Effective pair potentials of Molten AgBr, CuBr, CuI and RbBr estimated from the experimental partial structure factors

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Abstract

The effective pair potentials of molten AgBr, CuBr, CuI and RbBr have been obtained from measured structural information by solving the modified hypernetted-chain (MHNC) equation coupled with a predictor–corrector method, recently proposed for a binary system. The usefulness of the pair potentials obtained in this work was suggested by reproducing the particular pre-peak in the partial structure factor of Cu–Cu pair in molten CuBr and CuI, because such pre-peak could not be given while using the model potentials previously proposed for these two molten salts. Some characteristic features in these four molten salts were also detected in the bridge function, which was introduced to the MHNC equation as a many-body interaction contribution. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A clear understanding of the physical properties of molten salts is known to depend heavily upon their structure and pair potential at a microscopic level. It is also well recognized that the effective pair potentials estimated from the experimental structural data are quite useful, because they are considered to include, more or less, the particular features of liquid of interest. After the pioneer work of Johnson and March [1], the effective pair potentials of various liquids were estimated from measured structural information using Percus–Yevick (PY) equation and hypernetted-chain equation (HNC) [2].

For metallic liquids, the pseudo-potential theory is now well-recognized for estimating the effective pair potentials, because their characteristic features, including their long-range oscillatory behavior, are interpreted as dielectric screening of ions by conducting electrons. In case of a long-range Coulombic interacting system such as molten salts, asymptotic behavior of the direct correlation function is described by the form of \(1/r\) in the long distance region and this is known to induce a \(1/Q^2\) singularity at the low-wave vector \((Q)\) limit of the Fourier transformation for the direct correlation function. Thus, the reasonable effective pair potentials can be obtained for the Coulomb system, only when the \(1/Q^2\) singularity is carefully taken into account. With respect to this problem, a ‘predictor–corrector method’ proposed by Reatto, Leversque and Weis [3] is found to be quite useful in solving the modified hypernetted-chain equation (MHNC) [4]. However, no systematic result for molten salts is obtained yet.

The main purpose of this work is to estimate the effective pair potentials of molten salts of AgBr, CuBr, CuI and RbBr from the experimental partial structure factors by applying the MHNC coupled with the predictor–corrector method.

2. Fundamentals of data processing

The procedure for estimating the effective pair potentials of molten salts has already been described in detail [4]. Thus, only essential points and some additional details are given below.

A diagrammatic expansion for the pair distribution functions \(g_{\alpha\beta}(r)\) of a multicomponent liquid, provided that the particles interact through two-body additive potentials \(u_{\alpha\beta}(r)\) between \(\alpha\) and \(\beta\) components, leads to the following equation [2],

\[
  g_{\alpha\beta}(r) = \exp \left[ - \frac{u_{\alpha\beta}(r)}{k_B T} + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) + B_{\alpha\beta}(r) \right] 
\] (1)
where \( h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \) and \( k_B \) is the Boltzmann constant and \( T \), the absolute temperature. Direct correlation function \( c_{\alpha\beta}(r) \) is defined through the following Ornstein–Zernike relation,

\[
h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\gamma} n_{\gamma} \int h_{\alpha\gamma}(r - r')c_{\gamma\beta}(r')dr' \tag{2}
\]

where \( n_{\gamma} \) is number density of the \( \gamma \)th component. \( B_{\alpha\beta}(r) \) is called a bridge function, which is a sum of the contribution of all elementary graphs in a cluster expansion.

By means of these equations, when the experimental structural data are given, the effective pair potential of the liquid can be estimated through the following equation,

\[
u_{\alpha\beta}(r) = k_B T [h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - \ln g_{\alpha\beta}(r) + B_{\alpha\beta}(r)]. \tag{3}
\]

The relations between Ashcroft–Langreth partial structure factors \( S_{\alpha\beta}(Q) \) and the Fourier transform of the direct correlation functions \( \hat{C}_{\alpha\beta}(Q) \) can be given by the following equations,

\[
n_1 \hat{C}_{11}(Q) = \frac{(S_{11}(Q) - 1)S_{22}(Q) - S_{12}(Q)^2}{M(Q)},
\]

\[
n_2 \hat{C}_{22}(Q) = \frac{(S_{22}(Q) - 1)S_{11}(Q) - S_{12}(Q)^2}{M(Q)},
\]

\[
\sqrt{n_1 n_2} \hat{C}_{12}(Q) = \frac{S_{12}(Q)}{M(Q)}, \tag{4}
\]

where \( M(Q) = S_{11}(Q)S_{22}(Q) - S_{12}(Q)^2 \).

The most simple way to solve this inverse problem is to set \( B_{\alpha\beta}(r) = 0 \) (hypernetted-chain approximation). However, this is not suitable to obtain the pair potentials from measured structural information, because \( B_{\alpha\beta}(r) \) could not be neglected in near neighbor region for dense liquids.

For ionic liquids, the long-range Coulomb interaction appears to play an important role in determining their structure and the low wave vector limit of the structure factor must satisfy the following condition [2]

\[
|z_1|S_{11}(0) = |z_2|S_{12}(0) = |z_2|S_{22}(0), \tag{5}
\]

where \( z_\alpha \) is the charge of \( \alpha \)th ion. This can be readily attributed to the long-range behavior of the direct correlation function.

\[
c_{\alpha\beta}(r) \approx -\frac{\nu_{\alpha\beta}(r)}{k_B T} \approx -\frac{z_1 z_2 e^2}{r} \frac{1}{k_B T} \quad (r \to \infty). \tag{6}
\]

The value of \( \hat{C}_{\alpha\beta}(Q) \) in the low-wave vector region is estimated to give a consistent value of \( S_{\alpha\beta}(0) \), with the isothermal compressibility at a given temperature, as follows

\[
\frac{1}{n_1} S_{11}(0) = \frac{1}{n_1 n_2} S_{12}(0) = \frac{1}{n_2} S_{22}(0) = k_B T \chi_T. \tag{7}
\]

For this purpose, the solution of the MHNC equation with an appropriate model potential which includes the long-range Coulombic nature is used, coupled with the asymptotic form of the solution satisfying Eq. (6) at the long-wavelength limit.

In the first step, for determining the bridge function \( B_{\alpha\beta}^{(0)}(r) \), Percus–Yevick equation was solved for each case by using the repulsive part of the so-called Huggins–Mayer type potential, except for the long-range Coulombic region [5].

In the second step, MHNC equation was solved using the model potential in the whole range and the bridge function \( \varepsilon B_{\alpha\beta}^{(0)}(r) \) was adjusted to satisfy the relation given by Eq. (7), where \( \varepsilon \) is a scaling factor of the bridge function.

The structure factor of liquids in the low wave vector region is usually limited to the value around \( 0.5 \text{ Å}^{-1} \) mainly due to the experimental difficulties. Therefore, in this work, the solution of MHNC equation from the second step is superposed on the experimental data in the low wave vector region. As a result, we can obtain a complete data set for calculating \( c_{\alpha\beta}(r) \) and \( g_{\alpha\beta}(r) \).

Further, for the estimation of the effective pair potentials from the experimental structure data, the ‘predictor–corrector’ method originally proposed by Reatto et al. [3] was utilized. On the first predictor stage, Eq. (3) was solved with the bridge function as \( B_{\alpha\beta}(r) = 0 \) in order to obtain the initial pair potential \( \nu_{\alpha\beta}^{(0)}(r) \). In the next corrector stage for simulation, we used the Monte Carlo (MC) simulation technique. Computer simulation was made with 4096 particles (2048 cations and 2048 anions), with corresponding cell size \( L \) at given temperatures. Coulomb potential energy was calculated by Ewald method. The real space and reciprocal space summation of the potential energy was made with parameters \( R_{\text{max}} = L/2 \) and \( kL = 6 \). The reciprocal space was evaluated by interpolation from the nearest mesh point of the table including 200^3 points in the cell. In each case, for the first corrector stage employing the MC method, at least 10^7 trials were carried out to realize the equilibrium state. For the next iterations, 3 \times 10^6 trials were found to be sufficient to obtain the equilibrium state. All necessary values and sources are given in Table 1 for convenience.

### 3. Results and discussion

#### 3.1. Molten RbBr

The resultant effective pair potentials of molten RbBr are shown in Fig. 1 together with the model potentials for comparison. The present results are found to agree well with the model potential, although there are small differences in detail. This means molten RbBr is quite likely to be described by the concept of simple ionic liquids such as molten NaCl. Fig. 2 shows the experimental pair distribution functions together with those of simulated results using both potentials for molten RbBr. The present authors maintain the view that the agreement between the simulated
Table 1
Values of effective charge, temperature, number density, isothermal compressibility and sources of model potentials and experimental partial structure factors of molten AgBr, CuBr, Cul and RbBr utilized in this work.

|                | AgBr | CuBr | Cul  | RbBr |
|----------------|------|------|------|------|
| Effective charge | 0.66 | 0.48 | 0.6  | 1.0  |
| Temperature $T$ (K) | 753  | 810  | 923  | 955  |
| Number density $\rho$ ($\text{m}^{-3} \times 10^{-30}$) | 0.0354 | 0.0350 | 0.0304 | 0.0190 |
| Isothermal compressibility $\chi_T$ ($\text{m}^2 \text{N}^{-1} \times 10^{-10}$) | 0.95 | 1.91 | 1.9  | 4.54 |
| Partial structure factors sources $S_{\alpha\beta}(Q)$ | Saito et al. [15] | Saito et al. [16] | Waseda et al. [17] | Waseda et al. [18] |
| Model potential sources | Vashista et al. [19] | Stafford et al. [20] | Stafford et al. [20] | Woodcock et al. [21] |

results using potentials presently determined and the experimental data is good by reducing discrepancies detected in the first peak region of the pair distribution functions in the model potential case, particularly for the Rb–Br pair. This may be attributed to the difference in the depth of the Rb–Br pair potential of molten RbBr as seen in Fig. 1.

From the results for partial pair distribution functions of molten RbBr in Fig. 2, it can be found that $g_{RbBr}(Q)$ and $g_{BrBr}(Q)$ are approximately in anti-phase to $g_{RbBr}(Q)$. This indicates well-defined charge (chemical) ordering. Considering some observed structural results, it is suggested that the symmetrical first coordination shell of Rb–Br pair can be described by the octahedral configuration, as it is in the crystalline state. These structural features are quite similar to the typical simple ionic liquid case of alkali chlorides [6–10].

3.2. Molten CuX (X = Br, I)

Fig. 3 shows the effective pair potentials of molten CuBr and Cul estimated in this work together with relevant model potentials. The Cu–Cu pair potentials for both molten salts show the negative deviations from the model potential in the range from 0.2 to 0.4 nm. The deviations from the model potentials are also recognized in the potentials of Cu–X and X–X pairs. These features contrast to the case of molten RbBr, in which the pair potentials are well described by the Coulombic and ionic core repulsion forces.

The pair distribution functions obtained by the MC simulation with the potentials presently obtained are shown in Fig. 4 together with the experimental data. The partial structure factors calculated from these pair distribution functions are also compared with the experimental partial structure factors in Fig. 5. The partial structure factors of molten CuBr are similar to those of molten Cul, except for the peak positions, in accordance with the anionic size effect. For example, the profiles of $S_{XX}(Q)$ and $S_{CuX}(Q)$ agree with those of simple ionic liquids such as molten RbBr, by observing that the first valley of $S_{CuX}(Q)$ is located at a $Q$ value where the principal peak in $S_{XX}(Q)$ is situated. In contrast, the partial structure factor of $S_{CuCl}(Q)$ is found to be rather structureless in both molten salts. Moreover, a
small pre-peak located at $Q = 10$ nm$^{-1}$ in $S_{\text{CuCu}}(Q)$ is clearly recognized in both molten CuBr and CuI. Such pre-peaks are considered particular density fluctuations associated with the Cu distribution, which is attributed to the effective pair potentials. The following remarks could be drawn from these results.

The pair potentials presently obtained are able to reproduce well the experimental pair distribution functions of Cu–Cu pair in molten CuBr and CuI by MC simulation. On the contrary, the simulated result using the model potentials clearly differs from the experimental data. Particularly, in the first neighbor region of the pair distribution functions, the experimental distribution functions indicate the characteristic like-ion penetration into the first unlike-ion coordination shell when compared with the model potential case. This could be attributed to the marked decrease in the repulsive core part of pair interaction between Cu ions detected in the range of $0.2–0.35$ nm. The present results of the Cu–Cu pair potential of molten CuX suggest a more free movement of Cu ions by making available a lower value at the repulsive core part, than the model potential case. As a result, we could obtain very weak Cu–Cu pair correlation. The calculated structure factors using the potentials obtained in this work also reproduce pre-peaks at about $Q = 10$ nm$^{-1}$. This may be attributed to the small positive deviation from the Coulomb potential

in the range from 0.4 to 0.8 nm. However, it is difficult to certainly identify the origin of the modulation of the two-body interaction in such medium range region from the presently available information alone.

The present results of the Cu–X pair potentials show shallow minima when compared with the model potential cases in the first neighbor region. It is also noticed that there are negative deviations from the model potentials (Coulombic form) in the range from 0.4 to 0.9 nm, which are opposite to the cases of the Cu–Cu pair potentials. The deviation of the Cu–X pair potential from the Coulombic form is considered essential for the understanding of the density fluctuation of Cu ions by keeping the charge neutrality in Coulomb liquids. As the evidence of the structureless feature of Cu ions in these liquid systems, the Cu–X correlation is also reduced rapidly in the long-distance region compared to the simulated results with the model potentials. It would also be noted that a particular feature can be easily seen in the depth of the first valley of the Cu–X partial structure factor shown in Fig. 5.

The present results of the X–X pair potential, in the authors’ view, are relatively close to the model potentials, and this contrasts the Cu–Cu and Cu–X cases. As a result, a
fairly good agreement is observed for the partial structure factors simulated using these two potentials, although there are differences in detail.

3.3. Molten AgBr

The resultant effective pair potentials of molten AgBr are shown in Fig. 6 together with the model potentials [19]. Calculated pair distribution functions from MC simulations are shown in Fig. 7 together with the experimental data. Fig. 8 shows the resultant partial structure factors compared with the experimental partial structure factors. Fig. 8 also includes the results of molten RbBr for convenience of the discussion with respect to the particular feature of cation–cation partial structure factor in molten monovalent metal bromides of RbBr, CuBr and AgBr. It is found in Fig. 8 that the Rb–Rb partial structure factor in molten RbBr shows a pronounced principal peak at a $Q$ value coincident with the position of the first minimum in $S_{++}(Q)$, as a typical ionic liquid. On the other hand, the Cu–Cu partial structure factor is found to be significantly structureless as shown in Fig. 5, so that the first peak is no longer well defined. Such

characteristic feature of cation–cation pairs is very common in the superionic conductors [11]. In the case of molten AgBr, as shown in Fig. 8, the Ag–Ag partial structure factor has a principal peak located at the same position of the first minimum in $S_{++}(Q)$ and this peak is much structured than the Cu–Cu case, but much flatter than that of Rb–Rb. Thus, the behavior of cation–cation correlation in molten AgBr seems to be intermediate between those of RbBr and CuBr. The following remarks could be given from these results.

The simulated results for the pair distribution function of Ag–Br pair using the model potential clearly differ from the experimental data. A significant difference was found in the inter-atomic distance for the nearest neighbor Ag–Br pairs. The first peak positions in the present result and model potential case are located at 0.27 and 0.24 nm, respectively. This could be attributed to the difference detected in the

Fig. 5. Partial structure factors of molten CuBr and CuI calculated by Fourier transform of the simulated pair distribution functions of Fig. 4. The effective pair potentials presently obtained (solid line) and model potentials (dotted line). The experimental data (open circles) are also shown for comparison.
position of the minimum for the pair potential. It is also stressed here that the present result of the inter-atomic distance for the nearest neighbor Ag–Br pair agrees well with the values determined by neutron diffraction [12,13].

The present potential for Br–Br pair in molten AgBr shows an oscillatory behavior against the model potential. Namely, positive deviation from the model potential is found in the range from 0.31 to 0.57 nm and from 0.86 to 1.10 nm. On the other hand, negative deviation is cited in the range from 0.6 to 0.8 nm. Over the range from 1.4 nm, present potential is found to be converged to the model potential. Such profile of Br–Br pair is rather similar, in authors’ view, to that in molten RbBr case (see Fig. 1). This may correspond to the common structural feature described by disordered close packing of Br ions in both cases of molten RbBr and AgBr.

The simulated results for the experimental pair distribution function of Ag–Ag pair using the model potential differ from the experimental data again. This may be attributed to slightly positive deviation from the model potential in the range from 0.37 to 0.52 nm. At the present stage, a clear explanation of the origin for broader and complex profile in experimental structure factors of Ag–Ag pair cannot be given. Nevertheless, this small difference in the potential could be related with the particular feature of molten AgBr.

Within the framework of the present approach, the effective pair potentials can be estimated from Eq. (3) only in the region where \( g_{ab}(r) \neq 0 \), due to the logarithm relation for this term. In the region where \( g_{ab}(r) \neq 0 \), the numerical values for the pair potentials are extrapolated to infinity for the application to MC simulation. Of course, the potentials extrapolated in this manner are not applicable for the solution of MHNC and PY equations.

The method employed in this work for the pair potential using the MHNC equation is not a unique mathematical procedure. Nevertheless, the effective pair potentials obtained in this work are considered to be, at least, in a sense of necessary condition at best by reproducing the experimental structural data by computer simulation, although they might be not sufficient condition.

In other words, the effective pair potentials systematically obtained in this work for molten RbBr, CuBr, CuI and AgBr could be considered one of the best approximations for representing the real interaction including many body correlations in these four molten salts.

Furthermore, the sum of elementary graphs enters the MHNC equation as a part of an effective pair potential and the bridge function must be specified in the region where the pair distribution function indicates its first minimum non-zero value [14]. The origin for disagreement among the results of various theories or their mutual disagreement with the MC simulation results should be attributed to the assumption used for the bridge function in this region. Therefore, it is interesting to see the contribution of bridge function to Eq. (3). This is particularly true in the near repulsive core part of the effective pair potential because, such a region appears to be important for describing the behavior of the low wave vector region of the structure factors.

Fig. 9 shows the bridge functions \( B_{ab}(r) \) obtained in this work as direct result from the ‘predictor–corrector’ scheme. It may be suggested that the profile of the bridge functions for Br–Br pair and unlike atom pair looks similar in molten salts of AgBr, CuBr and RbBr. Of course, the present results should be considered to reflect only with the partial behavior of real component, but there is one evidence of specific properties for these molten salts, because the bridge function is introduced to the MHNC equation for involving the so-called many-body correlation. On the other hand, disagreements in detail for the bridge function as exemplified by the Cu–Cu case in molten CuBr and CuI might be related to a consequence of different correlation in the respective salt.

4. Concluding remarks

The effective pair potentials of molten AgBr, CuBr, CuI
and RbBr have been estimated from measured structural information. The usefulness of the pair potentials presently obtained was confirmed by reproducing the particular pre-peak in the structure factor of Cu–Cu pair in molten CuBr and CuI. This contradicts with the case using model potentials previously proposed. For this reason, it would be interesting to extend the effective pair potentials to the calculation of some physical properties such as diffusion, viscosity and ion mobility of these molten salts. Then the validity of the effective pair potential estimated from the experimental partial structure factors may be tested in a rather wider base.

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