

Surface Tension of Liquid Binary and Ternary Chloride Mixtures

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The surface tension, γ , of binary liquid chloride mixtures of $\text{AlkCl} - \text{CaCl}_2$ and $\text{AlkCl} - \text{MgCl}_2$ have been measured by the pin detachment method. The covalent character of molten MgCl_2 is pointed out. The excess surface tension in molten mixtures is expressed as the deviation from modifications of the so-called Guggenheim equation:

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

In the ionic mixtures $\text{AlkCl} - \text{CaCl}_2$, the negative deviations found can be ascribed to polarization effects, and to the enrichment in the surface of the component with the lowest surface tension. In MgCl_2 -containing mixtures, the ionization of the partly covalent MgCl_2 -structure and the formation of MgCl_4^{2-} complexes are additional factors, contributing positively and negatively, respectively, to the excess surface tension.

The surface tension values of the ternary systems $\text{NaCl} - \text{CaCl}_2 - \text{MgCl}_2$ and $\text{KCl} - \text{CaCl}_2 - \text{MgCl}_2$ have also been determined and compared with values calculated from the component binaries. The agreement between experimental and calculated surface tension is within $\pm 3\%$.

As part of an investigation of the physico-chemical properties of the magnesium chloride electrolyte for the electrowinning of magnesium, the surface tension of several binary and ternary liquid chloride mixtures of potential interest have been determined.

Several methods have been used for measuring surface tension in molten salt systems. Among these are: The maximum bubble pressure method,¹ the capillary method,² drop methods,³ the ring method,⁴ the Wilhelmy method,⁵ and the pin method.⁶ In the present studies the pin method was selected, because it allows precise determinations of density and surface tension to be made in the same run.

The density studies have been described in a recent publication,⁷ and so have the principles underlying the surface tension measurements.⁸ In that paper⁸ it has been shown that the pin method is an absolute method, needing

no calibration constant. The surface tension is calculated by equating the detachment force ΔW_{\max} to the weight of the liquid lifted prior to detachment. Here ΔW_{\max} , the detachment force, is the difference between the weight of the sinker with the pin (Fig. 1) just before contact is broken and the weight when it is free from the melt. The weight of the liquid lifted is expressed as a function of the surface tension by the basic Laplace equation for liquid surfaces, when the density of the liquid and the dimensions of the pin are known.

Surface tensions determined this way were for most melts about 10% lower than those calculated from the simple intuitive relation

$$\gamma = \Delta W_{\max} / 2\pi r \quad (1)$$

where γ is the surface tension, and r is the radius of the pin.

EXPERIMENTAL

An electronic, recording thermobalance was employed. This balance is described in detail in connection with the density measurements.⁷ The density sinker with the pin for the surface tension measurements was made from Pt-10% Rh alloy (Fig. 1). The diameter of the pin was measured to be 1.98 mm at 25°C. To calculate the diameter in the actual temperature range, the thermal expansion data given by Barter and Darling⁸ were used.

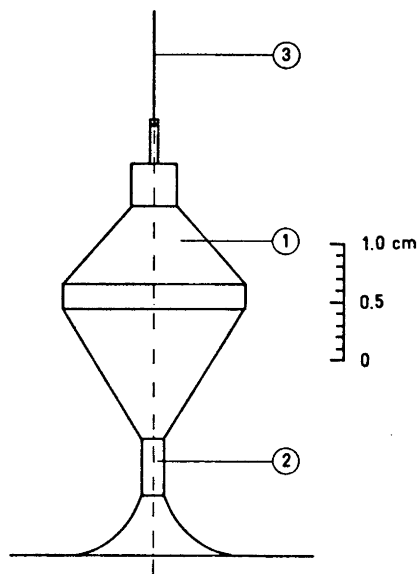


Fig. 1. Platinum sinker for measurements of density and surface tension in molten salts. 1 Density sinker. 2 Pin for surface tension measurements. 3 Platinum/rhodium wire.

All salts were dried carefully according to the procedures described earlier.⁷

The surface tension measurements were performed in the following way. When contact is established between the melt surface and the Pt-pin, there is a sudden increase in the weight of the sinker. This increase is due to the effect of the surface tension on the pin. The supporter with the crucible that contains the melt is then lowered, slowly and continuously until contact is broken. During this procedure, the weight of the sinker is recorded by the balance.⁷ The weight exhibits a definite maximum just before contact is broken.

RESULTS

In Table 1 we have compared the surface tension for the pure, fused chlorides at 800°C from this work with available literature data. The reproducibility for our surface tension measurements was $\pm 1\%$.

Table 1. Surface tension (dyn cm^{-1}) and our observed temperature coefficient α ($\text{dyn cm}^{-1} \text{ degree}^{-1}$) for pure molten chlorides.

Salt	Lit. values and method (800°C)	This work (800°C)	$\alpha \times 10^3$
CaCl ₂	147.3 ^a (Max. bubble press.)	147.3	46
	150.6 ^b (Max. bubble press.)		
	148.9 ^c (Max. bubble press.)		
	145.6 ^d (Max. bubble press.)		
MgCl ₂	66.5 ^a (Max. bubble press.)	62.1	4
	71.8 ^e (Max. bubble press.)		
	66.0 ^f (Max. bubble press.)		
LiCl	123.2 ^b (Max. bubble press.)	116.2	70
	117.9 ^g (Max. bubble press.)		
NaCl	116.4 ^b (Max. bubble press.)	116.1	73
	118.0 ^h (Wilhelmy method)		
KCl	96.8 ^b (Max. bubble press.)	97.0	70
	98.7 ^c (Max. bubble press.)		
	99.0 ^h (Wilhelmy method)		
RbCl	90.8 ^b (Max. bubble press.)	88.6	77
	90.0 ^h (Wilhelmy method)		
CsCl	79.3 ^b (Max. bubble press.)	79.5	79
	78.2 ^c (Max. bubble press.)		
	79.8 ^h (Wilhelmy method)		

^a Zezyanov, S. P. and Iliehev, V. A. *Russ. J. Inorg. Chem. (English Transl.)* **11** (1966) 936.

^b Janz, G. J. *Molten Salts Handbook*, Academic, New York 1967, p. 80.

^c Lehman, D. J. *Diss.*, Indiana Univ. 1959, p. 1192.

^d Cantratov, M. F. *Zh. Prikl. Khim.* **34** (1961) 1249.

^e Reding, J. N. *J. Chem. Eng. Data* **11** (1966) 239.

^f Desyatnikov, O. G. *J. Appl. Chem. USSR* **29** (1956) 870.

^g Ellis, R. B. Progr. Dep. USAEC Contract No. At-(40-1)-2073 (1961).

^h Bertozzi, G. J. *Phys. Chem.* **69** (1965) 2006. (Read from curve.)

For NaCl, KCl, RbCl, and CsCl, where the different literature values show relatively small scattering, the present results are within 2% of the mean of the literature value. For CaCl₂ our value is 3% lower and for MgCl₂ 7% lower than the lowest value previously reported.

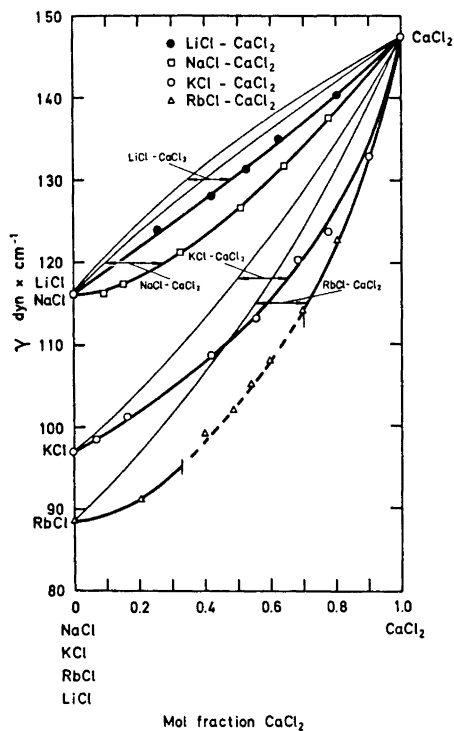


Fig. 2. Surface tension of binary liquid CaCl_2 -AlkCl mixtures at 800°C . (The values for the system CaCl_2 -RbCl with $0.3 < X_{\text{CaCl}_2} < 0.7$ have been found by extrapolation from higher temperatures.) Thinly drawn curves calculated by eqn. (10). The temperature coefficients $\alpha \times 10^3$ ($\text{dyn cm}^{-1} \text{ degree}^{-1}$) in $\text{LiCl}-\text{CaCl}_2$ are 70 (pure LiCl), 50, 75, 74, 50, 68, 46, (pure CaCl_2); in $\text{NaCl}-\text{CaCl}_2$: 73 (pure NaCl), 79, 77, 75, 71, 60, 53, 46, in $\text{KCl}-\text{CaCl}_2$: 70 (pure KCl), 68, 76, 70, 63, 60, 56, 50, 46; and in $\text{RbCl}-\text{CaCl}_2$: 77 (pure RbCl), 51, 62, 57, 59, 54, 58, 64, 46.

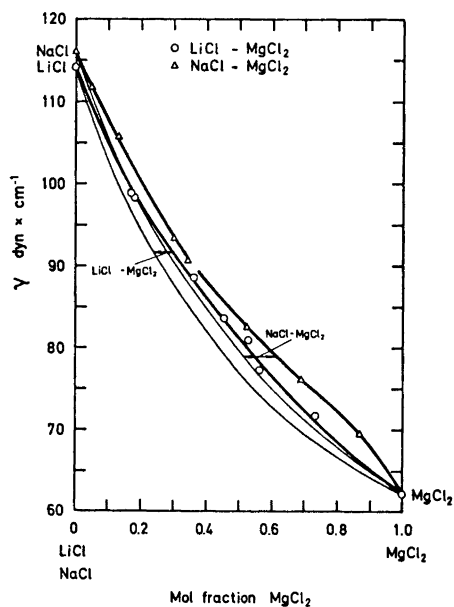


Fig. 3. Surface tension of the binary liquid $\text{LiCl}-\text{MgCl}_2$ and $\text{NaCl}-\text{MgCl}_2$ mixtures at 800°C . Thinly drawn curves calculated by eqn. (10). The temperature coefficients $\alpha \times 10^3$ ($\text{dyn cm}^{-1} \text{ degree}^{-1}$) of the $\text{LiCl}-\text{MgCl}_2$ mixtures are 70 (pure LiCl), 52, 49, 37, 25, 27, 26, 14, 4 (pure MgCl_2); and in the $\text{NaCl}-\text{MgCl}_2$ system 73 (pure NaCl), 65, 62, 44, 56, 45, 32, 14, 4.

Results for the binary mixtures of CaCl_2 and the alkali chlorides and of MgCl_2 and the alkali chlorides are given in Fig. 2 and Figs. 3 and 4, respectively. Surface tension values for the system $\text{CaCl}_2-\text{MgCl}_2$ are given in Fig. 5.

Surface tension values for the two ternary mixtures $\text{MgCl}_2-\text{CaCl}_2-\text{NaCl}$ and $\text{MgCl}_2-\text{CaCl}_2-\text{KCl}$ are given in special ternary diagrams in Figs. 6 and 7.

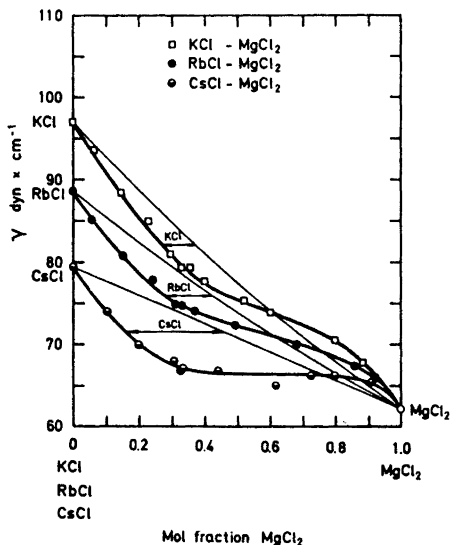


Fig. 4. Surface tension of the binary liquid KCl-MgCl₂, RbCl-MgCl₂ and CsCl-MgCl₂ mixtures at 800°C. Thinly drawn curves calculated by eqn. (10). The temperature coefficients $\alpha \times 10^3$ (dyn cm⁻¹ degree⁻¹) are KCl-MgCl₂: 70 (pure KCl), 56, 60, 61, 49, 45, 51, 49, 47, 43, 29, 12, 4 (pure MgCl₂); RbCl-MgCl₂: 77 (pure RbCl), 63, 64, 49, 52, 45, 52, 46, 40, 27, 18, 4; CsCl-MgCl₂: 79 (pure CsCl), 80, 55, 51, 66, 45, 50, 43, 35, 50, 21, 4.

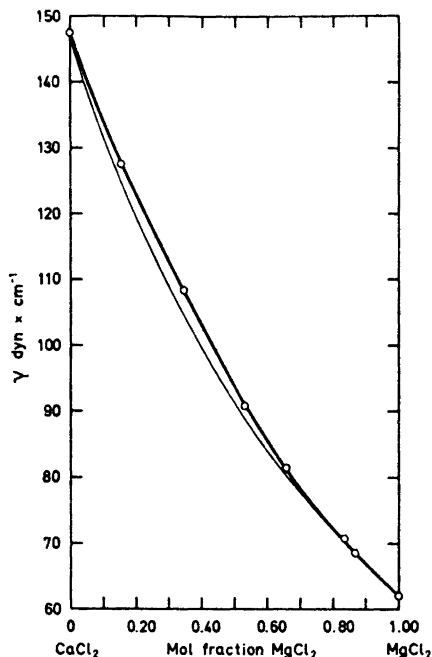


Fig. 5. Surface tension of binary liquid CaCl₂-MgCl₂ mixtures at 800°C. Thinly drawn curve calculated by eqn. (10). The temperature coefficients $\alpha \times 10^3$ (dyn cm⁻¹ degree⁻¹) are 46 (pure CaCl₂) 30, 21, 14, 11, 8, 7, 4 (pure MgCl₂).

DISCUSSION

1. Pure molten salts

The surface tension of the pure molten salts and of their binary and ternary mixtures were found to decrease linearly with increasing temperature, T , and can be described by the relation:

$$\gamma = \gamma_0(1 - \alpha(T - T_0)) \quad (2)$$

Values of α for the pure salts are given in Table 1 and for the binary and ternary mixtures in Figs. 2-7.

For a one-component system the surface thermodynamic functions per unit area are given as:¹⁰

$$G_s = \gamma; \quad S_s = -d\gamma/dT; \quad H_s = \gamma - T(d\gamma/dT) \quad (3)$$

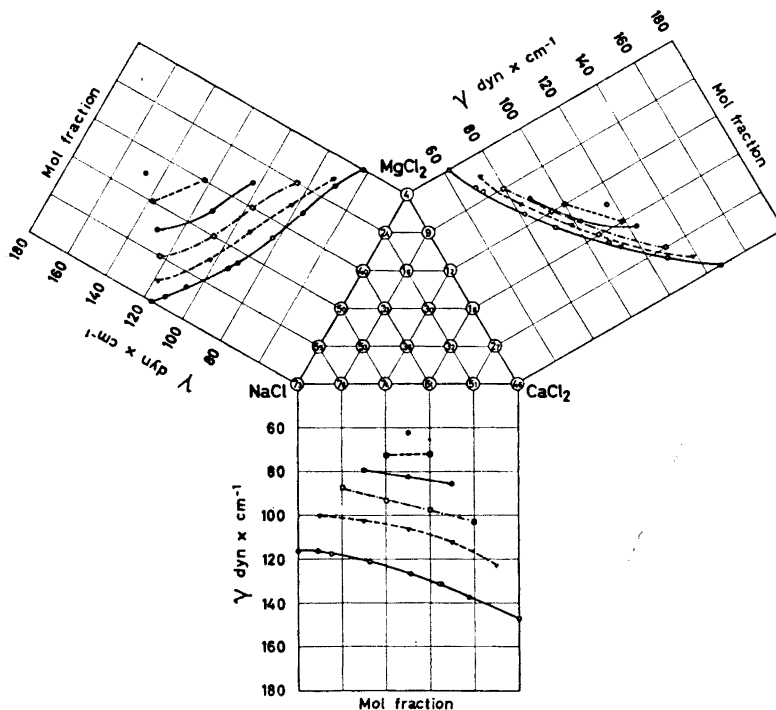


Fig. 6. Surface tensions of ternary mixtures in the system MgCl_2 – CaCl_2 – NaCl at 800°C . Surface tensions corresponding to the lines in the composition diagram are projected in the three rectangular diagrams.

- , ———: Binary system
- ▲, - - - - : Mol % of component with constant composition 20.
- , - . . . : Mol % of component with constant composition 40.
- , ———: Mol % of component with constant composition 60.
- , - - - - : Mol % of component with constant composition 80.
- : Pure components.

Given in circles: Temperature coefficient, $\alpha \times 10^3$ ($\text{dyn cm}^{-1} \text{ degree}^{-1}$).

Since the surface tension varies linearly with temperature, H_s is independent of temperature, and therefore useful for making comparisons between high- and low-melting liquids. In Table 2 it is seen that our surface enthalpy values fall in the range 150 – 200 dyn cm^{-1} for all the investigated salts except MgCl_2 .

Our surface enthalpy value of molten MgCl_2 (66 dyn cm^{-1}) is of the same order of magnitude as that of most organic liquids.¹¹ This supports the view originally advanced by Førlund,¹² that molten MgCl_2 has a partially covalent structure. We also want to point out that MgCl_2 , contrary to all the other salts in Table 2, has a temperature coefficient, $d\gamma/dT$, close to zero. A possible explanation for the low temperature coefficient of MgCl_2 may be a partial ionization of the covalent structure with increasing temperature, leading to

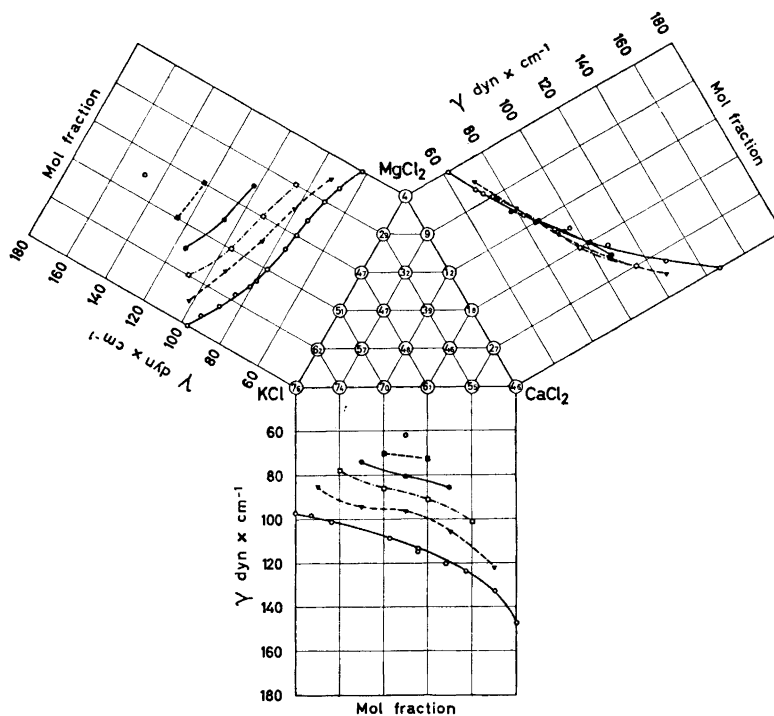


Fig. 7. Surface tensions of ternary mixtures in the system $\text{MgCl}_2 - \text{CaCl}_2 - \text{KCl}$ at 800°C . Surface tensions corresponding to the lines in the composition diagram are projected in the three rectangular diagrams.

- , ———: Binary system
 ▲, - - - - -: Mol % of component with constant composition 20.
 ◻, - . . . -: Mol % of component with constant composition 40.
 ●, ———: Mol % of component with constant composition 60.
 ■, - - - - -: Mol % of component with constant composition 80.
 ○: Pure components.

Given in circles: Temperature coefficient, $\alpha \times 10^3$ ($\text{dyn cm}^{-1} \text{ degree}^{-1}$).

Table 2. Surface thermodynamic functions of the pure molten salts at 800°C .

	H_s (dyn cm^{-1})	$S_s \times 10^3$ ($\text{dyn cm}^{-1} \text{ degree}^{-1}$)
LiCl	189	70
NaCl	194	73
KCl	170	73
RbCl	178	77
CsCl	164	79
MgCl_2	66	4
CaCl_2	196	46

higher surface tension and thus masking the generally observed decrease in surface tension with temperature.

Some covalency is also indicated for LiCl, H_s and γ being lower than for NaCl, and not higher as one would expect if only ionic forces were present.

2. Binary systems

Surface tensions are generally not expected to be additive quantities as given by the relation

$$\gamma = X_1\gamma_1 + X_2\gamma_2 \quad (4)$$

where X is mol fraction and γ_1 and γ_2 are the surface tensions of the pure components.¹⁰ The equilibrium value of the surface tension is obtained by minimizing the total energy of the system, this being a balance between low surface tension and a surface composition not too far from the bulk concentration. This will result in a preference in the surface layer for the component with the lowest surface tension.

According to Guggenheim¹³ the surface tension of an ideal solution can be calculated from the following expression

$$\exp(-\gamma a/RT) = X_1 \exp(-\gamma_1 a/RT) + X_2 \exp(-\gamma_2 a/RT) \quad (5)$$

where a , the surface area per molecule, is assumed equal for the two components.

From eqn. (5) it is seen that an additive surface tension is only predicted for solutions where the surface tensions of the components are not too different. For ideal solutions with $\gamma_1 \neq \gamma_2$ a negative deviation from additivity is predicted, due to enrichment of the component with the lowest surface tension in the surface layer.

Guggenheim¹³ has also derived an expression for the surface tension of regular solutions. At the 50:50 mol% composition the surface tension is then given by:

$$\exp(-\gamma a/RT) = \frac{1}{2}(\exp(-\gamma_1 a/RT) + \exp(-\gamma_2 a/RT)) + \exp(mw/4RT) \quad (6)$$

The parameter m expresses the number of neighbours in the adjacent layer, this parameter being 1/6 for a simple cubic lattice and 1/4 for a close packed structure, and $w/RT = b$ is the regular solution interaction parameter.

The regular solution formula has been used with some success to calculate surface tension in molecular liquids. According to this formula one should expect negative deviation from ideality when $w/RT > 0$, and positive deviation from ideality when $w/RT < 0$.

However, when dealing with molten salt mixtures, it is generally accepted that nearest neighbour as well as next nearest neighbour interactions will be changed during the mixing process. The regular solution formula is therefore not directly applicable.

In binary molten salt mixtures with a common anion the surface tension has generally been found to deviate negatively from additivity. Bertozzi *et al.*^{5,14,15} found that the maximum excess surface tension in charge symmetrical mixtures

$$\gamma_{\max}^E = [\gamma - (X_1\gamma_1 + X_2\gamma_2)]_{\max} \quad (7)$$

could be expressed as a linear function of the size parameter $[(d_1 - d_2)/(d_1 + d_2)]^2$ for each anion. Here d_1 and d_2 denotes the sum of the cation and anion radii (γ_{\max}^E may also be plotted as a function of the conformal solution parameter¹⁶ $\delta_{12} = [(d_1 - d_2)/(d_1 d_2)]^2$, since in both parameters the main variation is due to the $(d_1 - d_2)$ term). Bertozzi *et al.*^{5,14,15} concluded from their measurements that the observed negative deviation in surface tension is due to a change in Coulombic energy in the surface layer. This assumption is, however, open for discussion since other interactions, like the ion-induced dipole (polarization) interactions, may very well contribute more to the excess surface tension than the change in Coulombic energy does. Further, Bertozzi *et al.*^{5,14,15} claimed that the excess surface tension calculated from eqn. (7) is independent of the difference in surface tension between the two components, which is contrary to most models, for instance the Guggenheim equation (eqn. (5)).

We have calculated surface tension values for all the binary mixtures according to three different modifications of the Guggenheim equation, namely:

$$1: \exp(-\gamma a/RT) = X_1 \exp(-\gamma_1 a/RT) + X_2 \exp(-\gamma_2 a/RT) \quad (8)$$

The surface area per molecule has been taken to be

$$a = \left[\frac{M_1 X_1 + M_2 X_2}{\rho N} \right]^{2/3} \quad (9)$$

where M is the molecular weight, ρ is the density of the mixture, and N is Avogadro's number.

$$2: \exp(-\gamma A/RT) = \phi_1 \exp(-\gamma_1 A/RT) + \phi_2 \exp(-\gamma_2 A/RT) \quad (10)$$

Here, mol fractions have been replaced by the volume fractions:

$$\phi_1 = \frac{V_1 X_1}{V_1 X_1 + V_2 X_2} \quad \text{and} \quad \phi_2 = \frac{V_2 X_2}{V_1 X_1 + V_2 X_2} \quad (11)$$

V is the molar volume, and the surface area per molecule is given by

$$A = \left[\frac{\phi_1 V_1 + \phi_2 V_2}{N} \right]^{2/3} \quad (12)$$

$$3: \exp(-\gamma A/RT) = \phi_1 \exp(-\gamma_1 A_1/RT) + \phi_2 \exp(-\gamma_2 A_2/RT) \quad (13)$$

In eqn. (13)

$$A_1 = \left[\frac{M_1}{\rho_1 N} \right]^{2/3} = \left[\frac{V_1}{N} \right]^{2/3} \quad (14a)$$

and

$$A_2 = \left[\frac{V_2}{N} \right]^{2/3} \quad (14b)$$

The reason for introducing eqns. (10) and (13) is that eqn. (8) was originally derived by assuming equal molar volumes and equal surface areas per molecule

for the two components. These two assumptions are not valid in molten salt mixtures as can be seen from molar volume data.⁷

Excess surface tensions have been obtained as the difference between the experimental values and those calculated from eqns. (8), (10), or (13), and are called $\gamma^E(1)$, $\gamma^E(2)$, and $\gamma^E(3)$, respectively.

In Figs. 8 and 9 the excess surface tensions of the CaCl_2 –AlkCl and MgCl_2 –AlkCl systems are plotted *versus* the conformal solution parameter for charge unsymmetrical systems as given by Davis¹⁷

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

Here d_1 and d_2 are the sums of the cation and the anion radii in the pure univalent and divalent salts, respectively. This has been done for the concentrations where the difference in excess surface tension for the various alkaline earth chloride–alkali chloride systems is largest, namely when $X_{\text{CaCl}_2} = 0.667$ and $X_{\text{MgCl}_2} = 0.333$ (*cf.* Figs. 3 and 4).

From Figs. 8 and 9 one sees that in the MgCl_2 –AlkCl systems, only $\gamma^E(2)$ and $\gamma^E(3)$, *i.e.* the excess values calculated from the volume fraction equation, eqns. (10) and (13), fit a straight line when plotted *versus* δ_{12} . The system MgCl_2 –LiCl is an exception, just as it is in the analogous plot of excess enthalpy.¹⁸ From Figs. 8 and 9 it is also seen that for the CaCl_2 –AlkCl systems, the plot of γ^E *versus* δ_{12} is linear for all three equations (eqns. (8), (10), and (13)). As these results might indicate that surface compositions calculated on the basis of volume fractions are more in accordance with the real concentrations of the components in the surface layer than surface concentrations calculated by use of the mol fractions, we will base the following discussion on the deviation from $\gamma^E(2)$, the surface tension calculated by use of volume fractions. The difference between $\gamma^E(2)$ and $\gamma^E(3)$ is always small, and unimportant in this context.

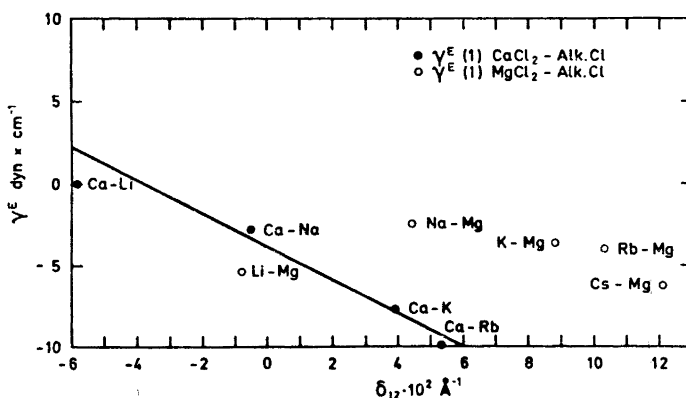


Fig. 8. Excess surface tension $\gamma^E(1)$, calculated relative to eqn. (8), plotted *versus* the size parameter δ_{12} for the charge unsymmetrical molten systems MgCl_2 –AlkCl and CaCl_2 –AlkCl at 800°C.

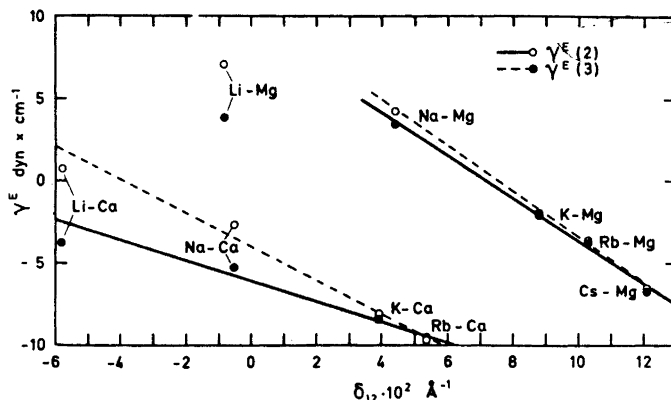


Fig. 9. Excess surface tension $\gamma^E(2)$, calculated relative to eqn. (10), and $\gamma^E(3)$, calculated relative to eqn. (13), plotted versus the size parameter δ_{12} for the charge unsymmetrical molten systems $\text{MgCl}_2 - \text{AlkCl}$ and $\text{CaCl}_2 - \text{AlkCl}$ at 800°C .

A. $\text{CaCl}_2 - \text{AlkCl}$ mixtures. Experimental and calculated surface tension values are compared in Fig. 2. The excess surface tension becomes more negative as the size of the alkali metal ion increases from Li^+ to Rb^+ . This trend can also be seen in Figs. 8 and 9.

The following should be stressed. The component with the lower surface tension (*i.e.* the alkali chloride) has somewhat lower bond energy in the mixture than in the pure molten salt due to stronger interactions between Ca^{2+} and Cl^- in the mixture. In addition the surface is richer in the component with the lower surface tension. This explains the negative excess surface tension found, and the trend towards more negative values when going from $\text{CaCl}_2 - \text{LiCl}$ to $\text{CaCl}_2 - \text{RbCl}$.

B. $\text{MgCl}_2 - \text{AlkCl}$ mixtures. Experimental and calculated values are compared in Figs. 3 and 4. The following observations can be made from the figures.

(i) In $\text{LiCl} - \text{MgCl}_2$ and $\text{NaCl} - \text{MgCl}_2$ only positive excess surface tensions are found.

(ii) In $\text{KCl} - \text{MgCl}_2$, $\text{RbCl} - \text{MgCl}_2$, and $\text{CsCl} - \text{MgCl}_2$ there are positive deviations on the MgCl_2 -side. These vanish, however, with moderate additions of alkali chloride to the magnesium chloride melt, and are gradually changed to negative excess surface tensions for melts with higher contents of alkali chloride.

The observed deviations may be explained in the following way:

By addition of an alkali chloride to molten magnesium chloride, ionization of the partly covalent magnesium chloride structure takes place. New species with higher surface tension than pure MgCl_2 (since they are more ionic) will be formed in the melt. For strong or medium field cations like Li^+ and Na^+ the ionization of the magnesium chloride melt will predominate. Thus the ionization effect explains why positive excess surface tensions are observed in these systems. When chlorides of the weak field cations K^+ , Rb^+ , and

Cs^+ are added, ionization of the magnesium chloride will again take place, but if the melt contains more than 50 mol % of the alkali chloride, there will now be a strong tendency to form complex species in the melt, like the tetrahedral complex MgCl_4^{2-} . We expect these complex compounds to have low surface tensions, resulting in negative deviations from the theoretical values.

C. CaCl_2 – MgCl_2 mixtures. Experimental and calculated curves are compared in Fig. 5. In this system the excess values are small and positive. This means that the ionization of the MgCl_2 -structure is the predominant factor, and that there is no tendency for complex formation in the system.

3. Ternary systems

We have compared our experimental surface tension values in the NaCl – CaCl_2 – MgCl_2 and KCl – CaCl_2 – MgCl_2 systems with values calculated from

Table 3. Experimental and calculated surface tension of mixtures in the two ternary systems NaCl – CaCl_2 – MgCl_2 and KCl – CaCl_2 – MgCl_2 .

System	N_{Alk}	N_{Ca}	N_{Mg}	$\gamma_{123}^{\text{calc}(1)}$	$\gamma_{123}^{\text{calc}(2)}$	$\gamma_{123}^{\text{calc}(3)}$	$\gamma_{123}^{\text{(exp)}}$
$(\text{Na} - \text{Ca} - \text{Mg})\text{Cl}$	0.6	0.2	0.2	103.1	102.3	102.6	102.4
	0.4	0.2	0.4	91.6	90.6	90.9	93.0
	0.4	0.4	0.2	108.4	107.4	107.9	106.1
	0.2	0.4	0.4	97.2	96.2	96.5	97.5
	0.2	0.6	0.2	115.4	114.5	114.8	112.3
	0.2	0.2	0.6	83.1	82.4	82.6	82.5
$(\text{K} - \text{Ca} - \text{Mg})\text{Cl}$	0.6	0.2	0.2	91.9	91.9	91.9	94.1
	0.4	0.2	0.4	84.4	84.2	84.2	86.1
	0.4	0.4	0.2	99.0	98.8	98.9	96.4
	0.2	0.4	0.4	91.6	91.3	91.3	91.2
	0.2	0.6	0.2	106.5	106.3	106.3	105.7
	0.2	0.2	0.6	80.2	79.6	79.6	80.7

the components' binary systems, according to the following semi-empirical equation:

$$\gamma_{123}^{\text{calc}(1)} = -\frac{RT}{a} \ln \left[\sum_{i=1}^3 N_i \exp(-\gamma_i a/RT) \right] + \sum_{i < j=1}^3 N_i N_j \lambda_{ij} \quad (15)$$

Here N_i is mol fraction of component i in the ternary system

$$N_i = \frac{n_i}{\sum_{k=1}^3 n_k} \quad (16)$$

and n is the number of moles. The surface area per molecule is

$$a = \left[\frac{\sum_{i=1}^3 N_i M_i}{N \rho} \right]^{2/3} \quad (17)$$

The interaction parameters are given as the binary excess surface tension (from eqn. (11)) divided by the product of the mol fractions in the binary system.

$$\lambda_{ij} = \gamma_{ij}^E(1)/X_i X_j \quad (18)$$

The surface tensions $\gamma_{123}^{\text{calc}}(2)$ and $\gamma_{123}^{\text{calc}}(3)$ have been calculated by similar equations using interaction parameters derived from eqns. (10) and (13), respectively, and on the basis of volume fractions.

In all cases the binary compositions, $X_i \cdot X_j$, are found as the points of intersection between the binary edge and the line drawn from its opposite corner in the triangle through the ternary composition point. As seen from Table 3, none of the calculated values differ more than $\pm 3\%$ from the experimental ones.

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