

Relative Permittivity of 1,2-Ethanol + 1,2-Dimethoxyethane from -10 to +30 °C

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The relative permittivities (ϵ) of 1,2-ethanol, 1,2-dimethoxyethane, and nine binary mixtures were measured at five temperatures from -10 to +30 °C. The experimental data were fitted vs composition of the mixture (x_1) in order to investigate the existence of solvent/cosolvent complexes, their stoichiometric ratios, and their thermostability. The formation of these complex species may be interpreted on the basis of specific interactions between the components of the mixed solvents.

Introduction

Some recent papers from our laboratory have been concerned with the chemical, physical, and thermodynamic properties of a chosen "guide solute" picric acid in some binary liquid mixtures of solvents of practical and electroanalytical interest.

At first, we have investigated the binary solvent systems composed of 1,2-ethanol, 2-methoxyethanol, *N,N'*-dimethylformamide, and water, crossing the components with each other, and in a wide temperature range (1-5). In this way, it is possible to elucidate some peculiarities of the selected solute/solvent systems because the chosen binary mixtures make possible the variation "in continuum" of the extrathermodynamic parameters such as density, viscosity, relative permittivity, and any other intensive chemophysical properties of liquids that influence the real behavior.

Now, continuing our interest in this field, we have extended these investigations to 1,2-ethanol + 1,2-dimethoxyethane.

In order to evaluate the experimental dissociation constant (β) of a solute in a solvent system by a conductometric technique, it is necessary to know the extrathermodynamic functions. In this paper we report the results of the studies about the relative permittivity (ϵ) of the selected solvent system in the $-10 \leq t/^\circ\text{C} \leq +30$ range, with thermal scanning of 10 °C. The excess dielectric property ϵ^E was calculated in order to assess the deviations from ideality as a function of binary composition. Furthermore, the trend of this function is a very powerful tool to investigate the possibility of forming different complex solvent/cosolvent adducts, as far as their stoichiometrical composition and their thermostability.

Experimental Section

Materials. The solvents 1,2-ethanol and 1,2-dimethoxyethane (both containing water <0.10% by mass, found by Karl-Fischer titrations) were high purity grade reagents from Carlo Erba (Milan). 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 water amount, keeping the middle fraction only (bp 83 °C) for the measurements. The 1,2-ethanol was used without further purification. The final purity of both solvents was checked by gas chromatography (99.5% diol, 99.7% ether).

Apparatus and Procedures. The mixtures were prepared by mass just before use by using a Mettler PM 4800 Δ -range balance, operating in a drybox to avoid the atmospheric mois-

ture. Samples were maintained dry by 3A molecular sieves. The probable error in the 1,2-ethanol mole fraction (x_1) is estimated to be $<1.5 \times 10^{-4}$.

Relative permittivity measurements were made by the heterodyne beat method with a WTW DM 01 dipolmeter, working at a radiofrequency of 2.0 MHz, equipped with two thermostated stainless steel cylindrical cells: MFL2 type ($7 < \epsilon < 21$) calibrated with dichloromethane, pyridine, 1-butanol, and acetone, and MFL3 type ($21 < \epsilon < 90$) calibrated with ethanol, methanol, glycerol, and water. All these calibrating nonaqueous solvents were Carlo Erba spectrograde quality, their purity being checked by gas chromatography, and were used as supplied. Water for the calibration cell was deionized by a MilliQ-plus apparatus (Millipore) and has a specific conductance $\leq 1.35 \mu\text{S}$ at 25 °C. All the reference dielectric constants were taken from the literature (7). A very good overlap of ϵ was observed at the borderline of the operative limits of the cells. The overall experimental uncertainty, expressed as standard deviation, was $\pm 0.2\%$, with a confidence interval of 95% for at least 10 runs at each selected temperature. Temperature control was provided by a Lauda K2R thermostatic bath maintained to ± 0.02 °C.

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

The relative permittivity of the two pure liquids and their nine binary solutions at the five temperatures are given in Table I. The temperature dependence of ϵ was fitted to the equation (7)

$$\ln \epsilon = \sum_0^I \alpha_i (T/K)^i \quad (1)$$

whose α_i coefficients (for $i = 1$) are summarized in Table II along with the standard deviations $\sigma(\ln \epsilon)$ for each binary mixture.

The polynomial expansion in the reduced form at the first power term (eq 1) appears to be completely adequate to represent the experimental data, and allows us to calculate the relative permittivity with an accuracy close to the experimental accuracy. The average uncertainty $\Delta(\epsilon)$ evaluated by means of the equation

$$\Delta(\epsilon) = \frac{\sum_i |\epsilon_{\text{calcd}} - \epsilon_{\text{expt}}|}{N} \quad (2)$$

where N is the number of experimental points, is ± 0.02 units of ϵ over the set of 55 values of Table I.

In order to carry out predictive calculations for this binary solvent system at different mole fractions than those reported, the following equation was used:

$$\ln \epsilon = \sum_0^J \beta_j x_1^j \quad (3)$$

to fit each isothermal set of experimental data. The results, for $j = 3$, obtained by a multilinear regression package TSP (β),

Table I. Experimental Relative Permittivity Values for 1,2-Ethanediol (1) + 1,2-Dimethoxyethane (2) at Various Temperatures

$t/^\circ\text{C}$	ϵ^E at various x_1										
	1.0000	0.9435	0.8813	0.8126	0.7355	0.6501	0.5516	0.4511	0.3170	0.1710	0.0000
-10	49.23	41.53	39.36	35.40	30.64	26.16	22.10	18.60	15.05	11.82	8.69
0	46.65	39.30	37.40	33.57	28.87	24.88	21.05	17.70	14.36	11.32	8.35
10	44.49	37.40	35.56	32.07	27.22	23.63	20.07	16.88	13.76	10.92	8.03
20	42.15	35.58	33.85	30.41	25.81	22.48	19.11	16.13	13.13	10.45	7.70
30	39.95	33.80	32.14	28.83	24.42	21.39	18.23	15.37	12.55	10.02	7.40

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

x_1	α_0	$\alpha_1 \times 10^3$	$\sigma(\ln \epsilon) \times 10^3$
1.0000	5.25120	-5.15416	1.1
0.9435	5.07106	-5.11662	1.8
0.8813	5.00098	-5.04850	0.6
0.8126	4.90605	-5.08990	2.3
0.7355	4.90893	-5.65721	2.5
0.6501	4.59005	-5.03922	0.6
0.5516	4.36079	-4.80912	0.5
0.4511	4.17039	-4.74383	1.1
0.3170	3.90387	-4.53233	0.9
0.1710	3.54923	-4.10195	2.3
0.0000	3.21741	-4.01037	0.6

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

$t/^\circ\text{C}$	β_0	β_1	$\beta_2 \times 10$	$\beta_3 \times 10$	$\sigma(\ln \epsilon) \times 10^2$
-10	2.16541	1.75611	-1.74783	1.27519	2.3
0	2.12563	1.73650	-1.84023	1.42307	2.3
10	2.08722	1.75452	-3.04326	2.36858	2.4
20	2.04602	1.74058	-3.07989	2.43432	2.3
30	2.00570	1.73518	-3.43176	2.71959	2.3

Table IV. Coefficients γ_{ij} of the Model Equation $\epsilon = \epsilon(T, x_1)$ for 1,2-Ethanediol (1) + 1,2-Dimethoxyethane (2)^a

ij	variable quantity	γ
00		9.07644
01	x_1	11.02105
02	x_1^2	10.66445
03	x_1^3	-5.65622
10	T	-1.66753×10^{-2}
11	Tx_1	-1.28157×10^{-2}
12	Tx_1^2	-3.33181×10^{-2}
13	Tx_1^3	2.43868×10^{-2}

^a $\sigma(\ln^2 \epsilon) = 0.14$.

are listed on Table III along with the standard deviations $\sigma(\ln \epsilon)$ at each investigated temperature. Equation 3 provides a set of calculated values within $\Delta(\epsilon) = \pm 0.35$.

In order to improve the analysis of experimental values and to quicken the procedures, a single function $\epsilon = \epsilon(T, x_1)$ has been derived by combining eqs 1 and 3 in the form

$$\ln^2 \epsilon = \sum_0^i \sum_0^j \gamma_{ij} T^i x_1^j \quad (4)$$

which allows us to calculate the relative permittivity for these binaries for any pair of independent variable quantities T and x_1 . This fitting equation, whose coefficients γ_{ij} are reported in

Table V. Excess Relative Permittivity ϵ^E for 1,2-Ethanediol (1) + 1,2-Dimethoxyethane (2) at Various Temperatures

$t/^\circ\text{C}$	ϵ^E at various x_1									
	0.9435	0.8813	0.8126	0.7355	0.6501	0.5516	0.4511	0.3170	0.1710	0.0000
-10	-5.41	-5.06	-6.24	-7.86	-8.89	-8.95	-8.38	-6.49	-3.79	
0	-5.19	-4.71	-5.91	-7.65	-8.37	-8.43	-7.93	-6.13	-3.58	
10	-5.03	-4.61	-5.59	-7.63	-8.10	-8.07	-7.59	-5.83	-3.34	
20	-4.62	-4.21	-5.28	-7.22	-7.62	-7.59	-7.11	-5.49	-3.14	
30	-4.31	-3.94	-5.02	-6.92	-7.17	-7.12	-6.71	-5.17	-2.94	

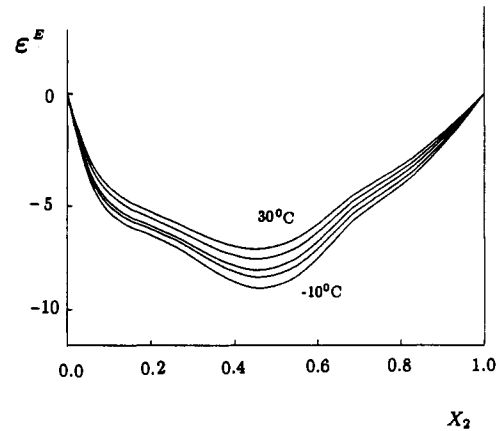
**Figure 1. Isothermal best-fit curves of the excess relative permittivity for the 1,2-ethanediol (1) + 1,2-dimethoxyethane (2) binary mixtures calculated by eq 6 at various temperatures.**

Table IV, provides a set of calculated values that match very well the experimental ones, with an average uncertainty $\Delta(\epsilon) = \pm 0.37$ units.

The Excess Function. According to Pajne and Theodorou (9), the following equation

$$\epsilon = \bar{\epsilon}_1 x_1 + \bar{\epsilon}_2 x_2 = \epsilon^E + \epsilon_1 x_1 + \epsilon_2 x_2 \quad (5)$$

was used to evaluate the shiftness of these binary mixtures from the ideal behavior of noninteracting components. In eq 5, $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ are the relative permittivities of the two solvents, ϵ^E is the excess function of the mixture, and ϵ_1 and ϵ_2 are the values for the pure species at each temperature.

The ϵ^E values summarized in Table V, are large and negative at all temperatures. In order to take into account also the variations of ϵ^E values for these polar-polar mixed solvents ($\mu = 2.28$ D (10) and 1.71 D (11) for 1,2-ethanediol and 1,2-dimethoxyethane, respectively) with composition, the data were isothermally fitted by a smoothing equation of the type (12)

$$\epsilon^E = x_1 x_2 \sum_{j=0}^4 c_j (x_2 - x_1)^j \quad (6)$$

whose c_j coefficients are listed in Table VI, along with the standard deviations $\sigma(\epsilon^E)$.

In Figure 1, the ϵ^E is shown as a function of the mole fraction of ether. This plot exhibits a pronounced minimum at each selected temperature, generally centered at $x_2 \approx 0.5$, that becomes more negative at lower temperature (maximum $\epsilon^E = -8.95$ at -10°C).

The excess relative permittivity gives an estimate of specific interactions between unlike molecules and the relative strength.

Table VI. Coefficients c_i of Equation 6 for 1,2-Ethanediol (1) + 1,2-Dimethoxyethane (2)

$t/^\circ\text{C}$	c_0	c_1	c_2	c_3	c_4	$\sigma \times 10$
-10	-36.73	11.47	44.27	5.49	-102.93	7.2
0	-34.64	11.18	39.80	5.12	-93.96	7.4
10	-33.22	11.82	36.87	4.69	-87.21	7.7
20	-31.11	11.37	31.78	3.57	-75.53	7.2
30	-29.20	10.91	27.36	3.58	-66.00	6.9

It has been postulated that small negative deviations on this excess nonthermodynamic property ($\epsilon^E \leq 5$) are a consequence either of weak dipole-dipole association phenomena or of hydrogen-bonded complexes (9). In this case, the presence of the minimum appears strictly related to the complex formation either by strong hydrogen bonds or by dipolar interactions ($\epsilon^E < -5$ at 30 °C).

Furthermore, the position of the minimum in Figure 1 indicates the formation of a stable complex adduct, consisting of one molecule of 1,2-ethanediol and one molecule of 1,2-dimethoxyethane at all the temperatures.

Registry No. 1, 107-21-1; 2, 110-71-4.

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High-Pressure Vapor-Liquid Equilibrium Data for Binary Mixtures Containing N₂, CO₂, H₂S, and an Aromatic Hydrocarbon or Propylcyclohexane in the Range 313–473 K

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Experimental binary vapor-liquid equilibrium data were obtained for mixtures of one light component, among nitrogen, carbon dioxide, and hydrogen sulfide, and one heavy component, among toluene, *m*-xylene, mesitylene, *n*-propylcyclohexane, and *n*-propylbenzene. Three static analytical methods differing by the sampling technique and one static synthetic method were used at about 313, 393, and 473 K.

Introduction

The data were tested according to the consistency test of Prausnitz-Keeler (2) in the range of low pressures and temperatures where it can be applied. Although some data had to be checked against other experimental methods (3) and rejected, all the other points given here were found consistent.

The experimental data reported here are part of a large data base collected by Gas Processors Association (GPA) and used to determine interaction parameters for equation of state models. Other relevant measurements from Ecole des Mines were presented in a previous paper (1).

Experimental Section

Apparatus. Equipment and procedure for each experimental method are described in previous publications: Legret et al. (4) for apparatus 1, Figuière et al. (5) for apparatus 2, Fontalba et al. (6) for apparatus 3, and Laugier and Richon (7) for apparatus 4.

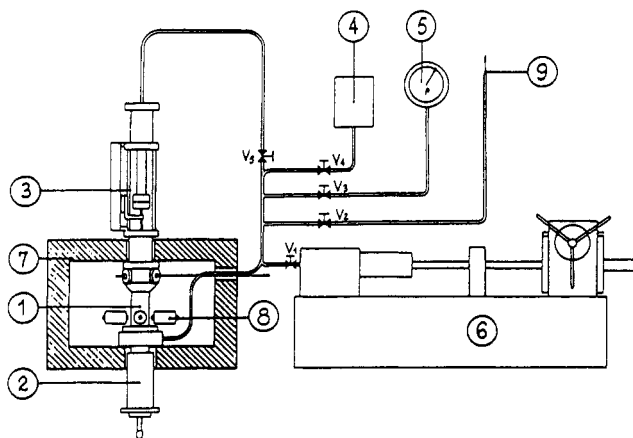


Figure 1. Static apparatus with variable volume cell, flow diagram: (1) equilibrium cell; (2) assembly for piston-level measurements; (3) assembly for interface level measurements; (4) pressurizing liquid reservoir; (5) manometer; (6) high-pressure pump; (7) air thermostat; (8) solenoids; (9) fitting to vacuum pump; (V_1 – V_5) shut-off valves.

Figures 1 and 2 refer to apparatus 3 based on a static synthetic method. The variable-volume cell (Figure 2) allows pressure P determinations as a function of the volume V up to 45 MPa and 423 K. Below the mixture critical pressure, the P – V curves display a break point at the bubble pressure and a volume corresponding to the saturated liquid molar volume. The composition of the saturated liquid at the break point is known by weighing the components into the systems during the loading procedure.