ABSTRACT

Liquid ZnCl$_2$ has been investigated up to 700°C using Raman and neutron scattering techniques. The results are critically analyzed for either a confirmation of, or a contradiction to, the interpretation of recent Brillouin scattering experiments which claimed a pronounced maximum in $C_p/C_v$ at 425°C. Our structural results show only minor changes above and below this temperature. The Raman results are interpreted as showing a gradual dissociation of the ZnCl$_2$ network.

INTRODUCTION

In recent years there have been a number of investigations that explore the possibility of the existence of phase transitions in liquids. It is clear that liquids which undergo dissociation as a function of temperature are, at least in a general sense, undergoing a transformation. Whether or not such transformations satisfy the thermodynamical criteria of true phase transitions is the point in question.

One possible candidate for exhibiting such a transformation is ZnCl$_2$. Diffraction studies of the liquid just above the melting point$^{1,2}$ indicate a highly connected network structure with well-defined ZnCl$_4$ tetrahedra. Such a structure is consistent with the macroscopic behavior, including the high viscosity above the melting point and also the relatively small latent heat of melting of ZnCl$_2$, compared with other divalent salts on the basis of volume change on melting:$^3$ the entropy deficit is presumably regained at higher temperatures when the network breaks up into smaller units. Furthermore, recent inelastic neutron scattering experiments$^4$ on ZnCl$_2$ at 347°C, 30°C above the melting point, show that the energy widths of the scattering function are much less than the Gaussian widths generally exhibited by liquids at high scattering vector $Q$, even at $Q$ values as high as 10 Å$^{-1}$, indicating unusually strong binding of the ions to the liquid network. This picture is consistent with a peak in the specific heat extracted from a simple two-state model.$^5$

More recently in a Brillouin scattering investigation of ZnCl$_2$$^6$ it was reported that the results could be interpreted as providing evidence for a very large anomaly in the ratio of specific heats ($\gamma = C_p/C_v$). The results of this investigation are shown in Fig. 1. The temperature of this maximum (= 425°C) is surprising since it lies above the melting temperature of crystalline ZnCl$_2$. Furthermore $C_p/C_v$ reaches a maximum of $\approx 4$ which is considered by many to be unrealistically large for any system.

The results shown in Fig. 1 are controversial since they are obtained with the use of simple hydrodynamic theory. It has been shown in similar Brillouin scattering investigations$^7,8$ that, if the generalized hydrodynamic theory is used, the experimental
data can be fit without invoking an anomalous $\gamma$. Since both approaches yield excellent fits to the experimental spectra it has not been possible to date to resolve the issue. We note that in the generalized hydrodynamic approach the usual hydrodynamic phenomenological material parameters are ad hoc, additionally assumed to be frequency dependent. It is one of these additional parameters which then exhibits anomalous behavior but, since this parameter has no clear microscopic origin, the significance of the anomaly is difficult to interpret.

The purpose of the present investigation was to perform both Raman and neutron scattering experiments to ascertain if there is any evidence for or against the existence of a $C_p/C_v$ anomaly which could be interpreted as a thermodynamic signature of a transformation.

**RAMAN SCATTERING RESULTS**

Figure 2 shows the temperature dependence of reduced polarized Raman spectra. The spectrum at 700°C has been fitted with three Lorenzians as indicated by the dashed lines: we found that at least three Lorenzians are required to produce a reasonable fit. Such fits show that neither the peak positions, nor line widths show any marked temperature dependence. The relative areas under each peak do however change dramatically with temperature. In Fig. 3 we have plotted the fraction of the total intensity of each one of the three peaks obtained from the fitting procedure. It shows that the peak at around 225 cm$^{-1}$ (307 cm$^{-1}$) decreases (increases) by a factor of around 3 as temperature is increased, while the one at 253 cm$^{-1}$ remains almost constant.

**NEUTRON DIFFRACTION RESULTS**

To examine possible structural changes over the temperature region of the anomalous behavior of the Brillouin scattering, neutron diffraction measurements were made at the GLAD facility at IPNS. The sample used was part of the high-purity, anhydrous sample used in the INS measurements, which had previously been shown to have negligible water content. It was contained in three vitreous silica tubes, 3 mm I.D., 4 mm O.D., and mounted in a vanadium furnace on the diffractometer. Diffraction patterns were obtained at 350°C and 500°C and corrected for container and furnace scattering, absorption and multiple scattering using standard procedures. The data were normalized with reference to a 0.635-cm diameter standard vanadium rod. The low-Q regions of the neutron-weighted average structure factors $S(Q)$ are shown in Fig. 4. The most obvious change with temperature is the shift in the position of the “first sharp diffraction peak”, which is known to be a signature of intermediate-range order. The peak center moves from 1.04 to 1.01 ± 0.01 Å$^{-1}$ over the temperature interval of the measurement, about a 3% decrease. According to the thermal expansion data discussed below, the volume change over this interval is also about 3%. The measurements of Allen et al. found a peak shift of 6% over a somewhat larger temperature interval, 330°C to 600°C, quite consistent with the present results.

Real space distribution functions were obtained by Fourier transformation of $S(Q)$ out to 18.0 Å$^{-1}$. Gaussian fits, made to the resulting $T(r)$ functions using standard
procedures,\textsuperscript{11} gave nearest-neighbor Zn-Cl coordination numbers of 4.31 and 4.15 ± 0.2 at 350°C and 500°C, respectively. These values are reasonably consistent with 4.3 ± 0.3 obtained by Biggin and Enderby\textsuperscript{1} at 327°C and with 3.93 and 3.67 ± 0.1 obtained by Allen \textit{et al.}\textsuperscript{2} at 330°C and 600°C, respectively. The positions of the first two coordination peaks changed negligibly (less than 1%), as did the second-neighbor (Zn-Zn and Cl-Cl) coordination number. This is also consistent with the earlier work. Thus, coordination changes with temperature in the short-range structure appear to be limited to a small decrease in the Zn-Cl coordination, about 2.5 · 10^{-4}/°C, comparable in relative magnitude to the decreases in the density and in the scattering vector of the first sharp diffraction peak.

**INTERPRETATION OF THE RAMAN RESULTS**

There have been two interpretations suggested for the features in the spectra in Fig. 2: (i) they are due to different chemical species\textsuperscript{5} of ZnCl\textsubscript{1} or (ii) different vibrational symmetry modes\textsuperscript{4,12} of ZnCl\textsubscript{4}. The first model is hard to reconcile with the observation of more than one peak even in the glassy state; the observed temperature dependence of the relative intensities of the various features is hard to reconcile with the second model. We have chosen to interpret our data along the lines of the first model where the three peaks are associated with different coordination states of the Zn atoms viz. ZnCl\textsubscript{4}, ZnCl\textsubscript{3} and ZnCl\textsubscript{2}. The intensity of each peak is assumed to be proportional to the total number of units with a specific coordination. Assuming that the probability of breaking a Zn-Cl bond, given by \exp(-E/kt), is independent of the number of broken bonds, it is straightforward to calculate the number of Zn atoms with zero, one and two broken bonds. If \(N_0\) is the total number of Zn atoms then we have

\[
\frac{N_1}{N_0} = \frac{1/(1 + \exp(-E/kt) + \exp(-2E/kt))}{1/(1 + \exp(-E/kt) + \exp(-2E/kt))}
\]

\[
\frac{N_2}{N_0} = \frac{\exp(-E/kt)/(1 + \exp(-E/kt) + \exp(-2E/kt))}{1/(1 + \exp(-E/kt) + \exp(-2E/kt))}
\]

\[
\frac{N_3}{N_0} = \frac{\exp(-2E/kt)/(1 + \exp(-E/kt) + \exp(-2E/kt))}{1/(1 + \exp(-E/kt) + \exp(-2E/kt))}
\]

Following Ref. 5 we also write

\[E = \Delta H - T\Delta S.\]  

Fitting the data in Fig. 3 to Eqs. 1 and 2 yields \(\Delta H = 4.0 ± 0.1\) kcal/mol and \(\Delta S = 5.7 ± 0.1\) cal/(mol K). Comfortingly fits to all three data sets yield almost identical values which are also in good agreement with those (\(\Delta H = 4.24\) kcal/mol and \(\Delta S = 5.86\) cal/(mol K)) extracted in Ref. 5 from volume vs. temperature data. The full lines in Fig. 3 are obtained with our values of \(\Delta H\) and \(\Delta S\) given above.

The above model leads directly to an expression for the volume expansion. If each bond breaking produces a change in volume \(\Delta V\) then the total volume of the system is given by

\[V = V_0 + \Delta V(N_2 + 2N_3)\]  

\[\text{(3)}\]
where \( V_0 \) is the volume at zero Kelvin. The temperature derivative of this expression yields the thermal expansion \( \alpha \): using our values of \( \Delta H \) and \( \Delta S \) we obtain the results given in Fig. 5. Note that since \( \Delta V \) is not known the absolute value of \( \alpha \) is also unknown. However, using the experimental\(^{13} \) values of \( \alpha \), also plotted (squares) in Fig. 5, allows us to make an estimate of its magnitude. Note that this scaling assumes that all the measured expansion originates from the bond breaking process.

The final step in our analysis comes by recalling the thermodynamic identity

\[
(\gamma - 1) = VT\alpha^2 B_S/C_p
\]  \hspace{1cm} [4]

where \( B_S \) is the adiabatic bulk modulus. Taking \( B_S = 10^{11} \) erg/cm\(^3\) and \( C_p = 24.1 \) cal/(mol K) from Refs. 6 and 14, and since all other parameters are known, allows us to calculate \( \gamma \): the result is shown in Fig. 6.

CONCLUSIONS

Over the temperature range where previous Brillouin results\(^6 \) indicated a maximum in \( C_p/C_V \) our neutron and Raman scattering experiments show only small and monotonic changes. However, the change in the relative intensities of the Raman peaks can be interpreted in the framework of a model in which the changes are associated with breaking of Zn-Cl bonds. This model leads directly to an expression for the thermal expansion which in turn allows the ratio \( C_p/C_V \) to be calculated: the results are in excellent qualitative agreement with the Brillouin results but there are large uncertainties in the absolute magnitude.

In summary: the results presented here neither confirm nor contradict the existence of an anomaly in \( C_p/C_V \) in ZnCl\(_2\). In order to resolve this issue it is necessary to await more accurate experimental data on both the specific heat and thermal expansion in this temperature range.

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REFERENCES

1. S. Biggin and J.E. Enderby, J. Phys. C: Solid State Phys. 14, 3129-3136 (1981).
2. D.A. Allen, R.A. Howe, N.D. Wood and W.S. Howells, J. Chem. Phys. 94, 5071-5076 (1991).
3. M.P. Tosi, D.L. Price and M.-L. Saboungi, Annu. Rev. Phys. Chem. 44, 173-211 (1993).
4. D.L. Price, M.-L. Saboungi, S. Susman, K.J. Volin, and A.C. Wright, J. Phys.: Condens. Matt. 3, 9835-9842 (1991).
5. C.A. Angell and J. Wong, J. Chem. Phys. 53, 2053 (1970).
6. M. Grimsditch and N. Rivier, Appl. Phys. Lett. 58, 2345 (1991).
7. M. Stoltwisch, J. Sukmanowski, D. Quitmann and M. Kuenzler, Mater. Sci. Forum 6, 571 (1985).
8. M. Stoltwisch, J. Sukmanowski and D. Quitmann, J. Chem. Phys. 86, 3207 (1987).
9. A.J.G. Ellison, R.K. Crawford, D.G. Montague, K.J. Volin and D.L. Price, J. Neutron Res. 1, 61-70 (1993).
10. S.C. Moss and D.L. Price, in Physics of Disordered Materials, ed. D. Adler, H. Fritzsche and S.R. Ovshinsky (Plenum, NY, 1985), pp. 77-95; D.L. Price, S.C. Moss, R. Reijers, M.-L. Saboungi and S. Susman, J. Phys.: Condens. Matt. 1, 1005-1008 (1989).
11. S. Susman, K.J. Volin, D.G. Montague and D.L. Price, J. Non-Cryst. Solids 125, 168-180 (1990).
12. F.L. Galeener, J.C. Mikkelsen, A.C. Wright, R.N. Sinclair, J.A.E. Desa and J. Wong, J. Non-Cryst. Solids 42, 23- (1980); M.L. Cacciola, S. Magazu, P. Migliardo, F. Aliotta and C. Vasi, Solid State Comm. 57, 513- 1986).
13. J.D. Mackenzie and W.K. Murphy, J. Chem. Phys. 33, 366 (1960); M. Goldsten and N. Nakonecznyj, Phys. Chem. Glasses 6, 126 (1965).
14. D. Cubicciotti and H. Eding, J. Chem. Phys. 40, 978 (1964).
Fig. 1. $C_p/C_v$ anomaly in ZnCl$_2$ obtained from Brillouin scattering experiments (Ref. 6).
Fig. 2. Representative polarized Raman spectra of ZnCl$_2$ at various temperatures. The dashed lines are three Lorenzians obtained from a fit to the 700°C data. The symbols are the sum of the three Lorenzians.
Fig. 3. Fraction of the total intensity under each of the three peaks in Fig. 2. The dots are experimental, the full lines represent Eqs. 1.
Fig. 4. Neutron weighted average structure factors $S(Q)$ at low scattering vector $Q$ for 
ZnCl$_2$ at 350°C and 500°C.
Fig. 5. Thermal expansion of ZnCl₂. The full line represents Eq. 3, the squares are experimental values from Ref. 13.
Fig. 6.  \( \frac{C_p}{C_V} \) calculated using Eq. 4 and the values given in the text.