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## Testing the Conformal Ionic Solution Theory for the Additive Ternary Molten Salt System

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The conformal ionic solution theory predicts excess chemical potentials of the components in a ternary additive molten salt system, if suitable thermodynamic data on the three subsidiary binary molten salt systems are available. The excess chemical potential of AgCl in the system AgCl—LiCl—KCl has been calculated theoretically, using the published data on binary molten salt systems AgCl—LiCl, AgCl—KCl and LiCl—KCl. The calculated values are compared with the corresponding data based on emf measurements in the ternary system, and discussed with respect to the use of the theory in the thermodynamics of additive molten salt systems.

### INTRODUCTION

The conformal ionic solution (CIS) theory is a statistical — mechanical perturbation theory which has been initially applied to binary molten salt mixtures,<sup>1</sup> and then extended to ternary additive and reciprocal<sup>2,3</sup> systems, taking into account second order perturbation terms. For additive systems the theory has been extended up to fourth order terms,<sup>4</sup> so that a thermodynamic function can be expressed as a power series in ionic fractions up to integral powers of the fourth order. Although the CIS theory originally assumed a pair-wise potential between hard spherical ions, it has been shown to apply to a more general pair potential,<sup>5</sup> taking into account different ionic radii of the component salts and long range interactions. Among other thermodynamic models of molten salts, mention can be made of the »surrounded ion model«,<sup>6,7</sup> then a model based on the concept of quasi-crystal lattice energy,<sup>8,9</sup> and several models based on the quasi-lattice theory.<sup>10-12</sup> They are usually less general and rigorous than the CIS theory, although also the latter has some shortcomings.<sup>4,6</sup>

In the present paper we shall test the CIS theory with respect to its capability to predict the excess chemical potentials of a ternary additive system from the data on the three subsidiary binary systems. So far, the theory has been tested with integral and partial enthalpies of mixing,<sup>4</sup> and it has been used to calculate phase diagrams.<sup>14</sup> In the latter case, however, some approximation and uncertain parameters are introduced, as, for example, the heat capacity of an undercooled liquid phase.<sup>9,15</sup> Since in the last ten years accurate emf measurements of formation cells in binary and ternary molten salt systems have been increasingly published, a direct approach to test the CIS theory by means of the chemical potential of an electrode active component seems feasible. Thus, in the present case, which deals with the system AgCl—KCl—LiCl, experimental data are available on the excess chemical potential of silver chloride,  $\mu_{\text{AgCl}}^{\text{E}}$ , in the ternary additive system,<sup>16</sup> and in two binary systems, AgCl—KCl<sup>17</sup> and AgCl—LiCl<sup>18,19</sup>. For the system KCl—LiCl, experimental data on  $\Delta\mu_{\text{LiCl}}$  are available only at 995 K for the concentration range 0.5—0.9 mole fraction of LiCl.<sup>13</sup> Values of chemical potentials can be also deduced by combining calorimetric<sup>20</sup> and cryoscopic<sup>21</sup> (phase diagram) measurements, and from activity coefficient equations proposed by Moser and Rzyman<sup>22</sup>.

#### CALCULATION OF EXCESS CHEMICAL POTENTIALS

The CIS theory applied to ternary additive molten salt systems (up to fourth order terms)<sup>4</sup> yields the following expression for the excess chemical potential of the component 1 in a mixture of salts 1—2—3:

$$\begin{aligned} \mu_{1(123)}^{\text{E}} = RT \ln \gamma_1 = & a_{12} x_2 (1 - x_1) + a_{13} x_3 (1 - x_1) - a_{23} x_2 x_3 + \\ & + b_{12} [2x_1 x_2 (1 + x_2 - x_1) - x_1^2] + b_{13} [2x_1 x_3 (1 + x_3 - x_1) - x_1^2] + \\ & 2b_{23} x_2 x_3 (x_3 - x_2) + c_{12} x_1 x_2^2 (2 - 3x_1) + c_{13} x_1 x_3^2 (2 - 3x_1) - 3c_{23} x_2^2 x_3^2 + \\ & + \alpha x_2 x_3 (1 - 2x_1) + \beta_1 x_1 x_2 x_3 (2 - 3x_1) + \beta_2 x_2^2 x_3 (1 - 3x_1) + \\ & + \beta_3 x_2 x_3^2 (1 - 3x_1) \end{aligned} \quad (1)$$

Here,  $x_i$  is the mole fraction of the component  $i$ ;  $a_{ij}$ ,  $b_{ij}$  and  $c_{ij}$  are the CIS-parameters of the subsidiary binary system  $i-j$ , while  $\alpha$ ,  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  are CIS-parameters relevant to the ternary system, which can be approximated in terms of the binary parameters:

$$\alpha \approx (b_{12}^{1/3} + b_{13}^{1/3}) (b_{21}^{1/3} + b_{23}^{1/3}) (b_{13}^{1/3} + b_{23}^{1/3}) \quad (2)$$

Here,  $b_{21} = -b_{12}$ ; and

$$\beta_i = 2 |c_{ij}|^{1/2} |c_{ik}|^{1/2} \quad (3)$$

Analogous equations are developed for  $\mu_{2(123)}^{\text{E}}$  and  $\mu_{3(123)}^{\text{E}}$ . The binary parameters  $a_{ij} \dots c_{ij}$  cannot be calculated *a priori*, but they can be obtained from experimental data on the three subsidiary binary systems. In the present work, the data relevant to the dependence of the excess chemical potential on the melt composition for a subsidiary binary system are always presented in the form:

$$\mu_{i(ij)}^{\text{E}} = (1 - x_i)^2 (A_{ij} + B_{ij} x_i + C_{ij} x_i^2) \quad (4)$$

In the case of the binary systems AgCl—KCl and AgCl—LiCl, eq. (4) is based on a least-square fit derived from emf measurements of the formation

cell in the binary melt. Thus,  $A_{ij} \dots C_{ij}$  are empirical parameters which give the best fit, and they are, in principle, temperature dependent. In case of the binary system KCl—LiCl, which does not form a measurable formation cell, we used the data of Thulin *et al.*<sup>13</sup>, obtained by emf measurements of a chlorine concentration cell containing pure LiCl in one half-cell and LiCl—KCl in the other half-cell. The two half-cells were separated by a Li-glass membrane. Only those results (at 995 K,  $x_{\text{LiCl}} = 0.5-0.9$ ) have been taken into account for which the junction potential was negligible.<sup>13</sup> From the data listed in Table I of reference 13, we obtained, by a least squares fit, the expression

$$\Delta \bar{S}_{\text{LiCl}}^{\text{E}} = (-8.49 + 5.11 x_{\text{LiCl}}) (1 - x_{\text{LiCl}})^2 / J \text{ mol}^{-1} \text{ K}^{-1}$$

and for the excess chemical potential of lithium chloride:

$$\mu_{\text{LiCl(LiCl-KCl)}}^{\text{E}} = (1 - x_{\text{LiCl}})^2 (-17900 + 8.49 T - 5.11 x_{\text{LiCl}} T) / J \text{ mol}^{-1}$$

The above equation reproduces the experimental excess chemical potentials of Thulin *et al.*<sup>13</sup> within  $\pm 3\%$ . With it one can calculate the excess chemical potential of potassium chloride:

$$\mu_{\text{KCl(KCl-LiCl)}}^{\text{E}} = (1 - x_{\text{KCl}})^2 (-17900 + 5.935 T + 5.11 T x_{\text{KCl}}) / J \text{ mol}^{-1} \quad (5)$$

Equation (5) is in the form compatible with eq. (4), and has been used in our CIS calculation of the ternary system. For the sake of comparison, two additional expressions for  $\mu_{\text{KCl}}^{\text{E}}$  in KCl—LiCl have been tested. One of them was derived by combining the enthalpies of mixing obtained calorimetrically<sup>20</sup> with a »regular solution« expression valid near the binary eutectic point<sup>21</sup> (from data based on phase diagram). The result is:

$$\mu_{\text{KCl(KCl-LiCl)}}^{\text{E}} = (1 - x_{\text{KCl}})^2 (-17949 + 6.91 T + 754 x_{\text{KCl}}) / J \text{ mol}^{-1} \quad (6)$$

Another expression has been recommended by Moser and Rzyman:<sup>22</sup>

$$\mu_{\text{KCl(KCl-LiCl)}}^{\text{E}} = (1 - x_{\text{KCl}})^2 (-17584 + 5.57 T) / J \text{ mol}^{-1} \quad (7)$$

The last equation is a »regular solution« expression which neglects asymmetric concentration terms, in contrast to eqs. (5) and (6).

The CIS parameters can be readily expressed in terms of the empirical coefficients of eq. (4). For example, if  $x_3 = 0$ , eq. (1) is reduced to eq. (4), and in the case  $i = 1$ ,  $j = 2$ , taking into account that now  $x_1 + x_2 = 1$ , one obtains:

$$\begin{aligned} \mu_{1(12)}^{\text{E}} &= (1 - x_1)^2 [(a_{12} - b_{12}) + (4b_{12} + 2c_{12}) x_1 - 3c_{12} x_1^2] = \\ &= (1 - x_1)^2 [A_{12} + B_{12} x_1 + C_{12} x_1^2] \end{aligned}$$

The last equation gives  $a_{12} - b_{12} = A_{12}$ ,  $4b_{12} + 2c_{12} = B_{12}$  and  $-3c_{12} = C_{12}$ . Generally, the following relations are valid:

$$a_{ij} = A_{ij} + B_{ij}/4 + C_{ij}/6 \quad (8a)$$

$$b_{ij} = B_{ij}/4 + C_{ij}/6 \quad (8b)$$

$$c_{ij} = -C_{ij}/3 \quad (8c)$$

Eqs. (8, a—c), (2) and (3) allow one to calculate the excess chemical potentials of the ternary additive system according to eq. (1). The empirical binary

coefficients (eq. (4)) and the CIS parameters (eq. (1)—(3)) for the system AgCl—KCl—LiCl are listed in Table I. The 5th column of that table gives the references relevant to the coefficients of eq. (4).

TABLE I

Empirical Coefficients for the Binary Systems (eq. (4)) and CIS Parameters (eq. (1)),  $J \text{ mol}^{-1}$ . All  $C_{ij}$ ,  $c_{ij}$ ,  $\beta_i$  Values Equal to Zero. Indices: AgCl 1, KCl 2, LiCl 3.

System (1) — (2)	Temp. K	$A_{ij}$	$B_{ij}$	Ref.	$a_{ij}$	$b_{ij}$	$\alpha$	Remark
AgCl—KCl (1) — (2)	873	—6145	—2675	17	—6814	—669		
	973	—6109	—2372		—6702	—593		
	1073	—6088	—2167		—6630	—542		
AgCl—LiCl (1) — (3)	873	8587	—	18, 19	8587	—		
	973	8693	—		8693	—		
	1073	8798	—		8798	—		
KCl—LiCl (2) — (3)	873	—12718	4461	13	—11603	1115	—1733	Based on eq. (5)
	973	—12125	4972		—10882	1243	—1730	
	1073	—11532	5483		—10161	1371	—1744	
KCl—LiCl (2) — (3)	873	—11917	754	20, 21	—11729	188.5	—726	Based on eq. (6)
	973	—11226	754		—11037	188.5	—681	
	1073	—10535	754		—10347	188.5	—649	
KCl—LiCl (2) — (3)	873	—12721	—	22	—12721	—	—	Based on eq. (7)
	973	—12164	—		—12164	—	—	
	1073	—11607	—		—11607	—	—	

Referring to Table I, it is interesting to note that in the binary system AgCl—KCl the excess chemical potential of silver chloride has a negative deviation from ideality, whereas in AgCl—LiCl its deviation from ideality is positive. This is obviously due to the difference in ionic size between the lithium and potassium cations and consequently to the difference in such contributions to the ion-ion interaction as ionic polarizability, dispersion and multipole interactions. It is also interesting to note that among the ternary CIS coefficients only  $\alpha$  which depends on the  $b_{ij}$  values, is important. Its absolute value is considerably below those of  $a_{ij}$ 's, but since the latter have opposite signs, its influence in a certain region of composition cannot be neglected.

## RESULTS AND DISCUSSION

The calculated excess chemical potentials of AgCl in the ternary system AgCl—KCl—LiCl, at various compositions of the melt and at three temperatures, are presented in Figure 1. The curves are functions of  $\mu_{\text{AgCl}}^E$  vs.  $x_{\text{AgCl}}$  according to eq. (1), at constant ratio of  $y = x_{\text{LiCl}}/(x_{\text{LiCl}} + x_{\text{KCl}})$ . The experimental points were obtained by emf measurements in the ternary system.<sup>16</sup> The full lines represent the CIS calculation in which the binary coefficients  $A_{ij}$  and  $B_{ij}$  for the system KCl—LiCl were taken from eq. (5), whereas the dashed lines and the series of points represent calculations in which those coefficients were taken from eqs. (6) and (7), respectively. One can easily note that the full lines fit much better the experimental data; the over-all standard deviation between the experimental and calculated

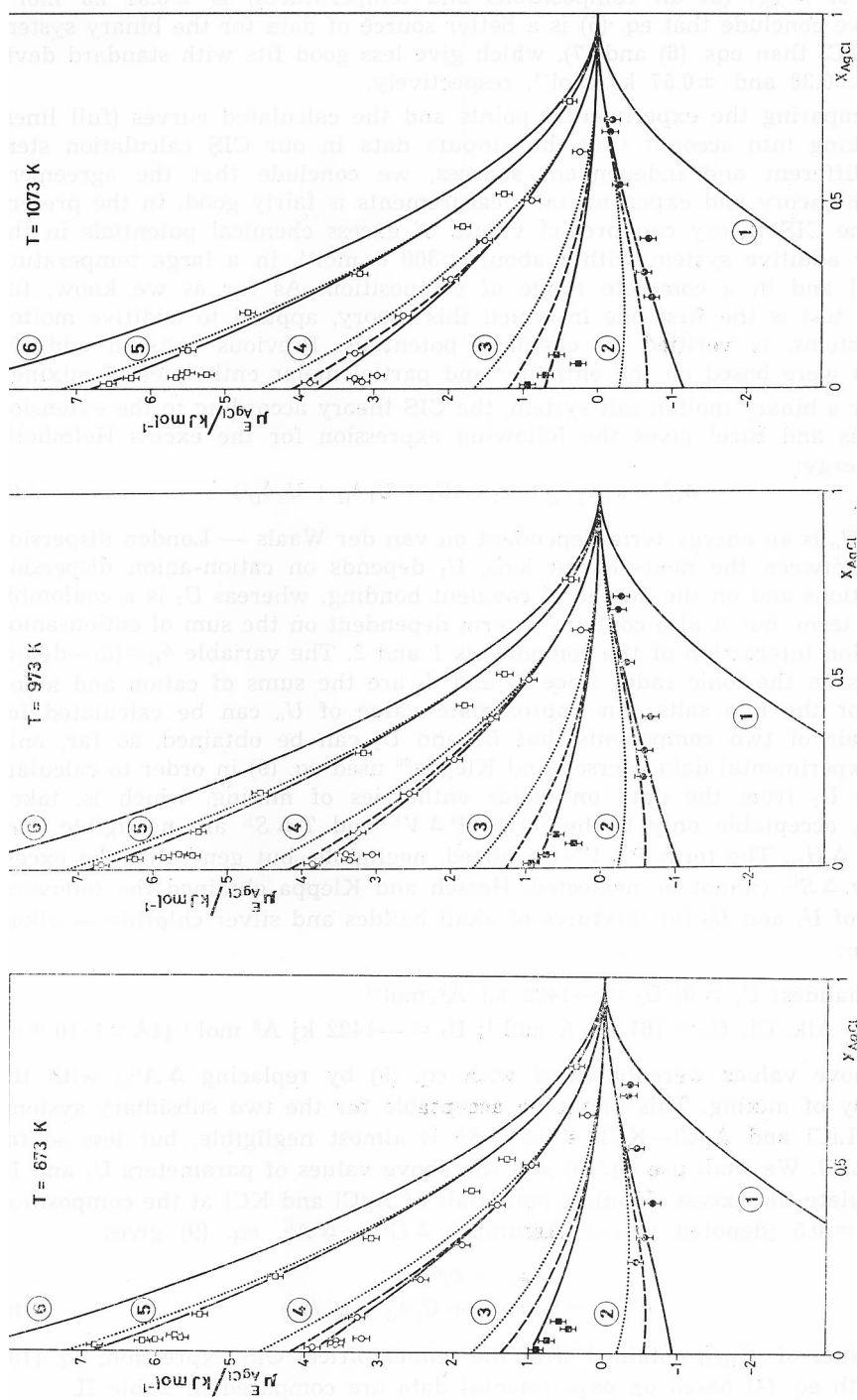


Figure 1. The excess chemical potential of AgCl vs. mole fraction of AgCl in the system AgCl—KCl—LiCl, at constant mole ratio  $y = x_{LiCl}/(x_{LiCl} + x_{KCl})$ . Experimental points from ref. 16, lines represent the CIS calculation (eq. 1), using the following data for the binary system KCl—LiCl:  $\frac{\mu_{AgCl}^E}{\text{kJ mol}^{-1}}$ : eq. (5),  $\frac{\mu_{AgCl}^E}{\text{kJ mol}^{-1}}$ : eq. (6), . . . . eq. (7). Values of the ratio  $y$ : 1) 0, 2) 0.25, 3) 0.35, 4) 0.526, 5) 0.750, 6) 1.00.

values of  $\mu_{\text{AgCl}}^E$  (at all compositions and temperatures) is  $\pm 0.31 \text{ kJ mol}^{-1}$ . Thus, we conclude that eq. (5) is a better source of data for the binary system KCl—LiCl than eqs. (6) and (7), which give less good fits with standard deviations  $\pm 0.38$  and  $\pm 0.57 \text{ kJ mol}^{-1}$ , respectively.

Comparing the experimental points and the calculated curves (full lines) and taking into account that the »input« data in our CIS calculation stem from different and independent sources, we conclude that the agreement between theory and experimental measurements is fairly good. In the present case, the CIS theory can predict values of excess chemical potentials in the ternary additive system within about  $\pm 300 \text{ J mol}^{-1}$ , in a large temperature interval and in a complete range of composition. As far as we know, the present test is the first one in which this theory, applied to additive molten salt systems, is verified by chemical potentials. Previous tests in additive systems were based on the enthalpy and partial molar enthalpies of mixing.<sup>4</sup>

For a binary molten salt system, the CIS theory according to the extension of Davis and Rice<sup>1</sup> gives the following expression for the excess Helmholtz free energy:

$$A_{12}^E = x_1 x_2 \lambda_{12} = x_1 x_2 (U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2) \quad (9)$$

where  $U_0$  is an energy term dependent on van der Waals — London dispersion forces between the next-nearest ions,  $U_1$  depends on cation-anion dispersion interactions and on the degree of covalent bonding, whereas  $U_2$  is a coulombic energy term, but it also contains a term dependent on the sum of cation-anion dispersion interaction of the components 1 and 2. The variable  $\delta_{12} = (d_1 - d_2)d_1 d_2$  depends on the ionic radii, since  $d_1$  and  $d_2$  are the sums of cation and anion radii for the two salts. An approximate value of  $U_0$  can be calculated for each pair of two components, but  $U_1$  and  $U_2$  can be obtained, so far, only from experimental data. Hersch and Kleppa<sup>20</sup> used eq. (9) in order to calculate  $U_1$  and  $U_2$  from the data on molar enthalpies of mixing, which is, taken strictly, acceptable only if the terms  $P \Delta V^E$  and  $T \Delta S^E$  are negligible, *i. e.*,  $\Delta A^E \sim \Delta H_m$ . The term  $P \Delta V^E$  is, indeed, negligible, but generally, the excess entropy  $\Delta S^E$ , cannot be neglected. Hersch and Kleppa obtained the following values of  $U_1$  and  $U_2$  for mixtures of alkali halides and silver chloride — alkali chloride:

alkali halides:  $U_1 = 0$ ;  $U_2 = -1422 \text{ kJ } \text{Å}^2 \text{ mol}^{-1}$

AgCl — Alk. Cl:  $U_1 = 167 \text{ kJ } \text{Å} \text{ mol}^{-1}$ ;  $U_2 = -1422 \text{ kJ } \text{Å}^2 \text{ mol}^{-1}$  ( $1 \text{ Å} = 1 \cdot 10^{-10} \text{ m}$ )

The above values were obtained with eq. (9) by replacing  $\Delta A_{12}^E$  with the enthalpy of mixing. This might be acceptable for the two subsidiary systems AgCl—LiCl and AgCl—KCl, since  $\Delta S^E$  is almost negligible, but less so for KCl—LiCl. We shall use eq. (9) and the above values of parameters  $U_1$  and  $U_2$  to calculate the excess chemical potentials of AgCl and KCl at the composition  $x_i = x_j = 0.5$  (denoted  $\mu_{i(0.5)}^E$ ). Assuming  $\Delta G^E \sim \Delta A^E$ , eq. (9) gives

$$\mu_{1(0.5)}^E = x_2^2 \lambda_{12} \\ \mu_{1(0.5)}^E = 0.25 ((U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2)) \quad (10)$$

The values of  $\mu_{i(0.5)}^E$  obtained with the semiempirical CIS expression, eq. (10), and with eq. (4) based on experimental data are compared in Table II.

TABLE II

A Comparison of  $\mu_{1(0.5)}^E$  Based on Experimental Data and on a Semiepirical CIS Expression (at  $x_1 = x_2$ , 973 K)

System (1) — (2)	$U_o/\text{J mol}^{-1}$ <sup>(a)</sup>	$\delta_{12}/\text{\AA}^{-1}$ <sup>(b)</sup>	$\mu_{1(0.5)}^E/\text{kJ mol}^{-1}$	
			exp. (eq. 4)	CIS (eq. 10)
AgCl—KCl	2427	-0.04385	-1.82	-1.91
AgCl—LiCl	5481	+0.05262	2.17	2.58
KCl—LiCl	619	-0.09647 <sup>(c)</sup>	-2.41 <sup>(d)</sup>	-3.15
			-2.71 <sup>(e)</sup>	
			-3.05 <sup>(f)</sup>	

<sup>(a)</sup> Calc., ref. 20

<sup>(b)</sup> Based on Pauling ionic radii, but for  $\text{Ag}^+$  a radius of 0.95 Å is adopted, as recommended by Blander (ref. 23) and used in the derivation of the  $U_i$  parameters (ref. 20).

<sup>(c)</sup> Index 1 refers to LiCl, in accordance with the derivation of  $U_i$  parameters (ref. 20).

<sup>(d)</sup> From eq. (5); <sup>(e)</sup> from eq. (6); <sup>(f)</sup> from eq. (7)

Table II shows that the agreement between the  $\mu_{1(0.5)}^E$  values is fairly good. Depending on the equation used to calculate  $\mu_{1(0.5)}^E$  for the system KCl—LiCl, values between -2.41 and -3.05 kJ mol<sup>-1</sup> are obtained, whereas the CIS value is -3.15 kJ mol<sup>-1</sup>. These discrepancies are well within the accuracy of estimating  $U_o$ ,<sup>20</sup> so that a difference of 0.6 kJ mol<sup>-1</sup> can be considered as an acceptable agreement.

Thus, we conclude that the conformal ionic solution theory is in reasonable agreement with the experimental chemical potentials obtained in the system AgCl—KCl—LiCl and its subsidiary binary systems.

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### IZVOD

#### Provera teorije konformalnog jonskog rastopa za aditivni ternarni sistem rastopa soli

Ivan J. Gal i István J. Zsigrai

Teorija konformalnog jonskog rastopa predskazuje dodatni («excess») hemijski potencijal komponenata u ternernom aditivnom sistemu rastopa soli ako su poznati termodinamički podaci za tri supsidijarna binarna sistema.

Na osnovu publikovanih podataka za binarne sisteme  $\text{AgCl-LiCl}$ ,  $\text{AgCl-KCl}$  i  $\text{LiCl-KCl}$  izračunat je dodatni hemijski potencijal  $\text{AgCl}$  u sistemu  $\text{AgCl-LiCl-KCl}$ . Izračunate vrednosti su upoređene sa odgovarajućim vrednostima dobijenim na osnovu merenja EMS u ternarnom sistemu i diskutovane u vezi s primenom teorije u termodinamici aditivnih sistema rastopa soli.