of the successive orders are illustrated in Figure 3. The fifth order was missing in the diffraction patterns of all but that of 2-tridecanone.

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Temperature Dependence of Diffusion and Viscosity in Aqueous Urea Solutions

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The temperature dependence of viscosity and the diffusion of zinc ion in aqueous urea solutions were measured over the range 298° to 319° K. The viscosities range from 0.593 cp (no urea, 319° K) to 1.378 cp (7*M* urea, 298° K). The diffusion coefficients, measured polarographically, range from 4.32 x 10^{-6} cm^2 sec^{-1} (7*M* urea, 298° K) to 10.63 x 10^{-6} cm^2 sec^{-1} (0*M* urea, 319° K). The viscosities and diffusion coefficients were fitted to Arrhenius equations; activation data for energy and entropy for seven solutions, 0*M* to 7*M* urea, are reported. These data suggest some transition in structure as urea concentration is increased, and that the transition affects differently the temperature dependence of these two transport properties.

The physical effects of urea added to aqueous solutions are of continuing interest in such areas as protein denaturation (*6*), diffusion (*2, 8*) and micelle formation (*7*). A review of these effects is available (*1*) and interpretations of these effects have recently been discussed (*4*).

The experimental data of the physical properties of aqueous solutions of urea, however, are as yet insufficiently complete to state definitively the mechanistic effect of urea in water. The temperature dependence of physical properties of aqueous urea solutions has not been extensively investigated and it has been recently suggested that such data should be revealing (*9*). Accordingly, we report here the concomitant effects of urea concentration and temperature upon the related transport properties of diffusion and viscosity. The diffusing species is zinc ion, 0.4*M* KNO_3, 0 to 7*M* in urea, over the temperature range 298° to 319° K. The viscosities range from 0.593 cp (no urea, 319° K) to 1.378 cp (7*M* urea, 298° K).

EXPERIMENTAL

All solutions were prepared in distilled water, using reagent-grade chemicals without further purification. The stock zinc nitrate solution was standardized chelometrically. The required concentrations of KNO_3 and urea were obtained by adding the required weights before dilution to volume.

Diffusion coefficients were measured using polarography at the dropping mercury electrode. A Leeds & Northrup electrochemograph was used: capillary and temperature characteristics were controlled using a Leeds & Northrup Polarotron.

Viscosity measurements were made with use of an Ostwald viscometer calibrated using distilled water. Density measurements were made using a Westphal balance calibrated using distilled water. By using a Sargent Thermonitor for temperature control (±0.01° C) and a Fisher thermometer having 0.1° C subdivisions for temperature measurements, the viscosity measurements (average of three determinations) were reproducible to ±0.5% and the density measurements were more precise, ±0.1%.

RESULTS

Diffusion. The experimental values of average current (i, μA), zinc ion concentration (C, mmole 1^{-1}), mercury drop time (t, sec), and mercury drop weight (m, mg sec^{-1}) were inserted into the expanded Ilkovic equation (*5*)

$$i = 607\, nD^{1/2}\, Cm^{2/3}t^{1/6} \cdot [1 + 34\, m^{-1/3}t^{1/6}D^{1/2}] \qquad (1)$$

where n is the number of electrons necessary for the electrochemical reduction of divalent zinc to metallic zinc at the mercury drop. The equation was then solved for D assuming $n = 2$, using successive approximations in APL language on an IBM 360/50.

These diffusion data of zinc ion in solutions 0 to 7M urea were determined over the temperature range 298° to 319° K at 3° increments. The results are expressed by an Arrhenius equation (*3*):

$$D = Ae^{-E_D/RT} \tag{2}$$

where D is the diffusion coefficient, A is an entropy-dependent constant, E_D is a constant termed the energy of activation, R is the gas constant, and T is the temperature corresponding to D. The experimental data (i, T, m, C) for each of seven solutions at each of the eight temperatures (298° to 319° K, 3° increments) were fitted to Arrhenius equations using the method of linear least squares programmed in APL language on an IBM 360/50. The results, by using the expanded Ilkovic equation for determining D, are given in Table I. Experimental reproducibility of these results was also incorporated into the APL program by calculating deviations of all experimental diffusion coefficients from the least-squares regression line. The magnitudes of the deviations using the diffusion data of Table I are confounded by the changing value of D with temperature as well as by the logarithmic compression. However, diffusion coefficients measured under these experimental conditions ranged from 4.32 to 10.63×10^{-6} cm^2 sec^{-1}. The range of deviations of experimental data from the regression line was ± 0.10 to $\pm 0.25 \times 10^{-6}$ cm^2 sec^{-1}. The maximum possible deviation is then 0.25/4.3 or 5.8% and most of our calculated deviations were less.

VISCOSITY

Since the diffusion coefficient of an electroactive species decreases as the viscosity increases, the viscosities of these solutions in this temperature range, 298° to 319° K, using 3° increments, were also determined; otherwise, the effect of urea *per se* upon the diffusion process could be misinterpreted.

Viscosity can also be described by an Arrhenius equation (*3*)

$$D = Be^{E_V/RT} \tag{3}$$

where B is an entropy-dependent constant and E_V is an energy of activation. The experimental data for these viscosities were also computer-treated, using the method of linear least squares (Table I). Again, in the program, deviations of experimental values from the least-squares regression lines were calculated. The experimental relative viscosities ranged from 0.593 to 1.378 cp. The range of deviations

Table I. Arrhenius Data for Diffusion and Viscosity

Urea Concentration, Moles Liter^{-1}	Diffusion		Viscosity		
	E_D, cal mole^{-1}	A, $\times 10^3$	E_V, cal mole^{-1}	B, $\times 10^3$	$D \times \eta$, $\times 10^6$
0	3835	4.39	3596	2.04	5.9
1	4146	7.67	3470	2.61	6.3
2	4177	7.67	3454	2.84	6.4
3	3598	2.76	3476	2.89	6.5
4	4006	4.84	3494	3.00	6.0
6	4140	5.23	3500	3.43	6.1
7	4253	5.81	3513	3.65	5.9

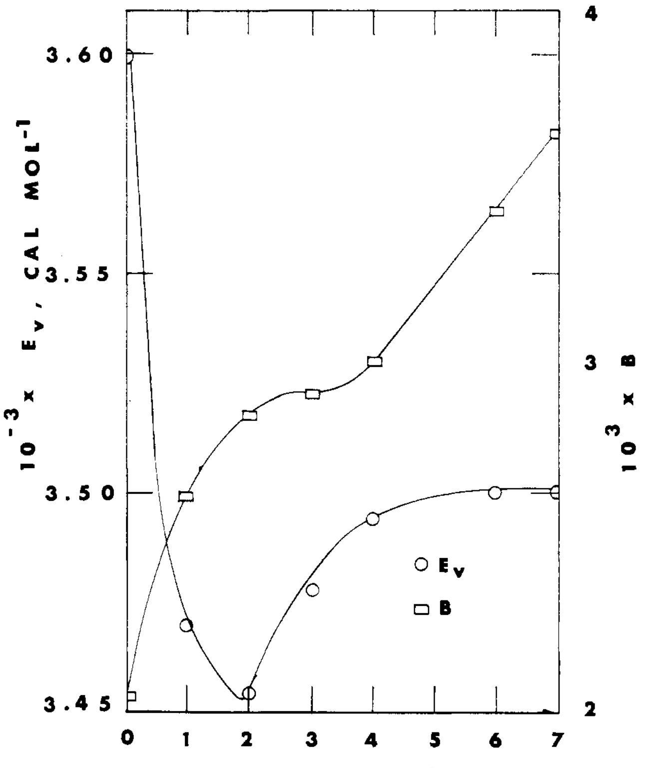

Figure 1. Arrhenius data for viscosity

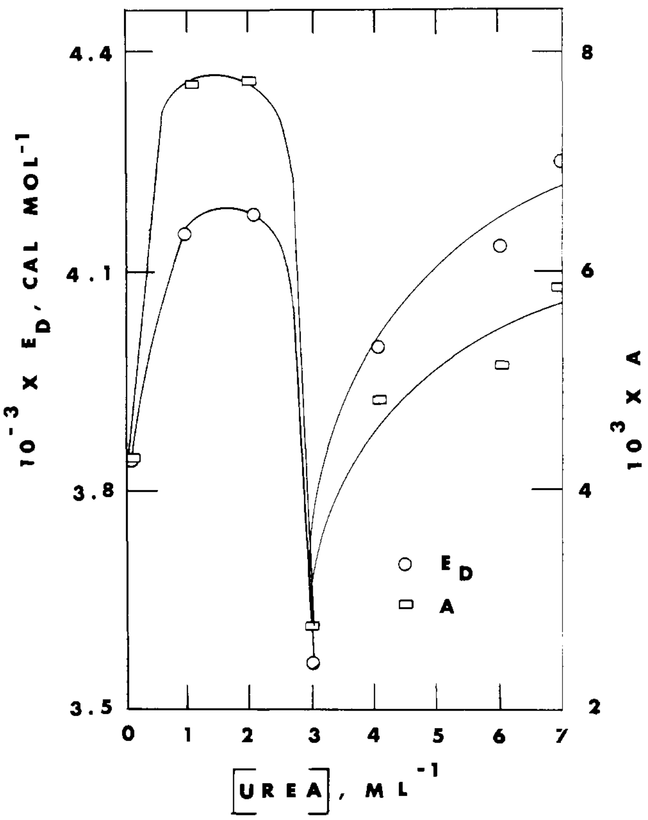

Figure 2. Arrhenius data for diffusion

from a regression line was 0.000 to 0.004 cp, the maximum possible relative deviation being less than 1%. As expected, the fit of the viscosity data to an Arrhenius equation is better than for the diffusion data, the viscosity data being from a more precise measurement technique.

DISCUSSION

The viscosity and diffusion data of Table I are plotted in Figures 1 and 2, respectively. These activation energies and entropies vary nonlinearly throughout the concentration range. Although the appearance of these plots cannot at present be rationalized, these complexities are not surprising, as the solution environment is being severely altered (at 7*M* urea there are about eight water molecules per one urea molecule). These results are of interest, since precise measurements of refractive indices at a single temperature did not show a concentration dependence *(10)* and it was concluded that urea solutions do not undergo a detectable transition in structure at some critical concentration of urea. The inflections and discontinuities of Figures 1 and 2 suggest some transition in structure that affects differently the temperature dependence of these two transport properties, although the Stokes-Einstein relationship (Table I) is apparently not affected.

These findings, as previously suggested (*9*), should be relevant to protein thermodynamics and protein denaturation.

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Thermodynamics of Hydrochloric Acid in 8.03, 20.76, 44.04, 70.28, and 87.71 Weight % 2-Propanol–Water Mixtures from E.M.F. Measurements at 0°, 15°, 25°, and 35°C

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The electromotive force measurements of the cell, Pt, H_2 (1 atm) | HCl (*m*), 2-propanol (*X*), water (*Y*) | AgCl, Ag were made for 8.03, 20.76, 44.04, 70.28, and 87.71 weight % 2-propanol at 0°, 15°, 25°, and 35° C. The cell was used to derive the standard e.m.f. of this cell for 2-propanol–water mixtures by using a polynomial curve-fitting technique, the mean activity coefficient of hydrochloric acid, the primary and secondary medium effects, the relative partial molal heat content and heat capacity of HCl, and the means of converting the values obtained from the mixed-solvent systems to those of the standard reference aqueous state. The curve-fitting program permits evaluation of the standard potential in mixed solvents, with elimination of some of the uncertainties encountered in the conventional linear graphical extrapolations where previous knowledge of the dielectric constant of the solvent, density of the mixed-solvent, and the ion-size parameter is required. The molality of HCl ranged from 0.1 to 0.001 mole kg^{-1}.

The properties of hydrochloric acid in aqueous-organic mixed solvents (*3–5, 7–11*) has long been a subject of interest. The normal graphical extrapolation (*3, 4, 7–9*) of the e.m.f. data of the cell Pt, H_2 (1 atm) | HCl (*m*), 2-propanol (*X*), water (*Y*) | AgCl, Ag, using Gronwall, LaMer, and Sandved's (*5*) extension of the Debye-Hückel theory usually exhibits errors and shows curvatures at the lower concentration, which is the region of greatest importance. The work reported here was undertaken to eliminate the errors encountered in the linear graphical extrapolations for the determination of E^0 and to interpret the e.m.f. data of hydrochloric acid in a medium of varying dielectric constant.

The binary 2-propanol-water solvent mixture of various compositions was chosen. These media are common laboratory solvents, and as such are used in the investigations of the acid-base properties of compounds that are not very soluble in water.

The scope of the investigation can be summarized as follows. The standard e.m.f. of the cell was evaluated by a polynomial curve-fitting technique. The mean activity coefficients, primary and secondary medium effects, relative

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