mixture quantity m

- ID ideal mixture
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#### **Literature Cited**

- Kouris, S.; Panayiotou, C. J. Chem. Eng. Data 1989, 34, 200.
   Teja, A. S.; Rice, P. Ind. Eng. Chem. Fundam. 1981, 20, 77.
   Bauer, H.; Meerlender, G. Rheol. Acta 1984, 23, 514.
   Prolongo, J.; Horta, A. J. Phys. Chem. 1984, 88, 2163.

- (5) Fischer, J.; Weiss, A. Ber. Bunsen.-Ges. Phys. Chem. 1986, 90, 896.
- (6) Tardajos, G.; Dlaz Pena, M.; Aicart, E. J. Chem. Eng. Data 1986, 31, 492.
- Wei, I. Ph.D. Thesis, Rice University, Houston, TX, 1984.
   Skubla, P. Collect. Czech. Chem. Commun. 1981, 46, 303.
   Lewis, G. L.; Smyth, C. P. J. Am. Chem. Soc. 1940, 62, 1529.
- (10) Musscle, M. J.; Verhoeye, L. J. Chem. Eng. Data 1975, 20, 46.
- Dizechi, M.; Marschall, E. J. Chem. Eng. Data 1982, 27, 358
- (12) Mamagakis, N.; Panayiotou, C. Z. Phys. Chem. (Munich) 1989, 162, 57.

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## Physical Behavior of Some Reaction Media. Density, Viscosity, **Dielectric Constant, and Refractive Index Changes of Ethanol–Cyclohexane Mixtures at Several Temperatures**

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### Georgios E. Papanastasiou\* and Ioannis I. Ziogas

Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Thessaloniki, 540-06 Thessaloniki, Greece

Viscosities, densities, dielectric constants, and refractive indexes were determined for ethanol-cyclohexane mixtures at 15, 20, 25, 30, 35 °C and over the whole composition range. These properties are represented by means of empirical relations wherein the composition and temperature effects are involved. These equations fit the experimental data with an uncertainty of the same order of magnitude with the corresponding experimental error. The analysis of data evidences the occurrence of changes In the self-association of ethanol with changing composition.

#### Introduction

This paper is a part of continuing research on the kinetics of S<sub>N</sub>2 reactions between ions and dipolar molecules in solvents where the ionic reactant associates to form ion pairs (1-4).

In previous papers we studied the kinetics of the reaction of sodium ethoxide and methyl iodide in ethanol-dioxane solvent systems (3), where the mixture of two organic solvents, in various proportions, enabled us to change the physical properties of the reaction media. In these investigations, in agreement with analogous literature data (5), we observed that the corresponding reactions are markedly accelerated as the dielectric constant of the medium is progressively decreased. This effect has been explained by assuming that the nonelectrostatic solute-solvent interactions are more important than the electrostatic ones. Thus, we assumed that the reactant-solvating ability of the medium is changed by the formation of a polar complex between dioxane and ethanol; the formation of such a complex has been detected in previous investigations (6).

In an attempt to supply further evidence for this assumption, we decided to extend our kinetic studies to binary ethanol-cyclohexane solvent systems, where the possibility of formation of polar associates through hydrogen bonds does not exist.

However, one problem, generally encountered in such studles, is to correlate reaction rate data with the physical properties of the corresponding media. It should be noted that, among the many intensive physical properties of liquids, the dielectric constant ( $\epsilon$ ), the viscosity ( $\eta$ ), and the index of refraction (n) remain the common solvent parameters used to interpret medium effects upon mechanisms of reactions for polar and lonic species, as well as upon electrochemical data and ionic equilibria (7-9).

Although extensive tabulation of values of these properties for pure solvents are generally available, literature data for various binary solvent systems are often incomplete and may be reported only as empirical graphs.

This situation has encouraged us to make a series of systematic measurements of density, viscosity, dielectric constant, and refractive index of ethanol-cyclohexane mixtures over the whole composition range and temperatures from 15 to 35 °C. An attempt has been made to express these properties by means of single equations, wherein the temperature and composition effects are involved. Some physical properties of the above-mentioned binary mixtures have been previously reported in the literature (10-14). However, these studies have been made at very different composition or temperature ranges than those used in our kinetic experiments.

#### **Experimental Section**

Reagents. Absolute ethanol (Fluka, p.a.) was further purified according to a recommended method (15).

Cyclohexane (Merck GR > 99.5%, bp =  $80.7^{\circ}/760$  mmHg) was refluxed and then fractionally redistilled. In all distillations only the middle fraction coming over at the reported boiling point and comprising about 75% was retained. Pure-component physical properties were measured and compared to average literature data to assure that there were no significant effects due to impurities (Table I). Mixtures were gravimetrically prepared on a Mettler analytical balance just before their use. The probable error in the cyclohexane mole fraction  $X_2$  is estimated to be less than 0.0001.

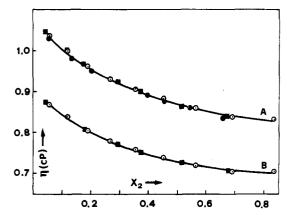
Measurements. The apparatus and procedure for the experimental measurements of density, viscosity, and dielectric constant were identical with those described previously (6). Refractive index measurements were carried out by means

of a thermostated Abbe refractometer (Jena). Values were

# Superscripts reference fluid /

Table I. Physical Properties of Pure Components

^	$\rho, \mathrm{g} \mathrm{cm}^{-3}$		η, cP		÷		n <sub>D</sub>	
temp, °C	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
				Ethanol				
15	0.793 69	0.79363 (16)	1.3182		26.24		1.3636	1.3633 (28)
20	0.78922	0.789 40 (16)	1.2050		25.41		1.3616	1.3614 (16)
25	0.78507	0.785 (13, 14, 17, 18)	1.0856	1.087 (13, 14)	24.55	24.42 (26, 27)	1.3597	1.3595 (16)
30	0.78076	0.780 79 (19)	0.9892	0.991 (25)	23.80	23.80 (27)	1.3577	
35	0.77681	0.7765 (13)	0.9061	0.908 (13)	23.06		1.3557	
				Cyclohexane				
15	0.78284	0.7831 (20, 21, 16)	1.0626	1.056 (16)	2.028		1.4285	1.4289 (16)
20	0.77836	0.7784(22, 23)	0.9781	0.980 (17)	2.023	2.023 (26)	1.4261	1.42623 (23)
25	0.77362	0.7737 (14, 23)	0.8942	0.890 (13, 14)	2.015	2.015 (26)	1.4234	1.42354 (23)
30	0.76879	0.769 14 (24)	0.8226	0.820 (16)	2.006	. ,	1.4206	
35	0.76401	0.7645 (13)	0.7592	0.757 (13, 16)	1.999		1.4180	



**Figure 1**. Variation of  $\eta$  (cP) with mole fractino  $X_2$  of cyclohexane for the ethanoi-cyclohexane system at (A) 25 °C and (B) 35 °C: (III) data from ref 13; ( $\bullet$ ) data from ref 14; ( $\odot$ ) data of this investigation.

obtained for the sodium D line, with an error of less than 0.0001 unit.

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

### **Results and Discussion**

The experimental density, viscosity, dielectric constant, and refractive index data at 15, 20, 25, 30, and 35 °C for the ethanol-cyclohexane solvent mixtures are listed in Table II. Only viscosity data of ethanol-cyclohexane mixtures covering the whole composition range at 25 and 35 °C have, to our knowledge, been previously reported (13, 14). These literature data are reported and compared to our values in Figure 1; the agreement is excellent.

**Densities.** As in the case of the ethanol-dioxane mixtures (6), the polynomial equation

$$\frac{1}{\rho} = \sum_{i=0}^{n} d_{i} X_{2}^{i}$$
(1)

was fitted at each temperature by a least-squares technique. On the basis of careful examination of the results of the fitting and taking into account that as the degree n of the polynomial is increased, the amount of smoothing is decreased, it was decided that the optimum degree n was equal to 4, namely much less than the number of data points. This degree minimizes the standard deviation  $\sigma$  defined by the following equation (29):

$$\sigma = \left[\frac{\sum_{i} \left( (1/\rho)_{i}^{\exp} - (1/\rho)_{i}^{\exp} \right)^{2}}{N - n - 1}\right]^{1/2}$$
(2)

where  $(1/\rho)_i^{exp}$  and  $(1/\rho)_i^{est}$  indicate the experimental and estimated, from regression eq 1, values of  $1/\rho$ . *N* is the number

Table II. Experimental Density  $(\rho)$ , Viscosity  $(\eta)$ , Dielectric Constant  $(\epsilon)$ , and Refractive Index  $(D_D)$  Data for Ethanol-Cyclohexane Mixtures at 15, 20, 25, 30, and 35 °C

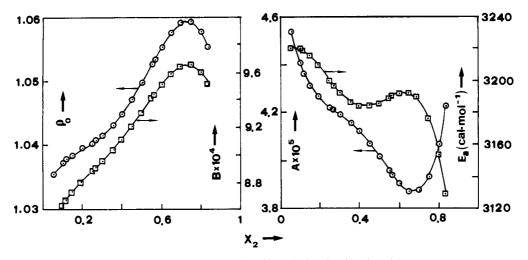
$X_2$	15 °C	20 °C	25 °C	30 °C	35 °C	
		ρ. 1	g/cm <sup>3</sup>			
0.0565	0.79037	0.786 26	0.78194	0.77770	0.77340	
0.1188	0.78797	0.78381	0.779 40	0.77512	0.77074	
0.1894	0.78576	0.78153	0.77698	0.77279	0.76810	
0.2674	0.78383	0.77981	0.77529	0.77084	0.76613	
0.3539	0.78273	0.77826	0.77396	0.76931	0.76458	
0.4506	0.78185	0.77736	0.77274	0.76812	0.76345	
0.5626	0.78130	0.77668	0.77222	0.767 30	0.76253	
0.6898	0.78127	0.77654	0.77175	0.76687	0.761 99	
0.8348	0.78112	0.77653	0.77185	0.76703	0.76216	
η, cP						
0.0565	1.2475	1.1427	1.0369	0.9470	0.8683	
0.1188	1.2000	1.0977	0.9995	0.9133	0.8383	
0.1894	1.1524	1.0535	0.9602	0.8784	0.8039	
0.2674	1.1166	1.0275	0.9303	0.8522	0.7793	
0.3539	1.0889	0.9953	0.9067	0.8288	0.7578	
0.4506	1.0602	0.9698	0.8821	0.8084	0.7384	
0.5626	1.0351	0.9436	0.8589	0.7860	0.7191	
0.6898	1.0095	0.9184	0.8388	0.7655	0.7052	
0.8348	1.0016	0.9099	0.8319	0.7647	0.7051	
			e			
0.0565	23.757	22.843	22.204	21.475	20.835	
0.1188	21.014	20.329	19.719	19.084	18.584	
0.1894	18.263	17.629	17.100	16.524	16.048	
0.2674	15.429	14.882	14.423	13.917	13.529	
0.3539	12.560	12.062	11.708	11.280	10.977	
0.4506	9.693	9.301	8.999	8.704	8.428	
0.5626	6.786	6.548	6.344	6.104	5.916	
0.6898	4.277	4.180	4.062	3.959	3.867	
0.8348	2.619	2.599	2.579	2.556	2.537	
n <sub>D</sub>						
0.0565	1.3682	1.3660	1.3635	1.3613	1.3590	
0.1188	1.3740	1.3712	1.3691	1.3664	1.3636	
0.1894	1.3798	1.3772	1.3738	1.3722	1.3687	
0.2674	1.3859	1.3832	1.3806	1.3780	1.3747	
0.3539	1.3921	1.3893	1.3869	1.3844	1.3821	
0.4506	1.3985	1.3964	1.3937	1.3913	1.3886	
0.5626	1.4062	1.4036	1.4011	1.3986	1.3960	
0.6898	1.4138	1.4116	1.4091	1.4061	1.4038	
0.8348	1.4213	1.4194	1.4167	1.4142	1.4117	

of experimental data. The values of the adjustable coefficients  $d_i$  are summarized in Table III along with the standard deviation  $\sigma$ .

The effect of temperature on the density of the mixtures was examined by assuming the validity of the following equation (27):

$$\rho = \rho_0 - BT \tag{3}$$

Calculated density data, by means of eq 1, were used in the plots of  $\rho$  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 ( $R^2 > 0.9997$ ). The



**Figure 2.** Variation of the constants  $\rho_0$ , B (eq 3) and A,  $E_v$  (eq 11) with mole fraction  $X_2$  of cyclohexane.

Table III. Coefficients and Standard Deviations  $\sigma$  for Representation of  $1/\rho$ , [R],  $\epsilon$ , and  $n_D$  of Ethanol-Cyclohexane Mixtures by Equations 1, 9, 17, and

Ethano	ol-Cyclohez	ane Mixtu	res by Equ	ations 1, 9,	17, and 24
	15 °C	20 °C	25 °C	30 °C	35 °C
		Equ	ation 1		
$d_0$	1.26065	1.267 48	1.27396	1.28101	1.28745
$10^2 d_1$	8.75256	8.394 53	9.573 49	9.266 02	10.7252
$-10d_{2}$	1.42397	1.22703	1.73560	1.48249	1.996 29
$10^2 d_3$	9.564 58	7.26588	15.9597	12.1496	19.8006
$-10^2 d_4$	2.04355	1.34766	6.21534	4.53542	8.43155
σ	1.44 ×	1.01 ×	1.67 ×	1.72 ×	1.31 ×
	10-4	10-4	10-4	10-5	10-4
		Εαι	ation 9		
Ro	33.7721	33.5898	33.3648	33.1599	32.9732
$R_1$	26.6902	26.5203	26.4337	26.3836	26.3442
σ	0.022	0.027	0.019	0.026	0.023
		Equ	ation 17		
$D_0$	26.5213	25.2526	24.6268	23.8057	23.0422
$-\check{D}_1$	52.0096	43.6174	44.4248	42.4406	39.7009
$D_2$	59.0154	18.0732	29.4408	23.7134	15.857
$-\bar{D}_3$	98.8860	1.1087	31.4684	17.2026	3.7800
$D_4$	106.0846	2.0386	37.0794	21.1404	11.0857
-Ď <sub>5</sub>	38.4892	-2.0180	12.7764	6.4230	3.9386
σ	0.018	0.013	0.010	0.024	0.037
		Equ	ation 24		
$D_0'$	1.36224	1.36093	1.35905	1.35617	1.35597
$10^{2}D_{1}'$	11.2587	9.047 55	8.015 86	9.45031	4.604 92
$10^2 D_{2'}$	-13.9006	-2.27563	1.74911	-8.517 51	18.1499
$10^2 D_{3'}$	22.3897	-3.86612	-9.989 56	20.5886	-42.6019
10D₄ <sup>7</sup>	-1.801 40	0.905841	1.28391	-2.79601	4.08479
$10^2 \dot{D_b}'$	4.72971	-5.599 17	-6.334 86	13.4452	-14.7314
σ	$1.4 \times 10^{-4}$	$1.8 \times 10^{-4}$	$4.1 \times 10^{-4}$	$9.4 \times 10^{-5}$	$3.3 \times 10^{-4}$

corresponding constants  $\rho_0$  and *B* were calculated by the least-squares method. The obtained results are graphically represented in Figure 2. On the basis of these data, the following relations were derived:

$$\rho_{0} = \sum_{i=0}^{7} C_{i} X_{2}^{i} = 1.03192 + 0.08218X_{2} - 0.36871X_{2}^{2} + 0.87062X_{2}^{3} - 0.71997X_{2}^{4} + 0.22572X_{2}^{5} - 0.13718X_{2}^{6} + 0.03460X_{2}^{7}$$
(4)  
$$\sigma_{\rho_{0}} = 1.69 \times 10^{-7}$$

$$10^{5}B = \sum_{i=0}^{2} B_{i} X_{2}^{i} = 8.28438 + 4.68475X_{2} - 15.7523X_{2}^{2} + 32.3426X_{2}^{3} - 25.8577X_{2}^{4} + 8.30678X_{2}^{5} - 4.98327X_{2}^{6} + 1.24761X_{2}^{7}$$
(5)  
$$\sigma_{B} = 5.5 \times 10^{-10}$$

It follows that the equation relating the density to the temperature, T, and the mole fraction of cyclohexane,  $X_2$ , is

$$\rho = \left(\sum_{i=0}^{7} C_{i} X_{2}^{i}\right) - \left(\sum_{i=0}^{7} B_{i} X_{2}^{i}\right) T$$
(6)

This equation fits the experimental data over the specified range of temperatures (15–35 °C) and compositions (0.07 <  $X_2 < 0.85$ ) with an uncertainty of 8.2 × 10<sup>-5</sup>, which is of the same order of magnitude with the experimental error.

**Viscosities.** In order to express the viscosity as a function of  $X_2$ , the rheochor [R] ( $\beta$ ) for various mixtures was calculated from the following equation:

$$[\mathsf{R}] = \frac{\bar{M}}{\rho} \eta^{1/8} \tag{7}$$

where

$$\bar{M} = (1 - X_2)M_1 + X_2M_1 \tag{8}$$

 $M_1$  and  $M_2$  being the molecular weights of ethanol and cyclohexane, respectively.

It should be noted that, because of the form of eq 7, even small errors in the experimental values of  $\rho$  cause large errors in [R]. To avoid these errors, smoothed values of  $\rho$ , calculated from eq 1, were substituted in eq 7.

In all temperatures studied, it was found that the plots of [R] vs  $X_2$  are fairly linear ( $R^2 > 0.99998$ ) of the general form:

$$[R] = R_0 + R_1 X_2 \tag{9}$$

whose coefficient  $R_0$  and  $R_1$  are listed in Table III.

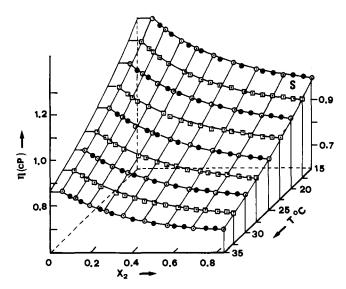
By combining eqs 1, 7, and 9, one obtains the following rational function (i.e., the ratio of two polynomials):

$$\eta^{1/8} = \frac{1}{\bar{M}} \frac{R_0 + R_1 X_2}{d_0 + d_1 X_2 + d_2 X_2^2 + \dots + d_4 X_2^4}$$
(10)

As previously (6), it was found in this investigation that, in all cases, eq 10 represents much better the reported data than a simple polynomial. The average deviation of the calculated values from the experimental ones, always less than  $\pm 0.25\%$  (approximate experimental accuracy), shows that eq 10 closely represents the experimental viscosity data. A comparison of experimental and calculated  $\eta$  data is presented in Figure 3.

The effect of temperature on the viscosity of the mixtures was examined by assuming the validity of the following equation, first pointed out by Guzmann (30):

$$\eta = A \exp\left(\frac{E_{\rm V}}{RT}\right) \tag{11}$$



**Figure 3.** Variation of  $\eta$  (cP) with mole fraction  $X_2$  and temperature T (°C): ( $\odot$ ) experimental values; ( $\oplus$ ) calculated from eq 10 values; ( $\boxdot$ ) calculated from eq 14 values.

where A is a constant and  $E_V$  is the energy barrier that must be overcome before the elementary flow can occur. The term  $\exp(E_V/RT)$  can then interpreted as a Boltzmann factor, giving the fraction of the molecules having the requisite energy to surmount the barrier. Thus,  $E_V$  is an activation energy of viscous flow.

Smoothed viscosity data, calculated by means of eq 10, were used in plots of ln  $\eta$  vs 1/T. Straight lines were obtained for each composition ( $R^2 > 0.9992$ ). The corresponding constants A and  $E_V$  were calculated by the least-squares method. The obtained results are graphically presented in Figure 2. The following relations were obtained:

$$10^{5}A = \sum_{j=0}^{\prime} A_{j} X_{2}^{i} = 4.8127 - 6.0682X_{2} + 24.0534X_{2}^{2} - 41.3531X_{2}^{3} + 7.3541X_{2}^{4} + 54.4976X_{2}^{5} - 61.4387X_{2}^{6} + 24.4315X_{2}^{7}$$
(12)

$$E_{V} = \sum_{j=0}^{7} E_{j} X_{2}^{j} = 3210.301 + 291.191 X_{2} - 2431.58 X_{2}^{2} + 5296.57 X_{2}^{3} - 3779.91 X_{2}^{4} + 531.597 X_{2}^{5} - 338.593 X_{2}^{6} + 84.5555 X_{2}^{7}$$
(13)

$$\sigma_{F_{11}} = 4.37 \times 10^{-3}$$

Consequently, the following equation expresses  $\eta$  as a function of  $X_2$  and T:

$$\eta = \left(\sum_{j=0}^{7} A_{j} X_{2}^{j}\right) \exp\left(\frac{\sum_{j=0}^{7} E_{j} X_{2}^{j}}{RT}\right)$$
(14)

Equation 14 explicitly represents the surface S in Figure 3. This equation predicts the experimental data with an overall uncertainty of  $\pm 0.0021$  cP.

The molar quantity  $E_V$  is known to be sensitive to molar associations (30-32). If the mixtures studied behave ideally, this quantity could be calculated for each composition by applying the additivity rule

$$E_{y}^{kl} = (1 - X_2)E_1 + X_2E_2 \tag{15}$$

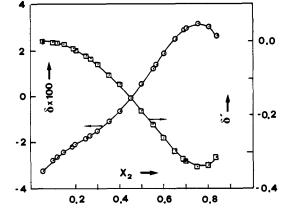
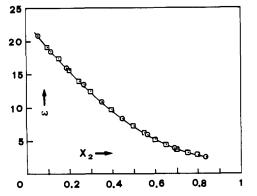


Figure 4. Variation of  $\delta$  (eq 16) and  $\delta'$  (eq 19, 35 °C) with mole fraction  $X_2$  of cyclohexane.



**Figure 5.** Variation of experimental ( $\odot$ ) and calculated ( $\Box$ ) dielectric constants with mole fraction  $X_2$  of cyclohexane for the ethanol-cyclohexane system at 35 °C.

 $E_1$  and  $E_2$  being the activation energies of pure ethanol and cyclohexane, respectively.

So, the values of the parameter

$$\delta = \frac{E_{\vee} - E_{\vee}^{\flat}}{E_{\vee}^{\flat}} = \frac{E_{\vee}^{\flat}}{E_{\vee}^{\flat}}$$
(16)

give an adequate approach to estimate molar associations. It was found that the maximum values of  $\delta$  occurs at  $X_2 \approx 0.75$  (Figure 4).

However, it has been well-known, for a long time, that alcohols in solutions in nonpolar solvents associate by means of hydrogen bonds into a series of *n*-mers (10-13, 33-41). 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, at concentrated solutions of alcohols only linear *n*-mers can be considered. On the other hand, Huyskens et al. showed that in solutions around the composition  $X_2 \approx 0.8$  the predominant hydrogen-bonded species of ethanol in cyclohexane is the cyclic trimer (13). It has been also postulated in this investigation that the cyclic species present greater viscosity than the linear ones.

Consequently, taking into account all these assumptions, we could attribute the observed values of  $\delta$  to all these effects. **Dielectric Constants**. The smoothing function

$$\epsilon = \sum_{i=0}^{n} D_i X_2^{i}$$
(17)

was fitted at each temperature by the least-squares method. In this case it was found that the optimum degree n was equal to 5. Values of the coefficients  $D_i$  and the corresponding standard deviations  $\sigma$  are summarized in Table III. The results

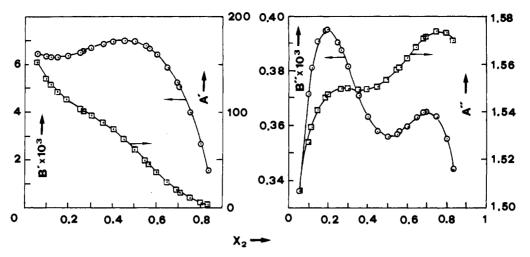


Figure 6. Variation of the constants A', B' (eq 20) and A'', B'' (eq 25) with mole fraction  $X_2$  of cyclohexane.

of fitting the data for 35  $^{\circ}\mathrm{C}$  are presented as an example in Figure 5.

In an attempt to study from a different point of view, than was previously studied, the self-association of ethanol, we examined the dielectric constant deviation from ideality. The ideal dielectric constants of the mixtures were calculated by using the Decroocq formula (42) in the most general form:

$$\epsilon^{\mathsf{ld}} = (1 - Y_2)\epsilon_1 + Y_2\epsilon_2 + 2\left(\frac{1}{\epsilon^{\mathsf{ld}}} - \frac{(1 - Y_2)}{\epsilon_1} - \frac{Y_2}{\epsilon_2}\right)$$
(18)

where  $\epsilon_1$  and  $\epsilon_2$  are the dielectric constants of pure ethanol and cyclohexane, respectively, and  $Y_2$  is the volume fraction of cyclohexane defined on the partial molar volume basis (43). This quantity has been determined by means of a method described previously (6).

Evidently, the values of the parameter

$$\delta' = \frac{\epsilon - \epsilon^{id}}{\epsilon^{id}} = \frac{\epsilon^{E}}{\epsilon^{id}}$$
(19)

give an adequate approach to estimate molar associations of ethanol.

It was found that  $\epsilon^{\text{E}}$  values are generally negative, and the corresponding curves  $\delta' = f(X_2)$  at each temperature present a pronounced minimum at  $X_2 \approx 0.75$  (Figure 4).

A point of interest is that the maximum relative deviations from dielectric ideality occur for all temperatures exactly in the same region of compositions where we observed the maximum value of  $\delta$ .

At the molecular level, it has been argued that the negative values of  $\epsilon^{E}$  for various systems are a consequence of the formation of polar associates of lower dipole moment (36, 41, 44, 45). Thus, 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. 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 hydrogenbonded species have a lower dipole moment. On the other hand, Huyskens et al. (34) showed that in solutions of some alcohols in hexane and cyclohexane the calculated apparent dipole moment of the corresponding alcohols changes with changing composition and passes through a minimum at  $X_2 \approx$ 0.8. This behavior has been attributed to the formation of nonpolar cyclic trimers.

Consequently, taking into account all these assumptions, we could attribute the observed deviations from dielectric ideality to all these effects.

The variation of dielectric constant with temperature was studied by means of the following equation (6, 26):

$$\epsilon = A' \exp(-B'T) \tag{20}$$

A similar form of calculation, as described before, was applied. The obtained results are represented in Figure 6. The following equations were obtained:

$$10^{-2}A' = \sum_{i=0}^{7} \alpha_i X_2^{i} = 1.8518 - 7.2757X_2 + 27.8283X_2^{2} - 61.5843X_2^{3} + 75.8432X_2^{4} - 82.5097X_2^{5} + 79.8437X_2^{6} - 34.3610X_2^{7}$$
(21)

$$\sigma_{A'} = 0.06$$

$$10^{3}B' = \sum_{i=0}^{7} \beta_{i} X_{2}^{i} = 6.7795 - 7.4941X_{2} + 28.343X_{2}^{2} + 33.272X_{2}^{3} - 283.82X_{2}^{4} + 539.52X_{2}^{5} - 506.04X_{2}^{6} + 185.13X_{2}^{7}$$
(22)

$$\sigma_{B'} = 8.52 \times 10^{-4}$$

By combining equations 20, 21, and 22, it follows that

$$\epsilon = (\sum_{i=0}^{7} \alpha_i X_2^{i}) \exp(-T \sum_{i=0}^{7} \beta_i X_2^{i})$$
(23)

This equation predicts the experimental data with an overall uncertainty of  $\pm 0.025$  unit, which is about equal to the experimental error.

Refractive Indexes. The coefficients of the smoothing function

$$n_{\rm D} = \sum_{i=0}^{5} D_i' X_2^{i}$$
(24)

calculated by the least-squares method are listed in Table III. The effect of temperature on  $n_{\rm D}$  was studied by using the following equation (6):

$$n_{\rm D} = A^{\prime\prime} \exp(-B^{\prime\prime}T) \tag{25}$$

In all cases it was found that the graphs in  $n_{\rm D}$  vs T were linear ( $R^2 > 0.998$ ). The obtained values of A'' and B'' for

various compositions are graphically shown in Figure 6. The corresponding curves were fitted to the following polynomials:

$$A'' = \sum_{i=0}^{7} \alpha_i X_2^{i} = 1.465590 + 0.931896X_2 -$$
  
3.740238 $X_2^2 + 6.384525X_2^3 - 3.689626X_2^4 -$   
1.106555 $X_2^5 + 1.814415X_2^6 - 5.488909X_2^7$  (26)

 $\sigma_{A''} = 8.4 \times 10^{-6}$ 

$$10^{3}B'' = \sum_{i=0}^{7} \beta_{i}' X_{2}' = 0.2546 + 1.8833X_{2} - 8.6274X_{2}^{2} + 16.068X_{2}^{3} - 12.897X_{2}^{4} + 3.7810X_{2}^{5} - 0.27621X_{2}^{6} - 0.0212X_{2}^{7}$$
(27)

The equation

$$n_{\rm D} = \left(\sum_{i=0}^{7} \alpha_i' X_2^{\ i}\right) \exp(-T \sum_{i=0}^{7} \beta_i' X_2^{\ i}) \tag{28}$$

fits the experimental data over the specified range of temperatures and compositions with an uncertainty of  $\pm 0.0001$  unit. which is about equal to the experimental error.

#### Glossary

ρ	density of the mixture, g cm <sup>-3</sup>
η	viscosity of the mixture, cP
δ	relative excess activation energy of viscous flow of the mixture
E	dielectric constant of the mixture
€ <sub>1</sub> ,€ <sub>2</sub>	dielectric constants of ethanol and cyclohexane, re- spectively
ε <sup>E</sup>	excess dielectric constant of the mixture
€ <sup>id</sup>	ideal dielectric constant of the mixture
δ'	relative excess dielectric constant of the mixture
n <sub>D</sub>	refractive index of the mixture for sodium D line
τ	absolute temperature
[R]	rheochor of the mixture defined by eq 7
X <sub>2</sub>	mole fraction of cyclohexane
$Y_2^-$	partial volume fraction of cyclohexane
$\rho_0, \boldsymbol{B}$	constants in eq 3
<b>M</b>	apparent molecular weight of the mixture
Α	constant in eq 11
E <sub>v</sub>	activation energy of viscous flow
A',B'	constants in eq 20
A",B"	constants in eq 25
d₀d₄	coefficient in eq 1
$R_0, R_1$	coefficient in eq 9
	coefficient in eq 17
D <sub>0</sub> 'D <sub>5</sub> '	

Registry No. Ethanol, 64-17-5; cyclohexane, 110-82-7.

#### Literature Cited

- Cayzergues, P.; Georgoulis, C.; Papanastasiou, G. J. Chim. Phys. 1977, 74, 1103; Ibid. 1977, 74, 1112; C. R. Séances Acad. Sci. (Paris) 1977, C183, 285.
   Papanastasiou, G.; Papoutsis, A.; Jannakoudakis, D. Chim. Chron., Non Constant Consta
- (3) (4)
- Papanastasiou, G.; Papoutsis, A.; Jannakoudakis, D. Chim. Chron., New Ser. 1984, 13, 99.
  Papanastasiou, G.; Papoutsis, A.; Jannakoudakis, D.; Georgoulis, C. J. Chim. Phys. 1985, 83, 907; 1985, 83, 913.
  Tsirtou, M.; Papoutsis, A.; Papanastasiou, G. 12th Hellenic Conference of Chemistry, Thessaloniki, Greece, 1988; p 483.
  Tchoubar, B. Bull. Soc. Chim. Fr. 1964, 2069 and references cited theorem (5)
- therein. (6)
- Papanastasiou, G.; Papoutsis, A.; Kokkinidis, G. Bull. Soc. Chlm. Fr. 1987, 589; J. Chem. Eng. Data 1987, 32, 377. Amis, E. S. Solvent Effects on Reaction Rates and Mechanisms; Aca-(7)
- (8)
- Annis, E. S. Scholm Enects on Reaction Parts and Mechanisms; Academic: New York, 1966; Chapters 1 and 2. Lagowski, J. J., Ed. The Chemistry of Nonaqueous Solvents; Academic: New York, 1978; Vol. VA, pp 121–178. King, E. J. Acid-Base Equilibria; Pergamon: Oxford, U.K., 1965; Chapters 7, 8, and 10. (9)
- (10)
- (11)
- (12)
- Chapters 7, 6, and 10. Staveley, L. A.; Taylor, P. F. J. Chem. Soc. 1956, 200. Ibbitson, D. A.; Moore, L. F. J. Chem. Soc. B 1967, 76. Hudson, R. F.; Stelzer, I. Trans. Faraday Soc. 1958, 54, 213. Bamelis, P.; Huyskens, P.; Meeussen, E. J. Chim. Phys. 1965, 62, (13) 158
- Wei, I.-C.; Rowley, R. L. J. Chem. Eng. Data 1984, 29, 332. Czernecki, S.; Georgoulis, C.; Prevosts, Ch. Bull. Soc. Chim. Fr. (14) (15) 1970, 3088.
- Timmermans, J. Physico-Chemical Constants of Pure Organic Com-(16)
- Immermans, J. Physico-Chemical Constants of Pure Organic Compounds; Elsevier: New York, 1964; Vol. II.
  Riddick, J. A.; Bunger, W. B. Organic Solvents. Techniques of Chemistry; Wiley-Interscience: New York, 1970; Vol. II.
  Mussche, M. J.; Verhoeye, L. A. J. Chem. Eng. Data 1975, 20, 46.
  Janz, G. J.; Tomkins, R. P. T. Nonaqueous Electrolytes Handbook; Academic: New York, 1972; Vol. I.
  Massart, L. Bull. Soc. Chim. Belg. 1936, 45, 76.
  Chavanne, G.; Van Risseghen, H. Bull. Soc. Chim. Belg. 1922, 31, 87 (17)
- (19)
- (20)
- (21) 87
- (22) Michielewicz, C. Rocz. Chem. 1938, 18, 718.
   (23) Forziati, A. F.; Giasgow, A. R., Jr.; Willingham, G. B.; Rossini, F. D. J. Res. Natl. Bur. Stand. 1946, 36, 129.
- (24) Scatchard, G.; Wood, S. E.; Mochel, J. M. J. Am. Chem. Soc. 1946,

- (24) Scatchard, G.; Wood, S. E.; Mochel, J. M. J. Am. Chem. Soc. 1946, 68, 1960.
  (25) Titani, T. Bull. Inst. Res. Jpn. 1927, 671.
  (26) Maryott, A. A.; Smith, E. R. Table of Dielectric Constants of Pure Liquids. Natl. Bur. Stand. Circ. 1951, No. 514.
  (27) Dannhauser, W.; Bahe, L. W. J. Chem. Phys. 1964, 40, 3058.
  (28) Dorochewsky, A. G. J. Russ. Phys. Chem. Soc. 1911, 43, 66.
  (29) Chatterjee, S.; Price, B. Regression Analysis by Example; John Wiley: New York, 1977; Chapter 3.
  (30) Grupberd, L.: Nissan, A. H. Trans, Faradex Soc. 1949, 45, 125 and
- (30) Grunberg, L.; Nissan, A. H. Trans. Faraday Soc. 1949, 45, 125 and references cited therein.
- (31) Glastone, S.; Textbook of Physical Chemistry; D. Van Nostrand: New York, 1946; p 501.

- York, 1946; p 501.
  (32) Moore, J. W. *Physical Chemistry*; Longman: London, 1972; p 926.
  (33) Prigogine, I.; Desmyter, A. *Trans. Faraday Soc.* 1951, 47, 1137.
  (34) Huyskens, P.; Henry, R.; Gillerot, G. *Bull. Soc. Chim. Fr.* 1962, 720.
  (35) Brot, C. J. *Chim. Phys.* 1964, 61, 139.
  (36) Syrkin, Y. K.; Dyatkina, M. E. *Structure of Molecules and the Chemical Bond*; Dover: New York, 1964, p 277.
  (37) Santos, J. D.; Pineau, P.; Josien, M.-L. J. *Chim. Phys.* 1965, 62, 528 and references cited therein.
  (38) Eletcher A. N.: Heller, A. C. *J. Phys. Chem.* 1987, 21, 3742.

- (38) Fletcher, A. N.; Heller, A. C. J. Phys. Chem. 1967, 71, 3742.
  (39) Ibbitson, D. A.; Moore, L. F. J. Chem. Soc. B 1967, 80.
  (40) Vinogradov, S. N. Hydrogen Bonding; Van Nostrand Reinhold: New York, 1971; pp 16, 127.
- (41) Kay, R. L.; Evans, D. F.; Matesich, M. A. Solute-Solvent Interactions; (41) N. D., Evalis, D. F., Matskill, M. A. Solide-Solven The M. Dekker: New York, 1976; Vol. 2, p 133.
  (42) Decrocq, D. Bull. Soc. Chim. Fr. 1963, 127.
  (43) Reynaud, R. Bull. Soc. Chim. Fr. 1972, 532.
  (44) Payne, R.; Theodoroy, I. J. Phys. Chem. 1972, 76, 2892.
  (45) Koolling, O. W. Anal. Chem. 1985, 57, 1721.

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