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VISCOSITY, AND A SUPERCRITICAL VISCOSITY-CONDUCTANCE
ANOMALY, IN FUSED ZINC CHLORIDE + PYRIDINIUM CHLORIDE MIXTURES

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Viscosity, and a Supercritical Viscosity-Conductance
Anomaly, in Fused Zinc Chloride + Pyridinium Chloride Mixtures.

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Abstract

Following an earlier conductimetric study of the glass-forming system $\text{ZnCl}_2 + \text{PyHCl}$, viscosity data covering up to 5 orders of magnitude have been obtained for compositions in the region of a previously observed anomalous glass temperature vs. composition relation. Viscosity data may be fitted to Fulcher type equations using the same T_0 parameter which fits the conductance data. An anomalous relation between the temperature dependences of the two processes, previously noted for oxide glasses in network oxide-rich composition regions, is confirmed for the present system and interpreted as due to the influence of microscopic supercritical composition fluctuations on the solution viscosities.

Viscosity of Molten ZnCl_2 and Supercritical Behavior
in its Binary Solutions

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Recently we reported a detailed phase equilibrium and electrical conductance study on the system $\text{ZnCl}_2 + \text{PyHCl}$ which established this system as a low temperature analog of the classical oxide glass system $\text{SiO}_2 + \text{Na}_2\text{O}$.⁽¹⁾ We now present viscosity data which extend this analogy by establishing the existence, in the present system, of a composition region in which anomalous changes in the ratio of activation energies for the viscous flow and electrical conductance processes occur. Because of less severe temperature control and corrosion problems, this region is more accurately defined in our analog system than in the oxide glass case.^(2,3) Our interpretation of its origin leads to the prediction that similar regions should exist in many apparently unrelated binary systems.

ZnCl_2 and solutions of $\text{ZnCl}_2 + \text{PyHCl}$ of compositions listed in Table 1 were prepared as described earlier.⁽¹⁾ Their viscosities were measured to $\pm 3\%$ using a Brookfield Synchro-Lectric (Model LVT) rotating spindle viscometer over a temperature range determined by instrument limitations (10^{-1} poise) at high temperatures, and crystallization of the melt at low

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temperatures. Spindles were gold plated to avoid corrosion by the acidic melts, and calibrated using Cannon Instrument Co. standard viscosity oils.

Results and Discussion

Our ZnCl_2 viscosities lie 15-18% above those of Gruber and Litovitz,⁽⁴⁾ and are presumed to be more accurate since Gruber and Litovitz made no attempt to completely dehydrate their melt. The only other data on ZnCl_2 ⁽⁵⁾ are more seriously in error as discussed elsewhere.^(4,6) Hereafter we discuss fluidities ϕ rather than viscosities η ($\phi = 1/\eta$) in order to keep the signs of coefficients the same as for conductance.

The ZnCl_2 data, like the earlier conductance data, are well fitted by the VTF equation,

$$\phi = A_{\phi} T^{\frac{3}{2}} \exp (B_{\phi} / (T - T_0)) \quad \dots (1)$$

where A_{ϕ} , B_{ϕ} , and T_0 are constants. The least squares best fit value of T_0 for fluidity of ZnCl_2 , $260^{\circ} \pm 25^{\circ}\text{K}$ is within error the value $280 \pm 15^{\circ}\text{K}$ obtained from the conductance data.⁽¹⁾ These values in turn are close to the temperature, $T_{0(\text{cal})} = 250^{\circ} \pm 20^{\circ}\text{K}$, at which the extrapolated excess entropy of supercooled ZnCl_2 falls to zero⁽⁷⁾, as predicted by the relaxation theory of Adam and Gibbs.⁽⁸⁾ If, as this suggests, T_0 characterizes a thermodynamic property of the system (an "ideal" glass temperature, albeit an operationally defined one rather than a true transition temperature) then the same value should apply to fluid flow as to electrical conductance. Adopting $T_0 = 260^{\circ}$ for each process,^(all) the difference in temperature dependence between the processes appears in the B parameter. We find $B_{\phi}/B_{\Lambda} = 1.13$ (which is also the ratio of activation energies E_{ϕ}/E_{Λ} at any temperature) which is

similar to B ratios obtained for viscous ionic nitrate mixtures and hydrate melts. This suggests fluid flow and conductance processes involve the same structural rearrangements.

For the binary mixtures, similar findings are made. Best fit T_0 values for the data of Table 1 are plotted in Fig. 1(b) where they are compared with a smoothed plot of the more extensive data obtained from the electrical conductance study, and with directly measured⁽¹⁾ glass transition temperatures (T_g). Such similarity of T_0 values seems common when comparisons are made for melts in the fluidity range 10^2 - 10^{-2} P⁻¹, though it is not found at much lower fluidities where Eq. 1 itself becomes inadequate to describe the data.⁽⁹⁾

(Systematic deviations from Eq. 1 were observable for the most viscous of the present melts.) The coincidence of $T_{0(\phi)}$ and $T_{0(\lambda)}$ with $T_{0(cal)}$ is likewise limited to T_0 values obtained from this higher fluidity range. Possible explanations are discussed elsewhere.⁽⁹⁾

Finally, we focus attention on the peculiar composition dependence of the activation energy ratio, $E_\phi/E_\lambda(T)$, or, equivalently, the ratio B_ϕ/B_λ for $T_{0(\phi)} = T_{0(\lambda)}$. These quantities are shown in Figs. 1(e) and 1(d), respectively. On either side of the maximum the ratio falls to values typical of viscous nitrate melts.

The anomalous region, in which some additional factor enters the temperature dependence of at least one of the processes, corresponds with the region in which it was earlier⁽¹⁾ concluded these solutions tend to undergo liquid-liquid phase separation with decreasing temperature. Such unmixing is an established phenomenon in this composition region of the $\text{SiO}_2 - \text{Na}_2\text{O}$

system, and is also a known occurrence in other oxide systems in which similar $E_p/E_A(T)$ anomalies have been suggested by the limited data available.⁽³⁾ This leads us to believe that the anomaly is associated with the presence of fluctuations in composition in the region of incipient phase separation, and may, therefore, prove to be a phenomenon common to all supercritical solutions capable of conducting electricity.

There is considerable current interest in supercritical transport phenomena in multicomponent solutions.⁽¹⁰⁻¹⁶⁾ Effects of supercritical composition fluctuations may extend over large temperature intervals. Zarzycki and Naudin⁽¹⁷⁾ have measured Debye correlation lengths of 20 Å at temperatures 100° above T_c , and Simmons et. al.,⁽¹⁵⁾ showed supercritical composition fluctuations lead to anomalous increases in viscosity of oxide melts detectable at temperatures up to 20% above T_c . Molecular solutions show similar effects near T_c .^(11-14,16) In 1945 Onsager⁽¹⁸⁾ anticipated that composition fluctuations in systems with large positive deviations from Raoult's Law would lead to increases in viscosity because of interruption of the flow lines (similar to a colloid effect) while diffusivities would be little affected or slightly enhanced. This reasoning, which was recently verified for the system 3-methylpentane-nitromethane,⁽¹⁶⁾ suffices to explain our findings, because the electrical conductance process is linked phenomenologically with self-diffusion⁽¹⁹⁻²¹⁾ but not with viscosity⁽²²⁾. Therefore, viscosity but not electrical conductance should behave anomalously in supercritical solutions, and the distinction will be detected most

sensitively in the temperature coefficients for the processes, in the manner seen in Fig. 1(d) and (e).

The validity of this conclusion is currently being established through studies on well-characterized binary molecular systems.⁽²³⁾ A general rule connecting E_s/E_A ratios with unmixing tendencies in viscous liquids would be useful since the separation of phases is not easily observed directly.

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Table 1

Viscosities of ZnCl_2 and ZnCl_2 + PyHCl Mixtures

ZnCl_2		78.4% ZnCl_2		68.7% ZnCl_2		64.3% ZnCl_2	
T(°C)	η (poise)	T(°C)	η (poise)	T(°C)	η (poise)	T(°C)	η (poise)
443.0	1.08	226.5	1.35	226.9	0.496	232.8	0.192
432.2	1.43	215.3	1.81	214.2	0.650	220.1	0.219
422.8	1.75	203.9	2.44	202.1	0.878	195.2	0.337
413.8	2.16	192.9	3.41	189.7	1.22	183.6	0.430
392.8	3.66	182.2	4.95	178.7	1.69	171.4	0.582
384.1	4.54			169.4	2.32	157.5	0.873
374.6	6.13			160.7	3.28	145.2	1.33
360.5	9.23			150.1	5.02	135.2	1.96
352.7	12.0			139.8	8.33	125.5	3.04
340.3	18.1			130.0	13.9	115.9	4.98
334.4	23.1			120.9	24.2	108.3	7.77
332.8	24.3			104.4	82.4	100.7	12.9
324.5	32.6			96.9	162	92.9	23.6
				67.9	6434	85.4	48.4

Fig. 1.

Composition dependence of transport parameters.

- (a) Isothermal (250°C) variation of fluidity (full curve and data points) and equivalent conductance (dotted curve).
- (b) Glass transition temperature (full curve), "best-fit" values of T_g (data points) from viscosity measurements, and smoothed values of T_g (dotted curve) from conductance measurements.
- (c) B (dotted curve) and "best-fit" values of B_g (data points and full curve).
- (d) Ratios of B -coefficients and pre-exponential coefficients, for fluidity and conductance.
- (e) Ratio of conventional "activation energies" for fluidity and conductance at 150° and 250°C . To obtain values at 250°C it was necessary to make small upward extrapolation of the mixture data and a larger downward extrapolation of the pure ZnCl_2 viscosity data. The 150° value for pure ZnCl_2 involved a long extrapolation of both viscosity and conductance data and, although consistent with other points, is not reliable.