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**Relative Viscosity and Apparent Molal Volume
of Aqueous Sodium Sulfate at
Various Temperatures¹**

by Frank J. Millero, W. Drost-Hansen,
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Anomalous temperature dependencies of conductance² and sound velocity^{3,4} for aqueous Na₂SO₄ solutions have been reported near the transition point (32.38°) of the solid decahydrate (Na₂SO₄·10H₂O).

Glass and Madgin⁵ studied the viscosity of sodium sulfate solutions, specifically investigating the possibility that the viscosity data might show an anomaly in the temperature range of the transition point. The data obtained by these authors seem to suggest a change of slope near 32.5° (see Figure 1), but the authors did not feel justified in stating that this was a

transition. Recently, Kay, *et al.*,⁶ have shown that the conductance of aqueous Na₂SO₄ solutions near 32.4° does not possess any anomalous temperature dependence.

We have made precision measurements of the relative viscosity and apparent molal volume of a dilute aqueous Na₂SO₄ solution to determine if a transition occurs in these properties. Both precision density measurements (made with a magnetic-float densitometer)⁷ and precision viscosity measurements⁸ were made at 1° intervals from 20 to 40°.

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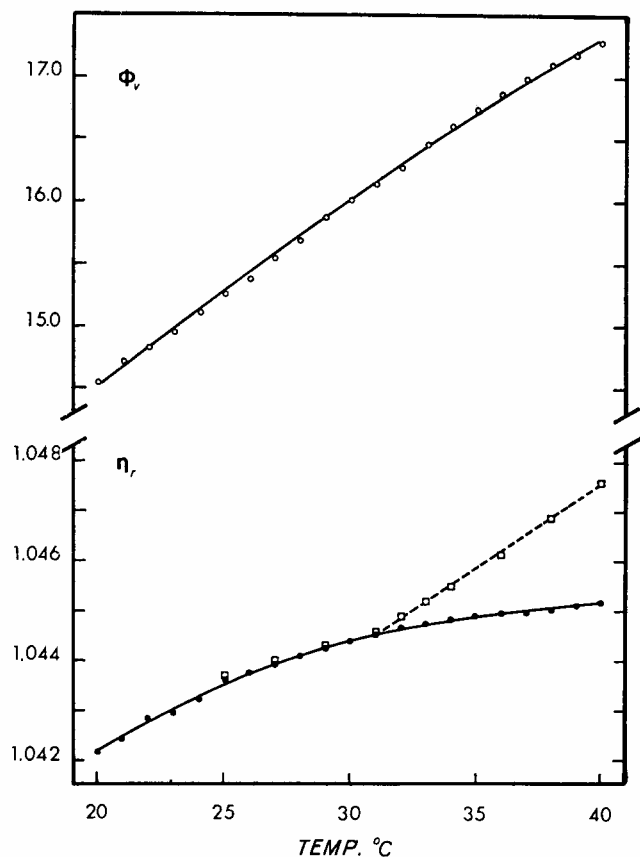


Figure 1. Apparent molal volumes, ϕ_v (open circles), and relative viscosities, η_r (closed circles), of aqueous (0.099579 *m*) sodium sulfate as a function of temperature. The η_r from Glass and Madgin's work are represented by the open squares.

Experimental Section

The (anhydrous) Na_2SO_4 was reagent grade Baker Analyzed. The salt was dried at 120° for 1 day and was used without further purification. The solutions were made by weight (corrected to vacuum) with doubly distilled water. Prior to making up the solution for the density runs, the water was degassed to remove dissolved gases and to prevent the formation of bubbles on the magnetic float.

The magnetic-float densitometer used to make the density measurements has been described elsewhere.⁷ The temperature of the bath in which the magnetic-float densitometer is submerged was controlled to $\pm 0.001^\circ$ with a Hallikainen regulator. The temperature of the bath was initially set and subsequently read to within $\pm 0.002^\circ$ with a Melabs platinum resistance thermometer.

A Cannon-Ubbelohde dilution type suspended level viscometer (Cannon Instrument Co.) with a flow time for water at 25° of about 244 sec was used to measure the viscosity of the Na_2SO_4 solution. The flow times were measured to ± 0.003 sec with a Rehovoth viscometer reader and a TSI universal counter.⁸ The temperature of the bath used to make the viscosity measurements was controlled to better than $\pm 0.001^\circ$

with a Hallikainen regulator. The temperature of the viscosity bath was read to within 0.0001° with a Hewlett-Packard quartz-crystal thermometer (Model 28-01A).

Results and Discussion

The density of 0.099579 *m* aqueous Na_2SO_4 solution has been measured at 1° intervals from 20 to 40° . The density (g/ml) was fit to an equation of the form

$$d_{\text{soln}} = A + Bt + Ct^2 + Dt^3 \quad (1)$$

where $A = 1.012761$, $B = 51.7 \times 10^{-6}$, $C = -8.06 \times 10^{-6}$, and $D = 0.04 \times 10^{-6}$. The expansion coefficient, $\alpha_{\text{soln}} = (\partial d_{\text{soln}} / \partial t)(-1/c_{\text{soln}})$, can be calculated from the equation

$$\alpha_{\text{soln}} = -(B + 2Ct + 3Dt^2) \frac{1}{d_{\text{soln}}} \quad (2)$$

where α_{soln} is equal to 274 deg^{-1} at 25° , compared to the value of 246 deg^{-1} calculated from the compilation of Harned and Owen.⁹

The apparent molal volume was calculated (Figure 1) from

$$\phi_v = \frac{1000\Delta d}{d_{\text{soln}}d_{\text{H}_2\text{O}}m} + \frac{M}{d_{\text{soln}}} \quad (3)$$

The ϕ_v at 25° can be compared to the literature value by using the equation

$$\phi_v = \phi_v^0 + S_v\sqrt{c} \quad (4)$$

Using the values $S_v = 12.16$ and $\phi_v^0 = 11.47 \text{ ml/mol}$ listed by Harned and Owen,⁹ we obtain $\phi_v = 15.30 \text{ ml/mol}$, compared to our value of 15.26 ml/mol at 25° . The apparent molal expansibility, $\phi_E = \partial\phi_v/\partial t$, was calculated from ϕ_v at the various temperatures. The average value of ϕ_E is 0.153 ml/mol deg , with a standard deviation of $\pm 0.027 \text{ ml/mol deg}$. This value is lower than the value (0.193 ml/mol deg) calculated from the compilation by Harned and Owen.⁹

The relative viscosity, η_r , of 0.099579 *m* aqueous Na_2SO_4 , defined by the equation

$$\eta_r = \eta_{\text{soln}}/\eta_{\text{H}_2\text{O}} \quad (5)$$

was also measured at 1° intervals from 20 to 40° . The viscosity of the solution, η_{soln} , was calculated from the measured flow times, τ , and densities, d_{soln} , from the equation

$$\eta_{\text{soln}} = K\tau d_{\text{soln}} - \frac{Ld_{\text{soln}}}{\tau^n} \quad (6)$$

K , L , and n were determined by measuring the viscosity of H_2O , $\eta_{\text{H}_2\text{O}}$, at various temperatures.⁸ Values

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," ACS Monograph No. 137, Reinhold Publishing Corp., New York, N. Y., 1958.

of $K = 3.6678 \times 10^{-3}$, $L = 82.1$, and $n = 1.95$ were found for the viscometer used in this study. Figure 1 shows η_r at 1° intervals from 20 to 40° ; Glass and Madgin's⁵ results are also shown for comparison. Our results agree very well with their results below 31° ; however, at higher temperatures they differ significantly.

If one assumes that the relative viscosity, η_r , of a 0.099579 *m* Na₂SO₄ solution can be represented by the Jones-Dole equation,¹⁰ it is possible to calculate the viscosity B coefficients

$$\eta_r = 1 + A\sqrt{c} + Bc \quad (7)$$

Using the values for A interpolated from Kaminsky's study,^{11,12} we have calculated B values equal to 0.375, 0.392, 0.398, 0.405, and 0.409, respectively, at 20, 25, 30, 35, and 40° . These B values may be compared with those taken from Kaminsky's work^{11,12} at the same temperatures; respectively, B equals 0.375, 0.381, 0.390, 0.398, and 0.409. A similar calculation from the relative viscosities obtained by Glass and Madgin's work⁵ gives similar results below 32° ; however, at higher temperatures one obtains B 's that are larger than both our values and those from Kaminsky's work^{11,12} (e.g., $B = 0.432$ at 40°).

A plot of all the B coefficients calculated from the present data fall on a smooth curve of a shape similar to the shape of the relative viscosity curve shown in Figure 1. Thus it appears that the B coefficients go through a maximum (i.e., dB/dT approaches zero) near 45 – 50° . The B coefficients obtained by Kaminsky increase linearly with temperature over the same temperature range. It should be kept in mind, however, that for sodium sulfate at a concentration of approximately 0.1 *m*, the Jones-Dole equation with only two terms may not represent the data with sufficient accuracy.

Since B coefficients are generally accepted as being proportional to the partial molal volumes of a salt, \bar{V} , or the hydration volume, one would expect dB/dT to be proportional to $d\bar{V}/dT$. The molal volumes for aqueous salt solutions have been shown by various workers^{13–15} to go through maxima between 40 and 60° . Thus one might postulate that B should also go through a maximum in this temperature range, as, indeed, observed in our data. We are presently measuring the viscosity and density of aqueous electrolyte and non-electrolyte solutions over a wide range of temperatures (0 – 75°), with the hope of being able to throw some light on various aspects of solute-solvent, solute-solute, and solvent-solvent interactions in these systems.

Based on absolute reaction rate theory, Nightingale¹⁶ has proposed an equation which permits the calculation of the energy of activation for viscous flow of an aqueous solution of a strong electrolyte in terms of the energy of activation for viscous flow of pure water and the B coefficient (of the salts) and its temperature derivative. Specifically, Nightingale¹⁶ proposed the equation

$$\Delta E^\ddagger_{\text{soln}} - \frac{R d \ln \eta^\circ}{d(1/T)} = \frac{R}{1 + BC} \frac{d(1 + BC)}{d(1/T)} \quad (8)$$

where $\Delta E^\ddagger_{\text{soln}}$ is the energy of activation for viscous flow of the solution, $(R d \ln \eta^\circ)/d(1/T) = \Delta E^\ddagger_{\text{H}_2\text{O}}$ is the energy of activation for viscous flow of pure water, R is the gas constant, B is the Jones-Dole B coefficient, C is the concentration, and the other symbols have their usual meaning.

Using the B coefficient obtained in the present study and the equation proposed by Nightingale, the difference between $\Delta E^\ddagger_{\text{H}_2\text{O}}$ and $\Delta E^\ddagger_{\text{soln}}$ is calculated to be -35.3 cal/mol; i.e., the energy of activation for viscous flow of the solution is less than that for the pure solvent, in agreement with the general notion that sodium sulfate acts as a structure breaker. Using $\Delta E^\ddagger_{\text{H}_2\text{O}}$, obtained experimentally⁸ (4000 cal/mol at 25° and $\Delta E^\ddagger_{\text{soln}}$ calculated from the temperature dependence of η_{soln} (4025 cal/mol), one obtains a difference of -25 cal/mol. The agreement is satisfactory, considering the magnitude of the difference between the two large numbers.

The results shown in Figure 1 for ϕ_v and η_r for Na₂SO₄ clearly demonstrate that there are no transitions near 32.4° in these properties. Furthermore, there is no evidence for an anomaly in the vicinity of 30° , owing to alleged structural changes in the properties of water.^{17,18} In a separate paper¹⁹ one of us (W. D.-H.) has speculated on the highly divergent opinions which have developed regarding the question of the existence or nonexistence of thermal anomalies in the properties of aqueous systems. Essentially, the conclusion which has been reached is that thermal anomalies may, indeed, be real, but that they are most likely to be manifestations of surface or interfacial effects. With the present experimental techniques, surface effects are expected to be minimal, and this, in turn, may explain the complete absence of any indications of anomalies in our results. While, in some cases, the surface effects may be suspected of contributing to anomalous temperature behavior, it is difficult to see where such surface phenomena could have entered into the measurements reported by Yasunaga and coworkers³ or those reported

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