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 ith component
T_0	coefficient in eq 11
T	absolute temperature
V_i	molar volume (cm^3 mol^{-1}) of the ith 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 ith 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
ρ_k^{-1}	coefficients in eq 1
ρ_i^{-1}	coefficients in eq 2
ρ_{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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Table I. Dielectric Constants (ϵ) for *N*,*N*-Dimethylformamide (1) + Ethane-1,2-diol (2)

	ϵ							
t/°C	x_1 = 1.0000	x_1 = 0.8848	x_1 = 0.7734	x_1 = 0.5609	x_1 = 0.3623	x_1 = 0.1758	x_1 = 0.0864	x_1 = 0.0000
−10	44.20	46.22	47.76	50.04	50.05	50.50	50.18	49.23
−5	42.89	44.98	46.63	48.25	48.29	48.34	48.39	47.80
0	42.06	43.91	45.54	46.74	46.64	46.65	46.65	46.65
5	41.16	42.89	44.54	45.09	–	–	–	45.41
10	40.24	41.89	43.55	43.64	–	–	–	44.49
15	39.30	40.94	42.53	–	–	–	–	43.17
20	38.48	39.98	41.51	–	–	–	–	42.14
25	37.59	39.08	40.60	–	–	–	–	40.97
30	36.74	38.16	39.58	–	–	–	–	39.95
35	35.78	37.22	38.70	–	–	–	–	39.00
40	34.94	36.33	37.47	–	–	–	–	37.99
45	34.16	35.57	36.57	–	–	–	–	36.98
50	33.36	34.79	35.73	–	–	–	–	36.06
55	32.64	33.95	34.92	–	–	–	–	35.13
60	31.94	33.21	34.16	–	–	–	–	34.30
65	31.20	32.44	33.59	–	–	–	–	33.44
70	30.50	31.71	32.89	–	–	–	–	32.67
75	29.88	31.03	32.05	–	–	–	–	31.84
80	29.09	30.29	31.25	–	–	–	–	31.02

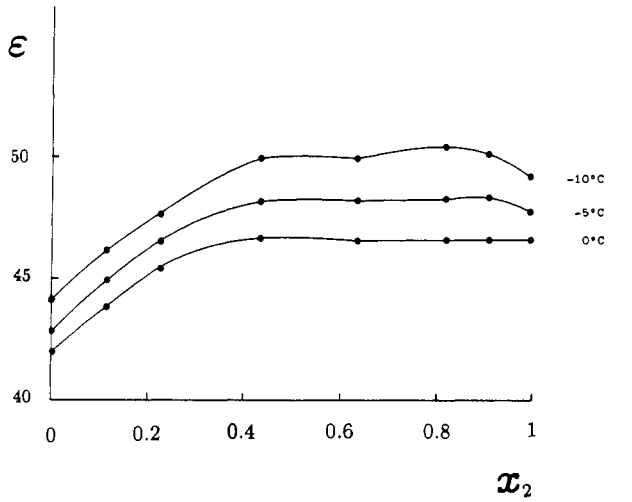

Figure 1. Experimental values for the dielectric constant (ϵ) for *N*,*N*-dimethylformamide (1) + ethane-1,2-diol (2).

Fischer titration) were Carlo Erba high-purity grade. The *N*,*N*-dimethylformamide was purified by passage through a neutral alumina column before use. The mixtures were gravimetrically prepared, on a Mettler analytical balance just before their use, under 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}.

Measurements. Dielectric constant measurements were carried out at 2.0 MHz by the heterodyne beat method with a Wissenschaftliche-Technische Werkstäten DM 01 dipolmeter. The thermostated measuring cell MFL3 type ($21 \leq \epsilon \leq 90$) was adequate to cover the dielectric constant range of DMF/DHE mixtures at the temperatures used. The overall experimental precision in ϵ values (standard deviation) was ±0.2%. With use of 10 replicate measurements, the estimated accuracy (95% confidence interval) was ±2 × 10^{-3}. The cell was previously calibrated with pure liquids like ethanol (ϵ = 24.30 at 25 °C), methanol (ϵ = 32.63 at 25 °C), glycerol (ϵ = 42.50 at 25 °C), and water (ϵ = 80.37 at 20 °C) (all literature values (*4*)). The temperature control was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C.

Refractive indexes for the sodium D line were measured with a thermostated Abbe refractometer (Officine Galileo, Milan) with a standard deviation of ±0.0001. Five replicate measurements were usually made at each composition and at each temperature, and the results were averaged.

The accuracy (95% confidence interval) was ±1.2 × 10^{-4}.

Table II. Coefficients of Equation 1 for *N*,*N*-Dimethylformamide (1) + Ethane-1,2-diol (2)

x_1	α_0	$\alpha_1 \times 10^3$/K	$\sigma \times 10^3$
1.0000	4.999 08	−4.609 47	1.96
0.8848	5.055 74	−4.662 13	1.71
0.7734	5.113 44	−4.738 67	3.89
0.5609	5.710 07	−6.832 96	1.25
0.3623	5.767 47	−7.047 68	0.41
0.1758	6.006 81	−7.927 56	3.29
0.0864	5.834 60	−7.292 22	0.08
0.0000	5.240 40	−5.117 38	1.77

Table III. Coefficients of Equation 2 for *N*,*N*-Dimethylformamide (1) + Ethane-1,2-diol (2)

t/°C	β_0	β_1	β_2	β_3	β_4	$\sigma_{(\epsilon)}$
−10	49.35	9.60	−23.90	20.19	−11.10	0.35
−5	47.90	3.95	−8.01	7.58	−8.59	0.22
0	46.70	−2.28	12.60	−15.94	0.91	0.16

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 of dielectric constant (ϵ) and refractive index (n) were measured for the pure components and for six mixtures, when possible, in the range −10 to +80 °C.

Dielectric Constant. The experimental dielectric constants given in Table I show many gaps in a large range of temperature and composition of binary mixtures. The reasons for this anomalous behavior probably lie in the great sensitivity of the specific conductance of the solvents (*7*) on the temperature and on the mixture composition.

The effect of temperature was studied by applying an equation of the type (*8*)

$$\ln \epsilon = \sum_{i=0}^{1} \alpha_i T^i \qquad (1)$$

whose coefficients α_i are reported in Table II with the corresponding standard deviation values. In order to take into account the dependence of ϵ on the composition of the binary mixtures, the polynomial equation (*9*)

$$\epsilon = \sum_{j=0}^{4} \beta_j x_1^j \qquad (2)$$

was used to fit the experimental data in the temperature range

Table IV. Refractive Index (n) for *N,N*-Dimethylformamide (1) + Ethane-1,2-diol (2)

	n							
t/°C	x_1 = 1.0000	x_1 = 0.8848	x_1 = 0.7734	x_1 = 0.5609	x_1 = 0.3623	x_1 = 0.1758	x_1 = 0.0864	x_1 = 0.0000
5	1.4358	1.4366	1.4378	1.4384	1.4380	1.4361	1.4355	1.4350
10	1.4350	1.4357	1.4366	1.4367	1.4366	1.4350	1.4343	1.4336
15	1.4328	1.4341	1.4350	1.4353	1.4351	1.4340	1.4333	1.4322
20	1.4308	1.4315	1.4326	1.4332	1.4335	1.4324	1.4312	1.4308
25	1.4282	1.4298	1.4308	1.4314	1.4315	1.4308	1.4298	1.4297
30	1.4263	1.4277	1.4284	1.4294	1.4297	1.4293	1.4284	1.4284
35	1.4231	1.4252	1.4264	1.4275	1.4282	1.4278	1.4269	1.4269
40	1.4220	1.4236	1.4251	1.4261	1.4269	1.4267	1.4258	1.4254
45	1.4196	1.4213	1.4226	1.4241	1.4250	1.4250	1.4246	1.4243
50	1.4177	1.4194	1.4208	1.4222	1.4232	1.4236	1.4234	1.4229
55	1.4150	1.4169	1.4180	1.4200	1.4211	1.4215	1.4218	1.4213
60	1.4131	1.4150	1.4168	1.4188	1.4200	1.4207	1.4204	1.4200
65	1.4109	1.4127	1.4140	1.4161	1.4175	1.4188	1.4182	1.4186
70	1.4083	1.4102	1.4118	1.4141	1.4157	1.4171	1.4169	1.4173
75	1.4058	1.4080	1.4097	1.4120	1.4137	1.4150	1.4151	1.4158
80	1.4039	1.4060	1.4077	1.4101	1.4120	1.4132	1.4137	1.4146

Table V. Coefficients of Equation 3 for *N,N*-Dimethylformamide (1) + Ethane-1,2-diol (2)

x_1	A'	$B' \times 10^4$	$\sigma \times 10^4$
1.0000	1.5655	−3.0804	3.4
0.8848	1.5611	−2.9551	3.4
0.7734	1.5588	−2.8792	3.2
0.5609	1.5492	−2.6549	2.6
0.3623	1.5399	−2.4465	2.6
0.1758	1.5249	−2.1377	3.2
0.0864	1.5194	−2.0323	2.6
0.0000	1.5136	−1.9149	0.8

−10 to 0 °C. Table III summarizes the β_j coefficients of eq 2 and the relative standard deviations (σ).

Refractive Index. A further tentative extension of our research on the solvent–cosolvent adducts formation has been made by working on the refractive properties of this binary solvent system. In fact, from Debye, Maxwell, and Lorentz–Lorenz theories (*7*, *10*), it is known that the dielectric properties of the materials are related to the polarization characteristics of their molecules.

The experimental values of the refractive index n, determined from 5 to 80 °C for the pure solvents and for all the mixtures, are reported in Table IV. Since instrumental problems occurred, it was impossible to measure the refractive index below 5 °C. The temperature effect was studied by means of the equation (*11*)

$$n = A' e^{B'T} \tag{3}$$

that reproduces the experimental data with an average difference of ±0.0002. The A' and B' coefficients (Table V), containing in implicit form the dependence on the binary solvent composition, were fitted by the polynomial equations of the type (*11*)

$$A' = \sum_{i=0}^{4} a_i' x_1^i \tag{4}$$

$$B' = \sum_{i=0}^{4} b_i' x_1^i \tag{5}$$

whose a_i' and b_i' coefficients are reported in the Table VI.

Now, by combining eqs 3–5, it is possible to write the relation

$$n = \left(\sum_{i=0}^{4} a_i' x_1^i\right) \exp\left[\left(\sum_{i=0}^{4} b_i' x_1^i\right) T\right] \tag{6}$$

that gives the dependence of the refractive index on T and x_1. The model equation (6) allows us to predict the experimental results of n in the whole miscibility field $0 \leq x_1 \leq 1$ and for temperatures varying in the $5 \leq t/°C \leq 80$ range, with an average deviation of ±0.0002 unit.

Table VI. Coefficients of Equations 4 and 5 for *N,N*-Dimethylformamide (1) + Ethane-1,2-diol (2)

	i = 0	i = 1	i = 2	i = 3	i = 4	σ
a_i'	1.5655	−0.0418	0.0741	−0.1718	0.0875	9.9e-4
$b_i' \times 10^4$	−0.3080	0.1199	−0.1885	0.3705	−0.1854	2.0e-6

Mixing Rules

The literature reports many equations that use mixing rules for analysis of the data for binary liquid mixtures. In order to check their validity and the relative merits, a test on model systems appeared to us, desirable. One test consists of comparing the measured refractive index of the mixtures with that calculated from the refractive index and the densities of the pure components and of the solutions (*12*).

One of the simplest early attempts to describe the refractive properties of the solutions is due to Arago and Biot (*13*) (AB equation):

$$n = \phi_1 n_1 + \phi_2 n_2 \tag{7}$$

where n, n_1, and n_2 are the refractive indexes of mixtures, solvent 1, and solvent 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the respective components in the mixtures.

Gladstone and Dale (*14*) formulated the following relation (GD equation):

$$n - 1 = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) \tag{8}$$

that may be reduced to eq 7 if one assumes volume additivity (no changes in volume on mixing).

Lorentz and Lorenz (*15*, *16*) gave a more commonly used mixing rule (LL equation) in the analysis of refractive index:

$$\frac{n^2 - 1}{n^2 + 2} = \phi_1\left[\frac{n_1^2 - 1}{n_1^2 + 2}\right] + \phi_2\left[\frac{n_2^2 - 1}{n_2^2 + 2}\right] \tag{9}$$

Wiener derived an equation that may be applied to isotropic bodies of spherical and symmetrical shape and that is valid for binary systems if volume additivity is assumed (*17*) (W equation):

$$\frac{n^2 - n_1^2}{n^2 + 2n_1^2} = \phi_2\left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right] \tag{10}$$

Finally, we have investigated the Heller equation (*18*), which was derived assuming the equivalence of the light scattering equations of Debye and Rayleigh, in the form (H equation)

$$\frac{n - n_1}{n_1} = \frac{3}{2}\phi_2\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right] \tag{11}$$

Table VII. Calculated Average Deviations $(\Delta n)_{av}$ for Different Mixing Rules at Various Temperatures

	$(\Delta n)_{av} \times 10^3$				
t/°C	AB[a]	GD[b]	LL[c]	W[d]	H[e]
5	0.87	0.87	0.87	0.87	0.87
10	0.79	0.79	0.79	0.79	0.79
15	1.03	1.03	1.03	1.03	1.03
20	0.84	0.84	0.84	0.84	0.84
25	0.91	0.91	0.91	0.91	0.91
30	0.77	0.77	0.77	0.77	0.77
35	1.05	1.05	1.05	1.05	1.05
40	0.96	0.96	0.96	0.96	0.96
45	0.95	0.95	0.95	0.95	0.96
50	0.92	0.92	0.92	0.92	0.92
55	1.10	1.10	1.10	1.10	1.10
60	0.79	0.79	0.79	0.79	0.79
65	0.81	0.81	0.81	0.81	0.81
70	0.81	0.81	0.81	0.81	0.81
75	0.79	0.79	0.79	0.79	0.79
80	0.66	0.66	0.66	0.66	0.66
av	0.89	0.89	0.89	0.89	0.89

[a] Arago–Biot equation (7). [b] Gladstone–Dale equation (8). [c] Lorentz–Lorenz equation (9). [d] Wiener equation (10). [e] Heller equation (11).

The results of this analysis are summarized in Table VII, where we have reported the average deviations of the refractive index differences, (Δn), expressed as

$$\Delta n = n_{exptl} - n_{calcd} \quad (12)$$

with n_{calcd} evaluated by means of different mixing rules. The five mixing rules tested are equivalent to each other, all reproducing the experimental data within the limits of experimental uncertainty over the range of temperature and composition studied.

Acknowledgment

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Glossary

A', B'	coefficients in eq 3
a_i'	coefficients in eq 4
b_i'	coefficients in eq 5
n	refractive index
t	Celsius temperature
T	absolute temperature, K

Greek Letters

α_i	coefficients in eq 1
β_j	coefficients in eq 2
ϵ	dielectric constant
ϕ_i	volume fraction of the ith component
σ	standard deviation

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

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Densities and Excess Molar Volumes of the 1,2-Ethanediol + 2-Methoxyethanol Solvent System at Various Temperatures

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Densities are reported for the binary mixture 1,2-ethanediol + 2-methoxyethanol in the whole composition range at 19 temperatures between −10 and +80 °C. The excess molar volumes, V^E, calculated from the density values, are negative at all concentrations and become more negative with increasing temperature.

Introduction

In recent papers we have reported some electroanalytical studies about acid–base equilibria which take place in solutions of 1,2-ethanediol and 2-methoxyethanol and in their binary mixtures operating at different temperatures in the range −10 to +80 °C (*1–4*). These alcohols appear very interesting from the point of view of practical and theoretical applications, being protic, protophilic, and dipolar, as well as potentially acidic, nonaqueous solvents. 1,2-Ethanediol is the simplest homologue of the diol series, largely utilized as thermoregulator fluid, as a controlling agent of density/viscosity reaction baths, and as emulsion coating owing to its unusual physicochemical properties (*5*).

On the other hand, 2-methoxyethanol is widely used for various industrial processes (*6*) and has unique solvating properties associated with its quasi-aprotic character (*5*). 2-Methoxyethanol, an ether alcohol, shows physicochemical characteristics midway between protic and dipolar aprotic solvents. It is a quite-toxic solvent, a weak narcotic, and a

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