Syracuse University SURFACE

Chemistry - Faculty Scholarship

College of Arts and Sciences

5-16-1979

# Surface Tensions of Molten Salt Mixtures

Jerry Goodisman Syracuse University

Follow this and additional works at: https://surface.syr.edu/che

Part of the Chemistry Commons

# **Recommended Citation**

Goodisman, J. (1980). Surface tensions of molten salt mixtures. Journal of Colloid and Interface Science, 73(1), 115-123.

This Article is brought to you for free and open access by the College of Arts and Sciences at SURFACE. It has been accepted for inclusion in Chemistry - Faculty Scholarship by an authorized administrator of SURFACE. For more information, please contact surface@syr.edu.

# Surface Tensions of Molten Salt Mixtures

## JERRY GOODISMAN

Department of Chemistry, Syracuse University, Syracuse, New York 13210

Received December 8, 1978; accepted May 16, 1979

It is always found that the surface tension of a mixture of molten salts lies below the mean of the surface tensions of the pure components, weighted by mole fractions. Part of this effect is certainly due to the well-known fact that the composition near the surface is enriched in the component of lower surface tension. We show that an effect of the long-range forces, present for fluids involving Coulombic interactions, is of greater importance. The effect is due to the electroneutrality constraint on the distribution functions. As we show by separate calculations, both effects must be considered to obtain good agreement with experimental results for alkali halide melts.

### I. INTRODUCTION

Molten salts are of theoretical as well as practical interest, in part because they can be thought of as ionic electrolytes with no solvent, so that one can neglect dielectric effects (1). The important concepts in molten salt theory have been reviewed by several authors (2, 3). Our own recent work (4, 5) has been concerned with the use of distribution functions of the bulk fluids to calculate surface tension and surface energy. It was found that, to obtain reasonable values for surface tension and surface energy, it was necessary to modify some of the bulk distribution functions in accordance with an electroneutrality constraint. The distribution functions which governed the contributions of the shortrange repulsions were not modified. The effect of the electroneutrality constraint extended rather far below the surface, as the long-range character of Coulombic forces would lead one to expect. Here, we apply the same ideas to generating a formula for the surface tension of a molten salt mixture in terms of properties of the component salts. Existing theories that do this are either thermodynamic (3, 6), involving

quantities undefined on the molecular level, or in terms of models (6, 7) like the cell model. A theory in terms of the liquid state distribution functions, while natural, does not seem to have been presented, possibly because only recently have liquids like molten salts begun to be understood on this level. We will be concerned with the mixture of two salts AX and BX, having a common anion.

In comparing the surface tension of a mixture of molten salts with the surface tensions of the pure components, it seems that at least two effects must be taken into account. The first is present for all mixtures: The composition of the liquid near the surface is different from the bulk composition. The concentration of the component of lower surface tension will be enhanced (2, 6), thus lowering the surface tension compared to the concentration-weighted mean. The second effect has to do with the action of the Coulombic forces, through the electroneutrality constraint, so is specific to ionic systems. As we will see, it also tends to lower the surface tension compared to the weighted mean. The present paper is concerned with this effect which is derived in Section III and tested in Section IV.

0021-9797/80/010115-09\$02.00/0 Copyright © 1980 by Academic Press, Inc. All rights of reproduction in any form reserved.

Journal of Colloid and Interface Science, Vol. 73, No. 1, January 1980

#### **II. EFFECT OF SHORT-RANGE FORCES**

Since the two cations are equivalent with respect to the Coulombic interactions and differ only in the short-range core repulsions, we consider that the changed concentration near the surface involves the short-range repulsions only. Ions with larger or more repulsive cores will have lower surface tensions, as repulsive forces make a negative contribution to surface tension. In mixtures, they will be overrepresented in the surface region, i.e., they will be surface-active, exhibiting positive adsorption, as is found experimentally (8, 9). Since it is due to short-range forces, the change in concentration should be largely close to the surface. Therefore, we calculate its effect using a simple lattice-like model given by Guggenheim (6), which assumes only the first layer of liquid is affected. Moiseev and Stepanov (8) reason similarly in developing their theory of the surface composition of molten carbonate mixtures.

Guggenheim (6) shows that for an ideal binary mixture, the quantity  $\exp(-\gamma a/kT)$ , rather than the surface tension itself, should scale with the mole fractions. If  $\tilde{\gamma}_{AB}$  is the surface tension of the mixture of A and B,

$$e^{-\tilde{\gamma}_{AB}a/kT} = X_A e^{-\gamma_A a/kT} + X_B e^{-\gamma_B a/kT} \quad [1]$$

with  $X_A$  the mole fraction of A and a the area of surface per molecule. We take  $a = \rho^{-2/3}$ where  $\rho$  is the bulk density of molecules in the mixture (which differs from the bulk densities in the pure components). For the mixtures of salts AX and BX which interest us, we consider that the combination of positive and negative ions constitutes the molecule. Then  $\rho$  is equal to the total cation density or the total anion density. Other choices of a are possible; one found in the literature is the average of  $\rho^{-2/3}$  for the pure components. This choice would give essentially the same results as ours.

Equation [1] makes  $\tilde{\gamma}_{AB}$  lower than the mean of  $\gamma_A$  and  $\gamma_B$ , weighted by mole fractions; the difference

Journal of Colloid and Interface Science, Vol. 73, No. 1, January 1980

$$\gamma_C = \tilde{\gamma}_{AB} - (X_A \gamma_A + X_B \gamma_B) \qquad [2]$$

is more negative for larger values of a. If we use  $a = \rho^{-2/3}$  for our systems, we find values of  $\gamma_C$  which are too small (see Table I), although our systems behave as ideal mixtures in other respects. This implies an effect due to the long-range forces, ignored in the calculation of  $\gamma_C$ . The value of  $\gamma_C$ , representing the effect of short-range forces through changed surface concentrations, will be added to the surface tension calculated by [14], which includes the effect of the long-range electrostatic forces. The changed surface composition is ignored in developing this equation, which is the subject of the next Section.

### **III. EFFECT OF LONG-RANGE FORCES**

We will take the cations A and B, and the anion X, as the components of the system. The relation of this choice of components to the use of the neutral salts has been discussed by us elsewhere (10). For a multicomponent system, the surface tension is given by (5, 11)

$$\gamma = \sum_{i,j} \int dz_1 \int d\tau_{12} \\ \times \frac{x_{12}^2 - z_{12}^2}{2r_{12}} u'_{ij} \rho_{ij}^{(2)}(z_1, \vec{r}_{12}) \quad [3]$$

where the sum is over species *i* and *j*,  $u_{ij}$  is the interaction potential between a particle of species *i* and a particle of species *j*, and  $\rho_{ij}^{(2)}$  is the two-particle distribution function, giving the number of pairs of particles such that a particle of species *i* is at  $\vec{r}_1$  and a particle of species *j* is at  $\vec{r}_2$ . Planar geometry has been assumed, with the *z* axis normal to the surface planes. For the distribution function we write

$$\rho_{ij}^{(2)}(z_1, \vec{r}_{12}) = \rho^{(1)}(z_1) \rho^{(1)}(z_2) \\ \times g_{ij}(z_1, z_2, r_{12}) \quad [4]$$

where  $\rho_i^{(1)}$  is the one-particle distribution (particle density) for species *i*, and  $g_{ij}$  the

Mole fraction CsCl	Measured density (g/cm <sup>3</sup> )	Measured surface tension (dyn/cm) <sup>a</sup>	$X_{\text{KCl}}\gamma_{\text{KCl}} + X_{\text{CsCl}}\gamma_{\text{CsCl}} $ (dyn/cm)	<i>a/kT</i> , see Eq. [1] (cm/dyn)	$\gamma_c$ , see Eq. [2]	$ ho_{K^+}$ (mole/cm <sup>3</sup> )	ρ <sub>Cs</sub> + (mole/cm <sup>3</sup> )	$\gamma_{AX,BX}$ see Eq. [14]	Surface tension calculated as $\gamma_{AXBX} + \gamma_C$
0.00	1.5087	98.0	98.0	0.01275		0.02024	0.0		
0.10	$1.644_{0}$	96.0	96.2	0.01303	-0.21	0.01763	0.00196	95.3 <sub>4</sub>	95.1 <sub>3</sub>
0.25	1.830 <sub>5</sub>	91.8	93.6	0.01348	-0.42	0.01401	0.00467	91.57	91.1 <sub>5</sub>
0.45	2.0668	$88.0^{b}$	90.0	0.01394	-0.56	0.00974	0.00796	85.84	85.2 <sub>8</sub>
0.65	$2.287_{0}$	84.6	86.4	0.01439	-0.52	0.00591	0.01097	84.2 <sub>8</sub>	83.76
0.85	$2.494_{0}$	82.0	82.8	0.01481	-0.29	0.00242	0.01374	81.4 <sub>8</sub>	81.19
1.00	2.6576	80.1	80.1	0.01505		0.0	0.01578	_	

TABLE I Calculations for KCl-CsCl at 800°C

<sup>a</sup> Ref. (9).

<sup>b</sup> This value, calculated from formulas given in Ref. (9) is about 2 dyn/cm higher than the value plotted in Fig. 1 of the same reference.

correlation function between particles of species i and j. We also write

$$\rho_i^{(1)}(z_1) = \rho_i f(z_1)$$
 [5]

where  $\rho_i$  is the bulk liquid density of species *i* (number per unit volume).

We will assume that the density profile function f is the same for all species in the pure salts and the mixture, thus excluding the presence of a double layer. Then with the abbreviation

$$T = (x_{12}^2 - z_{12}^2)/2r_{12}$$
 [6]

the surface tension of the salt AX is given by

$$\gamma_{AX} = \int dz_1 f(z_1) \int d\tau_{12} f(z_2) T \bar{\rho}_A^2 \times (u'_{AA} \bar{g}_{AA} + 2u'_{AX} \bar{g}_{AX} + u'_{XX} \bar{g}_{XX})$$
[7]

where we have used overbars to label correlation functions and bulk densities for the pure liquids. A formula similar to [7] obtains for the pure salt BX, while the formula for the mixture is

$$\gamma_{AX,BX} = \int dz_1 f(z_1) \int d\tau_{12} f(z_2) T[\rho_A^2(u'_{AA}g_{AA} + u'_{XX}g_{XX} + 2u'_{AX}g_{AX}) \\ + \rho_B^2(u'_{BB}g_{BB} + u'_{XX}g_{XX} + 2u'_{BX}g_{BX}) \\ + 2\rho_A \rho_B(u'_{XX}g_{XX} + u'_{AB}g_{AB} + u'_{AX}g_{AX} + u'_{BX}g_{BX})]. [8]$$

If we could express  $g_{AB}$  in terms of  $g_{AA}$  and  $g_{BB}$ , and assume that the correlation functions  $g_{AA}$ ,  $g_{AX}$ , etc. were the same for the mixture as for the pure salts ( $\bar{g}_{AA}, \bar{g}_{AX}$ , etc.), we would have a simple interpolation formula, giving  $\gamma_{AX,BX}$  in terms of  $\gamma_{AX}$  and  $\gamma_{BX}$ .

Note that  $g_{AB}$  multiplies  $u'_{AB}$ , and  $u_{AB}(r_{12})$ consists of a Coulombic interaction  $\pm e^2/r_{12}$ and a core repulsion. With respect to the former, we have to consider integrals of  $g_{AB}/r_{12}^2$ , and  $g_{AB}$  are damped oscillating functions outside the range of the core repulsions. Since A and B have the same electric charge (so that  $g_{AB}$  is small out to almost twice the ionic core diameter), it seems reasonable here to replace  $g_{AB}$  by the average of  $g_{AA}$  and  $g_{BB}$ . The repulsion is shortrange, so that its contribution to  $u'_{AB}(r)$  differs from zero only in a limited region of r, near the ionic diameter  $\sigma_{AB}$ . The value of  $g_{AB}$  for a separation of  $\sigma_{AB}$  is small because of the Coulombic repulsion, so replacing it by the average of  $g_{AA}(\sigma_{AA})$  and  $g_{BB}(\sigma_{BB})$  should not lead (2) to important errors. Thus we may replace  $u'_{AB}g_{AB}$  by  $1/2(u'_{AA}g_{AA})$   $+ u'_{BB} g_{BB}$ ) for both the Coulombic and short-range repulsive parts of the potential. Using this in [8], we have:

$$\gamma_{AX,BX} = \int dz_1 f(z_1) \int d\tau_{12} f(z_2) T[(\rho_A^2 + \rho_A \rho_B)(u'_{AA}g_{AA} + u'_{XX}g_{XX} + 2u'_{AX}g_{AX}) \\ + (\rho_B^2 + \rho_A \rho_B)(u'_{BB}g_{BB} + u'_{XX}g_{XX} + 2u'_{BX}g_{BX})].$$
[9]

We now consider the relation between  $g_{AA}$  and  $\bar{g}_{AA}$ . For the salt AX, local electroneutrality is expressed by the requirements that (a) the total charge around a cation Aat position  $z_1$  must be -e, while (b) the total charge around an anion X at  $z_1$  must be +e. Condition (b) is written in terms of the distribution functions as

$$\left[\bar{\rho}_{X}^{(1)}(z_{1})\right]^{-1} \int d\tau_{12} \left[e\bar{\rho}_{AX}^{(2)}(z_{1},\vec{r}_{12}) -e\bar{\rho}_{XX}^{(2)}(z_{1},\vec{r}_{12})\right] = e \quad [10]$$

or, using [4] and [5],

c

$$\int d\tau_{12} f(z_2) [\bar{g}_{AX}(z_1, z_2, \vec{r}_{12}) \\ - \bar{g}_{XX}(z_1, z_2, r_{12})] = 1/\bar{\rho}_A \quad [11]$$

since  $\bar{\rho}_X = \bar{\rho}_A$ , and similarly for the salt *BX*. For the charge around an anion X in the AX-BX mixture to be +e,

$$\int d\tau_{12} f(z_2) [\rho_A(g_{AX} - g_{XX}) + \rho_B(g_{BX} - g_{XX})] = 1. \quad [12]$$

If we take  $g_{AX} = \bar{g}_{AX}$ ,  $g_{XX} = \bar{g}_{XX}$ , and  $g_{BX}$  $= \bar{g}_{BX}$ , there is a contradiction between [11] and [12]. Our previous work (4) showed that reasonable surface tensions could not be obtained if the local electroneutrality condition, a consequence of the long range of the Coulomb interaction, was not satisfied. This was done by correcting differences of correlation functions such as those appearing in [11], but leaving sums such as  $g_{AX} + g_{XX}$ unchanged from their bulk values. In the present case, we maintain local electroneutrality in the mixture by "scaling" the cor-

relation functions for the pure fluids, as follows:

$$g_{AX} - g_{XX}$$
  
=  $[\bar{\rho}_A / (\rho_A + \rho_B)](\bar{g}_{AX} - \bar{g}_{XX})$  [13a]  
 $g_{BX} - g_{XX}$ 

$$= [\tilde{\rho}_{B}/(\rho_{A} + \rho_{B})](\bar{g}_{BX} - \bar{g}_{XX}). \quad [13b]$$

In Appendix I, we show that consideration of the pressure (11), which should be the same for the mixture as for the pure liquids, lead to the conclusion that  $2u'_{AX,S}g_{AX}$  $+ u'_{AA,S}g_{AA} + u'_{XX,S}g_{XX}$  must be  $\bar{\rho}_A/(\rho_A + \rho_B)$ times the corresponding quantity for the pure salt. Here, the subscript S refers to the short-range part of the potential. As a result, we show that

$$\gamma_{AX,BX} = \frac{\rho_A}{\bar{\rho}_A} \gamma_{AX} + \frac{\rho_B}{\bar{\rho}_B} \gamma_{BX}.$$
 [14]

We combine the correction for long-range forces with the correction for short-range forces to give our predicted surface tension for the mixture:

$$\gamma_{AX,BX} = \frac{\rho_A}{\bar{\rho}_A} \gamma_{AX} + \frac{\rho_B}{\bar{\rho}_B} \gamma_{BX} + \gamma_C. \quad [15]$$

The quantity  $\gamma_c$  is given by [2].

If the mixture were ideal, we could calculate its density from the densities of the pure components. In the mixture, the density of ions A is  $\rho_A = X_A N_0 / \bar{V}$ , where  $N_0$ = Avogadro's number, and  $\bar{V}$  is the volume per mole. For an ideal solution

$$\bar{V} = X_A \bar{V}_A + X_B \bar{V}_B$$
[16]

where  $\bar{V}_A$  is the partial molar volume of A

Journal of Colloid and Interface Science, Vol. 73, No. 1, January 1980

119

and  $\bar{\rho}_A = N_0/\bar{V}_A$ , and  $\bar{V}_A$  is the same in the mixture as in the pure liquid.

## **IV. CALCULATIONS**

Let us consider first a mixture of NaCl and KCl. As a function of composition, the surface tension varies smoothly, so that a prediction of the surface tension of the equimolar mixture (plus knowledge of surface tensions for the pure components) probably gives all the information needed. Bertozzi (12) has measured surface tensions for mixtures of these salts at 800°C (1073°K). In order to minimize the effects of experimental errors, we use his values of surface tension (read off his plots), for the pure salts as well as the mixtures, in our calculations:  $\gamma_{\text{NaCl}} = 118.5 \text{ dyn/cm}, \gamma_{\text{KCl}} = 99.5 \text{ dyn/cm},$  $\gamma_{eq} = 106.5$  dyn/cm. For the densities, we turn to Sandonnini's (13) data, which give specific weights for the mixture at 850°C and 900°C of 1.482 and 1.451, which extrapolates to 1.513 at 800°C. Similar linear extrapolation gives 1.542 and 1.496 for pure NaCl and pure KCl at 800°C. Thus  $\rho_{\rm Na}/\tilde{\rho}_{\rm Na}$ = 0.4312 and  $\rho_{\rm K}/\bar{\rho}_{\rm K}$  = 0.5669, Eq. [14] predicts 107.5 dyn/cm for the equimolar mixture, which is lower than the average of the pure salt surface tensions, 109. From 107.5 dyn/cm, we must subtract  $\gamma_{\rm C}$  (Eq. [2]), representing the effect of the change in surface concentration. For the equimolar mixture,  $\rho = 1.3703 \times 10^{22}$  molecules (or cations) per cm<sup>3</sup>, which gives  $a = 17.463 \text{ Å}^2$ . Equation [1] then makes  $\tilde{\gamma}_{AB} = 108.47$ dyn/cm and (Eq. [2])  $\gamma_c = -0.53$ . Our predicted surface tension is 107.0 dyn/cm, which compares well with the measured value of 106.5 (12).

Smirnov and collaborators (8, 9) have recently reported both surface tensions and densities for various mixtures of alkali halides. However, some of the pure salt densities differ from those measured by other workers (14). We carry out calculations according to our formulas for KCl– CsCl, since in this case densities agree reasonably well. The results, given in Table I, again show agreement with experiment to 0.5 dyn/cm. Judging from deviations of Smirnov's tabulated data points from his smooth curves, this is apparently the experimental error.

Janz and co-workers have been critically reporting data (15, 16) for molten salts and molten salt mixtures, which enable us to perform sample calculations for mixtures of fluorides, bromides (15), or iodides (16). The results for a number of mixtures are shown in Table II. Although agreement with measured surface tensions is not as good in all cases, the electroneutrality correction of Eq. [14] is always more important than the surface composition correction of Eq. [2]. We also show, in Table II, results for the AgCl-KCl system, for which surface tensions are given by Sternberg and Terzi (17) and densities by Boardman et al. (18). It is quite possible that the ionic model we use is less applicable for AgCl. There is evidence (19) that Ag-halide melts are indeed not like other molten salts, involving covalent interactions.

#### V. DISCUSSION

Sternberg and Terzi ascribed (17) all of the differences between the mixture surface tension and the mole fraction weighted mean surface tension to the deviations of the surface composition from bulk composition, and used Eberhart's formula to take this into account:

$$\gamma_{AX,BX} = \frac{SX_{AX}\gamma_{AX} + X_{BX}\gamma_{BX}}{SX_{AX} + X_{BX}} .$$
 [17]

The "enrichment factor for the surface layer" S is supposed to be a constant and is determined from the experimental surface tensions themselves. Rearranging [17], one finds that a plot of  $\xi = (\gamma_{AX,AB} - \gamma_{AX})/(\gamma_{BX} - \gamma_{AX})$  vs  $\xi X_{AX}/X_{BX}$  should be linear with slope -S. Thus [17] cannot be considered as a prediction of surface tension for the mixtures; it is rather an interpola-

Calculations for Various Mixtures

Systems	Measured density (g/cm <sup>3</sup> )	Measured surface tension (dyn/cm)	$a/kT$ $a = \rho^{-2/3}$ (cm/dyn)	$\gamma_c$ , see Eqs. [1] and [2]	ρ <sub>x</sub> - (mole/cm <sup>3</sup> )	Mole- fraction weighted surface tension	<i>Ŷах.вх</i> see Eq. [14]	Surface tension calculated as $\gamma_{AXBX} + \gamma_C$
0.5 KBr + 0.5 NaBr,								
1100°K <sup>a</sup>	2.1274	89.8	0.01289	-0.28	0.01918	91.8	90.0	89.7
0.5 KBr + 0.5 CsBr,								
1073°K <sup>a</sup>	2.514	76.2	0.01508	-0.38	0.01515	78.0	76.7	76.4
0.5  KF + 0.5  LiF,								
1173°K <sup>b</sup>	1.779	152.0	0.00713	-9.3	0.04234	194.5	178.3	169.0
0.2 KCl + 0.8 AgCl,								
1073°K <sup>c</sup>	3.679	129.3	0.01017	-4.3	0.02839	150.5	145.4	141.1
0.6 KCl + 0.8 AgCl,								
1073°K <sup>c</sup>	2.406	103.5	0.01152	-6.0	0.02357	123.4	116.4	110.4
0.45  CsCl + 0.55  LiCl,								
$1000^{\circ} K^{d}$	2.229	88.2	0.01275	-3.5	0.02250	110.8	100.7	97.2
0.5  NaCl + 0.5  LiCl,								
$1110^{\circ} \mathbf{K}^{d}$	1.473	115.7	0.00965	-0.02	0.02922	117.2	116.8	116.8

<sup>a</sup> See Ref. (15).

<sup>b</sup> See Ref. (16).

<sup>c</sup> See Refs. (17) and (18). Densities are linearly interpolated from tables in the latter.

<sup>d</sup> Data from G. J. Janz, R. P. T. Tompkins, C. B. Allen, J. R. Downey, Jr., G. L. Gardner, U. Kreb, and S. K. Singer, J. Phys. Chem. Ref. Data 4, 871 (1975).

tion formula. Its success in fitting the variation of  $\gamma_{AX,BX}$  with composition, given the value of S (i.e., the surface tension at some intermediate compositions), simply implies that the variation is a smooth one. It has no relevance to correctness of the interpretation of S. Indeed, the size and importance of our correction (according to Eq. [14]) implies that electroneutrality, in addition to changed surface composition, is important.

Other interpolation formulas and relations between them are discussed by Schmidt (20) and Shereshefsky (7). Schmidt points out that each such formula implies a relation between the surface tensions of the three sets of binary mixtures which can be constructed from three components. For example, if S of formula (19) is evaluated for the AX-BX mixtures to give the value  $S_{AB}$ , and if the value  $S_{BC}$  is obtained similarly for BX-CX mixtures, then the value of S to use for AX-CX mixtures is (21)  $S_{AB}S_{BC}$ . The accuracy of the resulting predictions is a test of the assumptions of the theory. For KCl-AgCl, Sternberg and Terzi (14) found S = 4.34; for AgCl-NaCl, they obtained  $(3.508)^{-1}$ . Thus S for KCl-NaCl is 1.237. For an equimolar mixture of KCl and NaCl, Eq. [20] would then give  $(1.23 \times 99.5 + 118.5)/2.237 = 108.0$  dyn/cm. The lowering of 1.0 dyn/cm compared to the average is not at all in good agreement with the measured lowering of 2.5. To yield the correct result of 106.5 the ratio of S factors for KCl-AgCl and NaCl-AgCl would have to be 1.7.

The deviations of  $\gamma$  from linearity of mole fraction for these systems were correlated by Bertozzi (12) with the size parameter  $[(\sigma_{AX} - \sigma_{BX})/(\sigma_{AX} + \sigma_{BX})]^2$ , the  $\sigma$ s being interionic distances. Another parameter used to measure size discrepancies (2) is  $(\sigma_{AX} - \sigma_{BX})/\sigma_{AX}\sigma_{BX}$ . In our theory, a size parameter governs the density of the mixture relative to those of the pure components. That the deviation of  $\gamma$  from linearity should be proportional to  $(d_2 - d_1)^2/(d_1d_2)^2$ , where  $d_i$  is a scaling length for system *i*, follows from conformal solution theory (22). It can also be shown (23) that the deviation of the mixture surface tension from linearity in the mole fractions should be proportional to  $X_1X_2(d_1 - d_2)^2$ , as is borne out. In work on binary alkali nitrates, maximum deviations of surface tension isotherms from linearity were plotted (23) vs  $(d_1 - d_2)^2/(d_1 + d_2)^2$ . The use of the parameter  $(d_1 - d_2)^2/(d_1 + d_2)^2$  comes from calculations on Coulombic interactions on linear arrays.

Nissen and Van Domelen (24) have shown that regular solution theory can predict surface tensions of molten salt mixtures to good accuracy for most systems with a common anion. In additionn to density data for the melts, a single "interaction parameter" is required; its value is obtained from data on heats of mixing. Problems arise when one of the cations is Ag<sup>+</sup>; examining the origins of the difficulty, Nissen and Van Domelen (24) favor an explanation in terms of possible non-Coulombic effects, such as covalently bonded structure, in melts containing silver ion (17).

Grjotheim *et al.* (25) have given surface tensions for mixed sodium halides and noted the inadequacy of the Guggenheim formula, Eq. [1]. Using Eberhart's formula (17), they note that the values of S fail the consistency test,  $S_{AC} = S_{AB}S_{BC}$ . Moiseev and Stepanov (8) use the variation of surface tension with composition to derive adsorption isotherms for binary and ternary mixtures of molten  $Li_2CO_3$ ,  $Na_2CO_3$ , and  $K_2CO_3$ . The thermodynamic surface excess or Gibbs adsorptions is then interpreted as a changed concentration in the first monolayer as compared to the bulk. Since the Gibbs adsorption is defined thermodynamically, specific physical assumptions are always necessary to go from Gibbs adsorption to information about surface structures. Density changes are not taken into account.

The present paper calculates mixed salt surface tensions from density data (and surface tensions for the pure salts); there are no other parameters. The results presented here show that the long-range electroneutrality effect must be taken into account as well as the short-range composition effect. Indeed, the former seems to be the more important. Our method of including both effects by addition of the results of separate calculations is justifiable only when both effects are small. Otherwise, one requires a method for considering the two simultaneously. Presumably, this would involve a form for the distribution functions which reflects changed surface composition as well as electroneutrality.

#### APPENDIX I

Equations [13], which reflect the electroneutrality constraints for the pure salts and the mixture, involve differences of correlation functions for the surface region. Electroneutrality must also hold for the bulk fluids, so that  $g_{ij,B}$  and  $\bar{g}_{ij,B}(B \equiv \text{bulk})$  must be related by Eqs. [13] as well. We now consider the pressure (11) of the homogeneous fluid:

$$p = (\rho_A + \rho_B + \rho_X)kT - \frac{2\pi}{3} \int_0^\infty dr r^3 (\rho_A^2 u'_{AA} g_{AA,B} + \rho_B^2 u'_{BB} g_{BB,B} + \rho_X^2 u'_{XX} g_{XX,B} + 2\rho_A \rho_B u'_{AB} g_{AB,B} + 2\rho_A \rho_X u'_{AX} g_{AX,B} + 2\rho_B \rho_X u'_{BX} g_{XX,B}).$$

We now write  $u_{ij}$  as  $\pm e^2/r_{ij}$  plus a short-range repulsion  $u'_{ijs}$ , and substitute for  $g_{AB}u'_{AB}$  as  $\frac{1}{2}(g_{AA}u'_{AA} + g_{BB}u'_{BB})$ . Then we insert Eqs. [13] in the electrostatic terms and rearrange the result, to obtain

$$-\frac{2\pi}{3}\int_{0}^{\infty} drr^{3}[(\rho_{A}^{2}+\rho_{A}\rho_{B})(2u_{AX,S}^{\prime}g_{AX,B}+u_{AA,S}^{\prime}g_{AA,B}+u_{XX,S}^{\prime}g_{XX,B}) + (\rho_{B}^{2}+\rho_{A}\rho_{B})(2u_{BX,S}^{\prime}g_{BX,B}+u_{BB,S}^{\prime}g_{BB,B}+u_{XX,S}^{\prime}g_{XX,B})]$$

$$=p-2(\rho_{A}+\rho_{B})kT + \frac{2\pi e^{2}}{3}\int_{0}^{\infty} drr[\rho_{A}\bar{\rho}_{A}(2\bar{g}_{AX,B}-\bar{g}_{AA,B}-\bar{g}_{XX,B}) + \rho_{B}\bar{\rho}_{B}(2\bar{g}_{BX,B}-\bar{g}_{BB,B}-\bar{g}_{XX,B})].$$
 [A1]

Considering the pressure for the pure salt AX, we find

$$-\frac{2\pi}{3}\int_{0}^{\infty} dr r^{3} \bar{\rho}_{A}^{2} (2u'_{AX,S}\bar{g}_{AX,B} + u'_{AA,S}\bar{g}_{AA,B} + u'_{XX,S}\bar{g}_{XX,B})$$
$$= p - 2\bar{\rho}_{A}kT + \frac{2\pi e^{2}}{3}\int_{0}^{\infty} dr r\bar{\rho}_{A}^{2} (2\bar{g}_{AX,B} - \bar{g}_{AA,B} - \bar{g}_{XX,B}). \quad [A2]$$

We multiply [A2] by  $\rho_A/\rho_{\bar{A}}$  and its counterpart for  $A \leftrightarrow B$  by  $\rho_B/\rho_{\bar{B}}$ , and subtract both from [A1]. The result is:

$$-\frac{2\pi}{3}\int_{0}^{\infty} dr r^{3}[\rho_{A}(\rho_{A}+\rho_{B})(2u'_{AX,S}g_{AX,B}+u'_{AA,S}g_{AA,B}+u'_{XX,S}g_{XX,B}) -\rho_{A}\rho_{\bar{A}}(2u'_{AX,S}\bar{g}_{AX,B}+u'_{AA,S}\bar{g}_{AA,B}+u'_{XX,S}\bar{g}_{XX,B}) +\rho_{B}(\rho_{A}+\rho_{B})(2u'_{BX,S}g_{BX,B}+u'_{BB,S}g_{BB,B}+u'_{XX,S}g_{XX,B}) -\rho_{B}\rho_{\bar{B}}(2u'_{BX,S}\bar{g}_{BX,B}+u'_{BB,S}\bar{g}_{BB,B}+u'_{XX,S}\bar{g}_{XX,B})] = p\left(1-\frac{\rho_{A}}{\bar{\rho}_{A}}-\frac{\rho_{B}}{\bar{\rho}_{B}}\right).$$

The pressure for these liquids is always very small compared to either the electrostatic or short-range contributions, and the factor multiplying p will only be a fraction of a percent. If we put the right side of this equation equal to zero, it implies that the quantity  $Q = (2u'_{AX,S}g_{AX,B} + u'_{AA,S}g_{AA,B} + u'_{XX,S}g_{XX,B})$  should be taken as  $\bar{\rho}_A/(\rho_A + \rho_B)$  times the corresponding quantity for the pure salt.

In our previous model (4, 5), Q is the same in the bulk and surface regions, so that the scaling of the corresponding term in  $\gamma$ , involving the surface correlation functions, should be done exactly as for Q (which involves bulk fluid properties) itself. Therefore, we may write

 $\gamma_{AX,BX}$ 

$$= (\rho_A^2 + \rho_A \rho_B) \int dz_1 f(z_1) \int d\tau_{12} f(z_2) T[(e^2/r_{12}^2)(2g_{AX} - g_{AA} - g_{XX}) \\ + (u'_{AA,S}g_{AA} + u'_{XX,S}g_{XX} + 2u'_{AX,S}g_{AX})] \\ + (\rho_B^2 + \rho_A \rho_B) \int dz_1 f(z_1) \int d\tau_{12} f(z_2) T[(e^2/r_{12}^2)(2g_{BX} - g_{BB} - g_{XX}) \\ + (u'_{BB,S}g_{BB} + u'_{XX,S}g_{XX} + 2u'_{BX,S}g_{BX})]$$

Journal of Colloid and Interface Science, Vol. 73, No. 1, January 1980

$$= (\rho_{A}^{2} + \rho_{A}\rho_{B}) \int dz_{1}f(z_{1}) \int d\tau_{12}f(z_{2})T\left[\frac{\bar{\rho}_{A}}{\rho_{A} + \rho_{B}}\left(\frac{2\bar{g}_{AX} - \bar{g}_{AA} - \bar{g}_{XX}}{r_{12}^{2}} + u_{AA,S}'g_{AA} + u_{XX,S}'g_{XX} + 2u_{AX,S}'g_{AX}\right)\right] + (\rho_{B}^{2} + \rho_{A}\rho_{B}) \int dz_{1}f(z_{1}) \int d\tau_{12}f(z_{2})T\left[\frac{\bar{\rho}_{B}}{\rho_{A} + \rho_{B}}\left(\frac{2\bar{g}_{BX} - \bar{g}_{BB} - \bar{g}_{XX}}{r_{12}^{2}} + u_{BB,S}'g_{BB} + u_{XX,S}'g_{XX} + 2u_{BX,S}'g_{BX}\right)\right].$$
 [A3]

Except for the bulk density factors, we recognize in [A3] the surface tensions of pure AX and pure BX. Specifically,

$$\gamma_{AX,BX} = \frac{(\rho_A^2 + \rho_A \rho_B)\bar{\rho}_A}{\rho_A + \rho_B} \frac{\gamma_{AX}}{\bar{\rho}_A^2} + \frac{(\rho_B^2 + \rho_A \rho_B)\bar{\rho}_B}{\rho_A + \rho_B} \frac{\gamma_{BX}}{\bar{\rho}_B^2} = \frac{\rho_A}{\bar{\rho}_A} \gamma_{AX} + \frac{\rho_B}{\bar{\rho}_B} \gamma_{BX}.$$
 [A4]

The mixed-melt surface tension is now written as a density-weighted average of the surface tensions of the pure molten salts.

#### REFERENCES

- 1. This is not strictly true, since the electronic polarizability of the ions themselves gives rise to a dielectric constant.
- Blander, M., *in* "Molten Salts" (G. Mamantov, Ed.). Marcel Dekker, New York, 1969; Braunstein, J., *in* "Ionic Interactions" (S. Petrucci, Ed.). Academic Press, New York, 1971.
- Stillinger, F. H., Jr., in "Molten Salt Chemistry" (M. Blander, Ed.). Interscience, New York, 1964; Nissen, D. A., and Van Domelen, B. H., J. Phys. Chem. 79, 2003 (1975).
- Pastor, R. W., and Goodisman, J., J. Chem. Phys. 68, 3654 (1978); Goodisman, J., and Pastor, R. W., J. Phys. Chem. 82, 2078 (1978).
- 5. Goodisman, J., J. Chem. Phys. 69, 5341 (1978).
- 6. Guggenheim, E. A., "Mixtures," Chap. IX. Oxford, London, 1952.
- Shereshefsky, J. L., J. Colloid Interface Sci. 24, 317 (1967).
- Moiseev, G. K., and Stepanov, G. K., Zh. Fiz. Khim. 40, 1056 (1966) [English Translation, Russ. J. Phys. Chem. 40, 569 (1966)].
- Smirnov, M. V., Sharov, A. F., and Stepanov, V. P., *Elektrokhimiya* 12, 597 (1976) [English Translation, *Soviet Electrochem.* 12, 572 (1976)].
- Badiali, J. C., and Goodisman, J., J. Electroanal. Chem. 91, 151 (1978).
- 11. Ono, S., and Kondo, S., in "Handbuch der

Physik," (S. Flugge, Ed.), Vol. 10. Springer, Berlin, 1960.

- 12. Bertozzi, G., J. Phys. Chem. 69, 2606 (1965).
- 13. Sandonnini, C., Gazz. Chim. Ital. 50, 289 (1920).
- 14. Janz, G. J., "Molten Salts Handbook. Academic Press, New York, 1967.
- Janz, G. J., Tompkins, R. P. T., Allen, C. B., Downey, J. R., Jr., and Singer, S. K., *J. Phys. Chem. Ref. Data* 6, 409 (1977).
- Janz, G. J., Gardner, G. L., Krebs, U., and Tompkins, R. P. T., *J. Phys. Chem. Ref. Data* 3, 1 (1974).
- 17. Sternberg, S., and Terzi, M., Rev. Roumaine Chim. 15, 527 (1970).
- Boardman, N. K., Darman, F. H., and Heymann, E., J. Phys. Colloid Chem. 53, 375 (1949).
- Hersh, L. S., and Kleppa, O. J., J. Chem. Phys. 42, 1309 (1965); Marcus, Y., "Introduction to Liquid State Chemistry." Wiley, New York, 1977.
- 20. Schmidt, R.-L., J. Phys. Chem. 71, 1154 (1967).
- 21. There seems to be an error in the way Eq. [7b] of Ref. (17) is written; from Eq. [7a], S(1,2) S(2,3) = S(1,3) follows.
- 22. Blander, M., Adv. Chem. Phys. XI, 83 (1967).
- Brown, W. B., Proc. Roy. Soc. London A 240, 561 (1957); Bertozzi, G., and Sternheim, G., J. Phys. Chem. 68, 2908 (1964).
- Nissen, D. A., and Van Domelen, B. H., J. Phys. Chem. 79, 2003 (1975).
- Grjotheim, K., Naterstad, T., and Øye, H. A., Acta Chem. Scand. A30, 429 (1976).