Physical Behavior of Some Reaction Media. 3.[†] Density, Viscosity, Dielectric Constant, and Refractive Index Changes of Methanol + Dioxane Mixtures at Several Temperatures

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Viscosities, densities, dielectric constants, and refractive indexes were determined for methanol + dioxane mixtures at 15, 20, 25, 30, and 35 °C. The variations of the properties with temperature and composition are represented by means of empirical relations, which fit the results with an uncertainty of the same order of magnitude as the experimental uncertainties. The results indicate molecular interactions between the components of the system.

Introduction

This paper is a part of continuing research concerning the kinetics of S_N2 reactions between ions and dipolar molecules in solvents where the ionic reactant associates to form ion pairs (1).

In the progress of these investigations we decided to extend our kinetic studies to binary methanol + dioxane solvent systems, where the ionic association of the nucleophilic reactant will be less important than in the case of the already studied ethanol + dioxane mixtures (1).

However, one problem, generally encountered in such studies, is to correlate reaction rate data with the physical properties of the corresponding media. For this purpose we decided to make a series of systematic measurements of density, viscosity, dielectric constant, and refractive index of methanol + dioxane mixtures over the whole composition range and temperatures from 15 to 35 °C. Some physical properties of the above-mentioned binary mixtures have been previously reported in the literature (2). However, this study has been made at a very different composition range than that used in our kinetic experiments.

Experimental Section

Reagents. Carlo Erba 1,4-dioxane (>99%, bp 101 °C) was further purified by refluxing with sodium metal for several days and redistilling; the whole procedure was repeated until the sodium remained bright after several hours. In all distillations only the middle fraction coming over at the reported boiling point and comprising about 75% was retained.

Absolute methanol (Fluka, puriss pa > 99.8%) was distilled once, and the first and last 10% fractions were rejected. The collected fraction was stored over 3A molecular sieves.

Pure-component physical properties were measured, and their values were compared with values of corresponding data obtained from the literature (Table I). Mixtures were gravimetrically prepared on a Mettler analytical balance just before their use. The error in the methanol mole fraction (x_2) is estimated to be ±0.0001.

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 cells (MFL 1/S, MFL 2/S, and MFL 3/S type) were adequate to cover the dielectric constant range of methanol + dioxane mixtures at the temperature used. The overall experimental uncertainty in ϵ values (coefficient of variation) was ±0.23%. The cells were previously calibrated with standard pure liquids in accordance with the manufacturer's specifications and with National Bureau of Standards Circular 514 (9).

Densities were measured with a Sprengel–Ostwald capillary pycnometer of about 25 cm³ capacity. The pycnometer was calibrated with distilled water at each temperature. The overall experimental uncertainty was ±0.008%.

Viscosities were measured with an Ubbelhode capillary viscosimeter (Schott Mainz Jena Glass C 2023). In all determinations the kinetic energy correction has been taken into account according to a recommended method (14). Flow times were measured with an electronic stopwatch with an accuracy of ±0.01 s. The estimated accuracy was ±0.17%.

Refractive indexes for the sodium D line were measured with a thermostated Pulfrich refractometer (Bellingham and Stanley) with an experimental uncertainty of ±0.000 01 unit.

In all cases temperature was controlled within ±0.01 °C by means of a Haake Ultrathermostat NBS.

Experiments were generally performed at least in five replicates for each composition, and the results were averaged.

Results and Discussion

The experimental density (ρ), viscosity (η), dielectric constant (ϵ), and refractive index (n_D) results at 15, 20, 25, 30, and 35 °C for the methanol + dioxane solvent mixtures are listed in Table II.

Densities. As observed previously for ethanol + dioxane and ethanol + cyclohexane (15, 16), the polynomial equation

$$\rho^{-1}/(\text{cm}^3 \cdot \text{g}^{-1}) = \sum_{i=0}^{n} d_i x_2^i \qquad (1)$$

fits the density data better than an analogous polynomial equation (of the same degree) relating ρ with x_2. Equation 1 was fitted at each temperature by a least-squares technique. It was found that the optimum degree (n) was equal to 6. The values of the adjustable coefficients (d_i) are summarized in Table III along with the standard error of estimate (σ).

The temperature dependence of the density of the mixtures was correlated by the following equation (10):

$$\rho = \rho_0 - BT \qquad (2)$$

Calculated density data, by means of eq 1, were used in the plots of ρ vs T. The mole fraction x_2 was kept as a constant parameter. For each composition and over the temperature range studied, straight lines were obtained (the linear correlation coefficient (R) was very close to unity). The corresponding constants (ρ_0 and B) were calculated by the least-squares

[†] Parts 1 and 2 of this paper are refs 15 and 16.

Table I. Physical Properties of Pure Components

	methanol		dioxane	
$t/°C$	this study	literature	this study	literature
		$\rho/(\text{g·cm}^{-3})$		
15	0.795 87	0.796 09 (3, 4), 0.796 02 (4)	1.039 25	1.039 22 (4, 5)
20	0.791 19	0.791 29 (3), 0.7916 (5)	1.033 66	1.033 64 (4), 1.033 61 (3, 4)
25	0.786 45	0.7872 (6), 0.786 64 (3)	1.028 12	1.027 97 (3), 1.028 02 (4)
30	0.781 65	0.7818 (5), 0.7819 (4)	1.022 23	1.022 30 (4, 5)
35	0.777 10	0.7766 (7), 0.7771 (5)	1.016 89	
		$\eta/(10^{-3}\ \text{Pa·s})$		
15	0.626	0.623 (4)	1.4256	1.439 (3-5)
20	0.581	0.581 (5), 0.5506 (3)	1.2972	
25	0.542	0.5526 (6), 0.545 (7)	1.1944	1.192 (12)
30	0.503	0.502 (5), 0.510 (4)	1.0937	1.087 (3-5)
35	0.469	0.476 (7), 0.477 (5)	1.0112	
		ϵ		
15	34.64		2.226	
20	33.66	33.6 (8), 33.62 (9)	2.218	2.235 (13)
25	32.63	32.62 (11), 32.63 (9)	2.209	2.2092 (2), 2.209 (9)
30	31.62	31.7 (5), 31.80 (10)	2.201	
35	30.64	29.9 (5)	2.192	
		n_D		
15	1.330 06	1.330 57 (3, 4)	1.424 06	1.424 36 (3, 4)
20	1.328 50	1.328 40 (3)	1.422 06	1.422 41 (3, 4)
25	1.326 61	1.326 52 (3)	1.419 99	1.4202 (4), 1.420 25 (3, 4)
30	1.325 28		1.417 71	
35	1.323 68		1.416 06	

Figure 1. Variation of viscosity η for dioxane (1) + methanol (2): ●, experimental values; O, values calculated from eq 9; (A) 15 °C; (B) 35 °C.

method. On the basis of these data, the following relations were derived:

$$10^2(\rho_0/(\text{g·cm}^{-3})) = \sum_{i=0}^{8} C_i x_2^i = 136.276 - 22.075x_2 +$$
$$38.378x_2^2 - 97.158x_2^3 + 81.234x_2^4 - 21.575x_2^5 -$$
$$10.084x_2^6 - 1.436x_2^7 + 3.508x_2^8 \quad (3)$$

$$\sigma(\rho_0)/(\text{g·cm}^{-3}) = 3.23 \times 10^{-7}$$

$$10^4(B/(\text{g·cm}^{-3}\cdot\text{K}^{-1})) = \sum_{i=0}^{8} B_i x_2^i = 11.227 - 4.459x_2 +$$
$$21.129x_2^2 - 58.068x_2^3 + 81.882x_2^4 - 56.438x_2^5 +$$
$$5.776x_2^6 + 13.842x_2^7 - 5.360x_2^8 \quad (4)$$

$$\sigma(B)/(\text{g·cm}^{-3}\cdot\text{K}^{-1}) = 2.95 \times 10^{-8}$$

It follows that the equation relating the density to the temperature (T) and the mole fraction of methanol x_2 is

$$\rho = \sum_{i=0}^{8} C_i x_2^i - (\sum_{i=0}^{8} B_i x_2^i)T \quad (5)$$

Equation 5 fits the experimental data over the specified range of temperatures (15–35 °C) and for $0 < x_2 < 1$. The average deviation of the density data calculated respectively from eqs 1 and 5 was $\pm 1.2 \times 10^{-4}$ g·cm^{-3}.

Viscosities. Two examples, depicting the trend in viscosity as a function of x_2, are given in Figure 1. The shape of these plots is quite different from that observed in the case of the ethanol + dioxane mixtures where the graphs of η against the mole fraction of dioxane presented a pronounced minimum (15).

However, as it has been argued in the literature (17), plots of the type shown in Figure 1 illustrate a general pattern for systems in which either complexes are not formed or complexes of low stability occur between the components of the mixture. In the latter case one can assume that the viscosity of the complexes may be less than that of the components of the system.

In an attempt to clear up this ambiguity, the rheochor [R] of the various methanol + dioxane mixtures, examined in this investigation, has been studied; this quantity being both additive and constitutive is known to be very sensitive to various intermolecular associations (18, 19).

The rheochor [R] was calculated from the following equation (15, 16, 19):

$$[R] = (\bar{M}/\rho)\eta^{1/8} \quad (6)$$

where

$$\bar{M} = (1 - x_2)M_1 + x_2M_2 \quad (7)$$

M_1 and M_2 being the molecular weights of dioxane and methanol, respectively.

As previously (15, 16), in all these calculations smoothed values of ρ, calculated from eq 1, were substituted in eq 6.

In all temperatures studied, it was found that the plots of [R] vs x_2 are not linear and that the corresponding data, at each temperature and for $0 < x_2 < 1$, can be fitted, by least squares, to a polynomial equation of the general form

$$10^6([R]/(\text{m}^3\ (\text{Pa·s})^{1/8}\ \text{mol}^{-1})) = \sum_{i=0}^{4} R_i x_2^i \quad (8)$$

Table II. Experimental Density ρ, Viscosity η, Dielectric Constant ϵ, and Refractive Index n_D for Dioxane (1) + Methanol (2) at 15, 20, 25, 30, and 35 °C

x_2	15 °C	20 °C	25 °C	30 °C	35 °C
			$\rho/(\text{g·cm}^{-3})$		
0	1.039 25	1.033 66	1.028 12	1.022 23	1.016 89
0.197 54	1.015 74	1.010 31	1.004 77	0.999 26	0.994 30
0.344 74	0.993 65	0.988 35	0.983 10	0.977 43	0.972 38
0.474 35	0.970 48	0.965 37	0.960 03	0.954 66	0.949 71
0.583 55	0.946 38	0.941 43	0.936 11	0.930 72	0.925 86
0.678 18	0.922 19	0.917 18	0.912 01	0.906 73	0.901 87
0.758 76	0.898 03	0.893 11	0.888 01	0.882 94	0.878 21
0.831 21	0.872 67	0.867 87	0.862 88	0.857 76	0.853 28
0.893 57	0.847 90	0.842 93	0.838 11	0.833 05	0.828 502
0.950 27	0.821 73	0.816 98	0.812 38	0.807 28	0.802 80
1	0.795 87	0.791 19	0.786 45	0.781 65	0.777 10
			$\eta/(10^{-3}\ \text{Pa·s})$		
0	1.4256	1.2972	1.1944	1.0937	1.0112
0.197 54	1.1407	1.0452	0.9612	0.8931	0.8310
0.344 74	0.9806	0.9049	0.8454	0.7780	0.7262
0.474 35	0.8783	0.8065	0.7506	0.6981	0.6503
0.583 55	0.7936	0.7327	0.6825	0.6349	0.5930
0.678 18	0.7330	0.6805	0.6352	0.5919	0.5507
0.758 76	0.6915	0.6441	0.6047	0.5568	0.5200
0.831 21	0.6595	0.6135	0.5780	0.5316	0.4970
0.893 57	0.6411	0.5998	0.5543	0.5157	0.4817
0.950 27	0.6298	0.5900	0.5443	0.5063	0.4725
1	0.6261	0.5811	0.5422	0.5028	0.4694
			ϵ		
0	2.226	2.218	2.209	2.201	2.192
0.197 54	3.609	3.562	3.500	3.451	3.394
0.344 74	5.485	5.348	5.215	5.085	4.958
0.474 35	8.046	7.843	7.622	7.387	7.199
0.583 55	11.069	10.767	10.408	10.100	9.775
0.678 18	14.435	14.012	13.560	13.150	12.733
0.758 76	18.070	17.500	16.945	16.410	15.861
0.831 21	22.017	21.349	20.672	19.968	19.358
0.893 57	26.036	25.242	24.44	23.661	22.952
0.950 27	30.321	29.427	28.516	27.617	26.762
1	34.636	33.663	32.634	31.617	30.636
			n_D		
0	1.424 060	1.422 063	1.419 993	1.417 705	1.416 056
0.197 54	1.415 181	1.412 973	1.411 063	1.409 202	1.407 288
0.344 74	1.406 567	1.404 542	1.402 441	1.400 87	1.399 057
0.474 35	1.397 501	1.395 56	1.393 605	1.392 134	1.390 420
0.583 55	1.388 506	1.386 323	1.384 147	1.383 069	1.381 428
0.678 18	1.378 832	1.376 996	1.375 05	1.373 704	1.372 086
0.758 76	1.369 386	1.367 66	1.365 675	1.364 048	1.362 304
0.831 21	1.359 592	1.357 693	1.355 718	1.354 256	1.352 685
0.893 57	1.350 12	1.348 116	1.346 339	1.344 771	1.343 278
0.950 27	1.340 116	1.338 257	1.336 387	1.334 852	1.333 665
1	1.330 056	1.328 497	1.326 613	1.325 284	1.323 676

whose coefficients R_i are listed in Table III.

By combining eqs 1, 6, and 8, one obtains the following rational functions (i.e., the ratio of two polynomials):

$$\eta^{1/8} = \frac{R_0 + R_1 x_2 + R_2 x_2^2 + \ldots + R_4 x_2^4}{\{(1 - x_2)M_1 + x_2 M_2\}(d_0 + d_1 x_2 + d_2 x_2^2 + \ldots + d_6 x_2^6)} \tag{9}$$

As previously (15, 16), it was found in this investigation that, in all cases, eq 9 represents the reported data better than a simple polynomial. The average deviation of the calculated values from the experimental ones, always less than $\pm 1.45 \times 10^{-6}$ Pa·s ($\sim \pm 0.3\%$), shows that eq 9 closely represents the experimental viscosity data. A comparison of experimental and calculated η data is presented in Figure 1.

If the mixtures studied behave ideally, the molar quantity [R] being both additive and constitutive could be calculated for each composition by applying the additivity rule:

$$[R]_{id} = (1 - x_2)[R]_1 + x_2[R]_2 \tag{10}$$

Table III. Coefficients and Standard Errors of Estimate σ for Representation of $1/\rho$, [R], ϵ, and n_D of Dioxane (1) + Methanol (2), Equations 1, 8, 19, and 26

	15 °C	20 °C	25 °C	30 °C	35 °C
			Equation 1		
d_0	0.962 24	0.967 44	0.972 65	0.978 25	0.983 39
$10^2 d_1$	8.3841	8.2734	8.6865	8.4259	7.6466
d_2	0.229 86	0.246 45	0.222 68	0.231 06	3.0022
$-d_3$	0.662 91	0.722 90	0.678 98	0.641 67	0.876 07
d_4	1.4878	1.5824	1.5926	1.4334	1.8362
$-d_5$	1.4336	1.4963	1.5729	1.3755	1.7167
d_6	0.589 32	0.604 05	0.648 55	0.569 48	0.683 30
$10^4 \sigma$	1.73	1.23	1.39	2.08	2.10
			Equation 8		
R_0	37.3723	37.1324	36.9480	36.7561	36.5882
$-R_1$	25.9211	25.3433	25.3113	24.9206	24.6515
R_2	7.457 89	5.914 94	6.905 11	6.382 46	6.067 99
$-R_3$	5.785 33	3.504 94	5.117 14	4.847 11	4.640 80
R_4	2.883 87	1.764 35	2.483 79	2.490 80	2.453 82
σ	0.0092	0.0068	0.0159	0.0058	0.0016
			Equation 19		
D_0	2.226 01	2.218 57	2.209 34	2.201 36	2.193 09
D_1	5.339 52	5.558 73	5.296 61	5.751 61	4.859 25
$-D_2$	-2.220 38	1.504 08	0.877 671	6.282 69	0.208 18
D_3	36.9048	46.7224	42.7656	56.0412	37.0405
$-D_4$	32.2776	45.0868	40.5319	55.7918	34.0954
D_5	20.2214	25.7546	23.7705	29.7033	20.8507
σ	0.0120	0.0163	0.0160	0.0086	0.0190
			Equation 26		
D_0'	1.424 054	1.422 057	1.419 990	1.417 715	1.416 053
$-10^2 D_1'$	3.6000	3.8991	3.6770	3.7057	3.9222
$-10^2 D_2'$	5.1294	3.7531	4.8335	3.2501	2.5338
$10^2 D_3'$	4.2557	2.2366	3.8825	0.803 28	0.023 483
$-10^2 D_4'$	4.9134	3.9371	4.7054	3.0894	2.7862
$10^4 \sigma$	1.42	0.654	1.35	0.896	1.98

$[R]_1$ and $[R]_2$ being the rheochors of pure dioxane and methanol, respectively.

So, taking into account that the rheochor is an extensive property, we consider that the values of the specific excess rheochor

$$\delta = \frac{[R] - [R]_{id}}{[R]_{id}} = \frac{[R]^E}{[R]_{id}} \tag{11}$$

give an adequate approach to estimate molar associations. It was found that the maximum deviations from the ideal behavior occur for all temperatures studied at $x_2 \approx 0.63$.

Alcohols in nonpolar solvents associate by means of hydrogen bonds into a series of n-mers (2, 7, 20-30). In very dilute solutions the predominant species are the unassociated (monomeric) molecules, while in more concentrated solutions both linear (acyclic) and (cyclic) n-mers coexist. Finally, in pure alcohols or in concentrated solutions of these substances only linear n-mers can be considered. Also, it has been argued that, in solvents such as dioxane, which can take part in hydrogen bond formation, the self-association of alcohols may be reduced in favor of hydrogen-bonded structures between the solute and the solvent (25, 26). On the other hand, there is experimental evidence for intermolecular association between methanol and dioxane (2, 31).

Consequently, taking into account all these assumptions, we could attribute the observed values of δ to all these effects. The maximum values of $|\delta|$ observed for all temperatures at molar ratio 1.7:1 ($x_1 = 0.37$) could be attributed to the formation of two complexes between dioxane and methanol of the types 1:1 and 1:2. It should be noted that this assumption is in agreement with the possibility that dioxane can be associated through H bonds to either of its oxygen atoms.
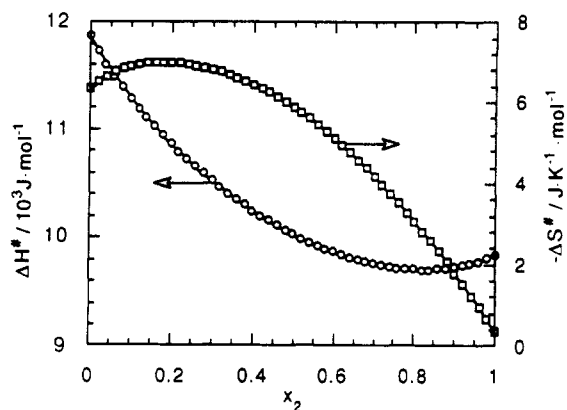
Figure 2. Variation of ΔH^* (activation enthalpy of viscous flow) and ΔS^* (activation entropy of viscous flow) for dioxane (1) + methanol (2).

The effect of temperature on the viscosity of the mixtures was examined by assuming the validity of Eyring's equation (*32*). This equation for a simple liquid is given by

$$\eta = (N_A h/V)\, \exp(\Delta G^*/(RT)) \qquad (12)$$

where N_A and h are respectively Avogadro's number and Plank's constants and ΔG^* is the free energy of activation for viscous flow. The molar volume (V) of a binary mixture is defined from the following equation:

$$V = \frac{x_2 M_2 + (1 - x_2)M_1}{\rho} \qquad (13)$$

On the other hand, since $\Delta G^* = \Delta H^* - T\Delta S^*$, it follows that

$$\eta = \{(N_A h/V)\, \exp(-\Delta S^*/R)\}\, \exp(\Delta H^*/(RT)) \qquad (14)$$

Since ΔS^* is being taken as a constant, eq 14 takes the form

$$\eta V = A\, \exp(\Delta H^*/(RT)) \qquad (15)$$

Equation 15 predicts a linear relationship between ln (ηV) and $1/T$. Alternatively, the experimental confirmation of such a correlation is an evidence of the validity of eq 12 over the specified range of temperatures.

Smoothed viscosity and molar volume data, calculated by using eqs 1, 9, and 13, were used in the plots of ln (ηV) vs $1/T$. Straight lines were obtained for each composition ($\sigma < 0.0045$). The corresponding values of the entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) were calculated by the least-squares method. The obtained results are graphically presented in Figure 2. The following relations were obtained:

$$-\Delta S^*/(\text{J·mol}^{-1}\cdot\text{K}^{-1}) = \sum_{i=0}^{8} S_i\, x_2{}^i = 6.3263 + 10.0726x_2 -$$
$$55.1587x_2{}^2 + 148.9820x_2{}^3 - 254.9143x_2{}^4 +$$
$$205.1922x_2{}^5 - 30.0198x_2{}^6 - 52.7177x_2{}^7 + 22.5804x_2{}^8$$
$$(16)$$

$$\sigma(\Delta S^*)/(\text{J·mol}^{-1}\cdot\text{K}^{-1}) = 7.9 \times 10^{-4}$$

$$\Delta H^*/(\text{J·mol}^{-1}) = \sum_{i=0}^{8} H_i\, x_2{}^i = 11860.4 - 6974.40x_2 +$$
$$14617.3x_2{}^2 - 32939.4x_2{}^3 + 51578.0x_2{}^4 - 42845.1x_2{}^5 +$$
$$13753.9x_2{}^6 + 2475.46x_2{}^7 - 1688.47x_2{}^8 \qquad (17)$$

$$\sigma(\Delta H^*)/(\text{J·mol}^{-1}) = 0.02$$
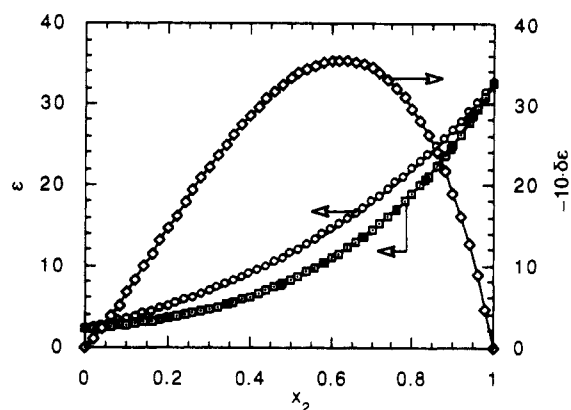
Figure 3. Variation of ϵ and $\delta\epsilon$ for dioxane (1) + methanol (2) at 25 °C: ■, experimental; ▣, calculated; ○, ideal dielectric constants.

Consequently, by combining eqs 5, 14, 16, and 17, we can write

$$\eta = \frac{N_A h\{\sum_{i=0}^{8} C_i\, x_2{}^i - (\sum_{i=0}^{8} B_i\, x_2{}^i)T\}\, \exp((\sum_{i=0}^{8} S_i\, x_2{}^i)/R)}{\{x_2 M_2 + (1 - x_2)M_1\}} \times$$
$$\exp((\sum_{i=0}^{8} H_i\, x_2{}^i)/(RT)) \qquad (18)$$

Equation 18, expressing η as a function of x_2 and T, fits the experimental data over the specified range of temperatures (15–35 °C) and for $0 < x_2 < 1$. The average deviation of the viscosity data calculated respectively from eqs 9 and 18 was $\pm 1.6 \times 10^{-6}$ Pa·s.

Dielectric Constants. The smoothing function

$$\epsilon = \sum_{i=0}^{5} D_i\, x_2{}^i \qquad (19)$$

was fitted at each temperature by the least-squares method. Values of the coefficients D_i and the corresponding standard errors of estimate σ are summarized in Table III. The results of fitting the data for 25 °C are presented as an example in Figure 3.

In an attempt to supply further experimental evidence for intermolecular associations in the binary systems studied, we examined the dielectric constant deviation from ideality. The ideal dielectric constants of the mixtures were calculated by using Decroocq's formula (*8*) in the most general form:

$$\epsilon^{\text{id}} = (1 - Y_2)\epsilon_1 + Y_2\epsilon_2 + 2\left(\frac{1}{\epsilon^{\text{id}}} - \frac{(1 - Y_2)}{\epsilon_1} - \frac{Y_2}{\epsilon_2}\right) \qquad (20)$$

where ϵ_1 and ϵ_2 are the dielectric constants of pure dioxane and methanol, respectively, and Y_2 is the volume fraction of methanol defined on the partial molar volume basis (*33*). This quantity has been determined by means of a method described previously (*15*).

Consequently, taking into account that the dielectric constant is an intensive property, we assume, in accordance with the literature (*8*, *33*, *34*), that the difference between experimental and ideal dielectric constant ($\delta\epsilon$) defined by

$$\delta\epsilon = \epsilon - \epsilon^{\text{id}} \qquad (21)$$

gives an adequate approach to estimate molar associations between the components of the system.

It was found that the values of $\delta\epsilon$ are generally negative, and the corresponding curves $-\delta\epsilon = f(x_2)$ at each temperature present a pronounced maximum at $x_2 \approx 0.63$ as it is shown by the example in Figure 3.

The maximum deviations from dielectric ideality occur at all temperatures exactly in the same region of compositions where

we observed the maximum relative deviations from the ideal behavior of [R]. The maximum values of $-\delta\epsilon$ are also attributed to the formation of two complexes between dioxane and methanol of the types 1:1 and 1:2.

At the molecular level, it has been argued that the negative values of $\delta\epsilon$ for various systems are a consequence of the formation of polar associates of lower dipole moment (35, 36). Also, it has been postulated that, in pure alcohols or in concentrated solutions of these substances in nonpolar liquids, the formed linear n-mers present a higher dipole moment (26). This behavior has been attributed to the fact that the O–H bond moment of these aggregates is increased through mutual induction. However, when the nonpolar solvent is added, these associates are broken up and the resulting hydrogen-bonded species have a lower dipole moment. On the other hand, it has been shown that the hydrogen-bonded complexes of dioxane of the type 1:2 present a negligible dipole moment (37). Consequently, taking into account all these assumptions, we could attribute the observed negative deviations from dielectric ideality to all these effects.

The variation of dielectric constant with temperature was correlated by the following equation (15, 16, 9):

$$\epsilon = A' \exp[-B'(T/K)] \qquad (22)$$

A similar fitting procedure, as described before, was applied. The following polynomials were obtained with optimum degree n equal to 9:

$$A' = \sum_{i=0}^{9} \alpha_i x_2^i = 2.77 + 10.35x_2 + 96.05x_2^2 -$$
$$214.40x_2^3 + 2.504\,06 \times 10^3 x_2^4 - 7.588\,81 \times 10^3 x_2^5 +$$
$$1.213\,437 \times 10^4 x_2^6 - 1.082\,449 \times 10^4 x_2^7 + 5.039\,21 \times$$
$$10^3 x_2^8 - 9.5495 \times 10^2 x_2^9 \qquad (23)$$

$$\sigma(A') = 1.27 \times 10^{-3}$$

$$B' = \sum_{i=0}^{9} \beta_i x_2^i = 7.51 \times 10^{-4} + 5.29 \times 10^{-3} x_2 + 7.064 \times$$
$$10^{-2} x_2^2 - 0.20435x_2^3 + 3.906 \times 10^{-2} x_2^4 + 0.76004x_2^5 -$$
$$1.63483x_2^6 + 1.59894x_2^7 - 0.78821x_2^8 + 0.15882x_2^9$$
$$(24)$$

$$\sigma(B')/K^{-1} = 2.19 \times 10^{-7}$$

When eq 22–24 are combined, it follows that

$$\epsilon = (\sum_{i=0}^{9} \alpha_i x_2^i) \exp(-T\sum_{i=0}^{9} \beta_i x_2^i) \qquad (25)$$

This equation, expressing ϵ as a function of x_2 and T, fits the experimental data over the specified range of temperatures (15–35 °C) and for $0 < x_2 < 1$. The average deviation of the ϵ data calculated respectively from eqs 19 and 25 was ±0.009 unit.

Refractive Indexes. The coefficients of the smoothing function

$$n_D = \sum_{i=0}^{4} D_i' x_2^i \qquad (26)$$

calculated by least squares are listed in Table III.

The effect of temperature on n_D was correlated by the following equation (15):

$$n_D = A'' \exp(-B''(T/K)) \qquad (27)$$

In all cases it was found that the graphs in n_D vs T were linear ($\sigma < 1.8 \times 10^{-4}$). The following polynomials were obtained:

$$A'' = \sum_{i=0}^{7} \alpha_i' x_2^i = 1.54660 - 8.00 \times 10^{-3} x_2 -$$
$$0.41160x_2^2 + 0.68175x_2^3 - 0.40550x_2^4 + 3.501 \times$$
$$10^{-2} x_2^5 - 1.666 \times 10^{-2} x_2^6 + 3.37 \times 10^{-3} x_2^7 \quad (28)$$

$$\sigma(A'') = 8.3 \times 10^{-7}$$

$$10^4 B'' = \sum_{i=0}^{7} \beta_i' x_2^i = 2.8652 + 0.7098x_2 -$$
$$7.9023x_2^2 + 13.5499x_2^3 - 6.3932x_2^4 - 0.8527x_2^5 +$$
$$0.7427x_2^6 - 0.3279x_2^7 \quad (29)$$

$$\sigma(B'')/K^{-1} = 3.1 \times 10^{-9}$$

The equation

$$n_D = (\sum_{i=0}^{7} \alpha_i' x_2^i) \exp(-T\sum_{i=0}^{7} \beta_i' x_2^i) \qquad (30)$$

fits the experimental data over the specified range of temperatures and compositions. The average deviation of the n_D data calculated respectively from eqs 26 and 30 was ±0.000 12 unit.

Glossary

α_i	coefficient in eq 23
α_i'	coefficient in eq 28
β_i	coefficient in eq 24
β_i'	coefficient in eq 29
δ	relative excess rheochor
ϵ	dielectric constant of the mixture
ϵ_1, ϵ_2	dielectric constants of dioxane and methanol
ϵ^{id}	ideal dielectric constant of the mixture
$\delta\epsilon$	difference between experimental and ideal dielectric constant of the mixture
η	viscosity of the mixture
ρ	density of the mixture
ρ_0, B	constants in eq 2
σ	standard deviation
A	constant in eq 15
A', B'	constants in eq 22
A'', B''	constants in eq 27
B_i	coefficient in eq 4
C_i	coefficient in eq 3
d_i	coefficient in eq 1
D_i	coefficient in eq 19
D_i'	coefficient in eq 26
$\Delta G^{\ddagger}$	activation free energy of viscous flow
H_i	coefficient in eq 17
$\Delta H^{\ddagger}$	activation enthalpy of viscous flow
$\bar{M}$	apparent molecular weight of the mixture
n_D	refractive index of the mixture for the sodium line
[R]	rheochor of the mixture defined by eq 6
R_i	coefficient in eq 8
$\Delta S^{\ddagger}$	activation entropy of viscous flow
S_i	coefficient in eq 16
T	absolute temperature
x_1, x_2	mole fractions of dioxane and methanol
Y_2	partial volume fraction of methanol

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Interfacial Tensions of Two-Liquid-Phase Ternary Systems

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Interfacial tensions of seven aqueous ternary systems containing propionic acid, 1-propanol, or 2-propanol as solute were measured at 25 °C with a DuNouy ring interfacial tensiometer. A simple equation is given for the estimation of the interfacial tensions with equilibrium compositions from binary data alone.

Introduction

The experimental data of interfacial tension are required by chemical engineers for the design of liquid-liquid contactors as well as by researchers for testing their methods used to predict or correlate interfacial tensions. The data for only 53 ternary systems were found in the literature (*1-8*). In the set of data of Murphy et al. (*1*) for 12 ternary systems containing acetic acid or acetone as solute, only the overall compositions of the whole liquid-liquid systems corresponding to the experimental interfacial tension data were given, and in that of Masamoto and Nakahara (*6*) for 5 ternary systems containing acetic acid as solute, only the mole fractions of solute in the two liquid phases were reported. For widening the data coverage for correlation, in the present work the interfacial tensions of seven ternary liquid-liquid aqueous systems are measured with a DuNouy ring tensiometer. We have given the compositions and densities of the two phases to more completely describe these seven ternary systems we have studied.

Experimental Section

All the measurements of interfacial tension were made at 25 ± 0.5 °C by use of a Kruss ring interfacial tensiometer with an accuracy of ± 0.1 mN m⁻¹ and a resolution of ± 0.05 mN m⁻¹. The data so obtained were corrected to the actual values by means of the Zuidema and Waters compensation for interface distortion (*9*).

The seven ternary systems studied are carbon tetrachloride + water + propionic acid, chloroform + water + propionic acid, benzene + water + propionic acid, toluene + water + propionic acid, n-heptane + water + propionic acid, cyclohexane + water + 2-propanol, and cyclohexane + water +

1-propanol. For all the systems, the points near the plait points are excluded since the data may be less reliable and they are of less importance in chemical engineering calculations; for instance, in liquid-liquid extraction where the operation near the plait point is usually avoided for the difficulty in phase separation. For the cyclohexane + water + 2-propanol system in the paper of Masamoto et al. (*6*), there was a mistake. The equilibrium compositions used for preparing the mixtures within the two-phase region are found to be those for the system containing cyclohexene instead of cyclohexane. No interfacial tension data of the other six systems appeared in the literature. For all the systems the component 1 and the component 2 are partially miscible, and the component 3 is completely soluble in both liquid phases.

Benzene, chloroform, carbon tetrachloride, and cyclohexane of spectroscopic grade and n-heptane, propionic acid, and 1-propanol of guaranteed purity (Tokyo Kasei Kogyo Co., Ltd., Japan) were used directly. Toluene and 2-propanol of analytical purity (Beijing Chemical Reagent Plant, China) were distilled in a laboratory column prior to use, retaining only the central portion of the distillate. The claimed minimum purity for the compounds is 99.0% or 99.5% (see Table I). Water was double distilled.

The densities and refractive indices of all the organic reagents at 20 °C were measured by using a pycnometer and an Abbe refractometer, respectively. The interfacial tensions of benzene, toluene, chloroform, carbon tetrachloride, n-heptane, and cyclohexane with water at 25 °C were also measured. A comparison between the measured values and those from the literature for the physical properties was listed in Table I.

The liquid-liquid equilibrium data for all the ternary systems were obtained from the literature (*10*). The three components forming the mixture with an overall composition within the two-phase region were weighed to an accuracy of about 0.1 mg into a sealed bottle. The bottles were kept in a thermostat and shaken several times during the period of at least 24 h allowed for equilibrium (*5*).

When the interfacial tensions of the two aqueous systems containing chloroform or carbon tetrachloride as the organic