	104.7	106.0	1.3

$S_{NaCl-NaF}=4.49$, $S_{NaBr-NaF}=6.13$ and $S_{NaBr-NaCl}=1.37$.

Comparison of surface tension values calculated in this manner and the experimental results is shown in Table 3. It can be seen that the agreement of the two sets of results is satisfactory, with an average deviation of 0.80. Relatively good prediction of all experimental data by eqn. (9) means that the determination of the surface tension for two of the binary systems is sufficient to predict the surface tension not only of the third binary system, as shown by Eberhart,[6] but also of all ternary compositions in that system.

Comparing results obtained by using previously reported [1] and optimized *S*-parameters it can be seen that the agreement with the experimental data is only modestly improved. While part of the explanation is that larger number of data were fitted, more significantly, the constraint imposed by eqn. (10) was applied. The effect of that is most evident in the binary system NaCl−NaBr, where calculated values are consistently high, indicating that the optimized *S*-parameter for that system is too low. Such behavior is probably caused by the non-ideality in the ternary system, as suggested previously.[1] It has been shown in another publication [2] that the molar volumes in this system show positive deviations from ideality, so non-ideality seems to be definitely present in the system. It can be concluded, therefore, that this model will predict surface tension values best in the systems in which deviations from ideality are very small.

CONCLUSIONS

The surface tensions of ternary compositions in the system NaF−NaCl−NaBr has been measured by the pin detachment method. Values of the surface tension at 900 °C were fitted by several proposed models. Guggenheims formula, derived for binary and here extended to ternary systems, correctly predicted negative deviations from additive behavior, but underestimated them. Equations employing volume fractions instead of mol fractions were shown to give better correlation, in agreement with earlier workers. The type of correction factors introduced for chloride mixtures [3,4] provides a substantial improvement in the agreement with experimental results, the calculated values lying well within the experimental error. Equation derived on the basis of Eberhart model, employing enrichment factors obtained in the corresponding binary systems, gave good agreement with experimental results. A new set of enrichment factors was calculated using all available experimental data, and

it was shown to provide satisfactory agreement between calculated and experimental data.

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