Interionic Potentials and MC Simulations of Molten AgCl

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Monte Carlo simulations on molten AgCl were carried out in order to test the applicability of the interionic potentials recently proposed for this salt in the solid phase. None of the literature potentials can be used as such: in all cases pairs of like ions reach too short distances of approach causing the collapse of the system. It was proved that, in order to obtain equilibration of the system, the pair potentials of like ions must be recalculated.

On the basis of these modified potentials, MC simulations of molten AgCl were carried out at 728 (m.p.), 1000 and 1500 K. The polarization energy effect was also analyzed with the use of a soft ion model.

Key words: Interionic potentials, Monte Carlo simulation, molten AgCl.

Introduction

Silver halides in the solid phase have been extensively studied on one hand because of their practical interest as materials [1], and on the other hand in order to establish from a theoretical point of view whether they should be considered totally or partially ionic salts [2].

Recently some authors have made the hypothesis that the peculiar features of the silver halides when compared to alkali halides (e.g. small lattice constants, large lattice energies, extremely low solubility in water, mobility of interstitial silver ions, etc.) are related to strong van der Waals interactions [3, 4, 5]. In this regard only little attention was devoted to silver halides in the molten state [6, 7].

The present work aims at evaluating the possibility to use the interionic potentials derived for solid AgCl in simulations of the molten state of this salt.

Interionic Potentials

The AgCl interionic potentials that can be found in literature were obtained, by using a fully ionic model, either on the basis of theoretical calculations or by fitting the bulk crystal data (principally the equilibrium condition for the lattice along with other physico-chemical properties).

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The classical interionic pair potential between ions i and j at distance r is written as

$$\varphi_{ij}(r) = \varphi^{C}_{ij} + \varphi^{W}_{ij} + \varphi^{R}_{ij}, \quad (1)$$

where $\varphi^{C}_{ij} = z_i z_j r^{-1}$, $\varphi^{W}_{ij} = -c_{ij} r^{-6}$ and $\varphi^{R}_{ij} = a_{ij} \exp(-b_{ij} r)$ are the Coulomb, the van der Waals (vdW) and the repulsive term, respectively, z_i, z_j are the ionic charges, while c_{ij}, a_{ij} and b_{ij} are parameters characteristic of the ionic pair i and j.

Numerical values for the pair potentials (1) were first given by Mayer in 1933 [8]: in this model, φ^{W}_{ij} is written as $-c_{ij} r^{-6} - d_{ij} r^{-8}$ in order to take into account, along with the induced dipole-dipole interaction ($-c_{ij} r^{-6}$), also the induced dipole-quadrupole interaction ($-d_{ij} r^{-8}$).

In 1979 Catlow, Corish, and Jacobs (CCJ) [3] proposed new values for the Buckingham part ($\varphi^{W}_{ij} + \varphi^{R}_{ij}$) of potential (1).

Bucher in 1984 [5] suggested other values for the interaction potentials of AgCl, introducing an additional three body interaction term in the computation of the vdW energy, which accounts for the deviation from the Cauchy relation between the values of the elastic constants of solid AgCl.

Table 1 reports the c_{ij} values that can be obtained from the literature. It should be noted that in order to have a direct comparison between the different sets of data, the original Mayer's values ($c_{+-} = 89$, $c_{--} = 133$, $c_{++} = 67$) were incremented by the contribution of the d_{ij} terms at the solid equilibrium distance, while those of Bucher's were roughly corrected in order to take

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Table 1. Van der Waals coefficients for AgCl (in 10^{-60} erg cm^6).

	c_{+-}	c_{--}	c_{++}
From Mayer's values [8]	109	151	73
CCJ [3]	352	120	359
From Bucher's values [5]	299	588	152

Table 2. values of a_{ij} (in 10^{-8} erg molecule^{-1}) and b_{ij} (in Å^{-1}) for φ^{R}_{ij}.

	a_{+-}	$-b_{+-}$	a_{--}	$-b_{--}$	a_{++}	$-b_{++}$
Mayer [8]	1.350	3.85	0.449	2.90	3.920	5.71
CCJ [3]	0.404	3.06	0.197	3.11	2.650	4.22
Bucher [5]	0.282	2.94	0.082	2.94	0.547	3.85

Table 3. Repulsive potentials (in erg molecule^{-1}) at r_0 for unlike and $\sqrt{2}r_0$ for like pairs ($r_0 = 2.775$ Å [9]).

	φ^{R}_{+-}	φ^{R}_{--}	φ^{R}_{++}
Mayer [8]	$3.34 \cdot 10^{-13}$	$5.56 \cdot 10^{-14}$	$0.85 \cdot 10^{-17}$
CCJ [3]	$8.81 \cdot 10^{-13}$	$0.99 \cdot 10^{-14}$	$0.19 \cdot 10^{-14}$
Bucher [5]	$8.56 \cdot 10^{-13}$	$0.87 \cdot 10^{-14}$	$0.17 \cdot 10^{-14}$

into account the repulsive contribution of the three body interaction. On the basis of the single contributions to the crystal properties of AgCl, a 24% reduction of the two body vdW terms should compensate, at least from the energetic viewpoint, the three body terms.

Table 2 reports the a_{ij} and b_{ij} values of the repulsive potentials. For a direct comparison of these data, Table 3 reports the φ^{R}_{ij} values calculated for the smallest lattice equilibrium distances.

Finally, Fig. 1 illustrates the behavior of the global potential between unlike ions $\varphi_{+-}(r)$, calculated according to the data previously cited.

For a comment on Mayer's repulsive terms, it should be noted that only φ^{R}_{+-} was deduced from AgCl experimental data since "the repulsion between Ag^+ pairs is probably negligible and is neglected, that between halide pairs is assumed to be the same function of r as in the alkali halides, and that between Ag^+ and halide ions is calculated from the constants of the crystal" [8]. This fact explains the abnormally small value of the φ^{R}_{++} reported in Table 3, that was fixed indirectly on the basis of particular ionic quantities. Moreover, the discrepancies between the φ^{R}_{--} values proposed by Mayer and those of the other sets of data should be underlined.

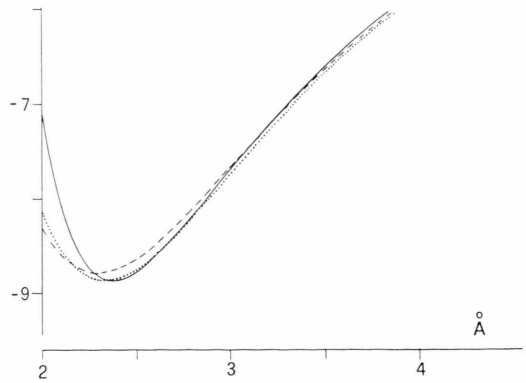

Fig. 1. Trend of the global potentials between unlike ions (in 10^{-12} erg molecule^{-1}). Solid line: Mayer's function [8]; dotted line: CCJ's function [3]; dashed line: potential curve obtained with the values derived from Bucher's function (see Table 1).

As regards the CCJ potentials, the φ^{W}_{++} term appears abnormally high in respect both to Mayer's and to Bucher's values.

For what concerns the values that can be deduced from Bucher's data, those pertinent to the chloride-chloride pair appear worthy of remark: in particular, φ^{W}_{--} is about five times larger than the corresponding value reported for the alkali halides. This is connected with the following relation used by Bucher to reduce the number of independent vdW parameters:

$$\frac{c_{++}}{c_{+-}} = \frac{c_{+-}}{c_{--}} = \frac{\alpha_+}{\alpha_-} = \frac{1.67}{3.29}, \tag{2}$$

where α_+ and α_- are the Ag^+ and Cl^- polarizabilities, respectively [10].

On the basis of the above interionic pair potentials attempts were made to simulate molten AgCl by the Monte Carlo method. No one of the three quoted sets allowed equilibration of the system to be reached: after a few hundreds of kilosteps, some pairs of like ions (Ag^+ in the case of Mayer's or CCJ's potentials, Cl^- in the case of the potential derived from Bucher's values) reached too low distances of closest approach, thus causing the collapse of the system. No one of these three potentials can therefore be used as such in MC calculations.

Thus, in order to obtain a potential function that could work within a MC simulation, the short-range potentials between like ions had to be re-examined.

The attention was focused on the potential proposed by Mayer. The values pertinent to the Ag–Cl ion pairs (evaluated on the basis of the crystal properties) and those for the Cl–Cl pairs (derived from the

alkali halide family) were kept fixed, whereas the Ag – Ag repulsive function was recalculated. In particular, by means of the Huggins model [11], and on the ground of the ionic dimensions, it was possible to estimate the ratio $\varphi^R_{--}/\varphi^R_{++}$: using for Cl^- the basic radius given in [11] and for Ag^+ a radius in between those of Na^+ and K^+, a value of 5 was obtained for the above ratio. As a result, the repulsive Ag – Ag potential is expressed as

$$\varphi^R_{++} = 0.90 \cdot 10^{-9} \exp(-2.90\, r) \text{ erg molecule}^{-1}. \quad (3)$$

MC Calculations

In the present paper, the MC method was used in the NpT version (at $p = 1$ atm) which allows a direct comparison with the experimental data [12]. Two body potentials type (1) were assumed to describe the interactions even if, within the single steps, the polarization energy of the system was also taken into account: the method used is the soft ion model (SIM) discussed in a previous work [13]. For comparison, the model without polarization energy (rigid ion model (RIM)) was also tested.

At first, for the short range terms of function (1), Mayer's original values [8] were used along with the φ^R_{++} given by (3). For the ionic polarizabilities those given by Bucher [10] were chosen. Simulations were carried out at three different temperatures: 728 (m.p.), 1000 and 1500 K.

Table 4 reports the values obtained for the molar volumes, V_m, and internal energies, U, of the melt according to the two models, together with the Coulomb, E^C, van der Waals, E^W, repulsive, E^R, and polarization, E^P, components of the average configurational energy, E. Energies U and E are related by $U = E + 3RT$.

For what concerns the experimental data, the literature reports density values in the range 759–1073 K [14] that were used to obtain the V_{exp} of Table 4. The agreement with the data calculated with the SIM model is very good. As regards the internal energy, the U values in Table 4 can be compared with those obtained from the crystal energy along with the molar heat capacity and the fusion enthalpy [15]. With the U_0 value calculated by Mayer (−203 kcal mol^{-1}) [8] or that by Ladd and Lee (−199) [16], one obtains energy data (e.g. at 1500 K: −180 and −176, respectively) in good agreement with those of Table 4. According to other authors [17, 18], however, the experimental U_0 value, calculated by a Born-Haber cycle,

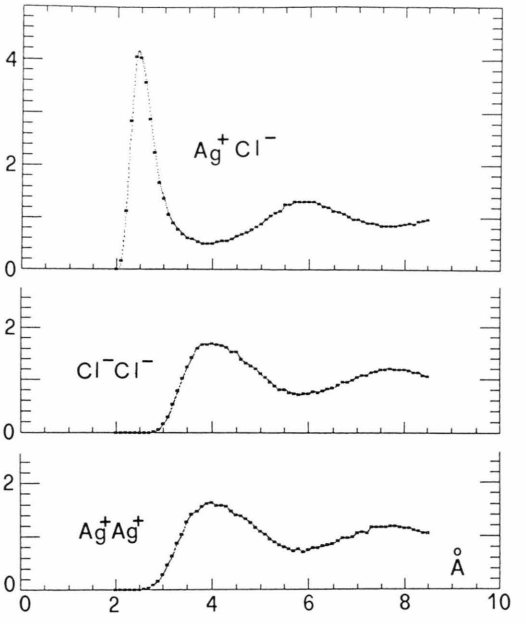

Fig. 2. Radial distribution functions according to the MC simulation of molten AgCl at 1500 K. The SIM model was used in the computations.

Table 4. Molar volumes and energies for molten AgCl (in cm^3 mol^{-1} and kcal mol^{-1}, respectively) obtained with the soft ion model (SIM) and the rigid ion model (RIM).

	728 K (m.p.)		1000 K		1500 K	
	SIM	RIM	SIM	RIM	SIM	RIM
V_m (calc.)	29.2	29.7	30.8	32.3	33.9	37.4
V_m (exp.)	29.4		30.9		34.1	
U	−187.8	−185.5	−184.3	−180.6	−177.6	−171.7
E^C	−207.7	−206.0	−204.4	−202.5	−199.4	−195.9
E^R	50.3	45.7	47.5	43.4	44.3	39.4
E^W	−31.1	−29.5	−29.2	−27.5	−26.0	−24.1
E^P	−3.6	−3.2*	−4.2	−4.2*	−5.4	−5.9*

* Mean values computed on static configurations apart from MC cycles.

should amount to about −(216÷218) kcal mol^{-1}, thus yielding a difference of about 15 kcal mol^{-1} in respect to the data in Table 4. It should be noted that Mayer's functions were constrained to r_0 and not to U_0.

Table 5 reports the principal features of the radial distribution functions (rdf) obtained for molten AgCl with the SIM model, from the histograms of the ion pair distances. In particular, the distance of minimum approach, d, the abscissa of the maximum of the main peak, r_{max}, and of the minimum following the main peak, r_{min}, are reported along with the apparent coor-

Table 5. Main features of the radial distribution functions for molten AgCl at 728, 1000 and 1500 K (distances in Å). The SIM model was used.

		728 K	1000 K	1500 K
Ag^+-Ag^+ pairs	d	2.6	2.6	2.4
	r_{max}	3.8	3.9	4.0
	r_{min}	5.8	5.8	5.9
	n	15.3	14.8	12.9
Ag^+-Cl^+ pairs	d	2.1	2.1	2.0
	r_{max}	2.5	2.5	2.5
	r_{min}	3.7	3.7	3.9
	n	5.0	4.8	4.5
Cl^--Cl^- pairs	d	2.8	2.7	2.6
	r_{max}	3.8	3.9	4.0
	r_{min}	5.8	5.8	5.9
	n	15.3	14.7	13.0
all ions	r_{max}	2.5	2.5	2.5
	r_{min}	3.1	3.1	3.2
	n	4.2	4.0	3.7

Table 6. Results for molten AgCl at 1500 K obtained using Mayer's modified potentials for like ions together with CCJ's function (Pot. I) or Bucher's (Pot. II) for unlike ions.

	V_m	U	E^C	E^R	E^W	E^P
Pot. I						
RIM	32.9	−186.6	−194.8	70.5	−66.8	−4.4
SIM	31.0	−187.8	−197.9	78.7	−73.1	−4.4
Pot. II						
RIM	36.0	−178.1	−190.0	58.1	−50.7	−4.4
SIM	33.3	−179.8	−194.3	66.0	−56.3	−4.1

dination number, n, at the three studied temperatures. Moreover, it was found that the "penetration" of like ions into the first coordination sphere is significant: at the m.p. and at 1000 K there are 0.1 Ag^+ ions on a total coordination of 4.2 and 4.0, respectively, whereas at 1500 K there are 0.2 Ag^+ and 0.1 Cl^- ions on 3.7.

Figure 2 shows the rdfs of molten AgCl obtained at 1500 K on the basis of the SIM model.

Further simulations were carried out based on the other two sets of potentials (namely CCJ's and those derived from Bucher's values) for the unlike terms, while the interactions between like ions were described by Mayer's values corrected with term (3).

The equilibration of the system was reached with no difficulty: this again proves that it is the like ions function of the above potentials that does not allow simulations of the equilibrium. Table 6 reports the results obtained at 1500 K. These values can be compared with those reported in Table 4: the set of potentials derived from Bucher's gives a good agreement for the volume and global energy, even though the distribution among the various energy components is quite different; the set derived from CCJ's yields a more contracted system with a U value closer to that predictable on the basis of the experimental U_0.

Thus, one can finally conclude that the MC simulations carried out on molten AgCl pointed out the inadequacy of some specified pair potentials of the literature when used in an MC simulation. In particular, Mayer's potentials can only be used if a harder Ag−Ag repulsive function is assumed, while the CCJ's and Bucher's potentials can be used to describe the unlike interactions only, and not the like ones.

Concerning the assumption of strong vdW interactions in AgCl, all the analyzed potentials between unlike pairs show an approximate balance of the repulsive and attractive components that does not allow a conclusive support.

Acknowledgement

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