PHASE EQUILIBRIA, ELECTRICAL CONDUCTANCE AND DENSITY IN THE
GLASS-FORMING SYSTEM ZnCl_2 + PYRIDINIUM CHLORIDE:
A DETAILED LOW-TEMPERATURE ANALOGUE OF THE SiO_2 + Na_2O SYSTEM

A. J. Easta1 and C. A. Angell
Department of Chemistry
Purdue University
Lafayette, Indiana 47907

Abstract

In a study of ZnCl_2 -based binary chloride melts which may serve as analogues of the well-known and technologically important glass-forming binary systems based on SiO_2 and BeF_2 as first component, a detailed phase-equilibrium, electrical conductance and density study of the system zinc chloride + pyridinium chloride has been carried out. In contrast to the better-known ZnCl_2 + alkali halide systems, this present system reproduces in great detail the phase relations and physico-chemical behavior of the classic Na_2O + SiO_2 system, though at temperatures reduced by a factor of about 1/3. Electrical conductance data have been analyzed in terms of the three parameter equation $\kappa = AT^{-1/2} \exp B/(T-T_0)$, and the "ideal" glass transition temperature T_0 found to closely parallel the experimentally measured glass transition temperature T_g . T_0 and T_g show complex composition dependences. A minimum at 33.3 mol% ZnCl_2 is interpreted in terms of formation of the orthochlorozincate ion ZnCl_4^{2-} , an approximately linear increase from 33.3 to 66 mol% is probably due to the formation of polymeric chains based on linked ZnCl_4 tetrahedra, and a plateau region at zinc chloride-rich compositions (65 - 90 mol%) is associated with the tendency to, or occurrence of, sub-liquidus liquid-liquid phase separation. The classical concept of "network-breaking" satisfactorily explains dramatic

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changes in conductivity in the region 90 - 100 mol% ZnCl_2 . There is some suggestion that the rapid decrease in "activation energy" for transport in this region may be associated primarily with changes in equilibrium thermodynamic properties (configurational heat capacity) rather than with changes in a purely kinetic energy barrier as is generally assumed.

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GLASS-FORMING CHLORIDE MELTS. I. PHASE EQUILIBRIA, ELECTRICAL
CONDUCTANCE AND DENSITY IN THE SYSTEM ZnCl_2 + PYRIDINIUM CHLORIDE

A. J. Easteal and C. A. Angell
Department of Chemistry
Purdue University
Lafayette, Indiana 47907

There are a number of good reasons for studying the physico-chemical behavior of binary systems containing ZnCl_2 . Perhaps the clearest is that they provide low-melting, hazard-free, non-corrosive analogues of the silica-based and beryllium fluoride-based systems of such importance to glass and nuclear reactor technology respectively. It might ^(for instance) be hoped that the greater precision achievable in those experimentally more tractable systems will permit more detailed analyses of some of the more perplexing features of the behavior of such highly structured liquids.

A second reason is that ZnCl_2 is a strong Lewis acid, and its interaction with chloride ions donated by a solvent chloride melt of suitable characteristics provides some of the least ambiguous cases available of the formation of "complex ions" in molten salt chemistry. Since this has been an area of contention in the field for a long time, new methods of characterizing such interactions are needed.

A further reason of special interest to us is that although the most obvious ZnCl_2 -based binary systems e.g. ZnCl_2 + alkali metal chlorides, crystallize readily at their liquidus temperatures, systems in which the second component is itself low-melting yield solutions of which bulk samples can be supercooled to the point of glass formation over a considerable range of compositions. Such non-crystallizing-composition regions provide

"windows" through which we can observe the behavior of liquids of variable composition as they approach the thermodynamic bottom of the liquid state. This low temperature limit is set by the vanishing of the difference between entropies of the liquid and crystalline states, the apparent inevitability of which can be argued, for the case of pure substances, from equilibrium thermodynamic data on liquid and crystalline states^(1,2).

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- (1) J. H. Gibbs, "Modern Aspects of the Vitreous State", Vol. 1, J. D. McKenzie, Ed., Butterworth and Co. Ltd, 1960, Chap. 7.
- (2a) C. A. Angell and C. T. Moynihan, "Molten Salts: Analysis and Characterization" Ed. G. Mamantov, Marcel Dekker, 1969.
- (2b) C. A. Angell, J. Chem. Ed., in press.
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Associated with the vanishing of the liquid excess entropy is a vanishing of the ionic (or molecular) mobility, a tendency which is reflected in the temperature dependence of liquid relaxation processes, Y , which are described to good precision over several orders of magnitude by the rate law

$$Y = A_Y T^{-1/2} \exp -B_Y/(T-T_0) \quad (1)$$

where A_Y and B_Y are constants characteristic of the particular relaxation process and T_0 is the low temperature vanishing excess entropy (or "ideal" glass transition) temperature. Behavior at T_0 , however, cannot be observed because the system inevitably falls out of internal equilibrium at a higher temperature, denoted T_g , when the relaxation times become of the same order as the time scale of the particular experiment being performed. Except in very highly structured liquids, T_g and T_0 are separated by only a small

temperature interval (~ 10 - 20°C) and in ideal solutions both appear to change linearly with composition between values for the two components⁽³⁾. Theories

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- (3) C. T. Moynihan, C. R. Smalley, C. A. Angell and E. J. Sare, J. Phys. Chem., 73, 2287 (1969).
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for Eq. 1, among which the entropy theory of Adam and Gibbs⁽⁴⁾ currently seems the most plausible⁽⁴⁾, have been discussed elsewhere^(2a), and will not

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- (4) G. Adam and J. H. Gibbs, J. Chem. Phys., 43, 139 (1965). (However, see M. Goldstein, J. Chem. Phys. 51, 3728, (1969), and R. Weiler, S. Blaser, and P. B. Macedo, J. Phys. Chem. 73, 4147, (1969)).
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be treated in any detail here.

Easteal and Hodge⁽⁵⁾ have given evidence from an Eq. 1 treatment of electrical conductance measurements that in binary solutions with covalent interactions (a tendency to complex ion formation) T_0 tends to a minimum at

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- (5) A. J. Easteal and I. M. Hodge, J. Phys. Chem., 74, 730 (1970).
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compositions of complex ion stoichiometry, but the certainty of these conclusions was limited by the fact that the liquidus temperatures in the system studied were high relative to T_0 and in consequence the departures from Arrhenius behavior from which T_0 is assessed were small. Since Angell and Moynihan^(2a) have discussed such minima in terms of the loss of Coulomb cohesive energy implicit in the covalent interaction (provided complexes are of high symmetry), and since ZnCl_2 -based systems combine strong covalent interactions with low liquidus temperatures and supercooling composition regions, it appeared that this interesting question could probably be clarified by the study of a ZnCl_2 -based system.

In choosing a system for study, three possibilities were available

(i) A system containing only a simple inorganic ionic species. A possible system would be $\text{ZnCl}_2 + \text{KI}$ ^(6,7) which has extensive glass-forming composition regions.

(6) I. Schulz, Naturwiss., 44, 536 (1957).

(7) A. J. Easteal, D. Chin, J. Wong, I. Hodge, and C. A. Angell,
Submitted to Phys. Chem. Glasses.

(ii) A system containing chloride anions and otherwise only inorganic constituents. A possible system would be the hydrate melt $\text{ZnCl}_2 + \text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2$ in which composition regions on the ZnCl_2 -rich side of the system are glass-forming.

(iii) A system containing only chloride anions and a simple organic cation. Numerous possibilities are available e.g. (a) $\text{ZnCl}_2 + \text{N}(\text{CH}_3)_4 \text{Cl}$ or other tetraalkyl cation chlorides, (b) $\text{ZnCl}_2 + \text{methylamine hydrochloride}$ or higher homologues, (c) $\text{ZnCl}_2 + \text{pyridine hydrochloride}$, etc. Examples of each of (a), (b) and (c) were examined and shown to have glass-forming composition regions.

Of the above possibilities (i) was rejected on the basis of the desirability in initial investigations of dealing with a single ligand species, and (ii) was excluded on counts of restricted glass-forming composition regions, and complications due to incomplete association of "hard base" water molecules with the "hard acid" Mg^{++} cation (though a study of this system will be reported elsewhere)⁽⁸⁾. Of the possibilities listed

(8) C. A. Angell and D. Chin, (to be published).

under (iii) the ZnCl_2 + pyridine hydrochloride system was selected because of the previous usefulness of pyridine hydrochloride in molten salt studies⁽⁹⁾,

(9) V. C. Reinsborough, Rev. Pure and Appl. Chem. 18, 281, (1968).

ease of purification, and low melting point. Potentially simpler systems incorporating the quasi-spherical tetraalkyl ammonium cations were avoided because the pure salts decompose before melting precluding the 0-100% ZnCl_2 liquid range study considered very desirable for this project.

Glass-forming regions and characteristics of these various glass-forming chloride systems are discussed jointly elsewhere⁽⁷⁾.

EXPERIMENTAL

Pyridinium chloride, hereafter referred to as PyHCl , was obtained from two sources: (a) by fractional distillation at atmospheric pressure of the Eastman Organic Chemicals salt, - the fraction distilling at $221-224^\circ$ being collected; and (b) by the method of Audrieth and co-workers⁽¹⁰⁾, viz.

(10) L. F. Audrieth, A. Long & R. E. Edwards, J. Am. Chem. Soc., 58, 428, (1936).

addition of concentrated aqueous hydrochloric acid (Baker and Adamson, "Reagent A.C.S" grade) to a slight (about 5%) excess of a solution of pyridine (J. T. Baker, "Analyzed" Reagent) in ethanol, and fractional

distillation (221-224°) of the mixture. The PyHCl prepared by both methods melted to a colorless liquid at 143.5°.

Zinc chloride was Fisher Certified A.C.S. grade material. It was purified by passing hydrogen chloride through the molten salt at 450-500°, for 1-4 hours depending on the quantity of salt, followed by purging with dry nitrogen for several hours. The fused commercial salt contains flecks of a black carbonaceous impurity which are generally completely removed by the HCl/N_2 treatment.

Except for the highest ZnCl_2 content melts, solutions for study were prepared by addition of molten zinc chloride aliquots initially to pure PyHCl , and subsequently to $\text{ZnCl}_2 + \text{PyHCl}$ solutions of known composition. Experiments were performed on several independently prepared sets of mixtures with overlapping composition ranges. At ZnCl_2 contents greater than 50 mol% solution was a slow process; temperatures in excess of 250°C were avoided because of the tendency of PyHCl to undergo some decomposition and discolor the melt. At compositions >85 mol% ZnCl_2 high solution temperatures could not be avoided: such solutions prepared by addition of PyHCl to ZnCl_2 were dark brown in color, and gave less reproducible results than the other compositions.

In preparation of samples for phase diagram determination ZnCl_2 was used in the form of easily handled glass beads (produced by dropwise pouring of purified fused ZnCl_2 into liquid nitrogen). All preparations involving the use of solid ZnCl_2 (beads) and PyHCl were performed in a low ^(-75°) dew-point dry box⁽¹¹⁾ (Kewanee Scientific).

(11) It is found that ZnCl_2 glass beads provide an excellent dryness detector for dry boxes. The beads, which are crystal bright as

prepared, frost over on the surface in the presence of very small traces of moisture.

Glass transition temperatures were determined using a differential thermal analysis method essentially the same as previously described⁽¹²⁾.

(12) C. A. Angell, E. J. Sare and R.D. Brassel, J. Phys. Chem., 71, 2759 (1967).

See also ref. 27b

The glasses were produced by quenching fused mixtures (in 5mm o.d. Pyrex tubes) either (a) in liquid nitrogen or (b) first in a trichloroethylene slush bath then in liquid nitrogen. Procedure (b) was used for mixtures in the composition regions 39-45 and 55-65 mole % ZnCl_2 , for which the greater initial quenching rate obtainable with the trichloroethylene slush (~ 28 deg. sec^{-1} compared with ~ 17 deg. sec^{-1} for liquid nitrogen) was required to circumvent crystallization.

The phase diagram for the system was investigated using the method of cooling curves for initial work, and differential scanning calorimetry (Perkin-Elmer DSC IB) using small ($\sim 2-6$ mg) samples encapsulated in aluminum pans to resolve uncertainties and establish the final diagram. Samples of mixtures in the composition region in which crystallization does not readily occur were caused to crystallize by fine grinding of the glassy samples.

A dip-type cell constructed from Pyrex glass (Fig. 1) in conjunction with a Wayne-Kerr Type B221 Impedance Bridge was utilized in measuring specific conductance. In addition to the cell components shown in Fig. 1 the transite cap carried two further tubes to provide a slow flow of dry nitrogen through the cell, in order to prevent absorption of water vapor by the melts. Measurements of conductance were made at a single frequency-1592 Hz⁽¹³⁾. The cell was calibrated using 1.0 and 0.1 Demal aqueous

(13) The frequency dispersion of conductance, which becomes very pronounced

at temperatures approaching T_g , as the liquid relaxation time and inverse bridge frequency match up, has been investigated and will be reported separately.

potassium chloride at 25.0° . The cell constant was $52.54 \pm 0.04 \text{ cm}^{-1}$ for one cell (A) and $25.77 \pm 0.02 \text{ cm}^{-1}$ for another cell (B) used for two melts. Cell A had overall length 15 cm, and the capillary was 2.5 mm i.d., 23 mm long. Cell B differed only in the length of the capillary. The electrodes were fixed relative to one another and to the capillary. The leads to the electrodes were immersed to different depths in different electrolytes, but it was found that the measured conductance of a given electrolyte was independent (within experimental precision) of the depth of immersion.

For the fused salt conductance measurements the cell was held in a cylindrical aluminum block furnace (Fig. 2), heated with two 250 watt "Firerod" cartridge heaters (Watlow Electric Mfg. Co.). The aluminum block was 7.5 cm in diameter and 16 cm long, the well in the center being 2.5 cm in diameter and 15.5 cm deep. The top of the cell was cooled with tap water, via a small copper coil.

Conductances were determined initially under both continuous cooling (up to 1 deg. cm^{-1}) and steady-state, i.e. constant temperature conditions. When $\ln K$ was plotted against $1/T$ for these mixtures, the steady-state and non-steady-state points fell on the same curves within experimental precision. Subsequently conductances were determined only under continuous cooling conditions (except in the case of pure ZnCl_2 , where both methods were used), with an approximately constant cooling rate. This was achieved by coupling the furnace heating elements to a Melabs Model CTC-1A proportional temperature controller in conjunction with a C1111 programmer and C1101 platinum resistance sensor. The sensor was located in the aluminum

block adjacent to one of the heaters (3mm separation). Using this arrangement cooling rates in the range $0.6 - 0.75 \text{ deg. min.}^{-1}$ were achieved, between 350° and 80° . For a given run the cooling rate was constant to within $\pm 10\%$.

Conductances were measured at temperature intervals of 2° for the most part. In the temperature region ca. $80^{\circ} - 20^{\circ}$ measurements were usually made at 1° intervals, provided crystallization did not intervene, in order to more precisely determine the temperature dependence of conductance at temperatures approaching T_g . In this region the temperature coefficient becomes very large (up to $40\% \text{ deg}^{-1}$).

Melt temperatures were determined with a calibrated chromel-alumel thermocouple, in association with a Leeds and Northrup Model K3 potentiometer.

The precision of temperature measurement was $\pm .05^{\circ}\text{C}$ and the accuracy is estimated as $\pm 1^{\circ}$. Apart from the effect of errors of temperature, specific conductances should be accurate to within $\pm 1\%$ ⁽¹⁴⁾, while mixture

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- (14) ~~Within~~ Within 60° of T_g , a spurious effect associated with the use of capillary cells under conditions of very long liquid structural relaxation times appeared; conductances measured for these temperature regions ~~are~~^{were} undoubtedly in error, and were omitted from the computer analysis of temperature dependence of conductance (see Results Section).
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compositions have an uncertainty of $\pm 0.5 \text{ mol\% ZnCl}_2$.

Densities were measured dilatometrically, using dilatometers constructed by fusing 5 ml pipettes, graduated in 0.1 ml (Kimax, No. 37020) to 10 ml

volumetric flasks (Pyrex or Kimax). A 10/30 ground glass socket was fused to the upper end of each dilatometer to allow a drying tube filled with Drierite to be attached. Dilatometers were calibrated with water at $25.00 \pm 0.02^\circ$, with precision 0.04%. They were loaded with pre-mixed fused salt using an auxiliary furnace, and transferred to an oil bath (Dow Corning 200 Electronic fluid) for the measurements. The temperature of the bath was controlled (to $\pm 0.2^\circ$) with a Melabs Proportional Controller. For two mixtures (82.3 and 92.8% ZnCl_2) the liquid temperature ranges were not accessible with the oil bath, and the dilatometer was heated in a conventional vertical tube furnace whose temperature was controlled with a Cole-Parmer Proportio Null (Series 1300) unit to within $\pm 0.5^\circ$. The temperature range of measurement for mixtures was from approximately the liquidus temperature to about 210° , except for the 82.3 and 92.8% ZnCl_2 mixtures.

RESULTS

The phase equilibrium study of the system indicates the existence of four congruently melting compounds: R_4ZnCl_6 , R_2ZnCl_4 , RZnCl_3 and RZn_2Cl_5 (R = pyridinium cation). An outline of the phase diagram is given in Fig. 3.

$\text{ZnCl}_2 + \text{PyHCl}$ fused mixtures can be quenched to the glassy state, in the composition ranges 39-45 and 55-100% ZnCl_2 . On heating, many of the glasses spontaneously crystallize at temperatures not far above their glass transition temperatures. In a restricted composition range (ca. 60-90% ZnCl_2) liquid mixtures can be supercooled slowly to the glassy state and the glasses reheated, without crystallization.

The variation of glass transition temperature with composition is indicated by the subliquidus points in Fig. 3. For each mixture T_g was

determined at a number of different heating rates, generally in the range 5-20 deg min⁻¹. For all except two mixtures (96.5 and 97.7% ZnCl₂) the values of T_g are those appropriate to a heating rate of 8 deg min⁻¹. The heating rates for the two exceptional mixtures were 10.5 deg min⁻¹ and 20 deg min⁻¹ for 96.5 and 97.7% ZnCl₂ respectively. The uncertainty in T_g for mixtures containing up to 91.5% ZnCl₂ is of the order ±2 deg. For the two mixtures richest in ZnCl₂ and for pure ZnCl₂ the uncertainty is larger, of the order ±5 deg, due to the relatively small change of heat capacity occurring at T_g. The value for pure ZnCl₂ agrees within experimental uncertainty with the value of 102.5°C determined dilatometrically⁽¹⁵⁾

15. M. Goldstein and M. Nakonecznyi, Phys. Chem. Glasses 6, 126 (1965).

by Goldstein and Nakonecznyi.

The specific conductances of all the mixtures studied (7.0 to 94.7% ZnCl₂) and of the two pure components, show non-Arrhenius temperature dependences. For the two pure salts and for mixtures containing up to 87.5% ZnCl₂ the temperature dependences are quite precisely (r.m.s. deviation 0.05 - 1%) described by analytic functions both of the form of Eq. (1) in logarithmic form with $Y \equiv \kappa$, and of Eq. (2)

$$\ln \kappa = A' - B'/(T - T'_0) \quad (2)$$

A', B' and T'₀ being constants for a given mixture. The difference between Eq. (1) and (2) lies in the inclusion or otherwise of the pre-exponential T^{-1/2} term. Since the most appropriate form is currently undecided, the "best-fit" parameters for both equations, evaluated by least-squares computer fit of experimental conductances, are presented in Table 1.

Note that only in the composition region 0 - 50% ZnCl_2 does the form of the equation have any important effect on the T_g and B values. Exercising a preference for Eq. (1) the composition variation of the best-fit parameters is shown in Fig. 4, in which glass transition temperatures are included for purposes of comparison. For mixtures with compositions in the range 58.4 - 87.5% ZnCl_2 the experimental data were analyzed in separate temperature ranges corresponding to equal ranges of conductance (excluding conductances for temperatures within 60° of T_g). The values of the transport parameters corresponding to the separate temperature ranges are shown as unshaded symbols in Fig. 4.

The best-fit parameters show some random scatter, particularly for mixtures towards the two extremes of the composition range. The reason for the scatter is principally the relatively short liquid ranges accessible in these composition regions. On the basis of the composition variation of the best-fit parameters and of T_g , we have chosen a set of smoothed values of T_g for which exist corresponding sets of smoothed values of A and B: the smoothed values of the parameters are represented with the shaded symbols of Fig. 4.

Dilatometer volumes were measured to $\pm 0.01 \text{ cm}^3$. Densities were computer fitted (method of least squares) to linear equations of the form

$$\rho = a + bT \quad (T \text{ in deg K}) \quad (3)$$

with precision (r.m.s. deviation) of the order $(0.4 - 1.2) \times 10^{-3} \text{ g.cm}^{-3}$. Best-fit parameters of Eq. (3) are given in Table 2. For the 92.8% ZnCl_2 mixture partial decomposition of the melt occurred, and the measured densities are less reliable for this mixture.

Fig. 5 shows the composition dependence of density, in the form of

isotherms for 150°, 250° and 350°, (the latter by extrapolation of measured values) in addition to the composition variations of molar volume (V_m) and thermal expansivity (α). The latter has been evaluated using the equation

$$\alpha = -b/\rho \quad (4)$$

b being the slope of the ρ versus T graph. Estimated uncertainties in α are shown as error bars in Fig. 5, and they vary from about 1% to 5%. The values of ρ , V_m and α for pure $ZnCl_2$ at 150° were calculated from published data ⁽¹⁵⁾, while the values for 350° are from the density data of Klemm ⁽¹⁶⁾.

16. W. Klemm, Z. Anorg. Chem. 152, 235 (1926).

From a large-scale plot of density versus composition, at 150°, 250° and 350°, densities for those mixtures whose specific conductances were measured have been estimated by interpolation, and the equivalent conductances (Λ) of these mixtures evaluated using the relationships

$$V_E = (X_E \cdot E_{ZnCl_2} + (1 - X_E) E_{PyHCl})/\rho \quad (5)$$

$$\Lambda = \kappa \cdot V_E \quad (6)$$

where V_E is equivalent volume ($cm^3 \text{ equiv}^{-1}$), E , the equivalent weight, and X_E the equivalent fraction of $ZnCl_2$ defined by

$$X_E = 2X_{ZnCl_2} / (1 + X_{ZnCl_2}) \quad (7)$$

where X_{ZnCl_2} is the mole fraction of $ZnCl_2$.

150°, 250° and 350° isotherms of Λ versus composition are given in Fig. 6. On account of the very large change in Λ from pure pyridinium chloride to pure $ZnCl_2$, isotherms of $\ln \Lambda$ are also given, to show more clearly the composition dependence for $ZnCl_2$ -rich mixtures.

The Conductance of Pure $ZnCl_2$

There are at least six published reports ⁽¹⁷⁻²²⁾ on the conductance

17. W. Biltz and W. Klemm, Z. Physik. Chem. (Leipzig), 110, 318 (1924).
18. J. D. McKenzie and W. K. Murphy, J. Chem. Phys., 33, 366 (1960).
19. F. R. Duke and R. A. Fleming, J. Electrochem. Soc., 104, 251 (1957).
20. J. O'M. Bockris, E. H. Crook, H. Bloom and N. E. Richards, Proc. Roy. Soc., A255, 558 (1960).
21. L. F. Grantham and S. J. Yosim, J. Chem. Phys., 45, 1192 (1966).

22. H. Bloom and I. A. Weeks, J. Chem. Soc., (A), 2028 (1969).

of pure ZnCl_2 and its temperature dependence. No two sets of data agree closely over a wide temperature range (e.g. 100°); in fact the variation in values for particular temperatures is very large. For example, at 336° the highest and lowest of the published specific conductances differ by almost 55% of the mean of the two values: at 400° the difference is 49%.

All sets of data show non-Arrhenius temperature dependence, however the curvature of $\ln \kappa$ versus $1/T$ plots varies widely from set to set. The literature data, together with the results of four of our experiments on pure ZnCl_2 have been analyzed using Eq. (1); the best-fit parameters are given in Table 3.

In the present study the conductance of ZnCl_2 has been measured in six separate experiments, in an attempt to obtain reproducible data and to ascertain the reliability of the purification procedure used. In each case the starting material was Fisher Certified A.C.S. grade ZnCl_2 , (maximum impurity listed as "substances not precipitated by $(\text{NH}_4)_2\text{S}$ ", 0.15%), which was dehydrated and purified using the procedure outlined above (Experimental Section). The results of these experiments are compared graphically with some of the literature data (for a limited temperature range) in Fig. 8. The results of our first experiment (points denoted by $\odot$ in Fig. 8) are in doubt due to possible contamination: black flecks of material of unknown identity were dispersed in the melt. In subsequent experiments the melts were colorless and transparent, with no visual evidence of contamination. In the second experiment ($\bullet$) a fresh sample of

ZnCl_2 was purified by the HCl/N_2 purging sequence and its conductance measured at 403.0° . The salt was then treated for a further period and the conductance remeasured (at 399.5° ; ■). The two values are in good agreement. The fourth experiment was done on a different batch of ZnCl_2 which yielded high results (●) due evidently to some prior contamination of the salt. For the last two experiments (Δ and ○) a previously unopened batch of ZnCl_2 was used. In the final experiment the salt was heated with HCl for seven hours followed by nitrogen for 16 hours. The results of the last two experiments agree well with the values obtained at 403.0° and 399.5° , and are in reasonable accord at some temperatures with some of the published data. However, there is an approximately uniform discrepancy of about 28% with the most recently published data (Bloom and Weeks⁽²²⁾).

It is noteworthy that the temperature dependence of κ found by us in the four experiments in which temperature was varied, is very similar, in that the values of T_0 (from Eq. 1) are all in the range $270 - 290^\circ\text{K}$. Also, these values of T_0 are consistent with that obtained from the temperature dependence of viscosity, which we have also determined. The best-fit value of T_0 from our viscosity data is $260 \pm 20^\circ\text{K}$. Both values are somewhat lower than an estimate, $T_0 = 336^\circ\text{K}$ ^(2a), made from the limited calorimetric data available.

It is apparent from Table 3 that several sets of published data show very poor precision: a notable exception is the data of Bloom and Weeks. The lack of precision is presumably due to instrumental factors and/or experimental technique. The large discrepancies in absolute values can probably be attributed to the highly developed network structure of

ZnCl_2 ⁽²³⁾: even very small amounts of contaminants can disrupt the network

(23) C. A. Angell and J. Wong, J. Chem. Phys., in press.

sufficiently to cause pronounced changes in ion mobilities. The discrepancies, in this interpretation, are attributable in large part to variations in the nature and concentration of impurities present in the various source materials which have been used.

In this respect a point in favor of the results of Bloom and Weeks is their distillation purification of the ZnCl_2 , a procedure not adopted in the present work.

Although the conductance and transport parameters of pure ZnCl_2 are of considerable interest per se, it must be emphasized that in the present study we have been concerned primarily with the composition variation of transport and other parameters, of mixtures of ZnCl_2 with PyHCl . While there may be some uncertainty in the values of the conductance of ZnCl_2 itself, any trace contaminants which may be present in the pure salt will have a negligible influence on the conductances of the binary solutions, less still on their composition dependences.

DISCUSSION

The general features of the behaviour of the present system closely parallel those which have been previously found for SiO_2 -based and BeF_2 -based binary systems, and it is with an exploration of the details of this behaviour that this discussion will be mainly concerned.

As in the analogous systems the most prominent feature, viz. the enormous increase in particle mobility resulting from addition of PyHCl to pure ZnCl_2 , is readily associated with the disruption of a highly structured 3-dimensional network liquid (details discussed elsewhere⁽²³⁾) by the breaking up of chloride-bridge bonds in proportion to the number of added chloride ions.

Details of the phase diagram for $\text{ZnCl}_2 + \text{PyHCl}$ will be discussed fully in a separate publication. However some features are worthy of comment in the context of the present study. In particular this system has two congruently melting compounds (R_4ZnCl_6 and RZnCl_3) which are not known to form in $\text{ZnCl}_2 +$ alkali metal chloride systems. The existence of these two compounds is probably evidence that the pyridinium ion acts in these mixtures as a very weak field cation i.e. it has a small effective ionic potential.

The compound RZnCl_3 has analogies in $\text{BeF}_2 +$ alkali fluoride mixtures. Thus NaF , KF , RbF and CsF all form 1:1 compounds with BeF_2 , while $\text{LiF} + \text{BeF}_2$ mixtures have been reported to form LiBeF_3 and LiBe_2F_5 as sub-solidus phases⁽²⁴⁾. In binary silicate systems the analogous "metasilicates" Li_2SiO_3 , Na_2SiO_3 , K_2SiO_3 , BaSiO_3 and CaSiO_3 are congruently melting compounds⁽²⁴⁾.

(24) E. M. Levin, C. R. Robbins and H. F. McMurdie, "Phase Diagrams for

Ceramists" American Ceramic Society, Columbus, 1964.

It is significant that liquid mixtures in the composition region of the 1:1 compound (~ 45 -55 mole % ZnCl_2) cannot be quenched to glasses without partial crystallization, even though the compound has a relatively low melting point (ca. 130° , $T_m/T_g = 1.56$). By contrast, mixtures of composition close to that of the compound RZn_2Cl_5 may be supercooled very readily without crystallization, in spite of the much higher melting point (ca. 195° , $T_m/T_g = 1.67$) of this compound. It is likely, therefore, that crystalline RZnCl_3 has a structure which is closely related to that of liquid mixtures of similar composition, whereas in order for RZn_2Cl_5 to crystallize rather severe changes in configuration of the liquid are necessary.

There is a close analogy here between the $\text{PyHCl} + \text{ZnCl}_2$ and $\text{Na}_2\text{O} + \text{SiO}_2$ systems. As in the case of the former melts, the sodium orthosilicate (Na_4SiO_4) melt does not form a glass, and glass formation does not readily take place at the metasilicate composition. Na_2SiO_3 (and Li_2SiO_3) has a crystal structure based on infinite chains of oxygen-bridged SiO_4 tetrahedra⁽²⁵⁾. In a number of other crystalline meta-

(25) A. Grund and M. M. Pizy, *Acta Cryst.*, 5, 837 (1952).

silicates there exist closed rings of tetrahedra, and the structure of sodium metaphosphate (NaPO_3), whose melt forms a stable glass, is also based on closed rings of (PO_4) tetrahedra. However, fused NaPO_3 contains bridged PO_4 chains⁽²⁶⁾; crystallization of the melt, therefore, requires

(26) G. W. Brady, *J. Chem. Phys.*, 28, 48 (1958).

fracture of a number of phosphorus-oxygen bonds, and supercooling to the vitreous state occurs readily. On the basis of these analogies - and the observation that $RZnCl_3$ forms acicular crystals - it seems likely that this compound has a crystal structure essentially similar to that of Na_2SiO_3 , and that melts of composition close to the trichlorozincate stoichiometry contain principally long chains of chloride-bridged $ZnCl_4$ tetrahedra.

The principal distinction between this work and the published work on the related systems is the greater detail on departures from Arrhenius behaviour in the present case, which have permitted the parameters of Eq. 1 to be determined with reasonable accuracy. The composition dependences of these parameters (Fig. 4) are of unusual interest. In the first place the close relationship of the measured glass transition temperatures to the T_0 parameter is to be stressed. The two curves are approximately parallel, except in the region 85-100% $ZnCl_2$, and in this region T_0 and T_g change in the same direction. The paralleling of T_0 by T_g is also characteristic of concentrated aqueous electrolytes⁽²⁷⁾ and lends weight

(27a) C. A. Angell and R. D. Bressel, unpublished work.

to the use^(27b) of the readily measurable T_g as a structure -

(27b) E. J. Sare and C. A. Angell, J. Chem. Phys., 52, 1058 (1970).

sensitive parameter for elucidation of the effects of composition variation on electrolyte constitution. T_0 is perhaps to be regarded as the

thermodynamically more meaningful parameter, but its evaluation depends on extrapolation of high precision transport data to temperatures which are generally well below the lowest temperature at which measurements can be made. T_g by contrast is directly measured at temperatures which in general are not far above T_o . The parallel behaviour observed for the two parameters therefore lends confidence to our interpretation of the variation of T_o , so that although T_g does not extend to compositions of less than 39% $ZnCl_2$, T_o continues to provide a probe for interparticle interactions. Since the parameters A and B show little sensitivity to composition except near pure $ZnCl_2$ and $ZnCl_4^{*}$ stoichiometries, most of the discussion of transport behaviour in this system can be made in terms of the behaviour of T_o .

The principal features are (a) an initial decrease, as $ZnCl_2$ is added to $PyHCl$, reaching a minimum at the stoichiometry of the tetrachlorozincate ion (b) a rapid increase region extending from the minimum to ca. 65% $ZnCl_2$ (c) a "plateau" region from 65-85% $ZnCl_2$ in which the variation is slight, and (d) a terminal region of sharply rising T_g to the high value for pure $ZnCl_2$. These regions and their origin will be examined in the following discussion but first it is appropriate to draw attention to a further example of the remarkable similarity in behavior of the present system and the classic Na_2O-SiO_2 system. Such data as exist for the glass transition temperature in the Na_2O-SiO_2 system⁽²⁸⁾, when scaled to the temperature of the present

(28) These data are actually "incipient softening temperatures" by Turner and Wicks, quoted in "Properties of Glass", by G.W. Morey, Reinhold, N.Y., 1954, 2nd Ed. p. 277.

system (by multiplying all T_g by the factor $T_g(PyHCl-ZnCl_2)/T_g(Na_2O-SiO_2)$ determined at one mole ratio) closely reproduce not only the rapidly increasing T_g below 65% $ZnCl_2$ but also the "plateau" region above. These data, displaced for clarity 7° lower on the temperature axis, are compared with the data for the present system in Fig. 3. Comparable data for BeF_2 -based melts are presently not available.

Composition Regions

(a) The T_o minimum. The variation in T_o and T_g is a manifestation of variation of the cohesive energy density of a liquid and hence reflects the effects of changing composition on the nature and strength of interparticle interactions. From this viewpoint the minimum in T_o near the

tetrachlorozincate composition seems significant. We interpret this minimum as a consequence of a decrease in Coulomb cohesive energy as the electrostatic charge density decreases. Assessing the volume of liquid containing one mole of $+ -$ charge from the molar volume plot (Fig. 5) we find this volume increases 24% (i.e. charge density decreases 19%) on addition of 33 mol% ZnCl_2 to PyHCl , if the liquid at this composition is considered to contain only PyH^+ and $\text{ZnCl}_4^{=}$ species. Some caution in accepting this interpretation ^{in detail} is, however, suggested by NMR studies of the acid proton chemical shift in this binary system ⁽²⁹⁾ (which suggest

(29) J. W. Shuppert, (private communication)

a role for a hydrogen bonding contribution), and ^{by} direct T_g determinations in this composition range in a related system with glass-forming organic salt ⁽³⁰⁾, (the T_g composition dependence differs from that of T_o in Fig. 4.)

(30) I. M. Hodge, (Private communication)

The minimum in T_o at the tetrachlorozincate composition indicates that a minimum in viscosity would also occur in this composition region. It is for this reason, we suggest, that melts such as $\text{BeF}_2 \cdot 2\text{LiF}$, which presumably are structurally similar to $\text{ZnCl}_2 \cdot 2\text{PyHCl}$, have the high-fluidity characteristics required of a nuclear reactor molten salt heat transfer and fuel-circulating medium.

Notwithstanding the doubts frequently expressed about the meaning of discreteness of complex ions in common molten salt solutions, (see e.g. ref. 2a) we feel $\text{ZnCl}_4^{=}$ may be correctly regarded as a true anionic "species"

in basic melts in the present system. The reason lies in the unusual "weakness" of the PyH^+ counter cation, which is responsible for the similarities, instanced several times in this discussion, between this system and $\text{Na}_2\text{O-SiO}_2$. SiO_4^{4-} is generally accepted as an anionic species in basic oxide melts, as is BeF_4^{2-} in basic fluoride melts⁽³¹⁾.

(31) K. A. Romberger and J. Braunstein, (private communication).

(b) The 35-65% ZnCl_2 T_o , T_g increase: polymer aspects. The increase of T_o with addition of ZnCl_2 to the melt of (ZnCl_4) stoichiometry is much more pronounced than that caused by addition of PyHCl . On the ZnCl_2 -rich side the chloride ion content is insufficient to satisfy individually the tetra co-ordination requirement of the Zn(II) ions, forcing ZnCl_4 tetrahedra to share corners in order to preserve the favored co-ordination number. This leads first, at 40 mol % ZnCl_2 , to the formation of $[\text{Zn}_2\text{Cl}_7]$ structural groups for which evidence has been presented elsewhere⁽³²⁻³⁴⁾ and then, as ZnCl_2 content increases beyond 40 mol%, to increasingly long, and/or

(32) C. A. Angell and D. M. Gruen, J. Phys. Chem. 70, 1601 (1966).

(33) W. E. Smith, J. Brynestad and G. P. Smith, J. Chem. Phys., (in press).

(34) We note that convincing Raman spectral evidence for a distinct

Al_2Cl_7^- species in alkali chloride melts has recently been presented

(S. J. Cyvin, P. Klaboe, E. Rytter and H. A. Oye, J. Chem. Phys., 52, 2776, (1970)).

complex associations.

The melt configurational restrictions associated with the build-up of these polymeric anions are no doubt responsible for the rapid increase in T_o and T_g in this composition region. Such an increase is predicted qualitatively by the Gibbs-DiMarzio lattice theory of the glass transition for chain polymers⁽³⁵⁾, although the theory is only quantitative for

(35) J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys., 28, 373 (1958).

chain lengths of more than several monomer units. For non-cross-linking chain polymers T_g approaches a constant value as the chain length approaches infinity which, in the simplest view, would correspond to 50 mol% $ZnCl_2$ in the present system. Since the present polymeric species are not restricted to one dimensional growth however, such behavior is not to be expected in our case. In fact the steady increase in T_g and T_o through the 1:1 composition up to 65 mol % suggests that the polymerization proceeds simultaneously and probably haphazardly in two directions, if not three.

The sharing of chloride ions between adjacent infinite

$$\left[\begin{array}{c} PyH^+ \\ | \\ Cl^- \\ | \\ Zn - Cl \\ | \\ Cl^- \end{array} \right] \text{ chains, for instance, is one way of generating the composition}$$

$PyH Zn_2Cl_5$ (66.7 mol % $ZnCl_2$) near which (66 mol%) the increase of T_g and T_o with increasing $ZnCl_2$ comes to a halt.

The 50 mol% composition is associated with distinct positive departures from molar volume additivity and maxima in expansion coefficient. This is of interest for two reasons: (a) in the related system $CsCl + ZnCl_2$ system

positive departures from volume additivity are most pronounced at 33 mol% ZnCl_2 ⁽³⁶⁾ while in the $\text{KCl} + \text{ZnCl}_2$ system no deviations were observed

(36) W. E. Smith and G. P. Smith, J. Chem. Eng. Data, 13, 123 (1968).

outside the ZnCl_2 -rich network-breaking region ^(23,37) (b) molar volume

(37) In the $\text{Na}_2\text{O} + \text{SiO}_2$ system measurements of ρ and α at 1400°C have been reported by J. O'M. Bockris, J. W. Tomlinson and J. L. White, (Trans. Faraday, Soc. 52, 299, (1956). These only cover the composition range 40-100% SiO_2 so comparisons are limited, and are complicated by the peculiar temperature dependence of the SiO_2 -rich solutions. However, it appears that while α shows positive deviations near 50 mol% SiO_2 , as in the present system, V_m does not.

deviations may often be correlated with glass temperature deviations while in the present case T_g varies linearly with composition through the region.

The maximum in α might reasonably be associated with a predominance of extended one-dimensional polymeric chains with little cross-linking between chains. The decrease in this parameter beyond 50% ZnCl_2 is consistent with a rapid increase in cross-linking and resultant "tightening" of the polyelectrolyte structure.

Eisenberg and Sasada ⁽³⁸⁾ have measured T_g in the 40-50% P_2O_5 region

(38) A. Eisenberg and T. Sasada, "Physics of Non-Crystalline Solids, Ed. J. A. Prins, North Holland, 1965, p. 99.

of the related $\text{Na}_2\text{O} + \text{P}_2\text{O}_5$ system. Evidence for polyphosphate chain structure in this region is strong⁽³⁹⁾, yet T_g showed only a weak composition

(39) A detailed chromatographic study of distribution of chain lengths as a function of composition was performed by T. R. Meadowcroft and F. D. Richardson, Trans. Faraday Soc., 61, 54, (1965). There is a strong presumption that similar chains exist in $\text{Na}_2\text{O}-\text{SiO}_2$ liquid and glass in this composition region but the dissolution-chromatography technique cannot be successfully applied to prove this.

dependence in the phosphate system. This was attributed to a strong sodium ion cross-linking effect, which is surprising. Again the present system is found to resemble more closely the $\text{Na}_2\text{O} + \text{SiO}_2$ system, in which T_g increases rapidly with increasing SiO_2 content in the corresponding composition region.⁽³⁸⁾

Other polymer-related aspects of the present system will be discussed in a separate publication.

(c) The 65-85% ZnCl_2 T_g , T_o plateau. The origin of the plateau region is obscure. There is some empirical evidence from other systems^(27b,28,40)

(40) R. L. Green, J. Am. Ceram. Soc., 25, 83 (1942).

that a levelling off in the T_g -composition relation is associated with a tendency of the supercooled liquid to separate into two immiscible liquid phases. It is known that in the $\text{Na}_2\text{O}-\text{SiO}_2$ system this sub-liquidus unmixing does actually occur⁽⁴¹⁾ although the kinetics of the process are

(41) R. J. Charles, J. Am. Ceram. Soc., 49, 55 (1966).

so slow that the growing particles only reach the dimensions of visible light wavelengths with special heat treatment: thus the unmixing phenomenon can usually only be observed in electron microscope studies. Drawing on the parallel with the $\text{Na}_2\text{O}-\text{SiO}_2$ behavior seen in Fig. 3, we can suppose the present system microscopically phase separates in the same composition region. This being the case, the upswing in T_g occurs at or about the critical composition of the miscibility dome, (90% SiO_2 in the $\text{Na}_2\text{O} + \text{SiO}_2$ system.) The structure of the liquid above the critical temperature will be one in which large fluctuations in composition occur, the different microregions probably tending to the compositions and structures of pure ZnCl_2 and some ZnCl_2 -poor liquid, possible ~66% ZnCl_2 in the present case⁽⁴²⁾.

(42) This type of structure was first suggested for $\text{Na}_2\text{O} + \text{SiO}_2$ melt by Bockris et al. (see footnote 37) as an alternative to their own "discrete ion" model. Structures of this type can explain the otherwise puzzling persistence of ZnCl_2 "polymer" bands in the Raman spectra of ZnCl_2 + alkali chloride solutions (see e.g. J. R. Moyer, J. C. Evans and G. Y-S. Lo, J. Electrochem. Soc., 113, 158 (1966), R. B. Ellis, *ibid.*, p. 485).

As the composition of the liquid increases in ZnCl_2 beyond the consolute composition the structure will change from ZnCl_2 -rich cryptophase regions dispersed in a ZnCl_2 -poor "matrix", to ZnCl_2 -poor cryptophase regions dispersed in a ZnCl_2 -like "matrix". If, as seems reasonable, the viscous properties of the solution are most strongly influenced by the character of the "matrix" cryptophase, then the plateau passing into a steeply rising region in the vicinity of 90% ZnCl_2 , can be qualitatively understood. A more quantitative treatment will be reserved for a later publication.

(d) The 85-100% ZnCl₂ region. This region, as mentioned at the start of this discussion, closely parallels the behavior of the SiO₂ + basic oxide systems and is interpreted in the classical network-breaking terms. Most striking is the rapid increase in A_K and B_K parameters (in both smoothed and unsmoothed forms). It is not clear whether the erratic behavior of T₀ and large standard deviation of best fit reflects a real failure of Eq. (1), or the small temperature range which could be studied before crystallization occurs (Table 1) and the increasing difficulty of preparing decomposition-free solutions in this composition region. Our inclination has been to attribute the rapid rise in the B_K parameter to the increase in some energy barrier term as the network perfection increases and more bonds need to be broken to permit the local structure rearrangement to occur. However, in our T_g studies we have observed, in this region, a rapidly decreasing d.t.a. signal, suggesting the change of heat capacity at T_g decreases rapidly as pure ZnCl₂ is approached. According to the Adam-Gibbs⁽⁴⁾ theory, the parameter B_y (Eq. 1) contains, besides invariant terms, the ratio of a free energy barrier ($\Delta\mu_y$) and the change in heat capacity at T_g (ΔC_p).

$$B_y = \text{constants} \times \frac{\Delta\mu_y}{\Delta C_p}$$

It would, of course, be of great interest if the thermodynamic term, ΔC_p , should prove of greater importance than the kinetic term $\Delta\mu$; it would also render invalid an important assumption made by one of us⁽⁴³⁾ in

(43) C. A. Angell, J. Am. Ceram. Soc. 51, 117 (1968).

It is hoped to perform the necessary heat capacity measurements in the near future.

The Role of the Organic Cation

Finally, some comments on the nature of the organic cation are necessary to relate the present system to the more commonly studied alkali chloride + zinc chloride systems. The first point of interest is whether the pyridinium cation is really a cation i.e. whether the full +1 charge can be associated with pyridinium ion. NMR studies⁽²⁹⁾ designed to answer this question (a suggestion of C. T. Moynihan) are affirmative only for compositions in which "free" chloride ion is absent. ^{Also, it is evident that} the charge, when fully transferred, remains localized on the nitrogen atom.

The second point of interest is that, in chloride-free regions the pyridinium cation functions as a much "weaker" cation than an alkali metal cation such as K^+ . T_0 estimates for $KCl-ZnCl_2$ solutions⁽⁴⁴⁾, for instance, fall $69^\circ C$ above those of corresponding pyridinium solutions, and measured T_g in solutions of composition $K PyH_{(1-x)}Cl + ZnCl_2$ increases sharply with increasing x ^{at a rate which confirms the estimated T_0 difference} (44). Since the size of the pyridinium cation (ring radius

(44) C. A. Angell, unpublished work.

⁰
~ 2.1 Å) is not so much greater than that of the larger univalent inorganic cations, it seems likely that the charge asymmetry of the organic cation leads to orientation towards a near neighbor negative charge center and consequent appearance, to more distant neighbors, of an apparent ^(cation radius) (distance from positive charge center) greater than actual.

Clearly there is great opportunity for manipulation of melt properties through choice of cation⁽⁴⁵⁾, and it is hoped to develop this aspect of

(45) It has already been found (I. H. Hodge, private communication) that addition of a methyl group to the pyridinium ring can completely eliminate the T_g plateau region characteristic of the present system (Fig. 3), giving substantially reduced T_g values in this composition range.

these studies in the future.

Concluding Remarks

Comparison of the plot of the Eq. (1) parameters, Fig. 4, with the comparatively featureless conductance isotherms plotted in Fig. 6 emphasizes the advantages of this type of analysis for extracting information on variations in particle interactions in molten salt systems. It is notable, however, that many of the useful observations could have been made on the basis of the much simpler T_g measurements taken alone. It is hoped that parallel studies of viscosity in this system will permit more to be said about the kinetic, as opposed to the system thermodynamics, aspects of the mass transport process in these solutions.

Acknowledgement

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Table 1
Transport Parameters for $\text{ZnCl}_2 + \text{PyHCl}$ Mixtures

Nole Fraction ZnCl_2	A	B	T_0	$\sigma \times 10^3$	A'	B'	T'_0	Temp. Range ($^{\circ}\text{C}$)
0.0	3.989	668.3	212	0.9	0.4967	526.3	228	139 - 211
7.0	4.111	762.7	200	3.3	0.6088	611.7	215	116 - 217
12.6	4.230	831.3	197	1.3	0.7390	684.1	210	110 - 200
17.5	4.147	827.4	208	2.0	0.6506	681.8	221	120 - 214
21.5	4.304	953.0	196	1.8	0.7462	773.1	212	138 - 221
26.9	4.441	1039.2	185	0.6	0.9136	648.6	198	134 - 203
32.2	4.548	1215.9	159	0.8	0.9450	994.7	176	178 - 216
36.0	4.140	1005.6	189	0.9	0.5634	812.8	206	154 - 240
38.6	3.942	932.9	200	1.4	0.4237	774.6	213	112 - 236
40.5	3.843	882.1	209	2.6	0.3984	758.9	218	99 - 206
45.2	3.765	896.9	215	1.9	0.2986	754.2	225	113 - 215
53.6	3.697	895.4	229	2.5	0.2579	781.2	237	111 - 215
58.4	3.645	887.0	241	3.3	0.1781	766.4	250	124 - 244
58.4	3.129	733.6	255	3.5	-0.0474	702.3	256	72 - 122
63.2	3.717	930.6	248	1.4	0.2771	823.5	255	138 - 254
63.2	3.137	764.0	262	3.7	-0.0994	720.2	264	92 - 136
63.2	3.766	908.8	252	6.3	0.6038	877.0	253	66 - 90
68.3	3.742	956.0	256	1.8	0.2533	831.3	265	150 - 274
68.3	3.383	864.3	262	3.4	0.0801	804.1	265	100 - 148
68.3	3.358	877.7	260	5.3	0.1012	829.5	262	74 - 98
73.1	3.884	1046.7	257	2.1	0.3590	906.4	267	162 - 297
73.1	3.921	1060.3	256	2.5	0.5936	991.6	259	112 - 160
73.1	4.573	1207.3	249	5.1	1.2408	1133.0	252	82 - 110
84.6	4.237	1313.9	257	1.9	0.6725	1153.4	267	196 - 308
84.6	2.214	963.8	260	4.3	-0.0111	898.6	263	96 - 130
87.5	3.003	1137.8	247	2.0	0.4396	1027.7	253	130 - 202
87.5	2.164	909.1	262	5.6	-0.0109	860.8	264	92 - 128
91.3	5.101	1958.0	235	1.7	1.4342	1728.3	247	253 - 325
94.7	6.141	2707.2	210	2.1	2.4314	2437.3	221	266 - 338
100.0	8.490	3617.4	280	5.6	4.7024	3343.2	288	301 - 454

σ is the r.m.s. deviation (in $\ln \kappa$) of the experimental points from the calculated curves.

Table 2

DENSITY PARAMETERS

$$\rho(\text{g.cm}^{-3}) = a + bT(^{\circ}\text{K})$$

Mole Fraction ZnCl_2	a	$-(b \times 10^3)$	$(\sigma \times 10^3)^*$	Temp. Range ($^{\circ}\text{K}$) [#]
0.000	1.395	0.588	0.5	418 - 471
0.052	1.434	0.579	0.6	400 - 460
0.153	1.528	0.586	0.7	387 - 465
0.204	1.602	0.628	0.6	386 - 464
0.312	1.700	0.613	0.6	456 - 480
0.334	1.720	0.600	0.6	461 - 490
0.383	1.808	0.675	0.4	429 - 479
0.452	1.886	0.694	0.8	403 - 479
0.530	2.025	0.799	0.6	404 - 475
0.621	2.152	0.792	0.5	391 - 480
0.716	2.311	0.791	0.4	412 - 481
0.823	2.551	0.799	0.9	513 - 588
0.928	2.931	1.002	1.2	563 - 609

* σ is the r.m.s. deviation (in ρ) of the experimental points from the calculated straight line.

[#] Temperature range of measurements.

Table 3

Transport Parameters for Pure ZnCl_2

Reference	A	B	T_0 ($^{\circ}\text{K}$)	$\sigma \times 10^3$	Temp. Range ($^{\circ}\text{K}$)
20	3.413	2345	339 ^a	29.7	602 - 970
21	6.677	2602	327	34.6	586 - 1136
17	5.965	1978	384	41.1	597 - 923
19	6.370	2173	375	1.9 ^b	748 - 923
18	0.503	255	521	4.6	593 - 673
22	7.384	2969	317	3.9	588 - 728 ^c
This work ^d	8.490	3617	280	5.6	574 - 727

^aThree of the published values appear to be significantly in error - they were excluded from the analysis.

^bThis analysis was made on smoothed data rather than raw experimental data - hence the value of σ is not necessarily a reflection of the precision of the experimental data.

^cBloom and Weeks' data extends to 851 $^{\circ}\text{K}$. Their data only for the range shown were analyzed in order to provide a more meaningful comparison with our own results.

^dAnalysis made on the combined results of four experiments (numbers 2, 3, 5 and 6).

FIGURE CAPTIONS

Fig. 1. Conductance cell.

Fig. 2. Furnace assembly used for conductance measurements.

Fig. 3. Phase diagram: $\text{ZnCl}_2 + \text{PyHCl}$. Open circles are experimental liquidus temperatures and horizontal broken lines indicate solid-state transitions. Values of T_g for $\text{ZnCl}_2 + \text{PyHCl}$ are shown as shaded circles: values of T_g' (see text for definition) for $\text{SiO}_2 + \text{Na}_2\text{O}$ are indicated by open squares.

Fig. 4. Composition variation of transport parameters and glass transition temperature.

Fig. 5. Composition variation of density, thermal expansivity and molar volume.

Fig. 6. Composition variation of conductance. $\log \Lambda$ is $\log_e \Lambda$.

Fig. 7. Comparison of published values with values found in this work, for the specific conductance of pure ZnCl_2 . $\log \kappa$ is $\log_e \kappa$.
Note inverted scale for κ .

- C: Container vessel
- E': Cylindrical Pt foil electrode
- E'': Disc electrode (Pt)
- G: Thermocouple guard tube
- T: Transite plug

Fig. 1

- A: Asbestos paper insulation
- B: Aluminum block
- C: Melt container
- H: Cartridge heater
- S: Pt resistance temperature sensor
- T: Transite disc

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7