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Comparison of the Activation Free Energies for Viscous Flow and for Diffusion in Dilute Solutions, Derivation of the Expression for the Effect of the Solute on the Activation Free Energy of Diffusion of the Solvent, and Application to Solutions of *N*,*N*-Dimethylformamide in Water, Methanol, and Acetonitrile

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The effect of a solute on the viscosity of a solution is determined by both its intrinsic rate of motion and its effect on the rate of flow of surrounding solvent molecules. Thus, the contribution of the solute to the activation free energy for viscous flow is the sum of two terms, one for each of these. In the viscosity experiment it is not possible to resolve these contributions unambiguously. In contrast it is possible to measure both the diffusion coefficient of the solute and the effect of the solute on the diffusion coefficient of the solvent. In this paper we report viscosity *B* coefficients and diffusion data for *N*,*N*-dimethylformamide in water, methanol, and acetonitrile and solvent diffusion for each of these as a function of solute concentration. The solvent diffusion data are found to obey an equation analogous to that of Jones and Dole for the solution viscosity. We also present a relationship for calculating the solute contribution to the activation free energy for diffusion of the solvent. Those for the diffusion of the solvent and for the solutes contribution to the activation free energy for viscous flow are calculated in the usual ways. Comparison of these activation free energies shows that the solute contribution to the free energy of activation for viscous flow is approximately equal to the sum of those for diffusion of the solute and that for the solute's effect on the diffusion of the solvent molecules. It is also found that the solute's affect on the motion of the solvent plays a major role in the aqueous system but makes only a minor contribution in the nonaqueous solvents.

Introduction

It was observed very early that the viscosities of solutions of small solutes could differ significantly from those of the pure solvent. That is, the introduction of the solute could either raise or lower the viscosity of the system. Jones and Dole[1] showed that the viscosities of dilute solutions varied simply with the solute concentration. The relationship for solutions of strong electrolytes is most commonly written as

$$\eta_r = \frac{\eta_{1,2}}{\eta_1} = 1 + A\sqrt{c} + Bc \qquad (1)$$

while that for solutions of nonelectrolytes is

$$\eta_r = \frac{\eta_{1,2}}{\eta_1} = 1 + Bc \qquad (2)$$

where η_1 and $\eta_{1,2}$ are the viscosities of the solvent and solution, respectively, and c is the solute concentration. The *A* coefficient in eq 1 represents the effects of ion−ion interactions in electrolyte solutions and can be calculated from interionic attraction theory.[2] In contrast, the *B* coefficient represents the effect of solute−solvent interactions on the viscosity.

The Jones−Dole *B* coefficients have been the subject of considerable interest.[3] In particular, the fact that they may be either positive or negative, that is the solute−solvent interaction may lower or raise the viscosity of the solution, is one of the central pillars in the argument that solutes may be structure makers or structure breakers.[4]

Feakins,[5] following arguments by Eyring, showed how the *B* coefficient is related to the solute's contribution to the molar free energy of activation for viscous flow. In considering the solute contributions to this activation free energy or, equivalently, the *B* coefficients, there is an immediate difficulty. Thus, the solute itself moves, passing over an energy barrier, and it will also affect the movement of solvent molecules in its vicinity, in effect perturbing the energy barriers to their movement. It has been suggested that the activation free energy for the movement of the solute could be approximated by those for diffusion or conductance of the solute[6] or by that for viscous flow of the solvent.[7] There is, however, no unambiguous method of separating these contributions from the measurement of solution viscosity.

At a molecular level the processes involved in viscous flow and in diffusion should be similar. That is, a solute molecule must diffuse over an energy barrier and equally may perturb the energy barrier of the flow of nearby solvent molecules. However, for diffusion, it is possible to unambiguously separate these, since the diffusion coefficients of solute and solvent can be measured independently.

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In this paper we report viscosity *B* coefficients and diffusion coefficients for *N*,*N*-dimethylformamide (DMF) in water, methanol, and acetonitrile and solvent diffusion coefficients for each of these as a function of DMF concentration. We find that the solvent diffusion coefficients follow a relationship similar to eq 2. We also show how the resulting B' coefficient is related to the solute's contribution to the activation free energy for diffusion of the solvent. Finally we find that the solute's contribution to the activation free energy for viscous flow is, to a good approximation, simply the sum of its measured free energy of activation for diffusion and its measured contribution to that for diffusion of the solvent.

Experimental and Results

Viscosity. The viscosity measurements were made using a Schött-Gerate AVS/S measuring system and Ubbelohde type suspended level capillary viscometer. The system was adapted to allow serial measurements to be made under computer control. The modification to the capillary viscometer involved replacing the lower reservoir by one with a volume of about 50 cm^3. The viscometer was suspended in a specially constructed water bath, which allowed the contents of the reservoir to be stirred using a magnetic stirrer. The temperatures of these systems were accurate to 0.02 K with temperature variations of less than ±0.001 K. The composition of the solution in the viscometer was altered by the addition of a stock solution, via a piston driven buret (Metrohm Dosimat 655, using a 1 cm^3 buret), through the sidearm of the viscometer. The AVS was controlled and interrogated via its RS-232 port, and the stirrer and buret were activated via reed relays under computer control. Thus, in an experiment a known weight of solvent was placed in the viscometer and its flow time measured. Subsequently, known volumes of a stock solution were injected into the viscometer, mixed by stirring, and the flow times of the resulting solutions measured. The weight of a 1 cm^3 injection of the stock solution was measured before and after the experiment, and the density of the final solution was measured as a check on the final solution concentration.

Diffusion. The self-diffusion coefficients of DMF and of the solvents in the solutions were obtained by applying the pulsed magnetic field gradient spin echo (PGSE) technique,[8,9] using a Minispec Pc 120 combined with a commercial pulsed-field gradient unit, both from Bruker. Sample temperature was controlled to ±0.2 K. In these experiments the component (solvent or solute) being studied was the ^{1}H compound and the other component was fully deuterated. Thus, the diffusion coefficients of DMF were determined in fully deuterated solvents. These data were corrected for the isotopic effects on diffusion using diffusion coefficients for water,[10] methanol,[10] and acetonitrile[10] containing ^{1}H and ^{2}H.

Density. Densities were measured using a vibrating tube densitometer (Anton Paar DMA-60) with two cells (DMA-601), one containing water, used as reference. This configuration has the advantage of minimizing the effects of variations in temperature. The cells were thermostated by circulating water from a thermostat; the temperature of the cells was controlled to ±0.01 K (the limit of precision of the platinum thermometer, Anton Paar DT 130). The system was fitted with an automatic sampler unit (Anton Paar SP-2). The apparatus was enclosed in an air thermostat kept at 0.5 K above the measuring temperature so that outgassing of samples was minimized.

Chemicals. DMF,[11] methanol,[12] and acetonitrile[13] were purified as described previously. Fully deuterated DMF (DMF-*d*$_7$, 99.5 atom % D) was obtained from Aldrich Chemicals and used without further purification. Water was distilled, passed through an ion exchange column and then redistilled; the conductivity of the water was less than 1 × 10^{-6} S cm^2.

Treatment of the Experimental Data

Feakins,[5,14] following Eyring's treatment of viscosities, showed that, if eq 1 (or 2) is obeyed, then

$$B = (\nu\bar{V}_1^\circ - \bar{V}_2^\theta) + \left(\frac{\bar{V}_1^\circ}{RT}\right)(\Delta\mu_{V,2}^{\theta\neq} - \nu\Delta\bar{G}_{V,1}^{\circ\neq}) \tag{3}$$

where the coefficient ν is 1 for an undissociated solute, as in the present work, and would be, for example, 2 for a fully dissociated univalent electrolyte. In eq 3 $\bar{V}_1^\circ$ and $\bar{V}_2^\theta$ are respectively the molar volume of the pure solvent and the partial molar volume of the solute at infinite dilution and $\Delta\bar{G}_{V,1}^{\circ\neq}$ is the molar free energy of activation for viscous flow of the pure solvent and $\Delta\mu_{V,2}^{\theta\neq}$ is the solute contribution to the molar free energy of activation for viscous flow.

By analogy with the Jones−Dole equation for solution viscosities we can write

$$\frac{\left\{\dfrac{1}{D_{1,2}}\right\}}{\left\{\dfrac{1}{D_1^\circ}\right\}} = 1 + B'c \tag{4}$$

where $D_{1,2}$ and D_1° are the diffusion coefficients of the solvent in the solution and in the pure liquid, respectively.

Eyring[15] writes, for the diffusion coefficient

$$D = \frac{kT}{h}\lambda^2 \exp\left\{\frac{-\Delta\bar{G}_D^{\neq}}{RT}\right\} \tag{5}$$

where λ is the jump distance and $\Delta\bar{G}_D^{\neq}$ is the molar free energy of activation for diffusion. For the pure solvent this gives

$$D_1^\circ = \frac{kT}{h}{\lambda_1}^2 \exp\left\{\frac{-\Delta\bar{G}_{D,1}^{\circ\neq}}{RT}\right\} \tag{6}$$

We take the jump distance as being simply related to the molar volume as

$$\lambda_1 = \left\{\frac{\bar{V}_1^\circ}{N_A}\right\}^{1/3} \tag{7}$$

where $\bar{V}_1^\circ$ and N_A are the molar volume of the solvent and Avogadro's number, respectively. Similarly, for the solvent in a solution we can write

$$D_{1,2} = \frac{kT}{h}\lambda_{1,2}^2 \exp\left\{\frac{-\Delta\bar{G}_{D,1,2}^{\neq}}{RT}\right\} \tag{8}$$

where $\Delta\bar{G}_{D,1,2}^{\neq}$ includes the effect of the solute on the activation free energy for diffusion of the solvent molecules. We can express this simply as

$$\Delta\bar{G}_{D,1,2}^{\neq} = \Delta\bar{G}_{D,1}^{\circ\neq} + x_2\Delta\mu_{D,1,2}^{\neq} \tag{9}$$

where x_2 represents the solute mole fraction (and x_1 is the solvent mole fraction).

If we assume that holes are created randomly in the solution then we can write

$$\lambda_{1,2} = x_1\lambda_1 + x_2\lambda_2$$
$$= x_1\left\{\frac{\bar{V}_1}{N_A}\right\}^{1/3} + x_2\left\{\frac{\bar{V}_2}{N_A}\right\}^{1/3} \tag{10}$$

which, for dilute solutions becomes

$$\lambda_{1,2} = x_1\left\{\frac{\bar{V}_1^\circ}{N_A}\right\}^{1/3} + x_2\left\{\frac{\bar{V}_2^\theta}{N_A}\right\}^{1/3} \tag{11}$$

where $\bar{V}_1^\circ$ and $\bar{V}_2^\theta$ are respectively the molar volume of the pure solvent and the partial molar volume of the solute at infinite dilution. Thus

$$1 + B'c = \frac{\dfrac{1}{D_{1,2}}}{\dfrac{1}{D_1^\circ}} = \frac{\lambda_1{}^2}{\lambda_{1,2}^2}\exp\left\{\frac{\Delta\bar{G}^{\neq}_{D,1,2} - \Delta\bar{G}^{\circ\neq}_{D,1}}{RT}\right\}$$
$$\cong \exp\{B'c\} \tag{12}$$

for small values of *c*. Thus

$$B'c = 2\ln\left(\frac{\lambda_1}{\lambda_{1,2}}\right) + \left\{\frac{\Delta\bar{G}^{\neq}_{\mathrm{D},1,2} - \Delta\bar{G}^{\circ\neq}_{D,1}}{RT}\right\}$$
$$= \frac{2}{3}\ln\left\{\frac{\bar{V}_1^\circ}{x_1\bar{V}_1^\circ + x_2\bar{V}_2^\theta}\right\} + \frac{(\Delta\bar{G}^{\circ\neq}_{D,1} + x_2\Delta\mu^{\neq}_{D,1,2}) - \Delta\bar{G}^{\circ\neq}_{D,1}}{RT}$$
$$= -\frac{2}{3}\ln\left\{1 - \frac{x_2(\bar{V}_1^\circ - \bar{V}_2^\theta)}{\bar{V}_1^\circ}\right\} + \frac{x_2\Delta\mu^{\neq}_{D,1,2}}{RT} \tag{13}$$

Taking the leading term of the Taylor's expansion of the logarithm leads to

$$B'c = \frac{2}{3}x_2\frac{(\bar{V}_1^\circ - \bar{V}_2^\theta)}{\bar{V}_1^\circ} + x_2\frac{\Delta\mu^{\neq}_{D,1,2}}{RT} \tag{14}$$

At low concentrations we can write

$$x_2 = \frac{c\bar{V}_1^\circ}{1000} \tag{15}$$

and eliminating *c* gives

$$B' = \frac{2(\bar{V}_1^\circ - \bar{V}_2^\theta)}{3\ \ 1000} + \frac{\bar{V}_1^\circ}{1000}\left\{\frac{\Delta\mu^{\neq}_{D,1,2}}{RT}\right\} \tag{16}$$

which rearranges to give

$$\Delta\mu^{\neq}_{D,1,2} = RT\left\{B' - \frac{2}{3}\frac{(\bar{V}_1^\circ - \bar{V}_2^\theta)}{1000}\right\}\left\{\frac{1000}{\bar{V}_1^\circ}\right\} \tag{17}$$

Results

The relative viscosities, η_r, of the systems studied here are reported in Table 1; the measured diffusion coefficients of water, methanol, and acetonitrile at different concentrations of DMF-d_7 are in Table 2, and the diffusion coefficients of DMF in water, methanol, and acetonitrile in Table 3. Table 4 lists the partial molar volumes of the solute and solvent, the viscosity *B* coefficients and the *B*′ coefficients from diffusion. The values of $\Delta\mu^{\theta\neq}_{V,2}$, $\Delta\mu^{\neq}_{D,1,2}$, and $\Delta\mu^{\neq}_{D,2}$, the molar free energy of activation for diffusion of *N*,*N*-dimethylformamide are listed in Table 5. The values of $\Delta\mu^{\neq}_{D,2}$ were calculated from the diffusion coefficients via eq 5 but taking λ as the mole fraction weighted average of solvent and solute hole sizes (eq 10).

TABLE 1: Relative Viscosities, η_r, of Solutions of *N*,*N*-Dimethylformamide at 298.2 K[a]

water		methanol		acetonitrile	
c_{DMF}	η_r	c_{DMF}	η_r	c_{DMF}	η_r
0.0000	1.00000	0.0000	1.00000	0.0000	1.00000
0.0268	1.00473	0.0111	1.00028	0.0173	1.00100
0.0495	1.00876	0.0217	1.00053	0.0322	1.00182
0.0690	1.01215	0.0317	1.00077	0.0452	1.00249
0.0935	1.01656	0.0417	1.00098	0.0618	1.00344
0.1138	1.02003	0.0503	1.00120	0.0758	1.00424
0.1308	1.02303	0.0672	1.00153	0.0877	1.00491
0.1538	1.02735	0.0826	1.00181	0.1040	1.00585
0.1719	1.03061	0.0967	1.00207	0.1171	1.00644
		0.1158	1.00240		
		0.1327	1.00268		

[a] Precisions in η_r are $\pm 5 \times 10^{-5}$; c_{DMF} is the DMF concentration expressed in mol dm^{-1}.

TABLE 2: Solvent Self-Diffusion Coefficients in Solutions of Fully Deuterated *N*,*N*-Dimethylformamide (or DMF-d_7) at 298.2 K[a]

water		methanol		acetonitrile	
c_{DMF}	D_{H_2O}	c_{DMF}	D_{CH_3OH}	c_{DMF}	D_{CH_3CN}
0.0000	2.30	0.0000	2.41	0.0000	4.37
0.1045	2.26	0.1375	2.40	0.1469	4.42
0.2038	2.22	0.2681	2.38	0.2599	4.38
0.2477	2.21	0.4167	2.39	0.4115	4.32
0.4312	2.15	0.5455	2.40	0.5442	4.30
0.5910	2.11	0.6874	2.39	0.6798	4.34
0.7914	2.05	1.0371	2.37	0.9097	4.23
1.2475	1.93	1.4014	2.37	1.3853	4.17
1.7251	1.81				

[a] Precisions in D_i are ±0.01; c_{DMF} is the DMF concentration expressed in mol dm^{-1}.

TABLE 3: Self-Diffusion Coefficients of *N*,*N*-Dimethylformamide (DMF) in Water, Methanol, and Acetonitrile at 298.2 K[a]

solvent	$D^b/10^{-9}$ m^2 s^{-1}	$D^c/10^{-9}$ m^2 s^{-1} [c]
water	0.85^d	1.04^d
	0.57^e	0.70^e
methanol	0.73^f	0.83^f
acetonitrile	2.99^g	3.15^h

[a] Precisions in D_i are ±0.01. [b] Values obtained in fully deuterated solvents. [c] Corrected for isotope effects (see text). [d] 2.0 *m* solution.[e] 6.0 *m* solution. [f] 3.4 *m* solution. [g] 0.87 *m* solution. [h] 2.6 *m* solution.

TABLE 4: Solute and Solvent Partial Molar Volumes, Viscosity *B* Coefficients, and *B*′ Coefficients from Diffusion for *N*,*N*-Dimethylformamide in Water, Methanol, and Acetonitrile at 298.2 K[a]

		water		
	$\bar{V}_1^\circ$/cm^3 mol^{-1}	$\bar{V}_2^\theta$/ cm^3 mol^{-1}	B/dm^3 mol^{-1}	B'/dm^3 mol^{-1}
water	18.07	74.3	0.178	0.16
methanol	40.73	75.6	0.020	0.01
acetonitrile	52.86	76.7	0.055	0.05

[a] Precisions are ±0.01 in $\bar{V}_1^\circ$, ±0.1 in $\bar{V}_2^\theta$, ± 0.002 in *B*, and ±0.01 in *B*′.

Discussion

The viscosity of a dilute solution may differ from that of the solvent in two ways, either because the solute moves more or

TABLE 5: Molar Free Energies of Activation at 298.2 K[a]

	water	methanol	acetonitrile
$\Delta\mu^{\neq}_{D,1,2}$/kJ mol^{-1}	26.4	2.0	2.9
$\Delta\mu^{\neq}_{D,2}$/kJ mol^{-1}	14.2	13.8	13.1
$(\Delta\mu^{\neq}_{D,2} + \Delta\mu^{\neq}_{D,1,2})$/kJ mol^{-1}	40.6	15.8	16.0
$\Delta\mu^{\theta\neq}_{V,2}$/kJ mol^{-1}	41.3	13.2	13.1
$\Delta\bar{G}^{\circ}_{D,1}$/kJ mol^{-1}	13.8	15.0	14.0
$\Delta\bar{G}^{\circ}_{V,1}$/kJ mol^{-1}	9.2	10.0	9.4

[a] Precisions of the calculated values are typically ±0.2 kJ mol^{-1}. $\Delta\mu^{\neq}_{D,1,2} \equiv$ the solute contribution to the activation free energy for diffusion of the solvent in a solution; $\Delta\mu^{\neq}_{D,2} \equiv$ the activation free energy for diffusion of the solute; $\Delta\mu^{\theta\neq}_{V,2} \equiv$ the solute contribution to the activation free energy for viscous flow in a solution; $\Delta\bar{G}^{\circ}_{D,1} \equiv$ the molar activation free energy for diffusion of the pure solvent; $\Delta\bar{G}^{\circ}_{V,1} \equiv$ the molar activation free energy for viscous flow of the pure solvent.

less rapidly than the solvent molecules or because the solute molecule affects the rate at which the solvent molecules move. Thus, $\Delta\mu^{\theta\neq}_{V,2}$ reflects both the activation energy for movement of the solute and the effect of the solute on the movement of the solvent molecules. In considering viscosity measurements there is no unambiguous way of separating these two contributions to $\Delta\mu^{\theta\neq}_{V,2}$. It has been suggested previously that the activation chemical potential for the movement of the solute could be approximated by those for diffusion or conductance of the solute or by that for the viscous movement of the solvent.

In contrast, the diffusion experiments allow these two terms to be independently determined. If we assume that the mechanisms of diffusion and viscous motion are similar, then we can write

$$\Delta\mu^{\theta\neq}_{V,2} \cong \Delta\mu^{\neq}_{D,2} + \Delta\mu^{\neq}_{D,1,2} \qquad (18)$$

The results in Table 5 are in good agreement with eq 18. We can note that the values of $\Delta\bar{G}^{\circ}_{V,1}$ and $\Delta\bar{G}^{\circ}_{D,1}$ differ systematically by around 5 kJ mol^{-1} so that the agreement is essentially quantitative within the approximations made.

These results, combined with the general constancy of the activation free energies for diffusion or conductance,[5] indicate that the variations in $\Delta\mu^{\theta\neq}_{V,2}$, or in the viscosity B coefficients, principally reflect the effect of the solute on the movement of the solvent molecules in the system.

The value of 25.0 kJ mol^{-1} for $\Delta\mu^{\neq}_{D,1,2}$ in water warrants some comment since it is more than half of the enthalpy of vaporization of water at the same temperature. Clearly the DMF perturbs the movement of a relatively large number of water molecules, raising their activation energies. The elevation in the activation energy could reflect stronger hydrogen bonds to the amide C=O or it could result from the caging of the methyl groups by the water. Given that $\Delta\mu^{\neq}_{V,2}$ is 75.4 kJ mol^{-1} for 2,2-dimethylpropan-2-ol (*tert*-butyl alcohol, TBA) in water, it seems likely that the latter effect predominates.

It is interesting to note that the value of $\Delta\mu^{\neq}_{D,1,2}$ for water is considerably larger than $\Delta\mu^{\neq}_{D,2}$ or $\Delta\bar{G}^{\neq}_{D,1}$ while those in both methanol and acetonitrile are much smaller. This suggests that water may be much more susceptible to the effect of solutes than most other solvents, which are of lower structural order and are composed of larger molecules.

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