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N,N-Dimethylformamide + 1,2-Dimethoxyethane Binary Mixtures. The Static Dielectric Constant from 40 to 80 °C

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The static dielectric constant (ϵ) has been measured at 2 MHz for *N,N*-dimethylformamide (1), 1,2-dimethoxyethane (2), and their nine binary mixtures covering the whole miscibility field ($0 \leq x_1 \leq 1$) in the 40–80 °C temperature range. The experimental ϵ values were fitted by empirical equations of the types $\epsilon = \epsilon(T)$, $\epsilon = \epsilon(x_1)$, and $\epsilon = \epsilon(T,x_1)$. The mixing quantity $\delta\epsilon$ has been evaluated and fitted by a Redlich–Kister equation. The trend of $\delta\epsilon$ vs mole fraction curves shows negative deviations from ideality, and makes evident the presence of a stable dipolar interaction between unlike molecules.

Introduction

In previous papers (*1–3*), we investigated the dielectric behavior of *N,N*-dimethylformamide (DMF) + 1,2-dihydroxyethane (DHE) over a wide temperature range. In this work we have extended the study to the *N,N*-dimethylformamide (DMF) + 1,2-dimethoxyethane (DME) binary system in order to improve our knowledge about the specific interactions between DMF molecules and other species. In particular, we report the static dielectric constants for the above-cited binaries from 40 to 80 °C for nine mixtures.

Experimental Section

Materials. *N,N*-Dimethylformamide and 1,2-dimethoxyethane (both containing less than 0.10% water by mass found by Karl-Fischer titrations) were Carlo Erba (Milan) high purity grade reagents. The *N,N*-dimethylformamide was purified by passage on a neutral alumina column. The 1,2-dimethoxyethane was further purified by double fractional distillation over $LiAlH_4$ to eliminate the traces of acids and peroxides and to reduce the total water amount, keeping the middle fraction only (bp 83 °C) for the measurements.

The solvents were stored over 3A type molecular sieves before use. The final purity of both solvents was checked by gas chromatography (99.8% by mass for DMF, 99.7% for DME), confirming the absence of other significant organic components.

Apparatus and Procedures. The solvent mixtures were prepared by mass using a Mettler PM 4800 Δ range balance, operating in a dry nitrogen atmosphere in order to avoid contact with atmospheric moisture, and then stored over 3A molecular sieves. The probable error in the DMF mole fraction (x_1) is estimated to be less than 1.5×10^{-4}.

Dielectric constant measurements were carried out at 2 MHz, by the heterodyne beat method, with a WTW-DM01 dipolmeter. The thermostated stainless steel measuring cells were of the MFL 2 ($7 < \epsilon < 21$) and MFL 3 ($21 < \epsilon < 90$) types. The sample cells were of the covered coaxial capacitor type with vacuum capacitances of 2 (MFL 2) and 0.5 pF (MFL 3). They were adequate to cover the dielectric constant range of the DMF + DME mixtures from 40 to 80 °C.

Results were checked for a good overlap when passing from the MFL 2 to the MFL 3 measuring cell, the difference lying always within the experimental accuracy of the equipment. The cells were calibrated with standard pure liquids, such as dichloromethane, pyridine, butan-1-ol, and acetone (MFL 2), methanol, ethanol, glycerol, and bidistilled water (MFL 3). With the exception of the bidistilled water, all these solvents were spectrograde quality, or better. The dielectric constants for the standards were taken from the literature (*4*).

The overall experimental uncertainty (standard deviation) in ϵ values was ±0.2%, with a confidence interval of 95% for at least 10 runs at each selected temperature. The thermostated measuring cells were encased in a polyurethane protective jacket, and the temperature control was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C. The temperature constancy was checked by a 100-Ω platinum resistance thermometer (Tersid, Milan) immersed in the sample, with the resistance measured by a Wayne Kerr 6425 precision component analyzer. Karl-Fischer titrations were performed for the water content of solvents with an automatic titration system (Crison Model KF 431) equipped with a digital buret (Crison Model 738).

Results and Discussion

Table I summarizes dielectric constants (ϵ) for DMF + DME mixtures in the $40 \leq t/°\mathrm{C} \leq 80$ range. The temperature dependence of ϵ was represented by (*4*)

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

whose α_i coefficients, along with the standard deviations $\sigma(\ln \epsilon)$, are listed in Table II. Equation 1 reproduces the experimental values of Table I with an average deviation $\overline{\Delta\epsilon}$ defined as follows:

$$\overline{\Delta\epsilon} = \sum_{N} \frac{|\epsilon_{\mathrm{calcd}} - \epsilon_{\mathrm{exptl}}|}{N} \qquad (2)$$

where N is the number of experimental points, equal to ±0.03.

The nonlinear dependence of ϵ on mole fraction was expressed by a polynomial expansion of the type

$$\ln \epsilon = \sum_{j=0}^{k} \beta_j x_1^{\,j} \qquad (3)$$

whose β_j coefficients, for $k = 3$, are given in Table III together with the corresponding $\sigma(\ln \epsilon)$ at each investigated temperature. The goodness of this best-fitting procedure was ascertained by an average deviation $\overline{\Delta\epsilon} = \pm 0.19$.

By combining eqs 1 and 3, it is possible to obtain a single function stating the dependence of ϵ on T and x_1, which may

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Table I. Experimental Static Dielectric Constant ϵ for *N,N*-Dimethylformamide (1) + 1,2-Dimethoxyethane (2) at Various Temperatures

	ϵ at various x_1										
t/°C	1.0000	0.9252	0.8422	0.7575	0.6702	0.5744	0.4742	0.3704	0.2527	0.1291	0.0000
40	34.94	30.86	29.12	26.18	22.95	20.32	17.71	15.16	12.35	9.74	7.12
45	34.16	30.26	28.49	25.69	22.48	19.95	17.36	14.90	12.14	9.59	6.98
50	33.36	29.55	27.83	25.04	21.99	19.42	16.95	14.52	11.80	9.35	6.83
55	32.64	28.90	27.20	24.49	21.46	19.06	16.63	14.22	11.64	9.16	6.70
60	31.94	28.29	26.61	23.88	21.09	18.66	16.28	13.95	11.41	9.00	6.57
65	31.20	27.64	25.97	23.37	20.47	18.29	15.86	13.64	11.18	8.82	6.46
70	30.50	26.98	25.40	22.89	20.20	17.88	15.59	13.36	10.96	8.64	6.31
75	29.88	26.43	24.87	22.33	19.74	17.51	15.26	13.09	10.64	8.48	6.21
80	29.09	25.75	24.25	21.70	19.19	17.09	14.88	12.78	10.41	8.28	6.09

Table II. Coefficients α_i and Standard Deviations $\sigma(\ln \epsilon)$ of Equation 1 for *N,N*-Dimethylformamide (1) + 1,2-Dimethoxyethane (2)

x_1	α_0	$\alpha_1 \times 10^3$	$\sigma(\ln \epsilon) \times 10^3$
1.0000	4.973 24	−4.533 30	1.3
0.9252	4.847 55	−4.522 13	1.5
0.8422	4.800 55	−4.562 37	0.8
0.7575	4.726 30	−4.658 69	2.3
0.6702	4.514 76	−4.408 97	3.2
0.5744	4.359 14	−4.300 99	1.8
0.4742	4.229 73	−4.326 44	1.9
0.3704	4.055 76	−4.266 07	1.6
0.2527	3.838 70	−4.224 10	4.1
0.1291	3.545 19	−4.047 99	2.0
0.0000	3.180 52	−3.893 11	1.3

Table III. Coefficients β_j and Standard Deviations $\sigma(\ln \epsilon)$ of Equation 3 for *N,N*-Dimethylformamide (1) + 1,2-Dimethoxyethane (2) at Various Temperatures

t/°C	β_0	β_1	β_2	$\beta_3 \times 10$	$\sigma(\ln \epsilon) \times 10^2$
40	1.966 77	2.521 27	−1.559 61	6.185 42	1.4
45	1.947 92	2.536 98	−1.599 47	6.399 96	1.4
50	1.926 78	2.497 26	−1.515 13	5.922 86	1.4
55	1.906 81	2.523 17	−1.590 08	6.397 21	1.3
60	1.887 07	2.533 00	−1.622 21	6.601 35	1.3
65	1.870 36	2.509 73	−1.603 72	6.585 27	1.3
70	1.847 28	2.524 21	−1.611 01	6.503 16	1.3
75	1.830 51	2.485 13	−1.542 53	6.167 57	1.3
80	1.810 04	2.475 67	−1.547 60	6.253 35	1.3

Table IV. Coefficients γ_{ij} and Standard Deviation $\sigma(\ln \epsilon)^a$ of the Model Equation $\epsilon = \epsilon(T,x_1)$ for *N,N*-Dimethylformamide (1) + 1,2-Dimethoxyethane (2)

ij	variable quantity	γ	ij	variable quantity	γ
00		3.192 55	10	T	$-3.915\,30 \times 10^{-3}$
01	x_1	2.842 16	11	Tx_1	$-9.915\,57 \times 10^{-4}$
02	x_1^2	−1.591 72	12	Tx_1^2	$4.472\,76 \times 10^{-5}$
03	x_1^3	0.530 96	13	Tx_1^3	$3.078\,16 \times 10^{-4}$

[a] $\sigma(\ln \epsilon) = 1.1 \times 10^{-2}$.

be written in the form

$$\ln \epsilon = \sum_i \sum_j \gamma_{ij} T^i x_1^{\,j} \tag{4}$$

The model eq 4, whose γ_{ij} coefficients were evaluated by a multilinear regression package (TSP) (*5*) and are summarized in Table IV, allows us to calculate ϵ for any T and x_1 of the binary solvent system under study. This equation fits the experimental data with an averaged uncertainty $\overline{\Delta\epsilon} = \pm 0.20$ over the temperature range $40 \le t/°\mathrm{C} \le 80$ and composition range $0 \le x_1 \le 1$.

The Mixing Quantity

The relationship (*6*)

$$\epsilon = \delta\epsilon + \epsilon_1 x_1 + \epsilon_2 x_2 \tag{5}$$

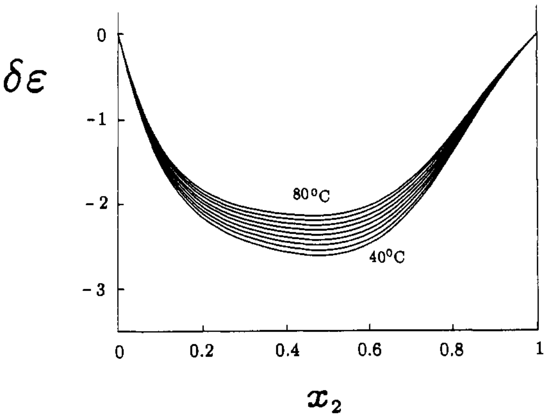

Figure 1. Isothermal best-fitting curves of the mixing quantity ($\delta\epsilon$) for *N,N*-dimethylformamide (1) + 1,2-dimethoxyethane (2) calculated by eq 6 at various temperatures.

may be employed in order to assess the difference ($\delta\epsilon$) between the experimental ϵ values of the mixtures and those calculated by using the mole fraction and the ϵ values of the pure solvents. Equation 5 is available in the limiting cases for apolar and for polar components in the binaries; $\delta\epsilon$ is $\simeq 0$ only in the case of very apolar and scarcely interacting components.

For the mixtures investigated here, the $\delta\epsilon$ quantities are always negative over the entire selected temperature range. Figure 1 represents the trend of $\delta\epsilon$ values vs x_2. The curves were obtained by fitting the isothermal $\delta\epsilon$ quantities by a smoothing equation of the type (*7*)

$$\delta\epsilon = x_1 x_2 \sum_{i=0}^{6} c_i (x_2 - x_1)^i \tag{6}$$

which allows us to recalculate the excess values in the limits of experimental error for each binary composition.

A brief examination of Figure 1 shows a flattened minimum at all the investigated temperatures, always centered at $x_2 \simeq 0.5$, which becomes more pronounced as the temperature decreases. The magnitude of the minimum never exceeds −2.9 at 40 °C.

Conclusions

The behavior of the static dielectric constant of these mixtures could provide useful evidence to investigate the nature and interactions between unlike species, as the dielectric properties are determined by the permanent electric moments of the molecules, by their polarizabilities, and by their mutual orientation when immersed in an external electrical field.

In regard to the DMF + DME mixtures, the $\delta\epsilon$ mixing quantity being always negative and less than $\sim|5|$, one may hypothesize that dispersive forces of a dipolar type occurred between unlike molecules (*6*), forming an approximately 1:1 ratio of low dipole moment aggregates.

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Literature Cited

(1) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *Can. J. Chem.* **1991**, *69*, 509.
(2) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *J. Chem. Eng. Data* **1991**, *36*, 360.
(3) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *J. Chem. Eng. Data* **1991**, *36*, 365.
(4) Maryott, A. A.; Smith, E. R. *Table of Dielectric Constant of Pure Liquids*; National Bureau of Standards Circular No. 514; U.S. Government Printing Office: Washington, DC, 1951.
(5) *TSP - Time Series Processor - User's Guide*; Hall, B. H., Ed.; TSP International: Stanford, CA, 1987.
(6) Kolling, O. W. *Anal. Chem.* **1985**, *57*, 1721.
(7) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 341.

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