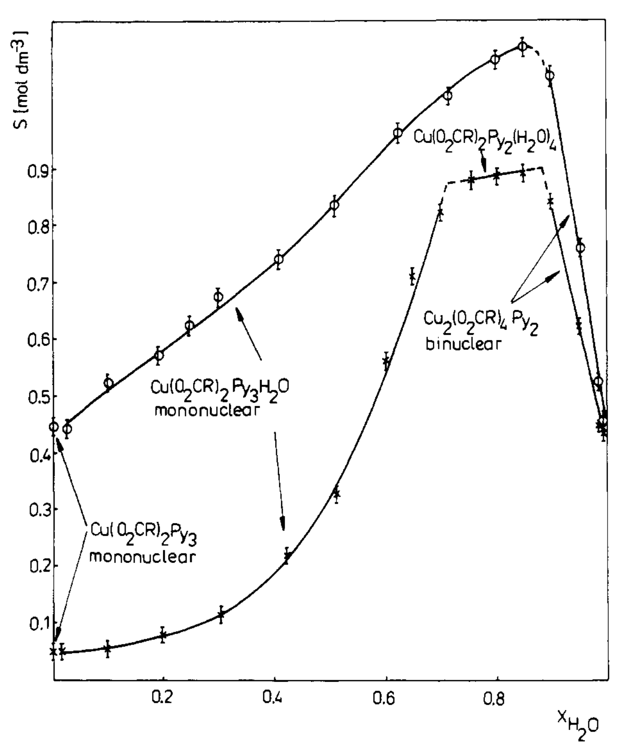

Figure 1. Solubility isotherms for $Cu(O_2CR)_2$ + pyridine + water systems, at 298.2 K: R = CH_3 (X); R = C_2H_5 (O). Solid phase in equilibrium with the saturated solutions indicated; *s* calculated per Cu atom.

= C_2H_5 and R = CH_3, respectively). At further dilution of the pyridine solutions with water, a gradual electrolytic dissociation and replacement of the pyridine molecules by water ligands occur. As could be expected, both processes are accompanied by an increase in solubility. For R = C_2H_5 the concentration of the saturated solutions increases up to $X_{H_2O} \simeq 0.9$, while for R = CH_3 there is a region of nearly constant solubility between $X_{H_2O} \simeq 0.7$ and 0.9. Above $X_{H_2O} \simeq 0.9$ the saturation curves of both systems drop very rapidly to the common value of $\simeq$0.45 mol dm^{-3} at $X_{H_2O} \simeq 1$. Now the solid phase becomes binuclear complex $Cu_2(O_2CR)_4Py_2$, retaining the pyridine molecules even at as low a pyridine content as X_{H_2O} = 0.99. The electronic spectra of the solutions saturated with the binuclear $Cu_2(O_2CR)_4Py_2$ correspond to mononuclear complexes only. The electronic spectra, solubilities, and conductivities of the two systems (R = CH_3 and C_2H_5) at pyridine concentrations approaching X_{H_2O} = 1 are very similar to each other, which suggests that the additional CH_2 group in the carboxylic ligand does not appreciably influence the solute-water interactions; at X_{H_2O} = 0.98 the mean molar absorptivity coefficients are 65 ± 3 at λ_{max} = 610 nm, and the conductivities at X_{H_2O} = 0.8 are 24 and 21 cm^2 Ω^{-1} equiv^{-1}, respectively. However this is not the case with the solute-nonpolar solvent interactions because the solubilities of two binuclear $Cu_2(O_2CR)_4Py_2$ in *n*-hexane and cyclohexane differ noticeably: they are 10^{-3} and 2×10^{-3} mol dm^{-3} for R = C_2H_5 and of the order of 10^{-4} mol dm^{-3} for R = CH_3. This difference is particularly great for aromatic solvents: 0.95 and 0.90 mol dm^{-3} for R = C_2H_5 in benzene and chlorobenzene and about 2×10^{-3} mol dm^3 in the two solvents for R = CH_3. Our attempts to obtain reliable (errors below 5%) solubility isotherms for analogous $Cu(O_2CR)_2$ complexes with longer hydrophobic chains (R > C_2H_5) were unsuccessful because of supersaturation effects. These effects increase rapidly with the length of R and make it difficult to obtain a real thermodynamic equilibrium between solid $Cu(O_2CR)_2Py_3H_2O$ and its saturated solutions. The results of the measurements for R > C_2H_5 are too poor to be a basis for any reliable interpretation.

Registry No. $Cu(O_2CCH_3)_2$, 142-71-2; $Cu(O_2CC_2H_5)_2$, 3112-74-1; pyridine, 110-86-1; $Cu(O_2CCH_3)_2Py_2$, 82872-28-4; $Cu(O_2CC_2H_5)_2Py_2$, 105033-58-7.

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The *N*,*N*-Dimethylformamide/Ethane-1,2-diol Solvent System. Density, Viscosity, and Excess Molar Volume at Various Temperatures

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Density (ρ), kinematic viscosity (ν), and absolute viscosity (η) are presented for mixtures of ethane-1,2-diol and *N*,*N*-dimethylformamide from −10 to +80 °C. The above properties were fitted by empirical equations stating their dependence on temperature and mole fraction of the mixture. Furthermore, some considerations regarding the meaning of the obtained adjustment parameters are made. The excess functions, such as molar volumes V^E, have been derived. The trends of V^E data vs mole fraction of the mixtures have exhibited markedly negative deviations from ideality, indicating extensive molecular interactions between the components of the binary solvent system.

Introduction

Among the most characterizing intensive chemical-physical properties of the solvent systems, density (ρ) and viscosity, either kinematic (ν) or dynamic (η), represent some of the common thermomechanical parameters that are in general useful in order to study and interpret the medium effects on the transport phenomena, on the electrolyte behavior, and on any other reaction mechanism that takes place in solution. In particular, in the field of conductometric studies, it's impossible to approach any problem without the preliminary knowledge of the above-mentioned solvent properties. In fact, if one thinks about the phenomena of electrolyte diffusion and electropho-

Table I. Experimental Density Values (g cm^{-3}) for the *N*,*N*-Dimethylformamide/Ethane-1,2-diol Solvent System

	x_1							
t, °C	1.0000	0.8848	0.7734	0.5609	0.3623	0.1758	0.0864	0.0000
-10	$0.981\,48_5$	$0.998\,20_2$	$1.013\,12_1$	$1.045\,86_1$	$1.080\,51_4$	$1.110\,46_8$	$1.123\,32_5$	$1.133\,63_4$
-5	$0.976\,03_8$	$0.992\,91_0$	$1.008\,09_3$	$1.041\,25_4$	$1.075\,30_2$	$1.105\,90_3$	$1.119\,61_1$	$1.130\,45_2$
0	$0.970\,70_4$	$0.987\,71_4$	$1.003\,19_1$	$1.036\,77_8$	$1.070\,58_4$	$1.101\,64_2$	$1.115\,87_4$	$1.127\,06_9$
5	$0.965\,52_5$	$0.982\,67_6$	$0.998\,67_5$	$1.032\,24_2$	$1.065\,81_7$	$1.097\,47_0$	$1.112\,28_3$	$1.123\,66_4$
10	$0.960\,45_6$	$0.977\,73_5$	$0.993\,72_5$	$1.027\,95_5$	$1.061\,42_4$	$1.093\,44_9$	$1.108\,68_0$	$1.120\,29_6$
15	$0.955\,30_2$	$0.927\,87_2$	$0.989\,10_4$	$1.023\,66_9$	$1.057\,03_3$	$1.089\,50_4$	$1.105\,00_5$	$1.116\,90_6$
20	$0.950\,45_3$	$0.968\,11_1$	$0.984\,55_7$	$1.019\,48_6$	$1.052\,96_5$	$1.085\,64_0$	$1.101\,42_2$	$1.113\,44_0$
25	$0.945\,59_7$	$0.963\,37_2$	$0.980\,00_9$	$1.015\,33_7$	$1.048\,82_8$	$1.081\,89_5$	$1.097\,86_7$	$1.109\,91_3$
30	$0.940\,69_1$	$0.958\,71_0$	$0.975\,60_2$	$1.011\,24_1$	$1.044\,94_8$	$1.078\,15_3$	$1.094\,21_6$	$1.106\,51_2$
35	$0.935\,81_4$	$0.954\,03_5$	$0.971\,15_6$	$1.007\,10_7$	$1.041\,00_6$	$1.074\,54_6$	$1.090\,67_3$	$1.103\,08_9$
40	$0.931\,03_0$	$0.949\,37_5$	$0.966\,75_5$	$1.003\,17_4$	$1.037\,27_5$	$1.070\,97_6$	$1.087\,10_8$	$1.099\,74_7$
45	$0.926\,28_2$	$0.944\,61_5$	$0.962\,33_0$	$0.999\,08_3$	$1.033\,46_0$	$1.067\,35_1$	$1.083\,55_9$	$1.096\,31_2$
50	$0.921\,54_8$	$0.940\,03_0$	$0.957\,91_1$	$0.995\,00_9$	$1.029\,68_1$	$1.063\,78_0$	$1.079\,82_2$	$1.092\,94_6$
55	$0.916\,71_6$	$0.935\,30_5$	$0.953\,40_4$	$0.990\,94_5$	$1.025\,85_6$	$1.060\,13_3$	$1.076\,24_5$	$1.089\,47_1$
60	$0.911\,97_1$	$0.930\,52_0$	$0.949\,09_7$	$0.986\,72_2$	$1.022\,07_8$	$1.056\,57_4$	$1.072\,65_4$	$1.086\,01_1$
65	$0.907\,02_5$	$0.925\,65_9$	$0.944\,47_1$	$0.982\,65_1$	$1.018\,14_5$	$1.052\,95_2$	$1.068\,90_6$	$1.082\,63_4$
70	$0.902\,25_8$	$0.920\,70_5$	$0.939\,82_6$	$0.978\,33_9$	$1.014\,15_3$	$1.049\,24_4$	$1.065\,33_2$	$1.079\,00_3$
75	$0.897\,21_9$	$0.915\,64_5$	$0.935\,12_8$	$0.974\,01_3$	$1.010\,06_0$	$1.045\,44_1$	$1.061\,78_5$	$1.075\,36_9$
80	$0.892\,24_7$	$0.910\,46_3$	$0.930\,38_1$	$0.969\,68_6$	$1.005\,89_3$	$1.041\,62_5$	$1.058\,14_6$	$1.071\,69_9$

retic migration (which are affected by the thermokinetic delay effects related to the viscokinetic properties of the solutions) (*1*), it is possible to understand the importance of the availability of the solvent extrathermodynamic parameters, such as ρ, ν, and η. As it is well-known, these properties are functionally dependent on temperature and, at least for binary mixtures, on composition of the solvent systems. The changes vs mole fraction of the above-cited parameters often provide more and more detailed evidence about the structural character of the systems themselves. The magnitude of the cited thermomechanical parameters of a liquid system is determined by the molecular packing degree and by the nature of the mutual orientation of the individual units that may constrain the medium to assume a significant liquid structure (SLS) (*2*); on the basis of these considerations, measurements of those properties should be a powerful tool to investigate the intermolecular forces and the local order of which these forces are responsible in a fluid mixture.

Although many tabulated values of the above thermomechanical properties are generally available for the pure solvents, literature data relative to various binary solvent mixtures are often either incomplete, or reported as graphs only, or quite lacking.

Very few studies are reported about amido-alcoholic solvent systems, and this fact has encouraged us to realize a series of systematic investigations on the solvent properties of these mixtures. For these aims, we have chosen, in the present case, *N*,*N*-dimethylformamide (DMF) and dihydroxyethane (DHE) as pure solvents and as components of binary mixtures, investigated in the −10 to +80 °C temperature range and in the whole composition range, expressed by x_{DMF} ($0 \le x_{\mathrm{DMF}} \le 1$).

Even if DMF has been already investigated (*3*–*8*), nowadays it's one of the most important solvent in analytical chemistry and for practical purposes, being a very good aprotic protophilic medium for a lot of organic and inorganic substances. These characteristics are probably due to its molecular properties, such as the high tendency to provide hydrogen bonds via acceptor sites of the amido group $-\mathrm{C(O)N}{=}$.

On the other hand, DHE is certainly one of the most interesting polyalcohols, being also the simplest homologue of the diol series, widely utilized in industrial applications (*9*) as a thermoregulating fluid and in chemical laboratories for its unusual viscosity and solvating properties (*10*–*12*), these last related to its character of protophilic solvent. Thus, further significant studies should be feasible on nonthermodynamic properties of binary (or higher) containing DHE solvent mixtures; the above properties are, in fact, tunable upon adding a more or less viscous dipolar cosolvent.

Experimental Section

Materials. *N*,*N*-Dimethylformamide and ethane-1,2-diol (both containing <0.10% g of water/g of solution found by Karl-Fischer titration) were Carlo Erba high purity grade. The *N*,*N*-dimethylformamide was purified by passage on a neutral alumina column before use. The mixtures were gravimetrically prepared on a Mettler analytical balance just before their use, operating in a dry nitrogen atmosphere at 26 °C. The probable error in the DMF mole fraction (x_1) is estimated to be less than 1.5×10^{-4}.

Apparatus. The densities were determined with a digital density meter Anton Paar Model DMA 60 equipped with a density measuring cell Model DMA 602, with a sensitivity up to 0.000 001 g cm^{-3}. For the measurements, we have selected the period of 10 000 oscillation cycles, keeping 30 readouts for every sample at each temperature.

Viscosity measurements were performed by using a Schott-Geräte AVS 400 viscosity measuring system, equipped with a series of Ubbelhode viscometers, covering the $0.6 \le \nu \le 3 \times 10^{-4}$ m^2 s^{-1} range. In all the determinations the kinetic energy correction has been taken into account according to Hagenbach in order to evaluate the absolute viscosity η. The temperature control was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C.

In all the cases the experiments were generally performed at least in five replicates for each composition and at each temperature, and the results were averaged. The overall experimental standard deviation was approximately equal to 1.6×10^{-6} for ρ and 1.4×10^{-3} for ν, respectively. The estimated accuracy (95% confidence interval) was $\pm 3 \times 10^{-6}$ for ρ and $\pm 4 \times 10^{-3}$ for ν.

Karl Fischer titrations were performed with an automatic titration system (Crison Model KF431) equipped with a digital buret (Crison Model 738).

Results and Discussion

Experimental values for density (ρ) and kinematic (ν) and absolute viscosities (η) were collected for the two pure components and for six mixtures of them in the whole composition range $0 \le x_{\mathrm{DMF}} \le 1$, working in the −10 to +80 °C temperature range.

1. Density and Excess Molar Volumes. The experimental density values, Table I, were fitted vs the variable quantity temperature by the polynomial equation

$$\frac{1}{\rho}(t) = \sum_{k=0}^{m} \frac{1}{\rho_k} t^k \qquad t(^\circ\mathrm{C}) \qquad (1)$$

Table II. ρ_i^{-1} Coefficients of Equation 2 for the *N*,*N*-Dimethylformamide/Ethane-1,2-diol Solvent System

t, °C	ρ_0^{-1}	$\rho_1^{-1} \times 10$	$\rho_2^{-1} \times 10^2$	$\rho_3^{-1} \times 10^3$	$\rho_4^{-1} \times 10^3$	$\sigma(\rho) \times 10^4$
-10	1.018659	-1.43673	3.09808	-10.2498	78.8208	6.09
-5	1.024393	-1.48227	3.34991	-9.61563	71.1531	4.52
0	1.030057	-1.52048	3.28794	-8.83137	64.6729	3.93
5	1.035657	-1.59067	4.89366	-10.5851	70.1766	3.13
10	1.041120	-1.60592	4.08896	-9.07480	61.8040	5.92
15	1.046755	-1.66167	4.79903	-9.53092	61.8818	4.92
20	1.052110	-1.68739	4.44989	-8.74234	57.4572	5.41
25	1.057534	-1.72181	4.55909	-8.74429	57.2166	6.18
30	1.063049	-1.76346	4.56772	-8.28094	53.9288	5.99
35	1.068599	-1.80754	4.93494	-8.62088	55.3089	6.06
40	1.074095	-1.83184	4.13066	-7.05638	47.3996	6.04
45	1.079625	-1.85134	3.37397	-5.78432	41.5030	5.94
50	1.085159	-1.87574	2.77644	-4.64513	35.8505	5.28
55	1.090884	-1.90139	2.13562	-3.48420	30.3993	5.47
60	1.096601	-1.93230	1.92419	-3.11581	29.1429	4.66
65	1.102586	-1.95157	0.711334	-0.925526	18.2022	4.90
70	1.108452	-1.95634	-0.402234	0.473242	13.0348	5.50
75	1.114721	-1.98641	-0.852482	1.19840	10.1000	6.53
80	1.120998	-1.99572	-2.17989	3.16416	1.49401	8.12

Table III. Coefficients ρ_{kl}^{-1} of Equation 3 for the *N*,*N*-Dimethylformamide/Ethane-1,2-diol Solvent System

ρ_{kl}^{-1}	coefficient value	ρ_{kl}^{-1}	coefficient value
ρ_{00}^{-1}	1.060973	ρ_{12}^{-1}	1.70273×10^{-3}
ρ_{01}^{-1}	-0.313556	ρ_{22}^{-1}	-1.53296×10^{-5}
ρ_{02}^{-1}	8.76020×10^{-2}	ρ_{32}^{-1}	-5.39986×10^{-7}
ρ_{03}^{-1}	-0.167449	ρ_{42}^{-1}	3.33609×10^{-9}
ρ_{04}^{-1}	0.119632	ρ_{13}^{-1}	1.23048×10^{-4}
ρ_{10}^{-1}	2.31357×10^{-3}	ρ_{23}^{-1}	-2.26218×10^{-5}
ρ_{20}^{-1}	1.15876×10^{-6}	ρ_{33}^{-1}	1.54140×10^{-5}
ρ_{30}^{-1}	2.41559×10^{-8}	ρ_{43}^{-1}	-9.76877×10^{-9}
ρ_{40}^{-1}	1.36583×10^{-10}	ρ_{14}^{-1}	-1.07718×10^{-3}
ρ_{11}^{-1}	-2.15335×10^{-3}	ρ_{24}^{-1}	3.66767×10^{-5}
ρ_{21}^{-1}	5.28824×10^{-6}	ρ_{34}^{-1}	-1.07461×10^{-6}
ρ_{31}^{-1}	1.20127×10^{-8}	ρ_{44}^{-1}	6.56791×10^{-9}
ρ_{41}^{-1}	7.55059×10^{-12}		

$\sigma(\rho) = 0.0007$

for each binary solvent system by the least-squares method. On the basis of a careful examination of the results obtained by using equations of different degree m, it was noted that the best correlation was obtained when $m = 4$. The rational eq 1 reproduces the experimental values better than the nonrational one of the type $\rho(t) = \sum_k \rho_k t^k$. In order to take into account the dependence of ρ on the composition of the binary mixtures, the polynomial equation

$$\frac{1}{\rho}(x_1) = \sum_{i=0}^{4} \frac{1}{\rho_i} x_1^{\,i} \tag{2}$$

was used to fit the experimental data at each temperature. Table II summarizes the ρ_i coefficients of eq 2 and the relative standard deviations (σ) at each investigated temperature.

These two equations (1 and 2) were simply combined in order to propose an empirical approach to solving the problem of a single function $\rho = \rho(t,x_1)$:

$$\frac{1}{\rho}(t,x_1) = \left[\frac{1}{\rho}(t)\,\frac{1}{\rho}(x_1)\right]^{1/2} \tag{3}$$

where $(1/\rho)(t)$ and $(1/\rho)(x_1)$ are eqs 1 and 2, respectively. The above equation, written in its expanded form, is composed of 25 terms that have been evaluated by fitting the set of experimental density values of Table I with the multilinear regression package TSP (*13*). These coefficients are summarized in Table III, together with the standard deviations (σ), and we may suppose that these differences should not be exceeded over all the points of the surface $\rho = \rho(t,x_1)$.

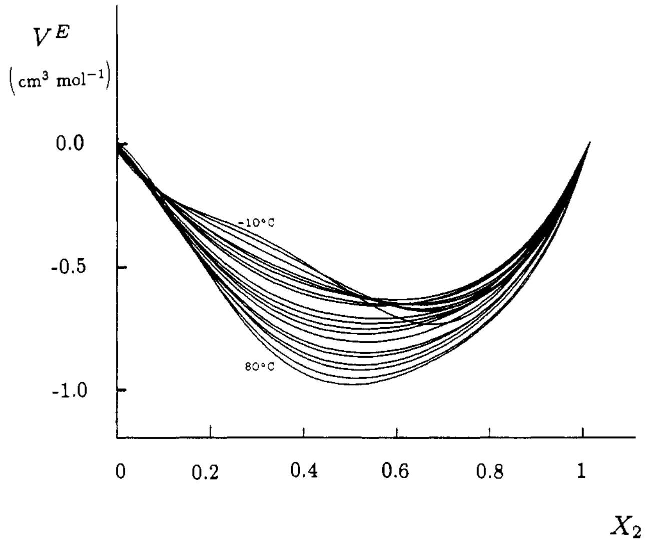

Figure 1. Excess molar volume V^E (cm³ mol⁻¹) curves for the *N*,*N*-dimethylformamide/ethane-1,2-diol solvent system at different temperatures.

The density values were converted into excess molar volumes V^E, assuming ideal mole fraction additivity of the molar volumes V_i. The equation

$$V^E = \frac{\sum_{i=1}^{2} x_i M_i}{\rho} - \sum_{i=1}^{2} x_i V_i \tag{4}$$

was used to evaluate the V^E quantity for each isothermal set of data, where M_i represents the molecular weight of the ith component. The values calculated by eq 4 have been fitted by a smoothing equation of the type

$$V^E = x_1 x_2 \sum_{k=0}^{3} a_k (x_1 - x_2)^k \tag{5}$$

where a_k are the adjustment coefficients.

Figure 1 shows the trend of excess volumes of mixing DMF and DHE ($V_1/V_2 = 1.38$ at 25 °C) at various temperatures; as it is particularly evident from the graph, the system exhibits negative deviations from ideality at all the investigated temperatures.

The trend of the curves is quite interesting, showing a continuous deformation with the temperature. At the lowest temperatures, the minimum of the V^E function is centered at $x_2 \simeq 0.7$ (molar ratio DMF:DHE $\simeq$ 1:2). By increasing the temper-

Table IV. Experimental Values of Kinematic Viscosity, ν (cS), and Ratio of Molecular Radii for the *N*,*N*-Dimethylformamide/Ethane-1,2-diol Solvent System at Various Temperatures

t, °C	x_1								r_2/r_1[a]
	1.0000	0.8848	0.7734	0.5609	0.3623	0.1758	0.0864	0.0000	
−10	1.397	2.072	3.151	7.632	19.02	45.78	67.40	98.91	0.994
−5	1.289	1.876	2.791	6.428	15.10	34.41	49.97	71.08	0.995
0	1.192	1.705	2.494	5.465	12.13	26.35	37.53	52.42	0.996
5	1.108	1.561	2.238	4.696	9.995	20.69	28.96	39.54	0.997
10	1.034	1.435	2.024	4.051	8.333	16.51	22.66	30.44	0.998
15	0.9693	1.326	1.842	3.558	7.017	13.43	18.06	23.89	0.999
20	0.9121	1.230	1.686	3.168	5.962	10.98	14.63	19.04	1.000
25	0.8605	1.147	1.549	2.818	5.130	9.170	12.06	15.44	1.000
30	0.8130	1.071	1.427	2.523	4.440	7.652	9.974	12.67	1.001
35	0.7712	1.003	1.323	2.273	3.885	6.536	8.374	10.49	1.002
40	0.7337	0.9428	1.226	2.058	3.424	5.601	7.107	8.806	1.002
45	0.6975	0.8907	1.139	1.875	3.037	4.845	6.097	7.481	1.003
50	0.6650	0.8416	1.067	1.720	2.709	4.237	5.252	6.434	1.004
55	0.6374	0.7971	0.9992	1.576	2.432	3.724	4.592	5.532	1.004
60	0.6102	0.7570	0.9401	1.452	2.197	3.287	4.014	4.777	1.005
65	0.5867	0.7210	0.8880	1.343	0.993	2.936	3.529	4.192	1.005
70	0.5635	0.6863	0.8380	1.247	1.818	2.632	3.134	3.688	1.006
75	0.5401	0.6560	0.7939	1.162	1.666	2.367	2.804	3.279	1.006
80	0.5210	0.6274	0.7553	1.088	1.537	2.159	2.544	2.910	1.007

[a] $r_2/r_1 = (M_2\rho_1/M_1\rho_2)^{1/3}$.

ature, starting from 15 °C up to the higher values, the minimum shifts to $x_2 \simeq 0.5$ (DMF:DHE = 1:1) and becomes more and more deep as the temperature increases. These observations could be very useful in order to try to verify the possibility of a solvent–cosolvent complex formation and to determine its hypothetical molar ratio composition. Indeed, the maximum degree of molecular packing is found in correspondence of a minimum value of V^E in the 1:1 and 1:2 DMF:DHE molar composition range.

By deriving eq 5 with respect to x_1 and x_2 (*7*), one obtains the relative partial molar volumes of the two components for each binary composition and temperature.

2. Kinematic Viscosity. Table IV reports the experimental values of the kinematic viscosities (ν) experimentally determined in the temperature range $-10 \leq t \leq 80$ °C with thermal scanning of 5 °C. The results of these measurements have been used to test the common empirical approach of McAllister (*14*), in order to try to predict the viscosities of the binary liquid mixtures not directly detected. In this treatment the author took into account the specific interactions between contiguous fluid layers of molecules that move of stationary motion. In this representation the molecules which have an activation energy that overcomes the potential barrier due to the velocity gradient may jump between adjacent layers, changing their individual motion conditions. For a binary mixture, McAllister derived the following cubic semiempirical equation for the kinematic viscosity:

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 + R_0 \quad (6)$$

where

$$R_0 = -[\ln (x_1 + x_2M_2/M_1)] + 3x_1^2x_2 \ln (2/3 + M_2/3M_1) + 3x_1x_2^2 \ln (1/3 + 2M_2/3M_1) + x_2^3 \ln (M_2/M_1) \quad (7)$$

Table V. Values of Adjustment Parameters and Standard Deviations $\sigma(\nu)$ for the McAllister Equation at Various Temperatures

t, °C	ν_{12}	ν_{21}	$\sigma(\nu) \times 10^3$
−10	3.954	23.59	2.6
−5	3.483	18.52	2.2
0	3.123	14.51	2.1
5	2.781	11.85	2.0
10	2.492	9.741	2.4
15	2.259	8.139	2.4
20	2.076	6.820	1.6
25	1.895	5.828	1.9
30	1.753	4.935	1.3
35	1.610	4.316	1.5
40	1.482	3.780	1.2
45	1.379	3.319	1.2
50	1.296	2.917	0.79
55	1.196	2.634	1.3
60	1.119	2.376	1.3
65	1.052	2.139	0.81
70	0.9843	1.954	0.85
75	0.9362	1.772	0.76
80	0.8741	1.670	2.0

In eq 6, ν_1 and ν_2 refer to the kinematic viscosities of the pure components having mole fractions x_1 and x_2, while in eq 7 M_1 and M_2 refer to their molecular weights. Equation 6 contains also the crossing terms ν_{12} and ν_{21} that are two adjustable parameters of the fit, characteristic of each binary system 1/2 and determinable by a least-squares method. The term R_0 can be calculated if one knows the binary composition of the solvent system and the molecular weight of the components. It is noteworthy that eq 6 may be used only if the ratio of the molecular radii of the two components in the mixture is smaller than 1.5. The choice and the use of this cubic equation is justified in all the investigated temperature range since, for each temperature value, the ratio of the radii is smaller than the imposed limit, as shown in Table IV. In Table V are summarized the adjustment parameters ν_{12}, ν_{21}, and the $\sigma(\nu)$ values for each isothermal experimental data fit. By analyzing a reasonably large set of these parameters, we can consider an assessment of their meaning. Figure 2 reports, in a graphic form, the obtained crossing terms ν_{12} and ν_{21} vs temperature and the curve represents a fit of the type

$$\nu_{ij} = C_0e^{C_1/T} \qquad \text{for } (i \neq j) = 1, 2 \qquad (8)$$

having, in its linear logarithmic form, a correlation coefficient $r = 0.999$ for ν_{12} and $r = 0.994$ for ν_{21}. Now, interpreting these parameters in terms of quantities related to the specific interactions between unlike molecules, it is possible to represent them in an oversimplified picture of the type {1–1–2}, {2–1–2} for ν_{12}, and {1–2–1}, {1–2–2} for ν_{21}, where the central molecule is involved in a hypothetical ternary aggregate. Obviously, the relative intensities of these interactions between a central unit and the surrounding molecules, or other aggregates, in any space direction are different for different neighboring arrangements. It is however reasonable to think that the nature of

Table VI. Experimental Viscosity Values (cP) for the *N,N*-Dimethylformamide/Ethane-1,2-diol Solvent System at Various Temperatures

	x_1							
t, °C	1.0000	0.8848	0.7734	0.5609	0.3623	0.1758	0.0864	0.0000
-10	1.371	2.069	3.192	7.983	20.55	50.84	75.70	112.2
-5	1.258	1.863	2.813	6.693	16.24	38.06	55.94	80.36
0	1.157	1.684	2.502	5.666	12.99	29.03	41.88	59.08
5	1.070	1.534	2.234	4.848	10.65	22.70	32.21	44.43
10	0.9933	1.403	2.011	4.164	8.844	18.05	25.12	34.11
15	0.9260	1.290	1.822	3.643	7.418	14.64	19.96	26.68
20	0.8669	1.191	1.660	3.230	6.277	11.93	16.12	21.20
25	0.8136	1.105	1.518	2.852	5.381	9.921	13.24	17.14
30	0.7647	1.027	1.392	2.551	4.639	8.250	10.91	14.01
35	0.7217	0.9570	1.285	2.289	4.044	7.023	9.133	11.58
40	0.6831	0.8951	1.185	2.064	3.551	5.998	7.725	9.684
45	0.6460	0.8415	1.096	1.873	3.139	5.171	6.606	8.203
50	0.6128	0.7911	1.022	1.711	2.789	4.507	5.671	7.032
55	0.5843	0.7455	0.9527	1.562	2.495	3.949	4.942	6.027
60	0.5565	0.7044	0.8921	1.433	2.245	3.473	4.305	5.188
65	0.5321	0.6674	0.8386	1.320	2.029	3.091	3.772	4.538
70	0.5084	0.6319	0.7876	1.220	1.843	2.761	3.339	3.978
75	0.4846	0.6007	0.7424	1.132	1.683	2.475	2.977	3.525
80	0.4602	0.5725	0.7044	1.055	1.546	2.249	2.692	3.117

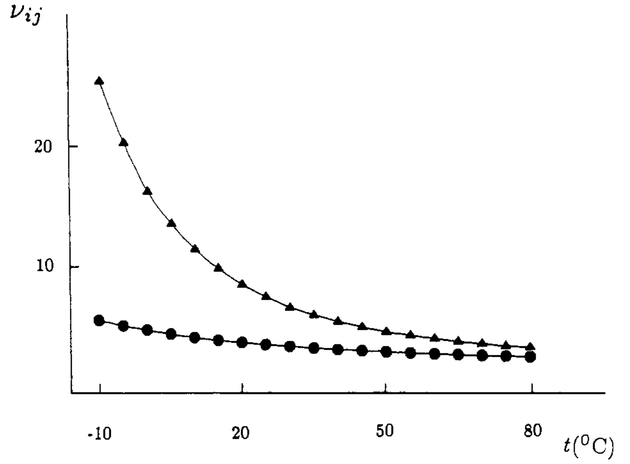

Figure 2. McAllister's equation ν_{12} (●) and ν_{21} (▲) parameters vs temperature.

these specific interactions is about the same either for the 1 or 2 central species. On the basis of these considerations, the crossing terms in the fit equations should have nearly the same statistical weight and consequently, for any fixed temperature, very little different values. For this binary solvent system, McAllister's equation provides adjustment parameters very different in magnitude, especially at the lowest temperatures, while, with an increase in the temperature, the relative differences δ_r evaluated as follows

$$\delta_r = \frac{|\nu_{12} - \nu_{21}|}{|(\nu_{12} - \nu_{21})_{\max}|} \tag{9}$$

are largely reduced. Therefore, McAllister's treatment appears to be more effective to describe this system at the highest temperatures, while probably it is less efficacious at the lowest ones. Equation 6 provides a set of calculated ν values with an average uncertainty of ±0.0031 cS.

3. Absolute Viscosity. The absolute viscosity values, Table VI, were obtained from the kinematic ones by the equation

$$\eta = \nu\rho \tag{10}$$

An interesting empirical treatment for the viscosity data fit vs temperature was provided by Williams-Landel-Ferry-Doolittle (*15*), and the three adjustment parameters equation WLFD

$$\ln \eta = \frac{A_0}{T - T_0} + A_1 \tag{11}$$

was used in order to check the validity of this theory for this binary solvent system. The results are reported in Table VII, and the reproducibility of the experimental η values is demonstrated by the average percent deviations $(\Delta\%)_{\text{av}}$, very close to the experimental standard deviation.

It is obvious from Figure 3 that the viscosity data are linear for this function over a wide temperature range, even if a sudden increase in this property at lower temperatures in the DHE-rich region is observed. In fact, the greatest values of η are due to the highly polymerized structure of the DHE solvent, in particular at the lower temperatures. This structure is easily depolymerized either by increasing the temperature of the system and/or by forming heteropolymers as a consequence of the increase in the cosolvent molar fraction. On the basis

Table VII. Adjustment Parameters and Average Percent Deviations $(\Delta\%)_{\text{av}}$, for the WLFD Treatment, Equation 11

x_1	A_0	A_1	T_0	$(\Delta\%)_{\text{av}}$
1.0000	648.28	-3.0603	71.00	0.16
0.8848	696.90	-3.1310	82.40	0.13
0.7734	771.10	-3.2746	89.21	0.12
0.5609	765.99	-3.2003	117.92	0.27
0.3623	832.53	-3.3314	132.07	0.12
0.1758	905.98	-3.4520	140.38	0.18
0.0864	993.93	-3.6477	138.54	0.21
0.0000	1034.3	-3.7239	140.61	0.22

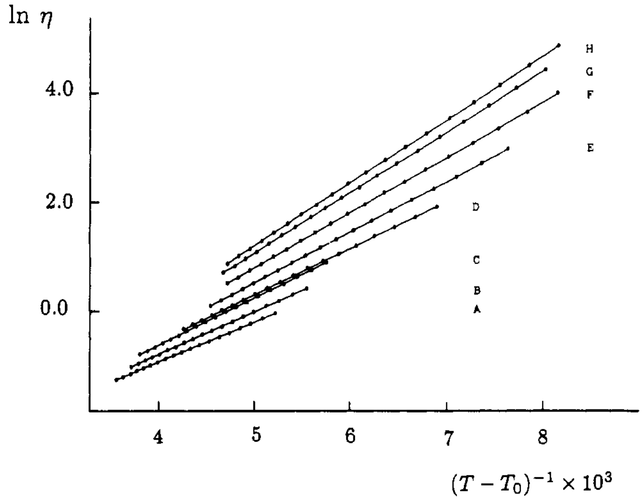

Figure 3. ln η of the *N,N*-dimethylformamide/ethane-1,2-diol solvent system as a function of $(T - T_0)^{-1}$.

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of these considerations, for these binary mixtures we may suggest the onset of a pseudo-glassy state in the region of the low temperatures and high molar fraction of DHE component. Therefore, expression 11 is not only an excellent three-adjustment-parameters fit equation of the experimental data but also may provide a model for low-temperature behavior as well.

The empirical meaning of the T_0 parameter is the temperature below which the system viscosity becomes infinite and, after WLFD theory, defines the temperature field below which the free intermolecular volume is not available for viscous flow. However, we have doubts about it. The melting points of the two pure components are -60.5 and -11.5 °C for DMF and DHE, respectively (*16*). Already at these temperatures one might observe a dramatic increase of the viscosity that becomes infinite in the solid state. Hence, the condition $\eta \simeq \infty$ may be achieved for temperature values higher than those reported in Table VII.

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Glossary

A_0,A_1	coefficients in eq 11
C_0,C_1	coefficients in eq 8
M_i	molecular weight of the *i*th component
T_0	coefficient in eq 11
T	absolute temperature
V_i	molar volume (cm^3 mol^{-1}) of the *i*th component
V^E	excess molar volume (cm^3 mol^{-1})
a_k	coefficients of eq 5
t	Celsius temperature
x_i	mole fraction of the *i*th component

Greek Letters

δ_r	relative differences in eq 9
η	absolute viscosity (cP)
ν	kinematic viscosity (cS)
ν_1,ν_2	kinematic viscosities of pure components
ν_{ij}	McAllister parameters in eq 6
ρ	density (g cm^{-3})
ρ_1,ρ_2	densities of the pure components
$\rho_k{}^{-1}$	coefficients in eq 1
$\rho_i{}^{-1}$	coefficients in eq 2
$\rho_{ki}{}^{-1}$	coefficients in eq 3
σ	standard deviation

Registry No. DMF, 68-12-2; ethane-1,2-diol, 107-21-1.

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The *N*,*N*-Dimethylformamide + Ethane-1,2-diol Solvent System. Dielectric Constant, Refractive Index, and Related Properties at Various Temperatures

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Dielectric constant (ϵ) and refractive indexes (n) were measured for pure *N*,*N*-dimethylformamide, ethane-1,2-diol, and their six mixtures over the entire composition range and, where possible, at nineteen selected temperatures ranging between -10 and +80 °C. The above properties were fitted by empirical equations stating their dependence on temperature (T) and mole fraction (x_1) of the mixture. The refractive indexes of the binary mixtures were used to test the validity of mixing rules at different temperatures.

Introduction

As a part of our studies on binary liquid mixtures and, in particular, on the influence of these solvents on the acid-base equilibria that take place (*1-3*), we report static dielectric constant (ϵ), refractive index (n), and some derived properties of *N*,*N*-dimethylformamide (DMF), ethane-1,2-diol (DHE), and six mixtures over, where possible, a temperature range from -10 to +80 °C.

The *N*,*N*-dimethylformamide is a very good aprotic protophilic solvent, with a high dipole moment (μ = 3.28 D at 25 °C) (*4*) and a medium dielectric constant (ϵ = 37.52 at 25 °C) in the general classification of Charlot (*5*).

The ethane-1,2-diol was chosen for its unusual solvent properties, such as the protic protophylic character, the high autoprotolysis constant (pK_{autoprot} = 15.8 at 25 °C) (*6*), and the high dipole moment (μ = 2.28 D), and, in particular, because it is almost isodielectric (ϵ = 37.7 at 25 °C) with *N*,*N*-dimethylformamide over the temperature range studied.

Experimental Section

Materials. *N*,*N*-Dimethylformamide and ethane-1,2-diol (both containing <0.10% g of water/g of solvent found by Karl-

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