The Maximum of the Conductivity of an Ionic Melt from MD Simulations at Various Temperatures

Isao Okada and Ryuzo Takagi
Department of Electronic Chemistry, Tokyo Institute of Technology, Yokohama, Japan

Z. Naturforsch. **36a**, 378—380 (1981); received January 27, 1981

Molecular dynamics simulations of molten TlCl are performed at 7 temperatures between 800 and 2600 K. The self-exchange velocity of neighbouring unlike ions divided by the molar volume, a quantity corresponding to the specific conductivity, is found to have a maximum as a function of temperature. The reason for the existence of the maximum is discussed.

Grantham and Yosim had discovered that the specific conductance vs. temperature curve of some molten salts shows a maximum [1, 2]. Also thallous chloride shows this phenomenon [3].

The main aim of this study was to check whether the maximum for TlCl can be reproduced by molecular dynamics (MD) simulations. In a previous MD simulation of molten (Li-Rb)Cl, we have shown that the internal mobilities are strongly related with the self-exchange velocities (SEV) of neighbouring unlike ions [4]. Since it takes extensive time to compute conductivities with MD simulations [5—8], we have tried to reproduce the maximum by calculating SEV's. Pair potentials of the Born-Mayer-Huggins type with the parameters presented by Mayer for the TlCl crystal [9] were adopted. The properties obtained by the simulation do not agree quantitatively with the experimentally obtained ones, perhaps partly because the parameters of the pair potentials are not quite adequate. Therefore, the melt dealt with in the present simulation should be regarded as a model ionic melt rather than molten TlCl.

The adopted pair potentials are expressed by

$$u_{ij}(r) = \frac{z_i z_j e^2}{r} + b_{ij} \exp\left(-\frac{r}{\varrho}\right) - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8}, \quad (1)$$

where z is the charge number, e the elementary charge, and b, c, d and ϱ are parameters whose values are given in Table 1.

The side length of a basic cell, L, was set from the density data of molten TlCl: $\varrho_\mathrm{d} = a_\mathrm{d} - b_\mathrm{d} T$ ($a_\mathrm{d} = 6.893 \times 10^3$ kg m^{-3}, $b_\mathrm{d} = 1.80$ kg m^{-3} K^{-1}, obtained from the range 708 K $\leq T \leq$ 915 K [10]). The basic cell contained 108 cations and 108 anions. The Ewald method was employed for the Coulombic force. The parameters in this method were chosen as follows: the cutoff distance was $L/2$, the maximum reciprocal vector $|\boldsymbol{n}|^2 = 27$ and the convergence parameter $\alpha = 5.6/L$. According to Ref. [11], given $\alpha = 5.6/L$ the simulation could have been improved by taking L as the cutoff distance and 60 as the maximum reciprocal vector. The step time was set as 5 fs. The MD simulation was performed so that the temperature in each run was kept constant following the way proposed by Woodcock [12], though in a correctly simulated system the temperature fluctuates.

The pair correlation functions of unlike ions, g_{+-}, at 3 temperatures are shown in Figure 1. The height of the first peak in g_{+-} has a minimum around 1600 K. In general, the first peak is higher in the solid and gaseous states than in the liquid state. Therefore, this minimum implies that the structure of the ionic melt is more "solid-like" and "gas-like" at lower and higher temperatures, respectively. The position of the first peak moves slightly towards the origin with rising temperature.

Some other computational data are tabulated in Table 2. The pressure was calculated from the virial

Table 1. Parameters in the pair potentials ($\varrho = 35.6$ pm).

pair	b (10^{-19} J)	c (10^{-79} J m^6)	d (10^{-99} J m^8)
+ +	1272	268	500
+ −	2429	179	346
− −	4508	133	268

Reprint requests to Dr. Isao Okada, Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan.

0340-4811 / 81 / 0400-0378 $ 01.00/0. — Please order a reprint rather than making your own copy.

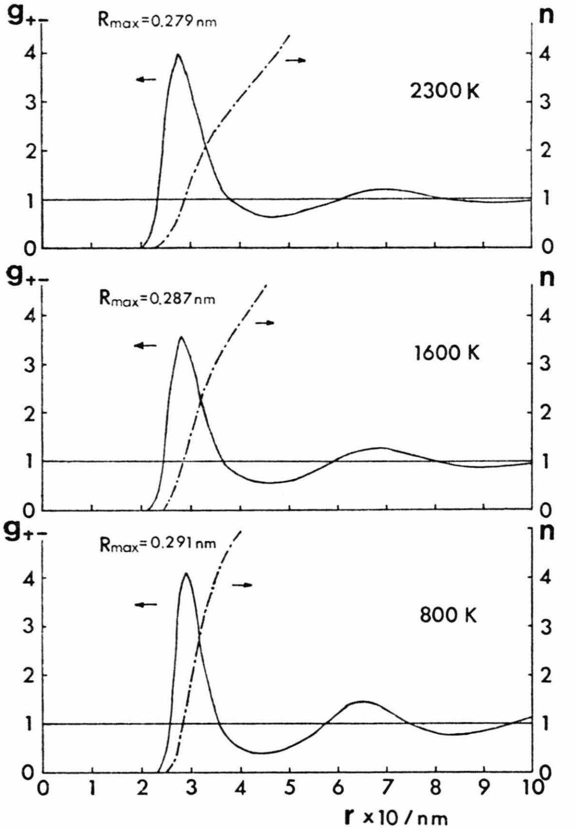

Fig. 1. Pair correlation functions between unlike ions, g_{+-}, and running integration numbers, n. The molar volumes are 44.0, 59.8 and 87.1 cm^3 mol^{-1} at 800, 1600 and 2300 K, respectively.

[13] averaged over 1500 time steps for each run. R_2 is the distance where g_{+-} crosses unity for the second time. As the temperature increases, R_2 increases, while the number of unlike ions within R_2, $n(R_2)$, decreases.

The SEV, v, is defined as [4]

$$v = (R_2 - \bar{R})/\tau , \tag{2}$$

where $\bar{R}$ is the average distance of unlike ions with distances $< R_2$, and τ the average time in which the average distance of these ions becomes R_2. The SEV was averaged for unlike ions surrounding totally 3240 reference ions.

It has been found that the internal mobility, b_i, is approximately proportional to v [4]:

$$b_i \simeq k v , \tag{3}$$

where k is a constant.

The combination of (3) with the equation $\varkappa = F b_i / V$ ($\varkappa$: specific conductivity, V: molar volume, F: Faraday's constant) yields

$$\varkappa \simeq k F v / V . \tag{4}$$

Therefore, as long as (3) holds, $\varkappa$ is approximately proportional to v/V. The SEV may be represented in the form

$$v = C \exp(- d_e/T) , \tag{5}$$

where C and d_e are constants. In the present case C and d_e are evaluated to be 400 ms^{-1} and 1975 K, respectively, while from the experimental internal mobility of molten TlCl (720—1160 K) at ambient pressure d_e is found to be 1720 K [14].

Since $V = M/(a_d - b_d T)$ (M: molecular weight), it follows from (4) and (5) that

$$\varkappa \simeq A (a_d - b_d T) \exp(- d_e/T) , \tag{6}$$

where A is a constant; consequently, $\varkappa$ has a maximum at

$$T_{max} = (d_e/2)\{\sqrt{1 + (4 a_d / b_d d_e)} - 1\} . \tag{7}$$

Table 2. Some computational data.

Temperature	(K)	800	1100	1600	1900	2100	2300	2600
Pressure	(MPa)	− 381	− 259	− 204	− 120	− 86	− 30	− 23
Potential energy	(kJ mol^{-1})	− 700.0	− 684.4	− 660.4	− 646.7	− 637.2	− 627.8	− 611.6
Coulombic energy		− 751.5	− 738.5	− 714.9	− 702.3	− 693.0	− 684.6	− 667.2
Repulsive energy		163.8	160.3	149.6	145.8	142.2	140.9	133.1
R_2	(nm)	0.359	0.362	0.369	0.373	0.377	0.380	0.397
$n(R_2)$		4.22	3.82	3.32	3.08	2.95	2.84	2.77
v	(m s^{-1})	30.5	70.6	114	139	163	168	186
v/V (10^{-7} mol m^{-2} s^{-1})		6.93	14.5	19.0	20.2	21.1	19.3	17.2
D_+	(10^{-9} m^2 s^{-1})	0.80	3.91	12.0	15.6	23.5	33.3	40.4
D_-		0.66	3.98	10.0	14.9	24.6	27.2	36.9

This is calculated to be 1930 K, while the experimental specific conductivity of molten TlCl at an unknown elevated pressure has a maximum around 1600 K [3].

For $T_{\max}$ to be detectable experimentally, it is required that both (a_d/b_d) and d_e be small. The quantity $1/[(a_d/b_d) - T]$ is the relative thermal volume expansion. A comparison of the literature values of (a_d/b_d) [10] reveals that for the salts for which a conductivity maximum has been detected these values are considerably smaller than for the other salts. The value of d_e would generally be small if the attraction between cation and anion is strong. Because the volume expansion is particularly unfavourable for the mobility if the ions are strongly attracted by the counter ions [4]. In the present case, the attraction is relatively strong owing to the large values of c_{+-} and d_{+-} in the pair potential, and the value of (a_d/b_d) is relatively small. These would be the reasons why the maximum occurs at a relatively low temperature.

An alternative equation to (5) is

$$v = g\sqrt{T} - f, \tag{8}$$

where f and g are constants. The values of v in the present case are expressed by (8) with $g = 6.90\ \mathrm{m\ s^{-1}\ K^{-1/2}}$ and $f = 161\ \mathrm{m\ s^{-1}}$. The experimental internal mobilities are well expressed by (8), even better than by (5) e.g. in the case of molten LiCl [14]. If (8) holds, it follows that

$$T_{\max} = \frac{1}{9}\left\{\left(\frac{f}{g}\right) + \sqrt{\left(\frac{f}{g}\right)^2 + \left(\frac{3\,a_d}{b_d}\right)}\right\}^2. \tag{9}$$

According to (9), $T_{\max}$ is 1960 K. If f equals zero, the temperature dependence of v becomes that of the thermal velocity of motion.

The calculated self-diffusion coefficients of the cation and anion (D_+ and D_-, respectively) are nearly equal and about one third of the measured ones [15–17]. The value of $(D_+ + D_-)/v\,T$ increases with rising temperature, which suggests that the Nernst-Einstein relation does not hold.

We are deeply indebted to Professor Klemm for helpful suggestions.

The computers HITAC M-180 and M-200 H at Institute for Molecular Science were used. The facilities and computer time made available to us are gratefully acknowledged.

[1] L. F. Grantham and S. J. Yosim, J. Phys. Chem. **67**, 2506 (1963).
[2] L. F. Grantham and S. J. Yosim, J. Chem. Phys. **45**, 1192 (1966).
[3] P. L. Spedding, Electrochim. Acta **18**, 111 (1973).
[4] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **35a**, 493 (1980).
[5] J. P. Hansen and I. R. McDonald, J. Phys. C: Solid State Phys. **7**, L384 (1974).
[6] J. P. Hansen and I. R. McDonald, Phys. Rev. **11A**, 2111 (1975).
[7] G. Ciccotti, G. Jacucci, and I. R. McDonald, Phys. Rev. **13A**, 426 (1976).
[8] A. Klemm, Z. Naturforsch. **32a**, 927 (1977).
[9] J. E. Mayer, J. Chem. Phys. **1**, 327 (1933).
[10] G. J. Janz, Molten Salts Handbook, Academic Press, New York 1967.
[11] M. J. L. Sangster and M. Dixon, Adv. Physics **25**, 247 (1976).
[12] L. V. Woodcock, Chem. Phys. Lett. **10**, 257 (1971).
[13] L. Schäfer and A. Klemm, Z. Naturforsch. **31a**, 1068 (1976).
[14] G. J. Janz et al. "Molten Salts: Vol. 1, Electric Conductance, Density, and Viscosity Data, NSRDS-NBS 15", Nat. Bur. Stand., Washington 1968.
[15] E. Berne and A. Klemm, Z. Naturforsch. **8a**, 400 (1953).
[16] C.-A. Sjöblom and A. Lundén, Z. Naturforsch. **18a**, 942 (1963).
[17] C. A. Angell and J. W. Tomlinson, Trans. Faraday Soc. **61**, 2312 (1965).