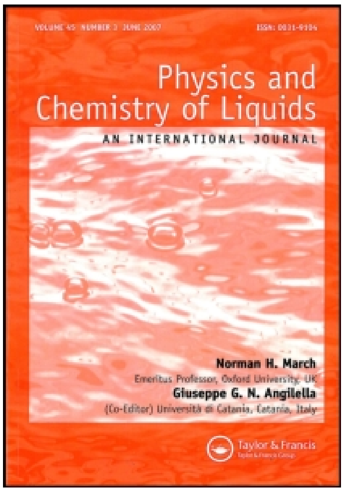

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Effective Charges and Ionicity in Molten Salts

H. B. Kavanoz[a]; M. Yilmaz[a]; H. gurbuz[a]; M. Silbert[b]
[a] Faculty of Science Physics Department, Yildiz Technical University, Turkey [b] Departamento de Fisica Teorica, Facultad de Ciencias, Universidad de Valladolid, Spain

To cite this Article Kavanoz, H. B. , Yilmaz, M. , gurbuz, H. and Silbert, M.(2002) 'Effective Charges and Ionicity in Molten Salts', Physics and Chemistry of Liquids, 40: 1, 115 — 121
To link to this Article: DOI: 10.1080/00319100208086653
URL: http://dx.doi.org/10.1080/00319100208086653

Phys. Chem. Liq., 2002, Vol. 40(1), pp. 115-121

Taylor & Francis
Taylor & Francis Group

EFFECTIVE CHARGES AND IONICITY IN MOLTEN SALTS

H. B. KAVANOZ[a], M. YILMAZ[a], H. GÜRBÜZ[a,*]
and M. SILBERT[b,†]

[a]*Yildiz Technical University, Faculty of Science Physics Department, 34210 Davutpaşa-İstanbul Turkey;* [b]*Departamento de Física Teórica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain*

(Received 28 November 2000)

We have used experimental values of the entropies, near melting, of molten salts to calculate their effective charges by using a charge α spheres model in the Mean Spherical Approximation (MSA).

We compare the values of the effective charges with the electronegativity differences for a number of 1 : 1 molten salts. We find a reasonable good correlation for the alkali halides, but no for the copper, silver and thallium halides, and we offer an explanation for these results.

Keywords: Effective charge; Ionicity; Entropy

1. INTRODUCTION

Akdeniz and Tosi [1] (AK) made use of an empirical relation, originally proposed by Tallon and Robinson [2], between the entropy and volume changes on melting. In their work AK provided useful insights about the melting mechanisms of molten salts. The relation used by AK is one of a range of useful semiempirical relations proposed to gain insights in, and help in the classification of, molten salts. Thus, for instance, Pietronero [3] proposed a melting criterion

---

[*] Fax: +90 212 449 1514, e-mail: gurbuz@yildiz.edu.tr

[†] Corresponding author. On Leave of Absence from the School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK.

ISSN 0031-9104 DOI: 10.1080/00319100290005712

for binary ionic compounds in terms of an instability due to the overlap between the larger ions (usually anions). More recently Koh [4] assumed a linear relation between the Szigeti charge and the density in order to obtain values for the former.

There have been, over the years, several important attempts to order binary compounds structural data, and to relate the data with suitable phenomenological approaches that makes possible the structural separation of binary compounds [5, 6]. Thus, it has been noted that binary compounds of atoms A and B with large differences in electronegativity tend to form rock-salt structures, while smaller differences in electronegativity favoured more open structures. When the difference in electronegativity is large, the heat of formation is large, providing a thermochemical meaning for the concept of electronegativity. The greater the difference in electronegativity, the more ionic the bond of a given compound A_mB_n is said to be, and the greater its heat of formation [7].

In this work, and following the preceding remarks, we attempt to establish a relationship between effective charges Z_i^* and the ionicity f of a number of 1 : 1 molten salts. Ionicity is related to electronegativity differences. We are using here for f Phillips ionicity scale [7]. Other choices are possible. However we submit that whatever the choice used for f will not alter the main findings of this work.

The ionicity, on the Phillips scale, varies between 0 and 1, and has been defined in terms of the optical properties of materials. $f=0$ stands for purely covalent bonding, while $f=1$ for purely ionic bonding.

Since we are concerned with the molten state we relate the effective charges to the entropy S of the molten salts. We specifically use the expression for the entropy of a system of charged spheres in the Mean Spherical Approximation (MSA). Blum [8] (see also Ref. [9]) obtained an analytic solution for a system of charged spheres within the MSA. Abernethy and Silbert [10] and Yokokawa and Kleppa [11] (see also Ref. [12]) gave explicit expressions for the entropy of charged spheres in the MSA, which they used to calculate the excess entropies of the molten alkali-halides near melting. Taking into account an error of a factor 2 in the third column of Table II of Ref. [10], the agreement between the calculated and experimental entropies is reasonably good.

The use of charged spheres in the calculation of the effective charges will also enable us, using only properties of the melt, to check on Pietronero's melting criterion for binary ionic compounds.

In the next Section we briefly outline the formalism used in our calculations. In Section 3 we present the results of our calculations. We complete the paper with a brief discussion of our results.

2. FORMALISM

The entropy of a system of charged spheres, in the MSA, may be written as the additive contributions of hard spheres (HS) and Coulomb (C) terms, namely

$$S = S_{HS} + S_C \tag{1}$$

For S_{HS} we use the entropy derived from the Percus-Yevick compressibility equation of state [10]. For S_C we write [10]

$$\frac{S_c}{Nk_B} = -\frac{\Gamma^3}{3\pi n} \tag{2}$$

where N is the total number of ions in the system, Γ a generalized Debye inverse screening length that reads

$$\Gamma^2 = \frac{\pi e^2 n}{\varepsilon_0 k_B T} \sum_i x_i X_i, \tag{3}$$

with n denoting the number density of the system, x_i the concentration of species i, and X_i is given by

$$(1 + \Gamma\sigma_i)X_i + \zeta\sigma_i^2 \sum_j n x_j \sigma_j X_j = Z_i^*. \tag{4}$$

In Eq. (4), σ_i and Z_i^* denote the ionic diameter and the effective charge respectively of species i; ζ is given by

$$\zeta = \frac{\pi}{2(1-\eta)}, \tag{5}$$

and $\eta = (1/6)\pi n \sum_i x_i \sigma_i^3$, denotes the packing fraction of the system.

3. RESULTS

We have used Eq. (1) to obtain the effective charges that yield the nearest values of the experimental entropies, for a number of 1 : 1 molten salts near melting. We have specifically chosen those alkali halides, noble metal halides and thallium halides for which we found the required experimental data.

In our calculations we have used as input data the experimental densities and temperatures near melting [13] and experimental entropies at that thermodynamic state [14]. For the molten alkali halides we have used the Fumi and Tosi diameters [15]. For molten AgBr, AgI, TlBr and TlI we have also used the ionic diameters given in Ref. [15], whereas for CuCl, AgCl and TlCl we have used those given by Shannon [16].

All of those input values are listed in Table I, where we have also included the values of the ionicity f, as well as the effective charges $|Z^*|$ thus obtained.

We note that the values of $|Z^*|$ for the molten alkali halides spread over a relatively small range of values that reflect, in some sense, the large ionicity of these systems. There is actually an almost linear relationship between $|Z^*|$ and f for the molten alkali halides studied in this work.

There is no point in looking for trends for the two noble metal halides studied here. Even if we had data to study more of these systems we doubt that any trend will be found. For the two cases studied here, we recall that both CuCl [17] and AgCl [18] exhibit strong premelting phenomena, so much so that CuCl resembles a superionic conductor in its behaviour, and that in AgCl the transition to a superionic phase is frustrated by melting. The values of the effective charge for these systems are only slightly higher than the unreasonably low effective charge used by Ginoza *et al.* [19] in an attempt to account for the structure of molten CuCl.

The behaviour of the molten thallium halides, both in their static and dynamic properties, are intermediate between the molten alkali halides and noble metal halides [20]. This is reflected in the effective charges found for molten TlCl and TlBr. However, the effective charge found for molten TlI is similar to that of molten CuCl.

TABLE I *Input data.* The experimental input data for the temperature T and density n are taken from Ref. [13]. The ionic diameters are taken from Ref. [15], except those marked with superscript a which are taken from Ref. [16]. The experimental values for the excess entropies ΔS are taken from Ref. [14]. The excess entropy is defined as that value for the entropy from which the ideal gas and ideal mixing contributions have been deducted

Salt	T(°K)	n ($Å^{-3}$)	σ_1($Å$)	σ_2($Å$)	$-\Delta S_{exp}/k_B$	$\|Z^*\|$	*Ionicity f*
LiF	1121	0.0836	1.632	2.358	7.2	0.952	0.915
NaF	1268	0.0558	2.34	2.358	7.2	1.120	0.946
KF	1131	0.0394	2.926	2.358	6.8	1.027	0.955
RbF	1048	0.0351	3.174	2.358	7.0	0.996	0.960
CsF	976	0.0289	3.44	2.358	7.4	1.054	–
LiCl	883	0.0426	1.632	3.17	7.2	0.866	0.903
NaCl	1073	0.0321	2.34	3.17	6.6	1.023	0.935
KCl	1043	0.0247	2.926	3.17	6.8	1.140	0.953
RbCl	995	0.0223	3.174	3.17	8.4	1.301	0.955
CsCl	918	0.0200	3.44	3.17	7.4	1.158	–
LiBr	823	0.0350	1.632	3.432	7.4	0.860	0.899
NaBr	1020	0.0273	2.34	3.432	6.8	1.037	0.934
KBr	1007	0.0215	2.926	3.432	6.8	1.115	0.952
RbBr	965	0.0197	3.174	3.432	8.2	1.002	0.957
CsBr	909	0.0177	3.44	3.432	7.6	1.213	–
LiI	742	0.0279	1.632	3.814	7.6	0.816	0.890
NaI	933	0.0221	2.34	3.814	6.8	0.989	0.927
KI	954	0.0177	2.926	3.814	6.8	1.105	0.950
RbI	920	0.0164	3.174	3.814	8.4	1.302	0.951
CsI	899	0.0147	3.44	3.814	6.8	1.124	–
CuCl	696	0.0456	1.2^a	3.17	2.45	0.325	0.746
AgCl	728	0.0409	2.3^a	3.17	4.37	0.21	0.856
AgBr	703	0.0357	2.3	3.432	3.12	–	0.850
AgI	831	0.0286	2.3	3.814	2.73	–	0.770
TlCl	702	0.0282	3.18^a	3.17	5.638	0.676	0.822
TlBr	733	0.0255	3.18	3.432	5.4	0.61	0.829
TlI	715	0.0226	3.18	3.814	4.97	0.359	0.821

4. DISCUSSION

The relationship sought between effective charges and ionicity appears to have limited applicability; it is only for the molten alkali halides that we find a clear trend. Such a trend is not present in the molten thallium halides and, while it is not possible to establish trends for data involving only two noble metal halides, we do not expect one for these melts either. The main reason is that in the thallium halides and the noble metal halides polarisation has an important effect on their properties.

Our findings are consistent with those of Pietronero [3], namely that his melting criterion is only applicable to the alkali halides. Our results also suggest that the freezing criterion proposed by Reiss *et al.* [21] is also limited to the alkali halides (see also March and Tosi [22] for a complete discussion of freezing theories). In both criteria the ratio of the ionic radii is a relevant parameter, and so is in our relationship through the calculation of the entropy.

Finally, it is clear from our work that the entropy of charged spheres will never be an adequate model for obtaining the entropies of the noble metal and thallium halides melts. Given the importance of the ionic polarization in the properties of these systems, it is unlikely that a system of soft spheres will be adequate either.

Acknowledgements

We thank Çetin Tasseven for his help in the earlier stages of this work. We also thank NATO Collaborative Research Grant (CRG971173) for financial support in carrying out this work. MS gratefully acknowledges the financial support of the Ministry of Education and Science of Spain.

References

[1] Akdeniz, Z. and Tosi, M. P. (1992). *Proc. R. Soc. London A*, **437**, 85.
[2] Tallon, J. L. and Robinson, W. H. (1982). *Phys. Lett. A*, **87**, 365.
[3] Pietronero, L. (1978). *Phys. Rev. B*, **17**, 3946.
[4] Koh, A. K. (1996). *J. Phys. Chem. Solids*, **57**, 51.
[5] Hafner, J., Hulliger, F., Jensen, W. B., Majewski, J. A., Mathis, K., Villars, P. and Vogl, P., *Structures of Binary Compounds* (North Holland: Amsterdam, 1989).
[6] Pettifor, D. G. (1986). *J. Phys. C: Solid State Phys.*, **19**, 285.
[7] Phillips, J. C. (1970). *Rev. Mod. Phys.*, **12**, 317.
[8] Blum, L. (1975). *Mol. Phys.*, **30**, 1529.
[9] Hiroike, K. (1977). *Mol. Phys.*, **33**, 1195.
[10] Abernethy, G. M. and Silbert, M. (1982). *Phys. Chem. Liq.*, **11**, 195.
[11] Yokokawa, H. and Kleppa, O. J. (1982). *J. Chem. Phys.*, **76**, 5574.
[12] Hoshino, K. and Young, W. H. (1986). *Phys. Chem. Liq.*, **15**, 229.
[13] Janz, G. J., Dampier, F. W., Lakshminarayan, G. R., Lorenz, P. K. and Tomkins, R. P., *Molten Salts, National Standard Reference Data Series*, National Bureau of Standards 15, 1988.
[14] Barin, I. and Knacke, O., *Thermodynamical Properties of Inorganic Substances* (Springer Verlag: Berlin, 1973).

[15] Sangster, M. J. L. and Dixon, M. (1976). *Adv. Phys.*, **25**, 247.

[16] Shannon, R. D. (1976). *Acta Cryst. A*, **32**, 751.

[17] Stafford, A. J., Silbert, M., Trullàs, J. and Giró, A. (1990). *J. Phys. Condens Matter*, **2**, 6631.

[18] Tasseven, Ç., Trullàs, J., Alcaraz, O., Silbert, M. and Giró, A. (1997). *J. Chem. Phys.*, **106**, 7286.

[19] Ginoza, M., Nixon, J. H. and Silbert, M. (1987). *J. Phys. C: Solid State Phys.*, **20**, 1005.

[20] Tasseven, Ç., Alcaraz, O., Trullàs, J., Silbert, M. and Giró, A. (1997). *J. Phys. Condens Matter*, **9**, 11061.

[21] Reiss, H., Mayer, S. W. and Katz, J. L. (1961). *J. Chem. Phys.*, **35**, 820.

[22] March, N. H. and Tosi, M. P., *Coulomb Liquids* (Academic Press, London, 1984).