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A DETAILED PHYSICO-CHEMICAL STUDY OF
ZnCl₂-BASED BINARY MOLTEN SALT SYSTEMS

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The overall purpose of the program is the study of the properties of ionic liquids over the maximum possible temperature range with special emphasis on extending the range of experimentation downwards in temperature toward the low temperature limit set by the glass transition phenomenon. This emphasis has restricted the systems of study, and most of the work has been performed on systems containing zinc chloride as one component. It was initially expected that these systems would provide interesting analogues of the BeF_2 -based molten salt solutions serving as fuel carrier and coolant in the molten salt reactor and work to date has shown this to be very much the case.

Studies have now been performed on:

1. Structure of glassy zinc chloride by spectroscopic methods.
2. Phase equilibria, molar volume, electrical conductance and glass transition temperatures in the ZnCl_2 -Pyridinium chloride system.
3. Viscosity of solutions in the ZnCl_2 -Pyridinium system.
4. Low temperature frequency dispersion of electrical conductance and dielectric constant in ZnCl_2 -Pyridinium chloride solutions.
5. Nuclear magnetic resonance studies of the proton shift in ZnCl_2 -pyridinium chloride solutions.
6. Phase equilibria and glass transition temperatures in the $\text{ZnCl}_2 + \text{KI}$ system.
7. Glass transition temperatures in zinc chloride + various substituted pyridine hydrochloride and other organic ammine hydrochloride solutions.
8. Dependence of co-ordination number of Ni(II) and electrical conductance on composition and temperature in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{ZnCl}_2$ solutions.

9. Dependence of co-ordination number of Ni(II) on pressure in molten organic chloride salt solutions.
10. Heat capacities of glassy and liquid nitrate mixtures and zinc chloride + pyridinium chloride solutions.

Of these, articles dealing with items 1 and 2 have been submitted for publication and accepted by J. Chem. Phys., and J. Phys. Chem. respectively. Items 3, 4, 5, and 8 are essentially completed studies and await writing up. Items 2 and 8 were partially described in the 1969 progress report.

B. RECENT RESULTS

1. Structure and thermodynamics of $ZnCl_2$ liquid and glass. (J. Long)

It is clear that if a program of study is to be performed on systems containing $ZnCl_2$ as a component common to all systems, the best possible understanding of the nature of this component is required. $ZnCl_2$ liquid and crystal phases have been the subject of quite detailed studies in the past but the glassy state has been ignored.

Raman spectra of the glass in thin capillary tubes were obtained using laser exciting sources, the far infrared spectra of thin films of glass formed between crystalline quartz plates were studied, and the spectra of Ni(II) and Cu^{2+} ions doped in trace quantities into the glass were determined and interpreted.

The Ni(II) spectra (Fig. 1) showed that the Ni(II) ions anomalously occupied tetrahedral sites when the liquid was quenched to the glass

indicating the existence of a tight structure in which Ni(II) is forced to occupy substitutionally the four-coordinate Zn(II) sites in some sort of network structure, a conclusion in accord with previous ideas on the structure of liquid zinc chloride.

A strong Raman band in the same spectral region as observed for liquid, but of considerably smaller half-width, was observed in the glass (Fig. 2) suggesting a more ordered structure in the glass as expected. The far infrared spectra were particularly informative. Here comparisons with spectra of the α - and β -crystal polymorphs of ZnCl_2 could be made, and it became clear (Fig. 3) that the glass was more closely related in short range order to the α polymorph than to the β polymorph. From reconstructions of the crystal lattices from X-ray determined structure data, it can be clearly seen that the α polymorph is essentially a 3 dimensionally extensive chloride bridged network, hence zinc chloride glass is well described as a 3 dimensional random network structure closely analogous to vitreous SiO_2 and BeF_2 .

A random network of such substances can be constructed in such a way that no bridging bonds are broken i.e. long range disorder can be achieved by a succession of small distortions of bond angles. However in order for fluid flow to occur some rupture of this network structure is obviously needed. It has been found possible to gain insight into the types of defect (broken bond) structure sustained by the glass and developed with increase of temperature, by doping in a bridging ligand which substitutes for the chloride bridge, but contains an internal degree of freedom which "signals" its chemical environment. Suitable probes are CN^- and CNS^- ions. By comparison of stretching frequency of these ions in very dilute solutions

in zinc chloride glass, with spectra of the ions in known bonding situations in crystal lattices (Fig. 4) we conclude that the glass contains, as expected, mainly fully bridging CN^- ions, but also smaller fractions of both singly broken and doubly broken bridges (the latter being essentially "free" cyanide or thiocyanate ions). The spectra of these three states are of similar half-width to the crystal bands, suggesting the bonded states are well defined in the glass i.e., there is no partial bonding. These observations have been utilized in constructing a lattice model for the thermodynamics of the glass transition referred to below.

2. Phase equilibria, molar volumes and electrical conductance of $ZnCl_2$ -PyHCl Solutions. (A. J. Easteal)

A crude phase diagram and a detailed report on electrical conductance data were given in the last progress report. The latter will not be repeated here. A detailed study of the phase equilibria in this system has now been completed and the results are shown in Fig. 5. Of special interest is the compound of 1:1 stoichiometry. No such compound is found in alkali metal chloride + $ZnCl_2$ systems, but compounds of this stoichiometry are found in SiO_2 -alkali oxide and BeF_2 -alkali fluoride systems.

In fact, the phase equilibria and physical behavior in the $ZnCl_2$ + PyHCl seem remarkably similar to those of the classical Na_2O + SiO_2 system. Outstanding in this comparison is the similarity of the composition dependences of the glass transition temperatures in the two systems, indicated in Fig. 5. This overall similarity has suggested $ZnCl_2$ + PyHCl solutions probably phase separate into $ZnCl_2$ -rich and PyHCl-rich fractions at temperatures near T_g , after the fashion of Na_2O + SiO_2 solutions, in the composition range 70 - 100% $ZnCl_2$.

The pyridinium cation thus appears to behave like a cation of $\frac{1}{2}$ the field strength of the alkali metal cations.

3. Viscosities of $\text{ZnCl}_2 + \text{PyHCl}$ Solutions. (A. J. Easta1).

To compare the temperature dependences of mass transport for two different processes, and in particular to find whether each yields the same value of T_0 , the "ideal" glass transition temperature, obtained from the general transport equation

$$P = P_0 \exp \frac{-B}{T-T_0} \quad (1)$$

where P is the transport property, and P_0 , B and T_0 are constants. Viscosities of several solutions in the above system have been measured over a range of temperatures. These have yielded interesting results. In the case of a 68.7 mole % zinc chloride solution, data were obtained in the viscosity range of $10^4 - 10^{-1}$ poise i.e. covering five orders of magnitude of viscosity change, and the analysis of the data according to Eq. (1) yielded a value for T_0 within the uncertainty, $\pm 3^\circ$, of the value of T_0 for conductance at the same composition. The value of the B parameter of Eq. (1) however was 33% larger in the case of viscosity. At other compositions difficulty was encountered with crystallization and the data were not obtained over such a wide range of viscosities. Nevertheless the best fit values of T_0 were in each case found, within the uncertainty of the analysis, to be the same as those for conductance. In order to determine how the ratio of B values for the two processes was changing with composition it was then assumed that the same value of T_0 could be attributed to each process, and the values of B corresponding to these T_0 values were compared. The ratio $B_\eta : B_A$ is shown as a function of zinc chloride content in Fig. 6, in which

the values for the glass transition temperatures over the same composition range are also shown. The maximum in the ratio which appears to correlate with the plateau in the glass transition temperature plot is a matter of some interest, and corresponds with expectations based on much less complete and less accurate data available in the case of some borate and silicate glasses. A detailed explanation of this interesting behavior is not yet at hand. The value found at 64.3% zinc chloride corresponds with values observed in other simple ionic liquids, and it is expected that further additions of pyridinium chloride would not change this value greatly.

4. Low Temperature Dispersion of Electrical Conductance and Dielectric Constant. (Dr. A. J. Easteal)

During the measurements of electrical conductance in these solutions, it was observed that, when using capillary cells, a temperature region was encountered during the cooling of the melt in which an anomalous increase in conductance with decreasing temperature was observed. In probing this phenomenon it was found that the anomaly disappeared when capillary cells were replaced by parallel plate cells, and that the effect should probably be attributed to a dispersion phenomenon known to occur in the presence of two dielectric phases of different dielectric constants. The observation, however, suggested that dispersion phenomena might be seen at lower temperatures when the bridge frequency began to coincide with the inverse of the structural relaxation time. Measurements made with all metal conductance cells have now given detailed information on this phenomenon and it has proven possible to get information on the fundamental structural relaxation times associated with the electrical conductance process in these solutions over a range of temperatures. This study has required the

investigation of the conductance as a function of frequency over a wide range of frequencies, obtained in our measurements by the use of both audio-frequency and radio-frequency conductance bridges. A typical set of results obtained on a solution of composition 72.0 mole% zinc chloride is shown in Fig. 7 and the data representation in terms of real and imaginary parts of a dielectric modulus, according to a theory by Macedo, is shown in Fig. 8. It is apparent that the conductance process requires description by a spectrum of relaxation times rather than a single value. The average relaxation time at a given temperature can be assessed from the maximum in the plot of G'' vs frequency in Fig. 8. Although crystallization of the melt limited the data obtainable, it appears from the movement of this peak with temperature, that the relaxation time would reach a value of the order of tenths of a second at a temperature corresponding to the glass transition temperature. This implies that the structural rearrangements involved in the electrical conductance process are the same as those involved in the viscous flow process. This conclusion is of interest as studies by Macedo and co-workers in alkali oxide + silica glasses have shown the conductance process to occur on a much shorter time scale than the viscous relaxation process.

5. Nuclear Magnetic Resonance Studies of the Proton Shift in $ZnCl_2$ -Pyridinium Chloride Solutions. (J. W. Shuppert).

In using the salt pyridinium chloride as a second component in zinc chloride-based solutions, the question has arisen as to what extent this salt can be considered to behave like the more commonly studied alkali metal chlorides. Pyridinium chloride itself is formed from the acid-base reaction of the base pyridine with HCl, and the extent to which the salt

can be considered to behave like a normal molten chloride depends on the extent to which the proton is transferred to the nitrogen atom in the acid-base reaction. In order to examine this question, proton magnetic resonance spectra have been run on pyridinium chloride and its solutions with zinc chloride. These measurements indicate the extent to which the proton is deshielded, greater shielding being expected when the proton is located very close to the nitrogen on the pyridine ring. The essential results of this study are contained in Fig. 9 where it is seen that there is a very rapid up-field shift in the resonance position (where shifts are measured relative to tetramethyl ammonium ion internal standard) as zinc chloride is added to the pyridinium salt. This indicates that as zinc chloride complexes the free chloride ions, the ability of the proton to hydrogen bond to the chloride decreases and the hydrogen retires to a better-shielded environment in close proximity to the nitrogen. We note that in the vicinity of 33-40 mole% of added zinc chloride there is a rapid change in the direction of shift with changing composition and conclude that in this composition region the supply of "free" chloride ion becomes exhausted. At this composition it is also observed that the originally sharp proton signal has become broadened and a triplet structure is observed, as expected for a proton closely located on the nitrogen atom. We conclude that for solutions richer in zinc chloride than about 40 mole% zinc chloride the pyridinium cation behaves as an essentially coulombic particle, whereas in pyridinium chloride the influence of the hydrogen bond between the pyridinium cation and chloride anion should be taken into account in interpretation of the salt behavior.

6. Phase Equilibria and Glass Transition Temperatures in the Zinc Chloride + Potassium Iodide System. (A. J. Easteal)

One of the interesting features of the zinc chloride plus pyridinium chloridy study described above was the evidence for liquid-liquid unmixing at low temperatures and high zinc chloride contents. Since this behavior was inferred rather than directly observed, it has become of interest to seek zinc chloride-based systems in which the phenomenon can be observed more directly. To this end a phase equilibrium study of the system zinc chloride plus potassium iodide has been undertaken, since preliminary observations, due to J. Wong, indicated that phase separation on a macroscopic scale could be observed at temperatures not far below the equilibrium liquidus temperature. The thermal behavior during warming and cooling of samples of different composition in this system has been determined by differential thermal analysis and the results, which are not considered complete at this point, are shown in Fig. 10. The most definite points are the liquidus temperatures, and it seems clear from the shape of this liquidus curve that the unmixing phenomenon is imminent at the liquidus temperature. The points indicated in the form of a dome beneath the liquidus in Fig. 10 were the temperatures at which an exothermic effect was observed during cooling of the melt, but whether this was due directly to the metastable liquid-liquid separation or to a crystallization which accompanied the separation, is not clear. Warmup behavior of quenched samples on the other hand showed clear evidence of there being more than one glass-forming phase present, hence it is concluded that extensive phase separation does indeed occur in these solutions over a wide range of compositions.

7. Glass Transition Temperatures in Zinc Chloride + Various Substituted Pyridinium Chloride and Other Organic Amine Hydrochloride Solutions.
(I. Hodga).

In view of the interest provoked by the glass transition temperature plateau in the zinc chloride-pyridinium chloride system, it was decided to perform glass transition temperature studies on a variety of other zinc chloride-organic chloride systems in order to determine what factors were affecting the existence, and the width, of the plateau and the inferred liquid-liquid immiscibility region. The results of measurements on seven different binary systems are summarized in Fig. 11. Interestingly enough, it appears that, so far, only the system containing pyridinium chloride yields the glass transition temperature plateau. The addition of a single methyl group to the pyridine ring can change the glass transition behavior drastically as indicated by the data for α -picolinium chloride-zinc chloride solutions in Fig. 11. Further evidence for the minimum in glass temperature at about 33 mole% zinc chloride, corresponding to the formation of the $ZnCl_4$ complex anion is provided by the results of this study. Although measurements in this composition region could only be determined directly for the case of the ethylamine hydrochloride solution, the trend of measured values at compositions to either side of this stoichiometry, particularly in the case of the quinolinium chloride solution, make clear the existence of the minimum.

8. Dependence of Electrical Conductance and of the Coordination Number of Nickel Cations on Composition and Temperature in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{ZnCl}_2$ Solutions.

This work unit was completed during the present year's work. The significant additions to the work reported in the previous progress report are principally the further investigation and definition of phase relations for this system. The phase diagram is broadly similar to that already described for the pyridinium chloride + zinc chloride system, however, the absence of the compound at the mole ratio 1:1 is notable.

9. Dependence of Co-ordination Number of Nickel Cations on Pressure, in Molten Organic Chloride Salt Solutions.

During this year the difficulties associated with determining the spectra of very small liquid salt samples held between diamond anvils in a miniature diamond high pressure cell, have been mastered. It has been found possible to obtain excellent spectra for nickel ions contained in approximately 2 mole % concentrations in various molten chlorides using the Cary 14R spectrophotometer without resort to additional beam condensing optics. Samples of about the size of a pinhead held within molybdenum gaskets between the diamond windows have been studied as a function of pressure within the pressure range 0 - ~15 kilobars. Ni(II) ions in 50 solutions of different compositions the system ethylamine hydrochloride + ethanolamine hydrochloride solutions have been examined and it is found in all cases that sufficient increase of pressure causes a coordination change for the nickel from tetrahedral 4 coordination to octahedral 6 coordination. It appears that the equilibrium is a simple two-species case, it being

speculated that the octahedral species contains two OH ligands in addition to the original four chlorides. Spectra from a representative run are shown (as recorded) in Fig. 12. The pressures indicated on the figure are nominal pressures, and require a correction due to the support of some of the load by the metal gasket. The magnitude of this correction is at the moment not known. The next stage in this investigation, now that it has been demonstrated that such coordination changes can be observed in detail, is to develop a reliable pressure calibration procedure. Methods using inserted crystals which undergo transitions at known pressures, and crystals with pressure sensitive optical bands, are being investigated. It is expected that coordination changes from tetrahedral to octahedral involving only chloride ligands, will be observable in systems such as zinc chloride + pyridinium chloride, or lithium chloride + α -picolinium chloride.

10. Heat Capacities of Glassy and Liquid Nitrate Mixtures, and Zinc Chloride + Pyridinium Chloride Solutions.

The heat capacities of a series of glasses from the systems calcium nitrate + potassium nitrate, and cadmium nitrate + potassium nitrate, have been investigated by differential scanning calorimetry. As the glass is heated through the glass transformation region, a rapid increase in heat capacity is observed. Insofar as this change in heat capacity indicates the accessibility of a new class of quantum states, this measurement may be viewed as of fundamental importance in gaining understanding of the glass transition phenomenon, and accordingly of the statistical thermodynamic character of the low temperature liquid state. It is also becoming evident, (and indeed is directly indicated in current theoretical developments from this laboratory), that the magnitude of the heat capacity change at the

glass transition is directly related to the temperature dependence of the mass transport processes at temperatures above the glass transition temperature.

It has been found that the molar change in heat capacity at T_g increases with increasing calcium nitrate content in calcium nitrate + potassium nitrate melts, but decreases with increases of cadmium nitrate in the corresponding cadmium nitrate + potassium nitrate system. In view of the fact that cadmium and calcium have the same ionic radii such a qualitative difference was not anticipated. It may be possible to correlate this effect with the greater polarizability of the cadmium ion and the associated tendency to covalent interactions between cadmium and nitrate ions. This may be related to the sharper far infrared spectra observed for cadmium nitrate + thallium nitrate glasses than for calcium nitrate + thallium nitrate glasses in recent work from this laboratory. The spectral differences were in this case interpreted in terms of the higher degree of short range order established in the presence of the cadmium cations.

More pronounced composition dependences of the change in heat capacity at T_g are anticipated for zinc chloride-based binary solutions at compositions approaching pure zinc chloride. Measurements have been performed on a pyridinium chloride - zinc chloride solution in the temperature region around T_g , but extension of measurements to higher temperatures has been precluded by the attack of these solutions on the aluminum sample pans. Progress in this investigation has been held up by delays in receipt of the necessary noble metal calorimeter sample pans. Data for the solution studied are shown in Fig. 13.

11. Theoretical Developments

During this year, principally as a consequence of spectral observations described in item 1 of this section, we have developed a promising zeroth order description of the thermodynamics of the glass transition. The essential feature of this model is the representation of the liquid by a "bond lattice" in which each element of the lattice represents the bond between the coordination centers of the liquid lattice e.g., the covalent bond between Ge atoms in amorphous germanium, or the (-Cl-) bridge bond between tetrahedrally coordinated Zn atoms in zinc chloride. The breaking of a bond is regarded as the elementary excitation of the liquid quasi-lattice and this corresponds to changing the state of a bond lattice element from "on" to "off". Each lattice element can thus have two distinct states in such cases as amorphous germanium (or water where a single hydrogen bond connects network centers) or three distinct states in the case of zinc chloride where there are two "breakable" parts to each bond lattice element. A simple statistical treatment of the distribution of "on" and "off" lattice elements leads to equations which describe the thermodynamic properties of the system, and which show that its configurational heat capacity should at first increase quite sharply (at a temperature determined by the bond energy and entropy characteristics) and then decrease with further increase in temperature. This is qualitatively the behavior observed at the glass transition.

By postulating that relaxation of the lattice can only occur when critical clusters of broken bonds occur, it proves possible to extend the model to account for the temperature dependence of mass transport properties characteristic of glass-forming liquids. The treatment, which

yields a direct relation between excess thermodynamic properties and mass transport properties is being prepared for publication. An account of the thermodynamic part of the theory is given in slightly different form in the article by Angell and Wong.

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F. FIGURE CAPTIONS

Fig. 1. For caption see figure.

Fig. 2. " " " "

Fig. 3. " " " "

Fig. 4. " " " "

Fig. 5. Phase diagram for the system zinc chloride + pyridinium chloride. Included in figure are the glass transition temperature vs composition relationship for ZnCl_2 - PyHCl solutions, and also for sodium oxide + silica solutions, at temperatures reduced by a factor of 3.

Fig. 6. Composition dependence of the ratio B_n/B_A for zinc chloride + pyridinium chloride solutions. (See Equ. 1 for definition of symbols.)

Fig. 7. Frequency dependence of the electrical conductance and the dielectric constant at various temperatures, for a zinc chloride + pyridinium chloride solution containing 72 mole% zinc chloride.

Fig. 8. Real (G') and imaginary (G'') parts of the dielectric modulus assessed from the frequency dependence of conductance and dielectric constant for a zinc chloride + pyridinium chloride solution. The relaxation time at each temperature is obtainable from the maximum in the G'' curve.

Fig. 9. Composition dependence of the proton chemical shift at 180°C for solutions of zinc chloride + pyridinium chloride.

(11)

Fig. 10. Approximate phase diagram for zinc chloride + potassium iodide system, showing glass transition temperatures attributed to the two separated amorphous phases, and region of phase separation based on thermal effects observed on cooling below liquidus.

Fig. 11. A plot of glass transition temperature as a function of composition for solutions of zinc chloride with various organic hydrochlorides. KEY: Q, quinolinium chloride; α , α -picolinium chloride; Py, pyridinium chloride; β , β -picolinium chloride; α , α -picolinium chloride; Et, ethylaminium chloride.

Fig. 12. Spectra of Ni(II) dissolved in solutions of ethylamine hydrochloride + α -picolinium hydrochloride at various pressures in the diamond anvil optical cell. Pressures are indicated on the curves.

Fig. 13. Heat capacity as a function of temperature for a zinc chloride + pyridinium chloride glass and supercooled liquid. Zinc chloride content 72 mole%.

FIG. 1. Spectrum of Ni(II) in molten ZnCl_2 at 320°C , in quenched ZnCl_2 glass, and in glass after successive 20-min annealing periods at 150°C . Also shown are spectra of Ni(II) in crystal lattices: a, doped into CaMgCl_2 crystals in which Ni(II) substitutes for Mg(II) regular octahedral sites; b, doped into Cs_2ZnCl_4 crystals in which Ni(II) occupies slightly irregular tetrahedral Zn(II) sites; c, doped into K_2ZnCl_4 crystals: structure of crystals unknown, but [Ni(II) substituted] Zn(II) sites presumed to be distorted tetrahedral.

FIG. 2. Room-temperature Raman spectrum of ZnCl_2 glass compared with spectrum of melt at 320°C by Irish and Young (Ref. 9) and spectrum of $\alpha\text{-ZnCl}_2$ crystals at room temperature.

FIG. 3. Far-ir spectra of ZnCl_2 in crystal, glass, and liquid states. (a) $\beta\text{-ZnCl}_2$, mull spectrum; (b) $\alpha\text{-ZnCl}_2$, mull spectrum; (c) vitreous ZnCl_2 , quartz-sandwiched thin film spectrum; (d) liquid ZnCl_2 , 280°C , from reflectance spectrum, by Wilmshurst, Ref. 6(a); (e) vitreous ZnCl_2 (containing some crystalline $\alpha\text{-ZnCl}_2$ contaminant): mull spectrum; (f) spectrum of sample studied in (e) after crystallization was completed by annealing at 150°C .

FIG. 4. Spectra, in frequency region of CN^- ion stretch, of ZnCl_2 glass slab containing (a) 1 mol % Zn(CN)_2 , (b) 0.024 mol % Zn(CN)_2 . Samples in "as-cast" condition. For comparison are shown spectra of Zn(CN)_2 (bridging CN^-); $\text{Na}_2\text{Zn(CN)}_4$ (singly bonded CN^-); and NaCN (ionic or "free" CN^-).

ZnCl₂ Mixtures