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Diffusion, Viscosity, and Refractivity Data on the Systems Dimethylformamide–Water and *N*-Methylpyrrolidone–Water at 5 °C

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Diffusion coefficients, densities, viscosities, and refractivities have been measured for the systems dimethylformamide–water and *N*-methylpyrrolidone–water at 5 °C through all the composition range. A minimum of the molecular mobility properties has been observed for both systems at solute/solvent intermediate composition. The results suggest that no strong solute–solvent complexes are present in solution. The observed extrema in the transport properties can be attributed to the growth of a two- or three-dimensional H-bond network connecting several molecules.

Dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) are solvents used to dissolve polymeric material for membrane casting with the technique of phase inversion. A polymer film solution spread on a flat surface is immersed in a large bath of a poor solvent that induces the membrane precipitation (*1*, *2*).

The mechanism of membrane formation is not readily explained in a quantitative manner. Several factors determine the casting of a good membrane and they are not well understood (*3*–*5*).

One of these factors is certainly the solvent–nonsolvent interdiffusion process.

Water is generally the nonsolvent used in membrane casting from DMF and NMP. We found a lack of accurate diffusion data for the DMF–H_2O and NMP–H_2O systems in the literature. So we thought it useful to present a set of isothermal diffusion data for these two systems through the entire composition range of solvent to nonsolvent. The data have been collected at 5 °C by using the Gouy interferometric technique. Density, refractivity, and viscosity data have also been measured at the same temperature.

Experimental Section

Material. Dimethylformamide and *N*-methylpyrrolidone, reagent grade (C. Erba Milan), were used without further purification. Solutions for all measurements were prepared by weighing both solute and solvent.

Diffusion runs were taken at 5 °C by using the Gouy interferometric technique (*6*). The experimental results are collected in Table I for both systems. Figure 1 is a graph of the diffusion coefficients drawn as a function of solute mole fraction for both systems.

Densities of solutions were measured with a A. Parr densitometer at 5 °C.

Viscosities were measured with an Ubbelhode viscometer (water flow time 180.7 s at 5 °C). Density and viscosity data are presented in Table II. Figures 2 and 3 show the graphs of density and viscosity.

Refractive indexes of solutions were computed by integration of the function $J_m/\Delta C_1 = f(C_1)$ (see Table I). The Gouy fringe number, J_m, is in fact a measure of the refractive index difference between top and bottom solutions, Δn:

$$J_m = (a/\lambda)\Delta n = 4.587 \times 10^4 \Delta n \tag{1}$$

where *a* is the diffusion cell thickness and λ the Hg green line wavelength (λ = 546.1 nm). The refractive index of water at 5 °C was computed from the data given in the International Critical Tables, Vol. 7, p 13: $n^{20}_{Hg} = 1.33447$ and $n^{5}_{Hg} = 1.33523$.

Table I. Diffusion Data

X_1[a]	ΔX_1[b]	J_m[c]	$10^5 D$[d]	ΔC_1[e]
		DMF–H_2O at 5 °C		
0			(0.625)	
0.0504	0.0051	91.95	0.558	0.214[f]
0.1515	0.0066	73.1	0.495	0.174[f]
0.2925	0.0233	122.2	0.477	0.355[f]
0.4032	0.0500	155.6	0.507	0.520[f]
0.5033	0.0512	100.8	0.565	0.396[f]
0.6127	0.0945	120.1	0.645	0.554[f]
0.7156	0.1092	92.6	0.771	0.500[f]
0.8120	0.0887	57.2	0.893	0.317[f]
0.8990	0.0808	39.9	1.035	0.241[f]
0.9602	0.0593	24.4	1.155	0.177[f]
1			(1.240)	
		NMP–H_2O at 5 °C		
0			(0.444)	
0.0300	0.0040	121.0	0.384	0.178[g]
0.0598	0.0023	64.9	0.343	0.083[g]
0.0984	0.0029	76.5	0.281	0.083[g]
0.1912	0.0052	64.2	0.238	0.093[g]
0.4974	0.0397	97.5	0.297	0.211[g]
0.5982	0.0607	102.3	0.324	0.241[g]
0.7001	0.0594	76.6	0.348	0.180[g]
0.8003	0.0608	59.1	0.415	0.149[g]
0.8988	0.0051	15.3	0.477	
0.9702	0.0399	25.5	0.562	0.071[g]
1			(0.600)	

[a] X_1 = mole fractions of DMF (or NMP). [b] ΔX_1 = mole fraction difference from upper and lower solution of each run. [c] J_m = number of Gouy fringes. [d] D = diffusion coefficient in $cm^2\ s^{-1}$. [e] ΔC_1 = concentration difference from upper and lower solution of each run. [f] Data were obtained from mole fractions by using the equation for density given in Table III. [g] Data were obtained from mole fractions by graphical interpolation of densities.

All experimental data have been fitted, where possible, with polynomial functions by the least-squares method. The polynomial coefficients are shown in Table III.

Density and viscosity data for the system NMP–water could not be fitted with any reasonable accuracy by the least-squares method. Graphical interpolation of densities was used to compute concentrations at intermediate mole fractions for this system.

Molar refractivity was obtained by using the equation

$$R_M = \frac{n^2 - 1}{n^2 + 2}(X_1 M_1 + X_2 M_2)/d \tag{2}$$

where X_1,M_1, X_2,M_2 are the mole fractions and molecular weights of solute and water, respectively.

The molar refractivity is almost a linear function of mole fraction for both systems, as seen in Figure 4. Table III gives the polynomial coefficients for R_M fitted both with a linear function and with a parabola. The parabolic function leads to a somehow smaller standard deviation for the R_M data, suggesting the presence of a small excess refractivity; however,

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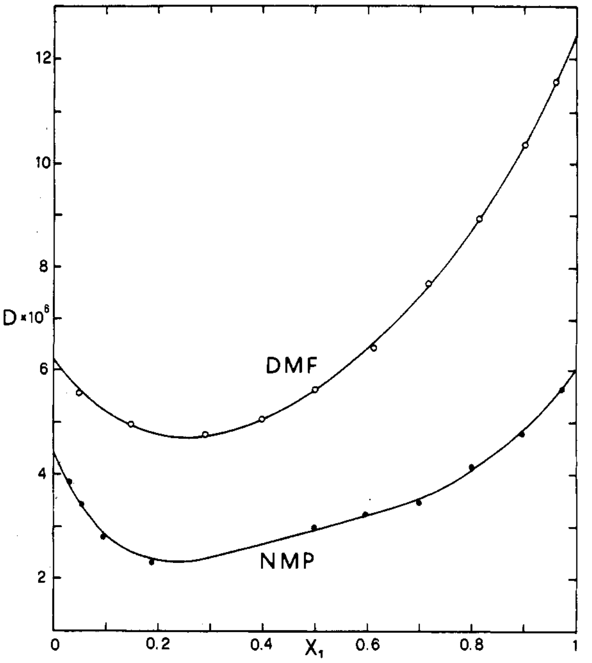

Figure 1. Diffusion coefficients (cm^2 s^{-1}) for the systems DMF–H_2O and NMP–H_2O at 5 °C as a function of component 1 mole fraction. Experimental points and curves computed with equation given in Table III.

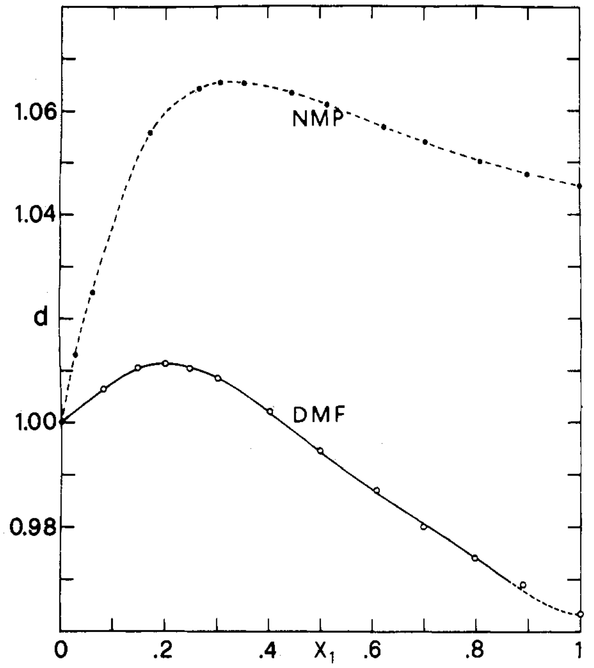

Figure 2. Density (g/mL) for the systems DMF–H_2O and NMP–H_2O at 5 °C as a function of component 1 mole fraction. Full line from equation of Table III.

such an excess is almost within the experimental error so we prefer not to speculate about it.

Discussion

A peculiar aspect of the diffusion coefficient trend for both systems is the presence of a minimum in the water mole fraction range of 0.7–0.75, corresponding to a X_2/X_1 ratio ~2–3 (see Figure 1).

A corresponding maximum is found in both the density and viscosity graphs (see Figures 2 and 3) (*7–10*). These maxima are interpreted as due to the presence of H-bond complexes between the organic molecules and water (*8*, *9*).

Table II. Density and Viscosity Data[a]

X_1[b]	d[c]	t[d]	C_1[e]	η/η_0[f]
DMF–H_2O at 5 °C				
0	0.999964	180.7	0	1.000
0.0814	1.00633	359.2	3.641	1.975
0.1495	1.01047		5.754	
0.2013	1.01138	566.0	6.995	3.097
0.2501	1.01058		7.952	
0.3021	1.00849	585.6	8.794	3.214
0.4022	1.00218	496.6	10.03	2.742
0.5005	0.99482	386.0	10.92	2.147
0.6095	0.98671	284.8	11.66	1.597
0.6988	0.98030	225.0	12.13	1.270
0.7982	0.97396	179.2	12.55	1.018
0.8897	0.96883	151.6	12.85	0.866
1	0.96324	128.8	13.18	0.740
NMP–H_2O at 5 °C				
0	0.999964	180.7	0	1.000
0.0331	1.01333	321.0	1.620	1.753
0.0615	1.02508	475.8	2.740	2.569
0.0997	*1.0382*	710.3	*3.965*	*3.787*
0.1754	1.05581	1226.5	5.744	6.428
0.2163	*1.0610*	1425.1	*6.453*	*7.432*
0.2568	1.06410	1499.4	7.034	7.798
0.3089	1.06542	1455.2	7.641	7.558
0.3564	1.06549	1330.8	8.092	6.908
0.4487	1.06339	1025.2	8.769	5.335
0.5148	1.06110	834.0	9.139	4.350
0.6232	1.05694	594.8	9.606	3.114
0.7020	1.05403	474.3	9.871	2.490
0.8080	1.05030	371.5	10.16	1.957
0.8993	1.04782		10.36	
1	1.04557	273.0	10.55	1.540

[a] Data in italics were computed by using graphical interpolation of density. [b] X_1 = mole fraction of DMF (or NMP). [c] d = density. [d] t = flow time in seconds. [e] C_1 = concentration in mol/L. [f] η/η_0 = viscosity relative to water (dt/d_0t_0).

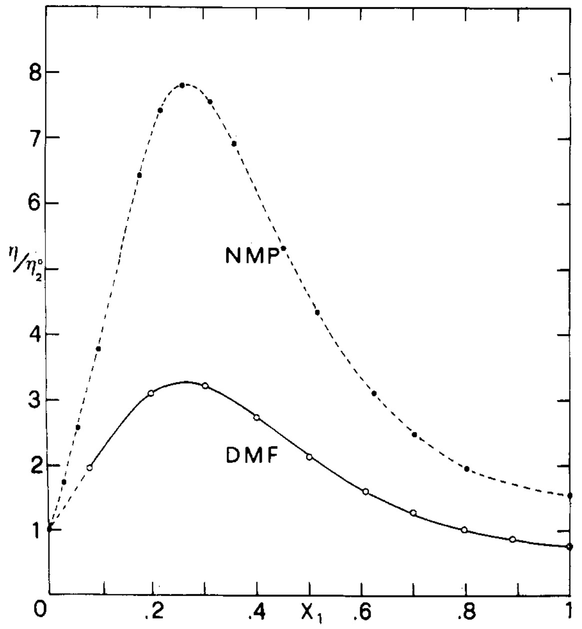

Figure 3. Relative viscosity (relative to water) for the systems DMF–H_2O and NMP–H_2O at 5 °C as a function of component 1 mole fraction. Full line from eq 3 of Table III.

Both DMF and NMP can bind two water molecules through their oxygen atoms, so a two- or three-dimensional H-bond network can grow.

Actually, it must be noted that, in spite of the presence of extrema in the density, viscosity, and diffusivity graphs, the molar refractivity is a very good linear function of mole fraction

Table III. Coefficients of the Equation

$$Z = A_0 + A_1 y + A_2 y^2 + \ldots + A_n y^n \pm \epsilon$$

Dimethylformamide (1)-Water (2) at 5 °C

Z	$10^5 D^a$	d	$J_m/\Delta C_1$	$n\mathrm{Hg}^b$	$R_M{}^c$	η/η_0	$R_M{}^c$
y	X_1	X_1	C_1	C_1	X_1	C_1	X_1
A_0	0.625	0.999964	422	1.33523	3.702	1.000	3.735
A_1	−1.345	0.07224	10.79	0.008722	16.213	0.7464	15.989
A_2	3.577	0.26014	−2.422	2.206×10^{-4}		−0.34230	0.227
A_3	−2.940	−2.63658		-2.214×10^{-5}		0.083982	
A_4	1.323	5.70976				-8.0945×10^{-3}	
A_5		−5.13396				2.5485×10^{-4}	
A_6		1.69185					
ϵ	0.0046	0.00035	18		0.031	0.011	0.024
			N-Methylpyrrolidone (1)-Water (2) at 5 °C				
A_0	0.444		287	1.33523	3.725		3.703
A_1	−2.333		343.6	0.006274	23.183		23.353
A_2	9.008		−62.78	0.003753			−0.178
A_3	−14.673		2.910	-4.571×10^{-4}			
A_4	11.026			1.589×10^{-5}			
A_5	−2.872						
ϵ	0.0055		33		0.027		0.023

[a] D = diffusion coefficient in $\mathrm{cm^2\ s^{-1}}$. [b] n_{Hg} = refractive index at the wavelength of Hg green light (546.1 nm). [c] R_M = molar refractivity (eq 2).

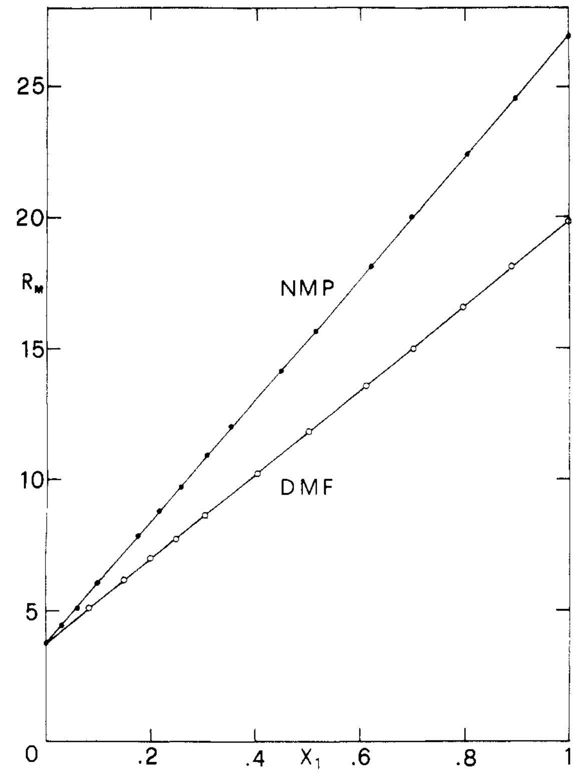

Figure 4. Molar refractivities (eq 2) for the systems DMF–H_2O and NMP–H_2O at 5 °C computed at the wavelength of Hg green line (546.1 nm).

for both systems (see Figure 4). This fact is an indication that no strong complexes are present in solution. So, the diffusion coefficient minimum and the corresponding, although not directly correlated, viscosity maximum are not due to an increasing dimension of the "statistical species" present in solution. Rather, they are due to the growth of a two-dimensional H-bond network connecting several molecules and decreasing, as a consequence, the local molecular mobility.

Finally, in connection with the membrane casting mechanism, we wish to point out that the density maximum at a water mole fraction of 0.7–0.75 may promote some convective motion inside the polymer solution during the coagulation process and may be in part responsible for the peculiar structure of asymmetric membranes.

Registry No. DMF, 68-12-2; NMP, 872-50-4.

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