THERMODYNAMIC PROPERTIES OF BINARY CHLORIDE MIXTURES BY MOLECULAR DYNAMICS COMPUTATION

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ABSTRACT

Experimentally, it has been shown that the interaction coefficients of binary molten salt mixtures are represented by $a(T,V)(g_1 - g_i)^2$; $a(T,V)$ is a constant for a class of mixtures and $g_i^{-1}$ is proportional to the sum of the radii of the cation and anion in the $i$th salt. Theoretically, this representation was explained by the conformal ionic solution (CIS) theory. Using the molecular dynamics technique, we have calculated $a(T,V)$ as derived from the CIS theory. In these computations, the particles interacted according to the Tosi-Fumi pair potential. The value obtained for $a(T,V)$ differed significantly from experimental data. Consequently, one can conclude that the repulsive contribution to the Tosi-Fumi pair potential is inadequate. Other models are needed to accurately represent molten salt properties.

I. INTRODUCTION

In recent years, computer simulation techniques have been widely used for studying the dynamics and thermodynamics of liquids, solids and gases. Monte-Carlo (MC) and molecular dynamics (MD) methods have proved to be powerful tools for such investigations, particularly for ionic liquid salts. Several machine simulations of molten alkali-halides have been performed at different temperatures and pressures; a more detailed review of the work in this field is given in Reference 1. However, one weakness of the numerical methods is related to the lack of a reliable pair potential defining the interactions between the particles present in the system. More precisely, in a large number of computer simulations, an empirical pair potential, derived by Tosi-Fumi from an extensive analysis of the properties of alkali-halides at room temperature, is used. Despite the approximation in the use of this pair potential to describe the liquid dynamics, the agreement obtained between calculations and observations of the studied properties was fairly good for most of the substances. However, for lithium salts and especially lithium iodide, the computed properties differed considerably from experiments. In addition, numerical difficulties are
encountered when polarizability contributions are included; a "catastrophe" occurs making the evaluation of the effect of polarizability impossible without an artifact in the calculations.3

To our knowledge, there have been only two computer simulations of ionic liquid mixtures. Such numerical investigations should provide valuable information on the structure of solutions and especially on the relative importance of different contributions to the thermodynamics of the system (such as contributions due to the short range repulsion, contributions due to coulomb interactions and contributions due to the cation-cation, anion-anion and cation-anion dispersive interactions). Larsen, Førland and Singer4 used MC techniques to study the mixing process:

\[
\text{NaCl}(l) + \text{KCl}(l) \not\sim (\text{NaCl}, \text{KCl})(l)
\]

and the related thermodynamic properties. In order to represent the interactions of the ions of the solution, a mathematical model for the binary mixture was suggested, which resulted in an adjustment of the coefficients of the Tosi-Fumi potential. The conclusions drawn from this work were more qualitative than quantitative: large relative errors affected the results since the MC data for the mixing process were obtained as small differences between large quantities.4

A more recent calculation by Adams and McDonald5 dealt mainly with the evaluation of the enthalpies of mixing of nitrate mixtures. The pair potential used was suggested by Blander6 in an analysis of dimensional methods. The conformal ionic solution (CIS) theory (developed by Reiss, Katz and Kleppa7 from an analogous theory for non-electrolytes by Longuet-Higgins8) which describes the binary mixtures in terms of the properties of a reference salt was reviewed in light of the results. For numerical reasons, the coefficient \( g_1 \) (which is defined as the ratio of the sum of the cation and anion radii in the reference salt, in this study KNO3, to the sum of the radii in the ith salt of the mixture, \( g_i = (d_{\text{KNO3}}) / d_i \)) was considerably larger than unity. Consequently, the second-order equations that Adams and McDonald tested are inadequate to accurately represent their calculated enthalpies of mixing. Higher order terms9 should be required and evaluated if one applies such large changes. The test of the CIS theory, as performed, is inconclusive.

These above considerations stimulated our interest in numerically investigating some of the thermodynamic properties of binary chloride mixtures. Recently, we demonstrated that for binary mixtures the equations for the enthalpy of mixing, \( \Delta H_m \), derived from the CIS theory agrees with calorimetric data10 not only in form, as shown by Reiss, Katz and Kleppa7 and by Blander,8 but also in sign. The second-order coefficient in the equation for \( \Delta H_m \) was shown to be proportional to the negative of an energy fluctuation and is therefore negative. This conclusion is valid regardless of the form of the repulsive part of
the pair potential. Qualitatively, the CIS theory has been proven to give reliable predictions. A quantitative test remains to be performed. The necessity of MC or MD sampling techniques in such a test is obvious if one considers the rather complicated multiple integrals in the equations. In this paper, we report on a computer simulation of binary chloride mixtures based on the CIS theory.

II. GENERAL CONSIDERATIONS ON THE CIS THEORY

Within the context of this work, the attractive feature of the CIS theory resides in the fact that the thermodynamic properties of the binary mixtures are related only to those of the reference salt. If one considers a binary mixture, AX-BX, three perturbation calculations are carried out generating the two pure salts, AX and BX, and the mixture from a reference salt with the same common anion. The resultant excess free energy of mixing, \( \Delta A_m^E \), is expressed as:

\[
\Delta A_m^E = a(T,V)(g_1 - g_2)^2 X_1 X_2
\]

Contributions up to only second-order terms in \((g_i - 1)\) are included in the above equation. The perturbation parameter \( g_i \) \((i = 1,2)\) is defined as \( g_i = \frac{d_0}{d_i} \) with \( d_0 \) and \( d_i \) being the characteristic sum of the anion-cation radii of the reference salt and of the \( i \)th salt, respectively; \( g_1 \) is used to scale the repulsive part of the pair potential. The quantity \( X_i \) represents the ionic fraction of the cation in the \( i \)th salt. The binary interaction coefficient can be written as:

\[
a(T,V) = \frac{kT}{2} \left[ \frac{N^3 D + N^3 (N-1) F}{Z'} - \left( \frac{A}{Z'} \right)^2 \right]
\]

where \( k \) is the Boltzmann constant and \( N \) is Avogadro's number. The coefficients \( Z' \), \( A \), \( D \) and \( F \) are combinations of multiple integrals; keeping the same notation as in Reference 9, one has

\[
Z' = \int \cdots \int \exp(-U_0/kT)(d\tau)^{2N}
\]

\[
A = \frac{N^2}{kT} Z'<a><c'a>
\]

\[
D = \left( \frac{1}{kT} \right)^2 Z'<a><c'a><c'a>
\]

and

\[
F = \left( \frac{1}{kT} \right)^2 Z'<a><c'a><c'a>
\]
The quantity $U_Q$ refers to the total potential energy of the reference salt, $c$ to a cation, $a$ to an anion, $dr$ to a volume element in configurational space, and the function $\phi_{ca} = \frac{\partial u_{rep}}{\partial g_{i}}$ where $u_{rep}$ represents the repulsive part of the pair potential. All these integrals can be calculated solely from properties of the reference salt. For any function of the coordinates, $<Q>$ designates:

$$<Q> = \frac{1}{Z'} \int \ldots \int Q \exp \left( -\frac{U_Q}{kT} \right) (dr)^{2N}$$

We have shown, that to a good approximation, Eq. (2) can be written as:

$$a(T,V) = \frac{N^2}{2kT(N-1)} \left[ <E_c^2> - <E_c>^2 \right]$$

with

$$E_c = \sum_{a=1}^{N} \phi_{ca}$$

According to Eq. (8), the second-order contributions to $\Delta H_m^E$ are always negative. The same conclusion holds for the second-order contributions to the enthalpy of mixing, $\Delta H_m$. In fact, a second-order perturbation calculation gives:

$$\Delta H_m = a'(T,P)(g_1 - g_2)^2 X_1X_2$$

The difference between $a(T,V)$ and $a'(T,P)$ is proportional to the excess entropy of mixing, $\Delta S_m^E$, which is generally small. Therefore,

$$a'(T,P) \approx a(T,V)$$

One can conclude from Eqs. (8), (10) and (11) that $\Delta H_m$ should be negative. The sign is in agreement with the calorimetric observations. In particular, at a 50%-50% composition, the variations of $\Delta H_m^E$ for chloride mixtures are linear in $(g_1 - g_2)^2$ and the reported slope is negative. This finding lends confidence in the CIS theory for representing the thermodynamic properties of mixtures. Consequently, in order to compare $a(T,V)$ as expressed in Eq. (8) with published data, one needs to evaluate $<E_c>$ and $<E_c^2>$. 

III. COMBINATION OF THE CIS THEORY AND MD TECHNIQUES

In this investigation, we used the MD procedure to evaluate $a(T,V)$ as defined in Eq. (8). More details on the algorithm of the method can be found in Appendix A of Reference 14. The test salt was selected to
be KCl, mainly because of good agreement between computed and observed thermodynamic properties. We chose a sample system consisting of 216 particles enclosed in a cubic box of size $L = 20.607 \text{ Å}$ and satisfying the usual periodic boundary conditions. The particles interacted according to the Tosi-Fumi pair potential, which reads as:

$$u_{ij} = \frac{Z_i Z_j e^2}{4\pi \varepsilon_0} \frac{1}{r_{ij}^6} + b_{ij} \exp[B_{ij} (d_{ij} - r)] + C_{ij} r^{-6} + D_{ij} r^{-8}$$  \hspace{1cm} (12)

where $Z_i$ is the charge of the ion $K$; $e$, the electron charge; $\varepsilon_0$, the vacuum permittivity; $r$, the distance between the two particles; $d_{ij}$, the characteristic size parameter; $b_{ij}$ and $B_{ij}$ are constants defining the repulsive interaction; and $C_{ij}$ and $D_{ij}$ are, respectively, the coefficients for dipole-dipole and dipole-quadrupole interactions. For KCl, the values of these coefficients are the following:

|      | $b_{ij}$ \text{(10^{-12} \text{ erg})} | $B_{ij}$ \text{(Å^{-1})} | $d_{ij}$ \text{(Å)} | $C_{ij}$ \text{(10^{-12} \text{ erg Å}^6)} | $D_{ij}$ \text{(10^{-12} \text{ erg Å}^8)} |
|------|---------------------------------|-----------------|----------------|-----------------|----------------|
| cc   | 0.423                           | 2.97            | 2.926          | -24.3           | -24.0          |
| ca   | 0.338                           | 2.97            | 3.048          | -48.0           | -73.0          |
| aa   | 0.253                           | 2.97            | 3.179          | -124.5          | -250.0         |

The constant $b_{ij}$ is the same for all alkali-halides; $B_{ij}$ has a common value for the three ion pairs in any salt. The quantities $C_{ij}$ and $D_{ij}$ are taken from the calculations of Mayer. According to Eq. (12), the expression for $E_c$ as introduced in Eq. (9) becomes:

$$E_c = \frac{Z_i Z_j e^2}{4\pi \varepsilon_0} + \sum_{a=1}^{n} \frac{b_{ca} B_{ca} d_{ca}}{c_a c_a c_a \exp[B_{ca} (d_{ca} - r)]}$$  \hspace{1cm} (13)

The averages of $E_c$ and $E_c^2$ were evaluated at $T = 1100 \text{ K}$ using 10,000 configurations. For a given cation, the values of $<E_c>$ and $<E_c^2>$ were calculated by including the anions located inside a sphere centered on the cation; for any radius $> 4.5 \text{ Å}$ the values do not differ significantly. This is expected since the repulsive potential drops off very rapidly with $r$. At $T = 1100 \text{ K}$, we obtained $a(T,V) = -1320 \text{ kcal \ mol}^{-1}$. The values derived for $a(T,V)$ from calorimetric data vary depending on the rather arbitrary choice of ionic radii. The first determination was given using the Pauling radii. The enthalpies of mixing, at a 50%-50% composition, for iodide, chloride, fluoride, bromide, and nitrate mixtures when plotted versus $\left(\frac{1}{d_i} - \frac{1}{d_j}\right)^2$ fall on a line, within
the experimental uncertainties, with a slope of -340. This leads to 
\( a(T,V) = -37 \text{ kcal mol}^{-1} \). Recently, a reevaluation \(^{18}\) of the slope was 
done for only chloride mixtures using ionic radii derived from the 
reduced molar volume of each salt. \(^{15}\) A different value of \( a(T,V) \) was 
obtained: \( a(T,V) = -130 \text{ kcal mol}^{-1} \). The remaining alkali-halides mix-
tures and the nitrate mixtures are found to define different slopes. \(^{18}\) 
Finally, one can extract other values for \( a(T,V) \) using a different 
self-consistent set of ionic radii as given by Goldschmidt \(^{20}\) or by 
Melnichak and Kleppa. \(^{21}\) Despite the differences in the determination 
of \( a(T,V) \) and the disagreement on the fact that the above mentioned 
slope varies with the common anion, our computed value of \( a(T,V) \) is too 
far from any derived from experiments to have physical meaning.

From another investigation by Ree and Holt \(^{22}\) on the crystal elastic 
constants, the Tosi-Fumi model did not give a satisfactory representa-
tion of the data. An analysis of the potential allowed Ree and Holt to 
conclude that the Tosi-Fumi potential appears to be too soft and re-
quires a deeper minimum. In fact, with a deeper minimum, the polariza-
tion "catastrophe" mentioned earlier would probably not occur, making 
possible the consideration of ion polarizabilities.

IV. CONCLUSION

This preliminary investigation underlines the fact that some phys-
ical properties are more sensitive than others to the form of the poten-
tial model used. In this case, the excess free energy of mixing for 
binary mixtures is not accurately represented by the Tosi-Fumi poten-
tial. MD computations performed using the empirical pair potential of 
Michielsen, Woerlee, Graaf and Ketelaar \(^{23}\) appear to give a more reason-
able value for the coefficient \( a(T,V) \). \(^{11}\) One conclusion could be that 
the repulsive contribution to the Tosi-Fumi potential does not lead to 
agreement between all calculated and observed thermodynamic properties.
The significance of this finding is that it is possible to test the 
adequacy of \( u_{REP} \) and thus to screen various forms suggested for repul-
sive contribution to the pair potential. Further computations are 
still needed to develop more criteria for testing other contributions 
to the pair potential. Given a variety of such criteria, we should be 
able to ultimately develop pair potentials adequate for a complete 
description of molten salt properties.

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