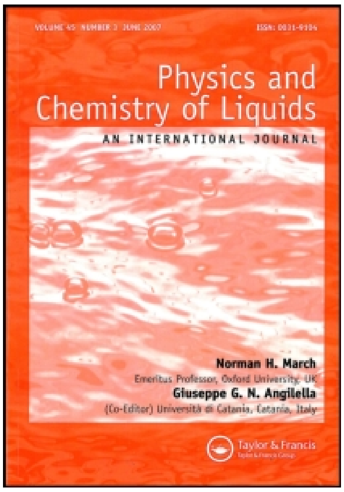

Physics and Chemistry of Liquids

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

Models for structural transitions in nitrates

Z. Akdeniz[a]; M. P. Tosi[b]
[a] Physics Department, University of Istanbul, Istanbul, Turkey [b] Classe di Scienze, Scuola Normale Superiore, Pisa, Italy

To cite this Article Akdeniz, Z. and Tosi, M. P.(2005) 'Models for structural transitions in nitrates', Physics and Chemistry of Liquids, 43: 4, 361 — 365

To link to this Article: DOI: 10.1080/00319100500115369

URL: http://dx.doi.org/10.1080/00319100500115369

Physics and Chemistry of Liquids
Vol. 43, No. 4, August 2005, 361–365

Taylor & Francis
Taylor & Francis Group

Models for structural transitions in nitrates

Z. AKDENIZ† and M. P. TOSI*‡

†Physics Department, University of Istanbul, Istanbul, Turkey
‡Classe di Scienze, Scuola Normale Superiore, Pisa, Italy

(*Received 26 February 2005*)

A number of alkali and alkaline-earth nitrates crystallize in ionic structures related to the NaCl and fluorite crystal structures, respectively. This suggests that their cohesive properties may be usefully described by means of a phenomenological ionic model (Z. Akdeniz, M.P. Tosi, *Zs. Naturforsch.*, **59a**, 957 (2004)). In the present work we discuss from this viewpoint the structural transitions that take place in these materials. We first present a Bragg–Williams type approach to the orientational disordering of the NO_3 groups and to positional melting in sodium nitrate. We then discuss the stability of the superionic CKN glass in terms of strongly bound $Ca_2(NO_3)_7$ units surrounded by highly mobile potassium ions.

Keywords: Orientational disorder and melting; Glass transition

1. Introduction

Nitrate glasses are formed from mixing the nitrate of a divalent metal ion M, such as Mg, Ca or Cd, with that of an alkali metal ion A such as Na or K [1]. The glassy state in these materials is stable over a very broad range of composition around the stoichiometric compound $M_2A_3(NO_3)_7$. The prototype of these systems is the CKN compound having a chemical formula $Ca_2K_3(NO_3)_7$, which melts at $T_m = 498\,K$ and has a glass transition temperature $T_g = 333\,K \cong 2T_m/3$.

The NO_3 group is a chemically saturated and very stable unit in the shape of a planar equilateral triangle with nitrogen at its center [2]. Its stability is attested by the experimental observations showing that the frequencies of its internal vibrational modes are almost independent of the metal–ion partners in a variety of molten nitrates of monovalent ions [3] as well as in the mixed nitrate glasses [1]. Various evidence indicates that the pure components of the nitrate mixtures conform to an ionic model with the NO_3 group acting as the negative ion. Thus, the ANO_3 compounds crystallize into a NaCl-like structure and the $M(NO_3)_2$ compounds crystallize into a fluorite-like structure, with some structural distortions that are due to the spatial

---

*Corresponding author. Email: tosim@sns.it

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2005 Taylor & Francis
DOI: 10.1080/00319100500115369

requirements of the NO_3 group [4]. Further evidence comes from the presence of an infrared-active vibrational mode in molten ANO_3 compounds, which is associated with oscillations of the alkali ions against the NO_3 groups [3].

Torsional oscillations of the NO_3 group around its equilibrium orientations form a low-frequency Raman-active mode in both molten and crystalline ANO_3 compounds [3,4]. Disorder in the orientations of the NO_3 groups has been reported to develop in crystalline $NaNO_3$ in the temperature range from 423 to 548 K, as evidenced by the weakening and ultimate disappearance of X-ray reflections due only to the oxygen atoms [4]. We have been unable to find evidence on ionic motions in the $M(NO_3)_2$ compounds, but diffraction studies carried out on $Pb(NO_3)_2$ up to 573 K have given no evidence pointing to the development of the type of hindered rotations of the nitrate ions that have been found in $NaNO_3$ [4].

In the present work we first use the phenomenology laid down by Pople and Karasz [5,6], as extended by Amzel and Becka [7], to discuss the orientational disorder of the nitrate groups that arises in $NaNO_3$ crystals before positional melting occurs at $T_m = 575\,K$. We then take advantage of a microscopic model for the structure of the CKN glass [8] to discuss its glass transition on the basis of theoretical results obtained for charged hard-sphere systems [9].

2. Orientational disorder and melting of sodium nitrate

Pople and Karasz [5,6] generalized the approach to positional disordering (melting) proposed by Lennard-Jones and Devonshire [10] to include the possibility of disordering in the orientation of anisotropic molecules. They considered only two possible orientations separated by an energy barrier for each molecule at each lattice site. The case of D molecular orientations with $D > 2$ was later treated by Amzel and Becka [7]. The general framework is that of the Bragg–Williams approximation to phase transitions.

In their model, Amzel and Becka [7] determined by free energy minimization the order parameters Q and S_i (with $i = 1, \ldots, D$) giving the mean fraction of molecules on a lattice site and the mean fraction of molecules having orientation α_i on each lattice site, respectively. Taking $S_i = (1 - S_1)/(D - 1)$ for $i \neq 1$, the model yields simultaneous equations for Q and S_1. These read

$$\frac{1}{2Q-1}\ln\frac{Q}{1-Q} = L\left[1 - S_1\left(2 - \frac{DS_1}{D-1}\right)y\right] \tag{1}$$

and

$$\ln\frac{S_1}{(D-1)(1-S_1)} = -2Ly\left[1 - \frac{DS_1}{D-1}\right](1 - 2Q + 2Q^2). \tag{2}$$

Here $L = ZW/(2k_BT)$ and $y = Z'W'/ZW$, with ZW being the energy required to move a molecule to an interstitial site and $Z'W'$ the energy barrier to turn a molecule to another orientation. One recovers from these equations the model of Pople and

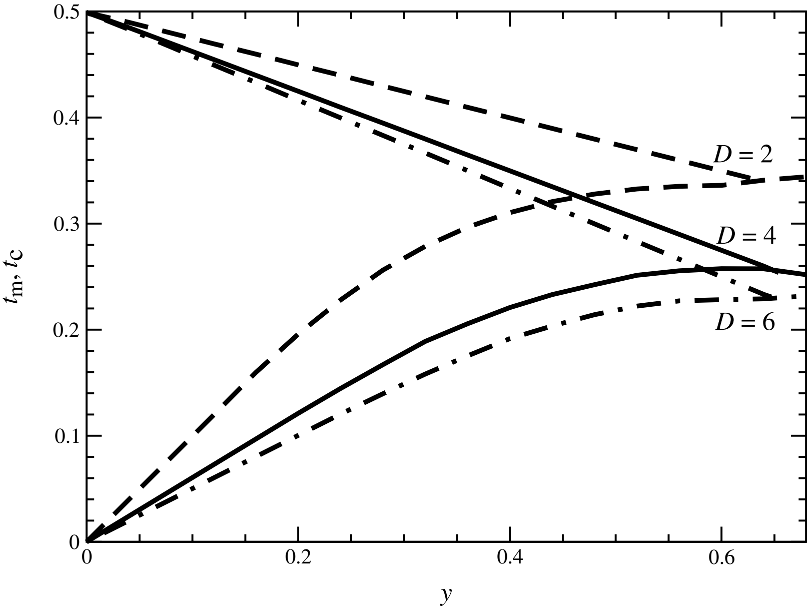

Figure 1. Reduced melting temperature $t_m = 2k_BT_m/ZW$ (upper line) and reduced orientational disordering temperature $t_c = 2k_BT_c/ZW$ (lower line) *versus* the parameter $y = Z'W'/ZW$ for the cases $D = 2$, 4, and 6.

Karasz by setting $D = 2$ (see also Ubbelohde [11] and Tozzini *et al.* [12]). The melting model of Lennard-Jones and Devonshire then follows by setting $y = 0$.

The solution corresponding to $Q = 1/2$ and $S_i = 1/D$ is realized at sufficiently high temperature and describes complete positional and orientational disorder as in an isotropic fluid state. At lower values of L, orientational disorder sets in before positional melting for a range of values of y lying appreciably below unity. Explicit solution of equations (1) and (2) shows that within this model the orientational disorder grows continuously as L decreases, before discontinuously dropping to its asymptotic value $1/D$.

Figure 1 plots for the cases $D = 2$, 4, and 6, the positional melting temperature T_m and the orientational disordering temperature T_c in the range $T_c \leq T_m$, both being measured in units of $ZW/2k_B$, as functions of the parameter y. This parameter has been assumed to be independent of temperature and volume. An increase in the number of local orientations is seen from figure 1 to lower both transition temperatures.

The relevant case for $NaNO_3$ actually is $D = 4$, since the nitrate group on a lattice site can reach physically indistinguishable orientations through four successive rotations by 30°. Taking $T_c/T_m = 0.95$ from experiment, we get $Z'W' \approx 0.55ZW$ in this material. At such values of the re-orientation energy barrier, the two disordering transitions are very close to each other and one expects that orientational disordering is strongly influencing the melting process.

3. Structure of the CKN glass

The transport properties of CKN in the melt have been measured over broad temperature ranges. The shear viscosity η obeys a universal modified Arrhenius law of the type $\eta \propto (T/T_0)\exp(qT_0/T)$ with $T_0 = 530\,\mathrm{K}$ and $q \cong 5.9$ [13]. The behavior of $\eta(T)$ classifies the melt as a fragile glass-former [14], implying that the glassy structure may reorganize itself over a variety of particle orientations and coordination states. The appropriate structural model of the CKN glass should therefore be thought of as a frozen disordered array of strongly bound units, rather than as an extended disordered network of chemical bonds. The orienting influence of non-spherical neighbors in liquids and glasses of rod-like or disc-shaped molecules is reviewed in Ubbelohde [11].

It has also been shown that in the CKN melt the relationship $\sigma T \propto (T/\eta)^m$ between shear viscosity and ionic conductivity σ is obeyed over nine orders of magnitude with $m \cong 0.8$ [15]. A nonlinear Stokes–Einstein law as displayed in these measurements indicates that the elementary mechanisms of momentum and charge transport are basically different. A consistent viewpoint is that electrical conduction is due to the motions of alkali ions through a disordered array of strongly bound $Ca_2(NO_3)_7$ units, which govern the viscosity of the material.

The equilibrium structure of a $Ca_2(NO_3)_7$ unit has been evaluated within an ionic model adapted to reproduce the available data on physical properties of the pure components of the CKN glass [8]. A notable result of the analysis given in [8] is that the electronic charge transfer from the alkali to the nitrate ion in alkali nitrates is relatively limited, corresponding to an effective ionic valence of about 0.6 elementary charges. This value accounts for the measured frequencies of the infrared-active mode in the nitrates of Na, K, Rb and Cs. The shape of a $Ca_2(NO_3)_7$ unit is then predicted to consist of two calcium ions in a fivefold coordination and sharing three nitrate groups. Around such a unit one finds a multiplicity of energetically equivalent positions for three potassium ions, thus accounting for the fast ion conduction property of the material.

If we allow for essentially free rotations of each $Ca_2(NO_3)_7$ unit around its main axis, the calculated shape of the unit is an ellipsoid with a length of roughly 8.8 Å and a radius of roughly 4.0 Å, corresponding to a volume of order 400 Å^3. On the other hand, the volume of the CKN glass per formula unit can be estimated as being somewhat in excess of 500 Å^3, from the experimental density data reported by Janz [16] for the melt near equilibrium freezing. The packing fraction of the constituent units in the CKN glass therefore is about 0.7. In this range the stability of the superionic-glass state is primarily determined by steric factors and is essentially independent of the strength of the Coulomb interactions [9]. The glass transition temperature of mixed nitrate glasses should therefore exhibit a strong dependence on pressure.

4. Conclusions

We have proposed a consistent picture for the cohesive properties of nitrates and for their structural transitions associated with melting and with the formation of plastic-crystal and superionic-glass states. This picture depends in a crucial manner on the nature of the nitrate group as a non-spherical object and on the magnitude of the electronic charge transfer from the metal ions to the nitrate ions. Similar ideas may be useful to describe the disordered states of other salts such as carbonates.

Acknowledgements

One of us (Z.A.) wishes to thank Scuola Normale Superiore for the hospitality during the completion of this work and acknowledges the support from TUBITAK and the Research Foundation of Istanbul University under Project Number YÖP-16/13082004.

References

[1] T. Furukawa, S.A. Brawer, W.B. White, *J. Chem. Phys.*, **69**, 2639 (1978).
[2] T. Ishiwata, I. Tanaka, K. Kawaguchi, E. Hirota, *J. Chem. Phys.*, **82**, 2196 (1985).
[3] M.H. Brooker, G.N. Papatheodorou, In *Advances in Molten Salt Chemistry*, G. Mamantov (Ed.), Vol. 5, p. 26, Elsevier, Amsterdam (1983).
[4] R.W.G. Wyckoff, *Crystal Structures*, Vol. 2, Chapter VII, Interscience, NewYork (1964).
[5] J.A. Pople, F.E. Karasz, *J. Phys. Chem. Solids*, **18**, 28 (1961).
[6] F.E. Karasz, J.A. Pople, *J. Phys. Chem. Solids*, **20**, 294 (1961).
[7] L.M. Amzel, L.N. Becka, *J. Phys. Chem. Solids*, **30**, 521 (1969). (We have corrected an evident printing mistake in equation (2) of this article.)
[8] Z. Akdeniz, M.P. Tosi, *Zs. Naturforsch.*, **59a**, 957 (2004).
[9] M. Cardenas, M.P. Tosi, *Solid State Commun.*, **133**, 667 (2005).
[10] J.E. Lennard-Jones, A.F. Devonshire, *Proc. R. Soc.*, **A169**, 317 and **A170**, 464 (1939).
[11] A.R. Ubbelohde, *The Molten State of Matter*, Wiley, New York (1978).
[12] V. Tozzini, N.H. March, M.P. Tosi, *Phys. Chem. Liq.*, **37**, 185 (1999).
[13] A. Voronel, E. Veliyulin, T. Grande, H.A. Øye, *J. Phys. Condens. Matter*, **9**, L247 (1997).
[14] C.A. Angell, *Science*, **267**, 1924 (1995).
[15] A. Voronel, E. Veliyulin, V.Sh. Machavariani, A. Kisliuk, D. Quitmann, *Phys. Rev. Lett.*, **80**, 2630 (1998).
[16] G.J. Janz, *J. Phys. Chem. Ref. Data*, **17**, 9 (1988).