Electrical Conductance and Viscosity of Concentrated H_2SO_4/H_2O Binary Systems at Low Temperatures: Correlation with Phase Transitions

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Density, viscosity, and electrical conductance of concentrated H_2SO_4/H_2O systems (above 66 wt % H_2SO_4) were measured in the subambient temperature region. The lowest temperature of measurement was 198 K. Density varied linearly with temperature. Viscosity and conductance data were fitted to the Vogel−Tammann−Fulcher (VTF) equation and also to the power-law equation, the latter being a better functional form to describe the temperature dependence of transport properties. Concentration dependences of viscosity, conductance, expansivity, and ideal glass transition temperature indicate the occurrence of structural changes in the H_2SO_4/H_2O system in the regions 83−85 and 92−94 wt % H_2SO_4 which are attributed to the formations of $H_2SO_4{\cdot}H_2O$ (at 84.48 wt% H_2SO_4) and the eutectic between $H_2SO_4{\cdot}H_2O$ and H_2O (at 93.8 wt % H_2SO_4), respectively. Above ∼75 wt % H_2SO_4 a direct correlation exists between the viscosity−concentration curve and the phase diagram of the H_2SO_4/H_2O system.

Introduction

Physical chemistry of the H_2SO_4/H_2O binary system in the low-temperature region is gaining importance due to its contemporary relevance to the global problem of ozone depletion since heterogeneous reactions causing ozone loss occur on the stratospheric background of the sulfuric acid aerosol layer. Accordingly thermodynamic, spectral, and calorimetric studies of sulfuric acid−water systems in the low-temperature region have been reported recently.[1−6] Investigations on sulfuric acid solutions are also being made with a view to ascertain accurately the temperature dependence of the dissociation constant of bisulfate ion.[7−10] However, not much attention has been focused on the transport behavior of the H_2SO_4/H_2O system at very high concentration and subambient temperature regions. The existing data on viscosity[11,12] and conductance[12,13] of this system were obtained mainly to cater to the needs of industries. Although these reported data[11−13] reveal the presence of maxima and minima in the viscosity (temperature range, 20−70 °C) and conductance (temperature range, ∼50 to −20 °C) versus concentration isotherms above ∼75 wt % H_2SO_4, no attempt has been made to address this unusual high-concentration transport behavior of H_2SO_4. In this work we have therefore made density, electrical conductance, and viscosity measurements of some of the concentrated H_2SO_4/H_2O systems in the subambient temperature region and conducted an analysis of the temperature and concentration dependence of these properties.

Experimental Section

Sulfuric acid (AR grade, SD Fine Chemicals, India) was used as supplied, and its concentration was determined by the conductometric acid−base titration method using standard NaOH solution. The actual concentration of the acid used was estimated to be 36.19 N (N = equiv dm^{-3}). Density measurements were made using a calibrated pycnometer of about 5.5 × 10^{-6} m^3 capacity. From the measured density the weight percent (wt %) of 36.19 N sulfuric acid was estimated to be 96.8. Dilute samples of sulfuric acid were prepared by carefully mixing weighed amounts of 96.8 wt % H_2SO_4 and double-distilled water. All compositions of H_2SO_4/H_2O solutions were analyzed by titration and estimated to be accurate within ±0.1 wt %.

For electrical conductance measurements sulfuric acid solutions were taken in sealed tubes containing a conductivity cell of cell constant 114.55 m^{-1}. The conductances were measured at 1 kHz using a Wayne Kerr B905 automatic precision bridge with a precision of ±0.05%.

Viscosity measurements were made using a Cannon-Ubbelohde suspended level viscometer of viscometer constant 0.2537 × 10^{-6} m^2 s^{-2}. After the viscometer was filled with the required amount of sulfuric acid solution, the three limbs of the viscometer were connected to stopcocks through pressure tubings. To the other ends of the stopcocks were connected fused $CaCl_2$ tubes in order to avoid moisture entering into the system during measurements. A vacuum pump was used to fill the upper bulb of the viscometer with sulfuric acid. Times of fall were measured using a stopwatch of 0.01 s least count.

All measurements were made in an ultra-low-temperature thermostat (INSREF-India). This thermostat is equipped with a two-stage refrigerating system and a digital proportional temperature controller. Methanol was used as the liquid medium in the bath. The digital temperature display of the thermostat was calibrated against a reference mercury thermometer at 25 °C. The temperature of the bath was also checked using an additional chromel−alumel thermocouple and a microvoltmeter (Systronics-India). The thermostat is designed to have a triple-glass window for the purpose of making density and viscosity measurements. Using this thermostat constant temperatures were maintained with better than ±0.1 °C thermal stability in the range ambient to about −20 °C. Below −20 °C the accuracy of the measured temperatures was found to be within about ±0.2 °C.

Duplicate measurements were made to check the reproducibility of the data. At low temperatures (<−20 °C) the density, conductance, and viscosity data were reproducible within ±0.02, ±0.01, and ±1%, respectively, and better reproducibilities were obtained at higher temperatures.

Results and Discussion

Temperature Dependence of Density, Conductance, and Viscosity. The experimental values of density, *d*, of sulfuric

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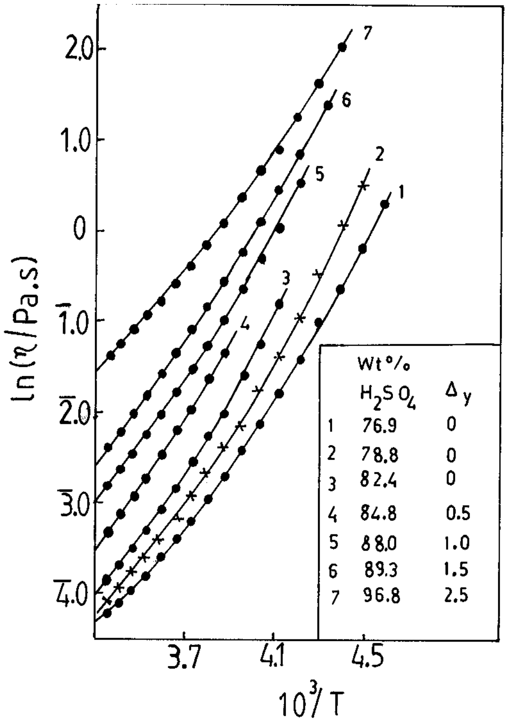

Figure 1. Plots of viscosity of H_2SO_4/H_2O systems vs $1/T$. Δy refers to the upward shift in the ordinate scale.

TABLE 1: Least-Squares Fitted Values of the Parameters of Eq 1

H_2SO_4 (wt %)	a (10^3 kg m^{-3})	b (kg m^{-3} °C^{-1})	SD in d (kg m^{-3})	temp range (°C)
96.8	1.8571	1.0090	0.9251	−47 to 21
89.3	1.8367	1.0813	0.8003	−49 to 15
88.0	1.8284	1.1149	1.0304	−44 to 19
84.8	1.7986	1.1240	0.5225	−32 to 16
82.4	1.7781	1.1241	0.5340	−42 to 18
78.8	1.7283	1.0271	0.3791	−45 to 20
76.9	1.7126	0.9457	0.9454	−53 to 15

acid solution have been found to vary fairly linearly with temperature in the temperature range of measurement. The density data are therefore presented in Table 1 in terms of the parameters a and b of a linear equation:

$$d = a - bt \qquad (1)$$

where t is the temperature in °C. The present values of density are found to be comparable within 0.2% with the reported data[11] at 15.6 °C.

The measured values of viscosity, n, and specific conductance, k, of sulfuric acid solutions as a function of temperature are shown in the form of Arrhenius plots in Figures 1 and 2. In Figures 3 and 4 viscosity and conductance data at some constant temperatures are also displayed. Some of the reported values of n and k are included in Figures 3 and 4 for comparison. An agreement of about ±2−3% has been estimated between the present and the reported data[11−13] of k and n. The lowest temperature of conductance measurement is −75 °C, and that of viscosity and density measurements is −55 °C.

The non-Arrhenius type of temperature dependence of k and n is normally explained by the Vogel−Tammann−Fulcher (VTF) equations of the forms:[14,15]

$$k = A_1 \exp[-B_1/(T - T_{01})] \qquad (2)$$

$$n = A_2 \exp[B_2/(T - T_{02})] \qquad (3)$$

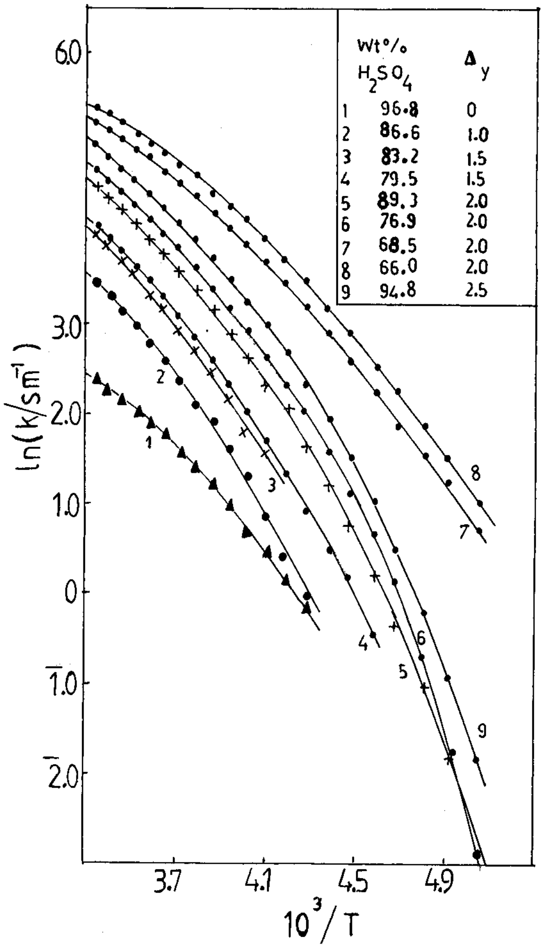

Figure 2. Plots of specific conductance of H_2SO_4/H_2O systems vs $1/T$. Δy refers to the upward shift in the ordinate scale.

The computed values of the parameters A_1, B_1, T_{01}, A_2, B_2, and T_{02} obtained by least-squares fitting the k and n data to eqs 2 and 3, respectively, are given in Tables 2 and 3 (in Supporting Information). For a particular system the computed value of T_{01} and T_{02} known as the ideal glass transition temperature is expected to be independent of the transport property.[16] Thus it is anticipated that $T_{01} \approx T_{02}$. On the contrary, agreement between T_{01} and T_{02} of a particular H_2SO_4/H_2O system is very poor as evident from Tables 2 and 3 and Figure 5.

Speedy and co-workers[17,18] employed a power-law equation of the form:

$$k = k_o[(T/T_{03}) - 1]^{\beta_1} \qquad (4)$$

to describe the temperature dependence of conductance of aqueous electrolyte solutions. A similar power-law equation has also been used to demonstrate the temperature dependence of viscosity and other relaxational properties of glass-forming systems.[19] The specific conductance data of sulfuric acid solutions were therefore least-squares fitted to eq 4, whereas the viscosity data were fitted to another equation of the form:

$$n = n_o[(T/T_{04}) - 1]^{-\beta_2} \qquad (5)$$

The computed values of the constant parameters k_o, T_{03}, β_1, n_o, T_{04}, and β_2 are given in Tables 4 and 5. Unlike T_{01} and T_{02}, the values of T_{03} and T_{04} are in good agreement (Figure 5) thereby confirming the view that the power-law equation works better than the VTF expression.[19] Although recently the validity of the VTF equation has been reasserted,[20] its inadequacy can be realized by examining the acceptability of best-fit parameters.

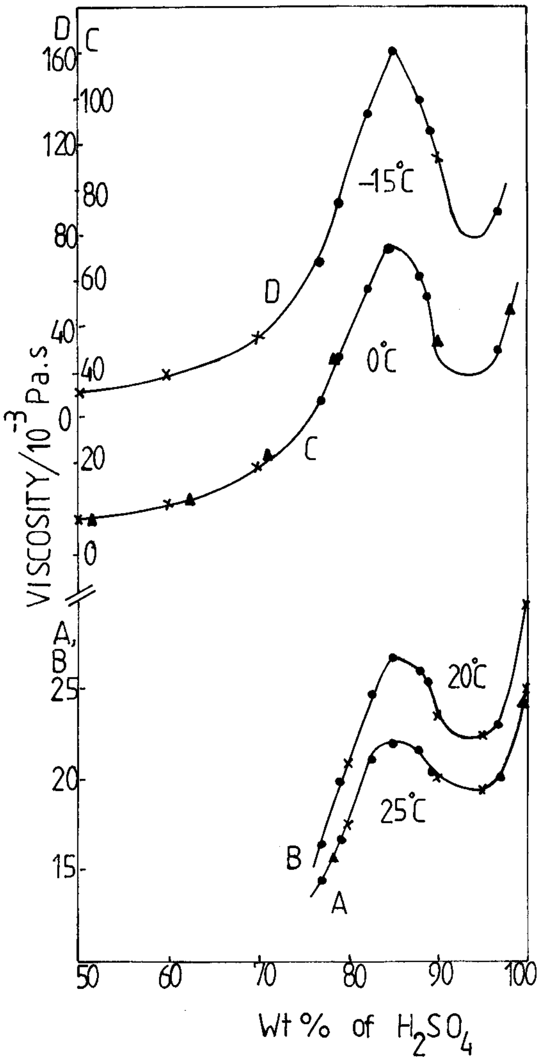

Figure 3. Viscosity vs concentration isotherms of H_2SO_4/H_2O systems at different temperatures (×, ref 11; ▲, ref 12).

For example, the reported[21,22] experimental glass transition temperature, T_g, of $H_2SO_4{\cdot}3H_2O$ is 160 ± 2 K. Estimated value of T_0 from the power-law equation (T_{03}) is 145 ± 2 K and from the VTF equation (T_{01}) is ~60 K, which is much less than even the temperature $T_2 = 133$ K at which configurational entropy of $H_2SO_4{\cdot}3H_2O$ becomes zero.[22] Therefore, in spite of the VTF equation providing good fit to the experimental data, the best-fit T_0 parameter is often unphysical, as observed by others[23] also. The failure of the VTF equation indicates that the free volume is not a satisfactory order parameter to explain the temperature dependence of transport properties of the H_2SO_4/H_2O system. The power-law equation, on the other hand, has been becoming more acceptable because it is shown to be based on the concept of mode-coupling theory (MCT),[24,25] a theory which has generated in recent years considerable interest in the dynamics of supercooled liquids and the mechanism of liquid−glass transition.[26−29] The exponents (β_1 or β_2) obtained in the present study are more by about 1−2 units than the exponent predicted by MCT[24] (in water[27] $\beta_2 = 2.05$), unlike the observation made by Murthy[19] in several glass-forming organic and inorganic liquids.

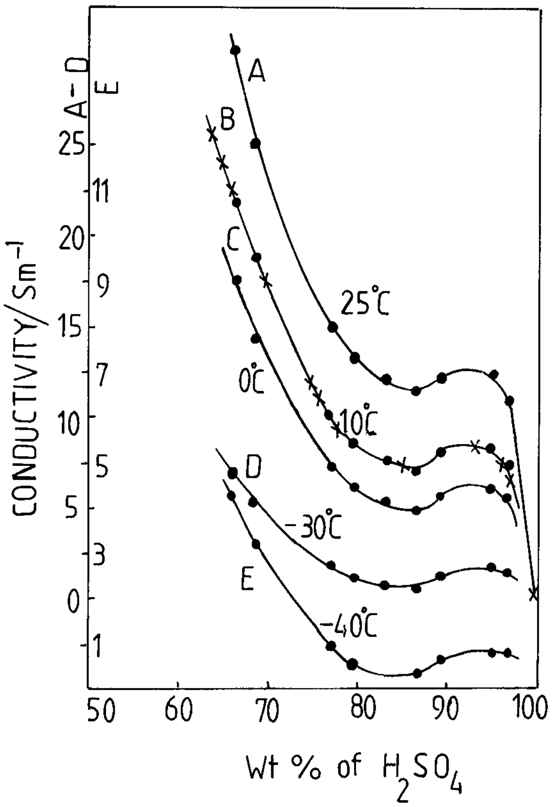

Figure 4. Conductance vs concentration isotherms of H_2SO_4/H_2O systems at different temperatures (×, ref 13).

TABLE 4: Least-Squares Fitted Values of the Parameters of Eq 4

H_2SO_4 (wt %)	ln k_o (S m^{-1})	β_1	T_{03} (K)	SD in ln k
96.8	4.0083	2.399	197.5	0.027
94.8	4.2093	3.301	184.7	0.051
89.3	4.3153	3.592	183.9	0.058
86.6	4.7322	2.788	206.8	0.034
83.2	4.7344	2.428	214.0	0.045
79.5	4.5753	2.960	196.6	0.082
76.9	4.5359	3.192	188.6	0.064
68.5	4.2182	3.017	171.0	0.069
66.0	3.6489	3.525	152.0	0.095

TABLE 5: Least-Squares Fitted Values of the Parameters of Eq 5

H_2SO_4 (wt %)	ln n_o (10^{-3} Pa s)	β_2	T_{04} (K)	SD in ln n
96.8	1.0046	3.051	195.0	0.022
89.3	0.8931	4.270	185.0	0.022
88.0	0.5746	3.586	199.0	0.023
84.8	0.2118	3.081	214.0	0.013
82.4	0.3013	3.201	209.0	0.029
78.8	0.4928	3.523	196.0	0.051
76.9	0.6742	3.678	187.0	0.043

Concentration Dependence of Density, Conductance, and Viscosity. Density of sulfuric acid solutions increases monotonically with increasing concentration up to 96.8 wt % H_2SO_4. On the other hand, expansivities of sulfuric acid solutions computed from the values of the b parameter of eq 1 exhibit a different type of concentration dependence as can be seen from the expansivity isotherms at 298 and 243 K (Figure 5). Concentration dependences of conductance, viscosity, and ideal glass transition temperature are illustrated in Figures 3−5. From the shape of all these isotherms it appears that structural changes take place in the H_2SO_4/H_2O system in the region 83−85 wt % and again in the region 92−94 wt % H_2SO_4. Similar inferences can also be made from the type of variations exhibited by k_o, n_o, β_1, and β_2 with wt % H_2SO_4. Moreover, the shape of the k, n, and expansivity isotherms does not vary with decreasing temperature.

Correlation with the Phase Diagram. The reported[30] phase diagram of the H_2SO_4/H_2O system has been shown in Figure 5c for the sake of comparison with the various isotherms given in Figures 3−5. The comparison reveals that the structural

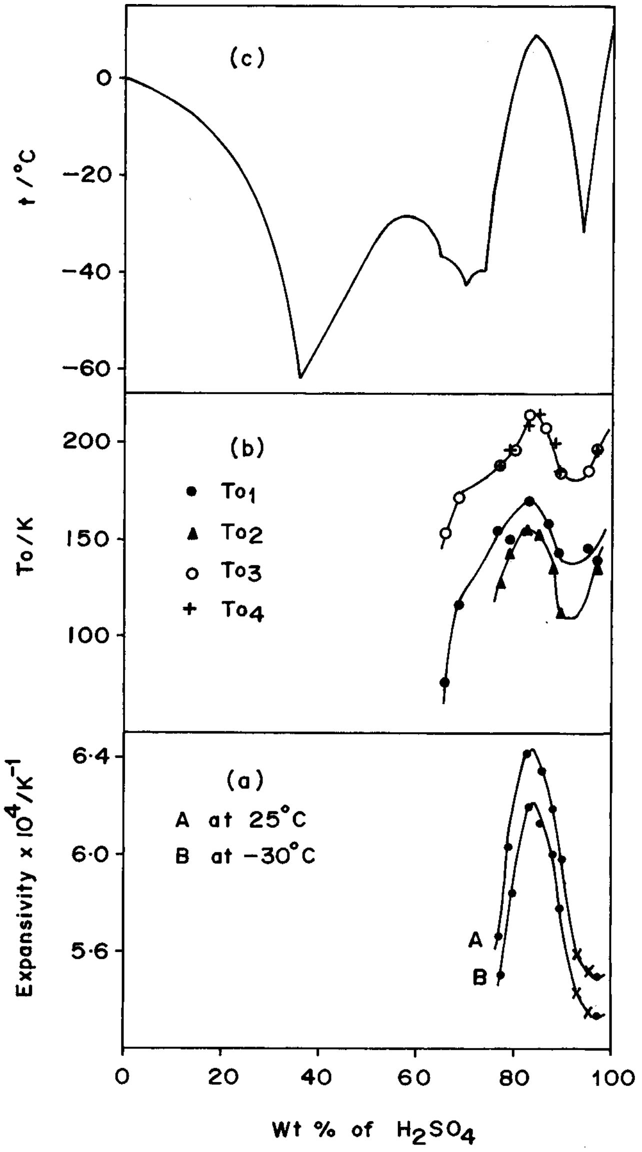

Figure 5. Variation of (a) expansivity (×, calculated by interpolation of the present data) and (b) ideal glass transition temperature with wt % H_2SO_4. (c) Phase diagram of the H_2SO_4/H_2O system (freezing points taken from ref 11).

transitions observed around 83−85 and 92−94 wt % H_2SO_4 correspond to the formations of $H_2SO_4 \cdot H_2O$ (at 84.48 wt % H_2SO_4) and the eutectic between $H_2SO_4 \cdot H_2O$ and H_2SO_4 (at 93.8 wt % H_2SO_4), respectively. It is therefore interesting to note that the formations of $H_2SO_4 \cdot H_2O$ hydrate and the eutectic mixture of $H_2SO_4 \cdot H_2O$ and H_2SO_4 are directly manifested in the *k* and *n* isotherms. On the other hand, no information can be gathered from the *n* and *k* isotherms regarding the formations of $H_2SO_4 \cdot 2H_2O$ (at ∼73 wt % H_2SO_4), $H_2SO_4 \cdot 3H_2O$ (at ∼64.5 wt % H_2SO_4), and $H_2SO_4 \cdot 4H_2O$ (at ∼57.6 wt % H_2SO_4). In the $Ca(NO_3)_2/H_2O$ system also the reported[16] conductance or viscosity isotherm does not indicate any structural change up to ∼75 wt % $Ca(NO_3)_2$, although $Ca(NO_3)_2 \cdot 4H_2O$ is formed around 64.5 wt % $Ca(NO_3)_2$. However, it has been reported[16,31,32] that the concentration dependences of the parameters of the VTF equation reflect on the structural changes taking place in binary aqueous electrolytic systems at low concentrations. It may therefore be concluded that in the very high concentration region of binary aqueous systems where the water to salt molar ratio is <2 a direct correspondence between the phase diagram of the binary system and its viscosity seems to exist since above the concentration of the conductivity maximum the concentration dependence of conductivity is in turn controlled by the viscosity itself. Besides an old report[33] on the correlation of viscosity curves to the freezing point curves in binary mixtures of organic salts, we have not found in the literature any report on the above type of viscosity−phase transition correlation in a concentrated electrolytic system. Lack of relevant data has therefore restricted us at the moment to establish whether the viscosity−phase transition correlation is of a general nature and common to binary solutions in the hyperconcentrated region.

However, it would be instructive to compare the present results with the reported[34] *n*, *k*, and T_g of the molten $ZnCl_2 \cdot RH_2O + LiCl \cdot RH_2O$ system ($R = 2.5$ or 4). On addition of $LiCl \cdot RH_2O$ to $ZnCl_2 \cdot RH_2O$ *n* and T_g decrease and pass through a minimum around 70 mol % $LiCl \cdot RH_2O$ whereas *k* increases and exhibits a maximum corresponding to the composition of minimum *n*. Similarly on addition of $LiCl \cdot RH_2O$ (R = 8, 6, 5, and 4) to $ZnCl_2$ melt *k* increases and T_g decreases and both show inflexions (around 70 mol % $LiCl \cdot RH_2O$ for $R = 4$) when plotted against concentration. However, phase diagrams of these molten systems are not reported.

The H_2SO_4/H_2O system under study can be treated in the region above 84.48 wt % H_2SO_4 as a binary mixture of $H_2SO_4 \cdot H_2O$ and H_2SO_4, and the eutectic composition then corresponds to 64 mol % H_2SO_4. The observed trends in the variation of *n*, *k*, and T_0 with the addition of H_2SO_4 to $H_2SO_4 \cdot H_2O$ now appear to be in accordance with the variations noticed in the above-referred molten systems. In fact, concentrated H_2SO_4/H_2O systems are reported[6] to behave like molten salt systems. In molten $ZnCl_2$[35,36] and hydrate melts[34] of $ZnCl_2$ a network type structure exists with $ZnCl_4^-$ as the predominant species. Addition of $LiCl \cdot RH_2O$[34] or KCl[37] breaks the network structure causing a decrease in *n* and an increase in *k*. Similarly it may be considered that when $H_2SO_4 \cdot H_2O$ is added to H_2SO_4 or vice versa disruption of the compact structure of pure solvent takes place causing *n*, k^{-1}, and T_0 to decrease from both concentration ends (i.e., 100% $H_2SO_4 \cdot H_2O$ and 100% H_2SO_4) resulting in a minimum at the eutectic composition. The decrease of T_0 with the addition of H_2SO_4 (or $H_2SO_4 \cdot H_2O$) to $H_2SO_4 \cdot H_2O$ (or H_2SO_4) may also be compared with the recent study of Johari and co-workers[38] on the effect of addition of LiCl to isomeric octanols. It has been reported[38] that when the solvent has a long linear structure (2-methyl-6-heptanol) addition of LiCl causes a decrease in T_g. Decrease in T_g has been reported by the addition of LiCl to water also.[39] This decrease in T_g is explained as due to the perturbation in the solvent structure caused by ion−solvent and ion−ion interactions.[38]

Finally, the observation made above in H_2SO_4/H_2O systems envisages that in concentrated sulfuric acid solution (>∼75 wt % H_2SO_4) the structure of the solid H_2SO_4/H_2O system is retained to a large extent by the liquid/supercooled liquid phase also. In fact absence of any significant change in the nature of the viscosity isotherm with the lowering of temperature supports this view. In pure H_2SO_4 also the structure of the liquid has been reported[40] to resemble the layer type structure of the solid H_2SO_4. Moreover, above ∼65 wt % H_2SO_4 it has been reported[1,6] that even the ionic equilibria of H_2SO_4 does not change with decreasing temperature whereas below 65 wt % H_2SO_4 cooling causes the amount of SO_4^{2-} species to increase at the expense of HSO_4^-. Generally, structures of liquids and solids are shown to be exceedingly similar.[41] In the absence of structural studies on H_2SO_4/H_2O systems, it may be worthwhile to refer to the work on the microscopic structures of concentrated electrolytes. The recent structural studies on $LiCl \cdot 6H_2O$[42] and $LiCl \cdot 4H_2O$[43] in the glass, supercooled liquid, and liquid states indicate that (1) there is no fundamental change in the intermolecular structure between the glass and supercooled liquid and (2) significant amounts of structures are present in the liquid state also except for the fact that correlations are not of long range order ($<\sim 8$ Å) and the intensities of the peaks of partial structure factors and partial pair distribution functions are reduced resulting in lower coordination numbers. Furthermore, it has been shown that the local ordering is different in liquid and supercooled liquid/glass states due to the changing balance between ionic and dipolar forces as the temperature decreases. Thus, the reported structural study on concentrated LiCl/H_2O systems[42,43] supports our above conclusion that in concentrated H_2SO_4/H_2O systems the structure of a solid $H_2SO_4 + H_2O$ mixture is largely retained in its corresponding melt.

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Supporting Information Available: Tables 2 and 3 (2 pages). Ordering information is available on any current masthead page.

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