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Dielectric Properties in Ternary Mixtures of Ethane-1,2-diol + 1,2-Dimethoxyethane + Water

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The static dielectric constant (ε) of ethane-1,2-diol + 1,2-dimethoxyethane + water ternary mixtures was measured as a function of temperature ($263.15 \leqslant T(K) \leqslant 353.15$) and composition, over the complete mole fraction range $0 \leqslant x_1, x_2, x_3 \leqslant 1$. The experimental values were analyzed by empirical relationships that accounted for the dependence $\varepsilon = \varepsilon(T)$ and $Y = Y(x_i)$. A comparison between calculated and experimental data shows that these fitting relationships can be reliably used to predict ε values, along with other related properties, in areas of experimental data gaps. Starting from the experimental measurements, some derived quantities such as molar orientational polarization (P), dipolar interaction free energy (F_μ) and the relevant thermodynamic excess mixing properties (F_μ^{E}, $\overline{F}_{\mu,i}^{\mathrm{E}}$), were obtained. The values of the excess quantities are indicative of the presence of specific interactions between different components in the mixtures. A discussion of data in terms of the Kirkwood theory also provides information on the short-range intermolecular interactions, suggesting the formation of stable two-component adducts rather than of more complex moieties involving all three molecular species.

KEY WORDS: 1,2-dimethoxyethane; ethane-1,2-diol; static dielectric constant; ternary mixtures; water.

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1. INTRODUCTION

For many theoretical or empirical investigations, as well as for many practical applications, a knowledge of the specific intermolecular interactions in the liquid state as a function of temperature and composition (for mixed solvent systems) is of utmost importance. From a microscopic point of view these interactions are responsible for the local intermolecular order that influences thus the macroscopic measurable physicochemical properties [1]. The study of the thermophysical and thermodynamic behavior of mixed systems represents a valuable tool in order to provide information complementary to spectroscopic techniques about specific intermolecular ordering which generally sustains the liquid structure. Nonelectrolyte polar solutions are excellent examples where important interactions take place. Therefore, each investigation about these systems can represent a useful contribution to improve our knowledge and to give a better foundation for theories and models describing the experimental behavior. Despite this need and the increasing literature in the field, there is little experimental information available about ternary and higher-order mixtures in the current literature [2].

Starting some years ago, our scientific interest has been focused on aquo-mixed polar solvents, choosing as nonaqueous liquids some species that pertain to the class of 1,2-ethanedyil (–CH_2–CH_2–) derivatives. Among these, the most representative chemical subjects for our studies have included ethane-1,2-diol (ED), 2-methoxyethanol (ME), 1,2-dimethoxyethane (DME), 2-chloroethanol (CE), and 1,2-dichloroethane (DCE), including other solvents such as DMF. These solvents were first mixed with each other in binary combinations and with water (W) when possible; successively we studied some ternary mixtures of them, like $\{ED(1)+ME(2)+W(3)\}$ [3, 4], $\{ME(1)+DME(2)+W(3)\}$ [5, 6], $\{DCE(1)+ME(2)+DME(3)\}$ [7], and $\{DMF(1)+ME(2)+DME(3)\}$ [8]. In our previous research, we studied some of the most common thermophysical properties such as density, viscosity and static dielectric constant at different experimental conditions for the ternary systems mentioned above.

The present paper is concerned with extending our database on dielectric properties of $\{ED(1)+DME(2)+W(3)\}$ ternary mixtures to cover different experimental conditions. For this aim we use binary data taken from our previous papers ($\{ED(1)+DME(2)\}$ [9]; $\{ED(1)+W(2)\}$ [10]; $\{DME(1)+W(2)\}$ [11]); and new experimental data collected for 14 three-component mixtures, whose composition range is $0 \leqslant x_1, x_2, x_3 \leqslant 1$, and at 19 temperatures in the $263.15 \leqslant T$ (K) $\leqslant 353.15$ range.

2. EXPERIMENTAL

2.1. Materials

The solvents ED and DME (both containing less than 0.10% of water by mass as determined by Karl–Fischer titrations) were Carlo Erba (Milan) high purity grade reagents. DME was purified by double fractional distillation over $LiAlH_4$ to eliminate traces of acids and peroxides and to reduce the total water content, retaining only the middle fraction (b.p. = 356.15 K) for the measurements. The purified solvents were preserved over 3Å molecular sieves for many days before use. The final purity was checked by gas chromatography (99.5% ED and 99.7% DME), confirming the absence of other significant organic components. Water for mixture preparation was deionized by a MilliQ-plus apparatus (Millipore) and had a specific conductance less than 0.70 $\mu S \cdot cm^{-1}$ at 298.15 K.

2.2. Apparatus and Procedures

The mixtures were prepared by mass just before use, by means of a Mettler PM 480 Δ-range balance, operating in a dry box to avoid atmospheric moisture. The probable error for each mole fraction (x_i) is less than 1.5×10^{-4}.

The dielectric permittivities of the pure compounds and of the mixtures were measured by the heterodyne beat method at a frequency of 2 MHz with a WTW—DM01 Dipolmeter, equipped with two thermostated stainless steel measuring cells of the type MFL 2 ($7 < \varepsilon < 21$) and MFL 3 ($21 < \varepsilon < 90$). The thermostated measuring cell was embedded in a thick polyurethane protective jacket, and the temperature control was provided by a Lauda K2R thermostatic bath maintained to ± 0.02 K. The temperature was checked by a thermoresistance Pt 100 (Tersid, Milan) immersed in the measuring cell. This device shows a slight quadratic dependence of the resistance with temperature [$R(T) = R_{273.15}(1 + AT + BT^2)$] in the investigated range, and with a tolerance of ± 0.01 K. The resistance values were collected using a Wayne Kerr 6425 PCA (Precision Component Analyzer).The experiments were generally performed for at least 10 replicate runs (without refilling the cell) for each composition and temperature, and the results were averaged. The reproducibility of measurements [standard deviations $\sigma(\varepsilon)$] was approximately ± 0.2%, and the estimated uncertainty (at a 95% confidence level) was in the range $\pm 2 \times 10^{-3}$ (for the largest ε measured) and $\pm 5 \times 10^{-4}$ (for the smallest ε measured).

Table I. Reference Dielectric Constant Values (ε) for ED, DME, and W Pure Species at Selected Temperatures

	ED			DME			W		
T (K)	ε	Ref.	This work	ε	Ref.	This work	ε	Ref.	This work
283.15							83.98	[19]	83.67
288.15	46.66	[12]	43.17						
293.15	38.66	[13]	42.14				80.37	[20]	80.11
298.15	37.70	[14]	40.97	7.20	[16]	7.55	78.54	[21]	78.31
	40.61	[15]		7.20	[17]		78.40	[19]	
				7.18	[18]				
313.15	34.94	[13]	37.99				73.19	[19]	73.23
							73.12	[22]	
328.15							68.33	[19]	68.45
333.15	31.58	[13]	34.30						
353.15	28.45	[13]	31.00						

Further details about the apparatus and procedures for the static dielectric constant measurements have been described elsewhere [7].

3. RESULTS AND DISCUSSION

For comparison purposes, Table I [12–22] summarizes some literature values of ε for the three pure species. There is fair agreement between the values we have measured and the literature results. The most probable sources of errors, variability, and discrepancies in such a type of analysis can be mainly ascribed to (i) the different measurement techniques employed in various laboratories; (ii) different experimental conditions (such as different frequency of the applied electric field for the same technique); (iii) different calibration procedures for experimental setups from various laboratories; and (iv) different sample purification procedures adopted by the authors. A more detailed discussion about these effects has been provided by Fogg et al. [23].

Even though DME has been proved to be an extremely interesting solvent for a lot of theoretical and practical applications, it seems that this chemical compound has been only slightly investigated and reviewed concerning its dielectric properties, in spite of its strategic importance in many laboratory and industrial applications, such as an electrolytic solvent for lithium batteries [24], among others. These facts led us to perform some extensive investigations about this species, and its multicomponent mixtures, over a reasonably wide temperature range.

3.1. Dielectric Constant Data Analysis

The experimental ε values of the three pure species and of the 14 ternary mixtures are listed in Table II, together with the ternary composition expressed as a mole fraction (x_i) of each of the three solvents.

The dependence of the measured ε values on the temperature (T in K) was studied by applying the following relationship [25]:

$$\ln \varepsilon = \sum_{j=0}^{1} \alpha_j T^j \tag{1}$$

where α_j's are empirical adjustment coefficients to be determined by a least-squares method [26]. The above equation, which is available for fitting over a wide temperature range in the approximate limits $170 < T(\mathrm{K}) < 420$ [13], yields the results presented in Table III, along with the standard deviations $\sigma(\ln\ \varepsilon)$ for each composition. This relationship interpolates the experimental values with an average absolute deviation (AAD), calculated by

$$\overline{\delta\varepsilon} = \frac{1}{N} \sum_{N} \left|\varepsilon_{\mathrm{calcd}} - \varepsilon_{\mathrm{exp\,tl}}\right| \tag{2}$$

where N is the number of data points (321) of Table II, and corresponds to $\overline{\delta\varepsilon} = 0.17\varepsilon$ units, well within the experimental uncertainty.

In the literature, dielectric constant data have been also reported as a function of temperature to conform to the equation [13, 27, 28],

$$\varepsilon = \sum_{j=0}^{1} \alpha'_j T^{-j} \tag{3}$$

where α'_j's are the new empirical parameters to be determined (Table III). This relation provides a set of calculated ε values to within an AAD, $\overline{\delta\varepsilon} = 0.70$ for the experimental data of Table II.

A more stringent test to evaluate the effectiveness of Eqs. (1) and (3) consists of comparing the relevant merits, which takes into account the relevant standard deviations (or the average uncertainty) of the results obtained by the different fitting procedures. As it appears from Table III, and on the basis of the above cited AAD, it is possible to assert that Eq. (1) is more effective than Eq. (3), when applied to our data set. In fact, to obtain the same performance level from the latter, it is necessary to introduce a further term ($j = 2$) into the polynomial expansion (the third empirical coefficient α'_j of Eq. (3)). For these reasons, and according to numerous literature suggestions [29], the better performance of Eq. (1), with respect

Table II. Ternary Composition (x_i) and Experimental Static Dielectric Constants (ε) for ED(1) + DME(2) + W(3) Mixtures at Various Temperatures T

	$x_1 = 1$	0	0	0.5100	0.1794	0.1328	0.4328	0.2853	0.6279	0.0123	0.2953	0.3060	0.8591	0.0820	0.4278	0.0387	0.6450
	$x_2 = 0$	1	0	0.0957	0.5441	0.1264	0.1994	0.3565	0.1499	0.0743	0.4761	0.1565	0.0593	0.8081	0.4887	0.3862	0.2899
T (K)	$x_3 = 0$	0	1	0.3943	0.2765	0.7408	0.3678	0.3582	0.2222	0.9134	0.2286	0.5375	0.0816	0.1099	0.0835	0.5751	0.0651
263.15	49.23	8.68	–	47.87	19.22	52.69	38.23	27.82	40.22	67.74	21.67	44.58	45.48	11.88	20.79	27.37	29.64
268.15	47.80	8.51	–	46.63	18.75	51.31	37.22	27.10	39.18	66.04	21.14	43.41	44.31	11.62	20.30	26.64	28.88
273.15	46.65	8.35	87.45	45.42	18.29	49.99	36.26	26.41	38.15	64.41	20.60	42.26	43.16	11.37	19.78	25.94	28.12
278.15	45.41	8.17	85.48	44.24	17.84	48.69	35.29	25.72	37.14	62.77	20.09	41.16	42.04	11.13	19.27	25.28	27.39
283.15	44.49	8.03	83.67	43.12	17.41	47.43	34.37	25.05	36.18	61.22	19.60	40.09	40.99	10.91	18.80	24.62	26.66
288.15	43.17	7.85	81.82	42.02	17.00	46.20	33.47	24.42	35.24	59.72	19.13	39.04	39.93	10.67	18.36	23.98	26.00
293.15	42.14	7.70	80.11	40.93	16.58	44.98	32.59	23.79	34.32	58.21	18.64	38.01	38.90	10.44	17.91	23.35	25.31
298.15	40.97	7.54	78.31	39.85	16.17	43.82	31.75	23.18	33.40	56.75	18.18	37.02	37.88	10.22	17.45	22.72	24.65
303.15	39.50	7.40	76.56	38.79	15.75	42.65	30.86	22.52	32.51	55.32	17.70	36.00	36.86	10.01	17.03	22.12	24.02
308.15	38.84	7.25	74.80	37.80	15.38	41.55	30.09	21.97	31.69	53.96	17.26	35.08	35.95	9.79	16.59	21.54	23.39
313.15	37.99	7.12	73.23	36.83	15.03	40.46	29.28	21.40	30.86	52.60	16.85	34.15	35.01	9.60	16.19	21.01	22.76
318.15	36.98	6.98	71.46	35.86	14.67	39.41	28.51	20.84	30.04	51.30	16.42	33.26	34.11	9.40	15.78	20.45	22.18
323.15	36.07	6.83	70.00	34.94	14.30	38.37	27.75	20.29	29.25	50.00	16.02	32.38	33.22	9.19	15.39	19.92	21.59
328.15	35.14	6.70	68.45	34.03	13.94	37.39	27.05	19.78	28.48	48.75	15.61	31.53	32.36	8.99	15.01	19.39	21.04
333.15	34.30	6.57	66.85	33.14	13.61	36.41	26.33	19.27	27.75	47.54	15.22	30.70	31.52	8.81	14.63	18.89	20.49
338.15	33.44	6.46	65.42	32.28	13.27	35.44	25.62	18.76	27.00	46.34	14.83	29.89	30.69	8.63	14.26	18.40	19.94
343.15	32.68	6.31	63.87	31.41	12.92	34.51	24.93	18.24	26.27	45.17	14.43	29.07	29.90	8.43	13.88	17.88	19.42
348.15	31.84	6.21	62.47	30.59	12.60	33.60	24.27	17.77	25.59	44.04	14.07	28.30	29.10	8.27	13.54	17.41	18.90
353.15	31.00	6.09	61.10	29.79	12.30	32.72	23.62	17.30	24.92	42.94	13.72	27.55	28.35	8.09	13.20	16.97	18.40

Table III. Coefficients and Standard Deviations of Eqs. (1) and (3) for {ED(1) + DME(2)+ W(3)} Ternary Solvent Mixtures

			Eq. (1)			Eq. (3)		
x_1	x_2	x_3	α_0	$10^3\alpha_1$	10^3 $\sigma(\ln\varepsilon)$	α'_0	$10^3\alpha'_1$	$10\sigma(\varepsilon)$
1	0	0	5.23852	−5.11391	1.6	−22.095	18.784	1.3
0	1	0	3.20086	−3.95421	1.4	−1.507	2.693	0.22
0	0	1	5.69777	−4.48755	0.81	−28.836	31.878	2.3
0.5100	0.0957	0.3943	5.25514	−5.26693	0.55	−23.031	18.715	1.1
0.1794	0.5441	0.2765	4.25920	−4.95115	0.87	−7.872	7.154	0.53
0.1328	0.1264	0.7408	5.35771	−5.29284	0.66	−25.665	20.679	1.1
0.4328	0.1994	0.3678	5.05012	−5.34329	0.56	−19.044	15.114	0.79
0.2853	0.3565	0.3582	4.71474	−5.27487	0.81	−13.437	10.891	0.64
0.6279	0.1499	0.2222	5.09428	−5.31815	0.44	−19.817	15.844	0.83
0.0123	0.0743	0.9134	5.54839	−5.06390	0.54	−29.524	25.675	1.5
0.2953	0.4761	0.2286	4.41303	−5.07675	0.91	−9.492	8.230	0.61
0.3060	0.1565	0.5375	5.20387	−5.34329	0.54	−22.204	17.624	0.94
0.8591	0.0593	0.0816	5.19905	−5.24895	0.49	−21.702	17.732	1.0
0.0820	0.8081	0.1099	3.59705	−4.26673	0.70	−2.961	3.921	0.34
0.4278	0.4887	0.0835	4.36400	−5.04756	0.95	−8.974	7.862	0.57
0.0387	0.3862	0.5751	4.70657	−5.30916	0.65	−13.426	10.763	0.56
0.6450	0.2899	0.0651	4.78223	−5.29164	0.55	−14.423	11.630	0.66

to Eq. (3), for fitting ε data of the {ED(1) + DME(2) + W(3)} ternary solvent system, is confirmed.

3.2. Dipolar Interaction Free Energy

From statistical considerations, Winkelmann and Quitzsch [30, 31] have concluded that the molar dipolar free energy (F_μ) of a pure associated liquid is given by the equation,

$$F_\mu = -\frac{RTLg\mu^2(\varepsilon-1)(\varepsilon_\infty+2)}{9k_B T\varepsilon_0 V(2\varepsilon+\varepsilon_\infty)} \tag{4}$$

where V is the apparent molar volume of the real system $\left(V = \frac{\sum_i x_i M_i}{\rho}\right)$, M_i is the molar mass of component i ($M_1 = 62.070$; $M_2 = 90.120$; and $M_3 = 18.015\ \mathrm{g\cdot mol^{-1}}$ for ED, DME, and W, respectively), ρ is the density at each experimental condition [32], k_B is the Boltzmann constant, L is Avogadro's number, μ is the dipole moment, ε_0 is the vacuum dielectric constant, ε_∞ is the limiting high-frequency permittivity of the medium, and the other symbols have their usual meaning [33]. Following that logic,

Table IV. Ternary Composition (x_i) and Molar Dipolar Free Energies $F_\mu(\mathrm{kJ \cdot mol^{-1}})$ for $\{\mathrm{ED(1)} + \mathrm{DME(2)} + \mathrm{W(3)}\}$ Solvent Mixtures at Various Temperatures

	$x_1 = 1$	0	0	0.5100	0.1794	0.1328	0.4328	0.2853	0.6279	0.0123	0.2953	0.3060	0.8591	0.0820	0.4278	0.0387	0.6450
	$x_2 = 0$	1	0	0.0957	0.5441	0.1264	0.1994	0.3565	0.1499	0.0743	0.4761	0.1565	0.0593	0.8081	0.4887	0.3862	0.2899
T (K)	$x_3 = 0$	0	1	0.3943	0.2765	0.7408	0.3678	0.3582	0.2222	0.9134	0.2286	0.5375	0.0816	0.1099	0.0835	0.5751	0.0651
273.15	−23.06	−3.01	−48.54	−22.94	−8.41	−25.83	−18.11	−12.87	−18.84	−34.47	−9.71	−21.49	−21.40	−4.71	−9.21	−12.68	−13.48
278.15	−22.87	−2.99	−48.29	−22.73	−8.33	−25.60	−17.93	−12.74	−18.66	−34.21	−9.61	−21.29	−21.21	−4.67	−9.12	−12.55	−13.34
283.15	−22.68	−2.96	−48.05	−22.52	−8.25	−25.37	−17.75	−12.60	−18.47	−33.94	−9.52	−21.08	−21.01	−4.63	−9.03	−12.42	−13.20
288.15	−22.47	−2.94	−47.78	−22.3	−8.16	−25.13	−17.56	−12.46	−18.28	−33.66	−9.41	−20.87	−20.81	−4.59	−8.93	−12.28	−13.06
293.15	−22.26	−2.91	−47.51	−22.08	−8.08	−24.88	−17.37	−12.32	−18.09	−33.38	−9.31	−20.65	−20.60	−4.55	−8.83	−12.14	−12.91
298.15	−22.05	−2.88	−47.23	−21.85	−7.99	−24.63	−17.17	−12.17	−17.89	−33.08	−9.20	−20.42	−20.38	−4.51	−8.73	−12.00	−12.76
303.15	−21.84	−2.85	−46.93	−21.61	−7.89	−24.37	−16.97	−12.02	−17.69	−32.78	−9.09	−20.19	−20.17	−4.46	−8.62	−11.86	−12.61
308.15	−21.61	−2.82	−46.64	−21.37	−7.80	−24.11	−16.77	−11.87	−17.48	−32.47	−8.98	−19.96	−19.94	−4.41	−8.52	−11.71	−12.45
313.15	−21.38	−2.78	−46.32	−21.13	−7.70	−23.84	−16.56	−11.72	−17.27	−32.15	−8.87	−19.73	−19.71	−4.37	−8.41	−11.56	−12.29
318.15	−21.15	−2.75	−46.01	−20.89	−7.60	−23.57	−16.35	−11.56	−17.06	−31.83	−8.75	−19.49	−19.48	−4.32	−8.30	−11.40	−12.13
323.15	−20.92	−2.72	−45.67	−20.64	−7.50	−23.29	−16.14	−11.40	−16.84	−31.50	−8.64	−19.24	−19.25	−4.27	−8.19	−11.25	−11.97
328.15	−20.68	−2.68	−45.34	−20.38	−7.40	−23.01	−15.92	−11.24	−16.63	−31.17	−8.52	−19.00	−19.01	−4.21	−8.07	−11.09	−11.81
333.15	−20.43	−2.65	−45.00	−20.13	−7.30	−22.73	−15.71	−11.08	−16.40	−30.83	−8.40	−18.75	−18.77	−4.16	−7.96	−10.93	−11.64
338.15	−20.19	−2.61	−44.64	−19.87	−7.20	−22.44	−15.49	−10.92	−16.18	−30.48	−8.27	−18.50	−18.53	−4.11	−7.84	−10.77	−11.47
343.15	−19.94	−2.57	−44.29	−19.61	−7.09	−22.15	−15.27	−10.75	−15.96	−30.14	−8.15	−18.25	−18.28	−4.05	−7.72	−10.61	−11.31

Davis and Douhéret [34–36] developed a very useful relationship that was adopted for the case of binary mixtures of Onsager liquids,

$$F_\mu = -RT(\varepsilon - 1)\sum_{i=1}^{2} \frac{x_i P_i(\varepsilon_{\infty,i} + 2)}{V_i(2\varepsilon + \varepsilon_{\infty,i})} \tag{5}$$

where P_i is the molar orientational polarization of the pure species, evaluated by applying the following relationship [33]:

$$P = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)V}{\varepsilon(\varepsilon_\infty + 2)^2} \tag{6}$$

When dealing with polar species, it is a common practice to choose $\varepsilon_\infty \cong 1.1n_D^2(n_D$ = refractive index at the Na-D line) at each temperature, this approximation being acceptable [37]. The molar orientational polarization data of this solvent system vary in the range 556 (ED at 273.15 K) $\geqslant P$ (cm^3· mol^{-1}) $\geqslant 123$ (DME at 343.15 K).

The formalism of Eq. (5) is particularly suitable for the extension of its applicability to a generic multicomponent system, and we tried to evaluate the quantity F_μ for the ternary solvent system under study. The results are listed in Table IV where, for simplicity, only results for the three pure components and the 14 three-component mixtures are reported. We observe that F_μ is always negative, with a decreasing trend with increasing temperature: the largest values, at $T = 298.15$ K, have been obtained in pure W (−47.23 kJ · mol^{-1}), DME shows the smallest negative values (−2.88 kJ · mol^{-1}), and ED values are located in the middle between these extremes (−22.05 kJ · mol^{-1}).

The property F_μ is a true additive thermodynamic quantity [35], and the equation,

$$F_\mu^{id} = \sum_i x_i F_{\mu,i} \tag{7}$$

represents an alternative definition of an ideal mixing process, where the molar dipolar free energy of pure component i, $F_{\mu,i}$, is evaluated by Eq. (4). On the basis of these considerations, it is possible to obtain an excess mixing property,

$$F_\mu^{\mathrm{E}} = F_\mu - F_\mu^{id} \tag{8}$$

which has been evaluated at each experimental condition. The results at 298.15 K are represented in graphical form in Fig. 1. This figure has been obtained by fitting the excess quantity to the equation [38],

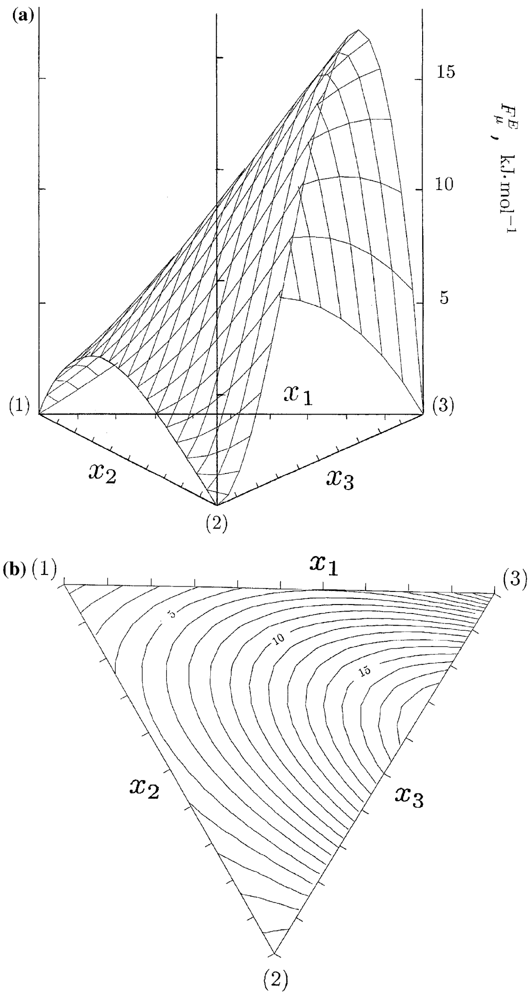

Fig. 1. (a) View of the excess molar dipolar interaction free energy, $F^{\mathrm{E}}_{\mu}(\mathrm{kJ \cdot mol^{-1}})$— composition, x_i, surface for ternary {ED(1) + DME(2) + W(3)} mixtures at 298.15 K; (b) computer-generated isolines at constant $F^{\mathrm{E}}_{\mu}(\mathrm{kJ \cdot mol^{-1}})$ at 298.15 K; (c) trends in the excess function, $F^{\mathrm{E}}_{\mu}(\mathrm{kJ \cdot mol^{-1}})$ with changing mole fraction, x_2, of binary subsystems at 298.15 K: (●) {ED(1) + DME(2)}; (■) {ED(1) + W(2)}; (▲) {DME(1) + W(2)}.

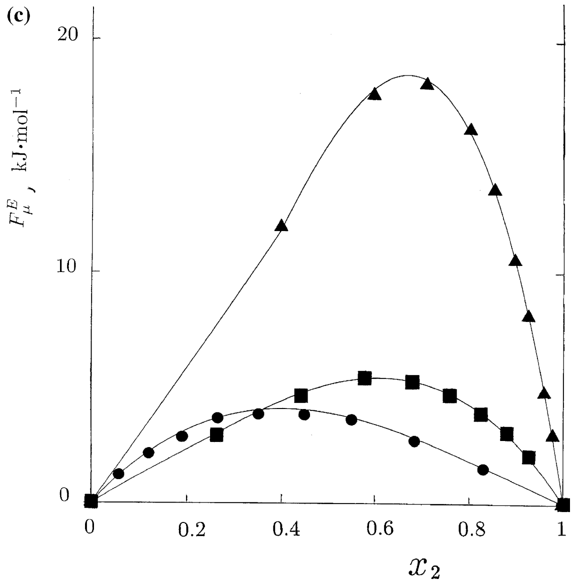

Fig. 1. Continued.

$$\begin{aligned} Y^{\mathrm{E}} &= d_1x_1x_2 + d_2x_2x_3 + d_3x_1x_3 + d_4x_1x_2(x_2-x_1) \\ &\quad + d_5x_2x_3(x_3-x_2) + d_6x_1x_3(x_1-x_3) + d_7x_1x_2x_3 \end{aligned} \tag{9}$$

which is formally derived from the well known Redlich–Kister equation [39], where Y^{E} is the excess property investigated, and d_ks are empirical coefficients to be determined at each temperature.

A common assumption for this relation is that the interactions in a ternary mixture are closely dependent on the specific intermolecular interactions involved in binary subsystems. The interactions in a ternary *i–j–k* mixture can be represented in terms of the interactions in the constituent *i–j*, *j–k*, and *i–k* binaries, eventually with a further additive contribution that accounts for the overall ternary mixture effects. The simplest procedure to represent these quantities is provided by the relation,

$$Y^{\mathrm{E}}_{ijk} = Y^{\mathrm{E}}_{ij} + Y^{\mathrm{E}}_{jk} + Y^{\mathrm{E}}_{ik} + \zeta_{ijk} \tag{10}$$

where the contributions due to the three binary subsystems are summarized, and each term Y^{E}_{ij} is represented by the equation [39],

$$Y^{\mathrm{E}}_{ij} = x_ix_j \sum_m d_m(x_j - x_i)^m \tag{11}$$

Table V. Coefficients d_k and Standard Deviations $\sigma(F_\mu^{\mathrm{E}})$ ($\mathrm{kJ \cdot mol^{-1}}$) of Eq. (9) for {ED(1)+DME(2)+W(3)} Ternary System at Various Temperatures

T (K)	d_1	d_2	d_3	d_4	d_5	d_6	$10^2 d_7$	$10\sigma(F_\mu^{\mathrm{E}})$
273.15	16.151	63.687	20.310	−6.395	60.794	−9.977	−157.71	6.3
278.15	16.064	63.421	20.357	−6.499	61.409	−10.097	−131.56	6.4
283.15	15.970	63.129	20.400	−6.588	62.002	−10.222	−106.36	6.5
288.15	15.887	62.839	20.429	−6.680	62.583	−10.334	−82.42	6.6
293.15	15.786	62.512	20.484	−6.740	63.144	−10.479	−64.21	6.7
298.15	15.677	62.177	20.514	−6.826	63.698	−10.573	−30.22	6.8
303.15	15.570	61.841	20.555	−6.920	64.185	−10.746	−22.42	6.9
308.15	15.464	61.500	20.588	−6.988	64.678	−10.861	−8.04	7.0
313.15	15.342	61.109	20.617	−7.049	65.170	−11.033	19.20	7.1
318.15	15.223	60.729	20.638	−7.132	65.644	−11.153	37.69	7.2
323.15	15.109	60.333	20.657	−7.166	66.090	−11.275	58.99	7.4
328.15	14.976	59.931	20.684	−7.200	66.479	−11.386	72.05	7.5
333.15	14.845	59.521	20.698	−7.271	66.820	−11.511	87.82	7.6
338.15	14.719	59.084	20.707	−7.302	67.217	−11.607	111.60	7.7
343.15	14.581	58.660	20.723	−7.347	67.527	−11.760	118.68	7.8

in the proper form. Equation (9) is obtained by truncating each polynomial in Eq. (11) in correspondence to the first power term, and introducing the overall-deviation coefficient d_7. A relation likes to Eq. (9) was previously employed by Katz et al. [38] to fit different thermophysical and thermodynamic excess quantities, and we have extended its use successfully to some other different mixing properties [3–8]. Equation (9), whose best fitting coefficients are listed in Table V along with the relevant standard deviation $\sigma(F_\mu^{\mathrm{E}})$ at each temperature, reproduces the initial data ($18 > F_\mu^{\mathrm{E}}$ ($\mathrm{kJ \cdot mol^{-1}}$) $\geqslant 0$) within an AAD $\overline{\delta F_\mu^{\mathrm{E}}}\% = 1.1\%$ for 748 F_μ^{E} values (3 pure species, 27 binaries, 14 ternary mixtures) in the $273.15 \geqslant T(\mathrm{K}) \geqslant 353.15$ temperature range.

At a molecular level, when strong deviations from linearity in Y^{E} are present, either a hypothesis of dipolar association phenomena between unlike molecules or an increase in dipolar association by one component to form self-aggregates of lower dipole moment [40–42], could be suggested in order to represent the experimental behavior obtained for ED(1) + DME(2) + W(3) ternary mixtures.

The trend for $F_\mu^{\mathrm{E}} = F_\mu^{\mathrm{E}}(x_1, x_2, x_3)$ is always positive, with consistent and largest deviations along the binary axis in the sequence {ED(1) + DME(2)} < {ED(1) + W(2)} < {DME(1) + W(2)}, and reaching a maximum of 4.0 $\mathrm{kJ \cdot mol^{-1}}$ at $x_2 \cong 0.35$ (2 ED: 1 DME, at 273.15 K), 5.24 $\mathrm{kJ \cdot mol^{-1}}$ at $x_2 \cong 0.6$ (2 ED: 3 W at 343.15 K), and 17.7 $\mathrm{kJ \cdot mol^{-1}}$ at

$x_2 \cong 0.65$ (1 DME: 2 W at 293.15 K). Similar behavior has been observed at all other experimental conditions.

A careful examination of Fig. 1 shows that no stable three-component adducts are probably formed in these nonelectrolyte solutions, and any singular point such as a relative minimum or maximum in the ternary domain is absent. However, it is possible to hypothesize that binary adducts may be formed through specific solvent–cosolvent interactions by hydrogen bonding or dipolar interactions of any kind [40–42].

To gain further insight about this property, we tried to explore the behavior of the partial molar excess dipolar interaction energies ($\overline{F}^{\mathrm{E}}_{\mu,i}$) for the three components in the mixtures, by applying the following equation [43]:

$$\overline{F}^{\mathrm{E}}_{\mu,i} = F^{\mathrm{E}}_{\mu,i} + (1 - x_i)\frac{\partial F^{\mathrm{E}}_{\mu,i}}{\partial x_i} \tag{12}$$

Then the partial molar dipolar interaction energies ($\overline{F}_{\mu,i}$) can be evaluated as follows:

$$\overline{F}_{\mu,i} = F_{\mu,i} + \overline{F}^{\mathrm{E}}_{\mu,i} \tag{13}$$

From Eq. (9), and using the fitting coefficients in Table V at each temperature, the quantity $\partial F^{\mathrm{E}}_{\mu,i}/\partial x_i$ is obtained and, as a consequence, using Eq. (13), the $\overline{F}_{\mu,i}$ values can be determined for each experimental condition. As an example, the results obtained at 298.15 K are presented in Fig. 2. It must be remembered that in such a type of analysis, the most significant aspects should involve the trends of the functions, rather than to the local and single values. However, with this fact in mind and to make more effective the descriptive comparisons, some reference to these data should be made.

As evidence, $\overline{F}^{\mathrm{E}}_{\mu,i}$ is generally positive for the three species, with only slightly negative values for the W(3) component at infinite dilution in DME(2) (Fig. 2c). Therefore, we can generalize that all components (with the exception noted above) sensibly increase the dipolar free energy by mixing with each other, but the DME molecules undergo the most significant electrostatic stress and energetic perturbation when dispersed at infinite dilution in water ($\overline{F}^{E}_{\mu,i} = 125.9\,\mathrm{kJ \cdot mol^{-1}}$ at 298.15 K).

These results about liquid structural effects in the selected system seem perfectly consistent with those obtained by studying different thermophysical properties, such as density [32], viscosity [44], and some related quantities at the same experimental conditions.

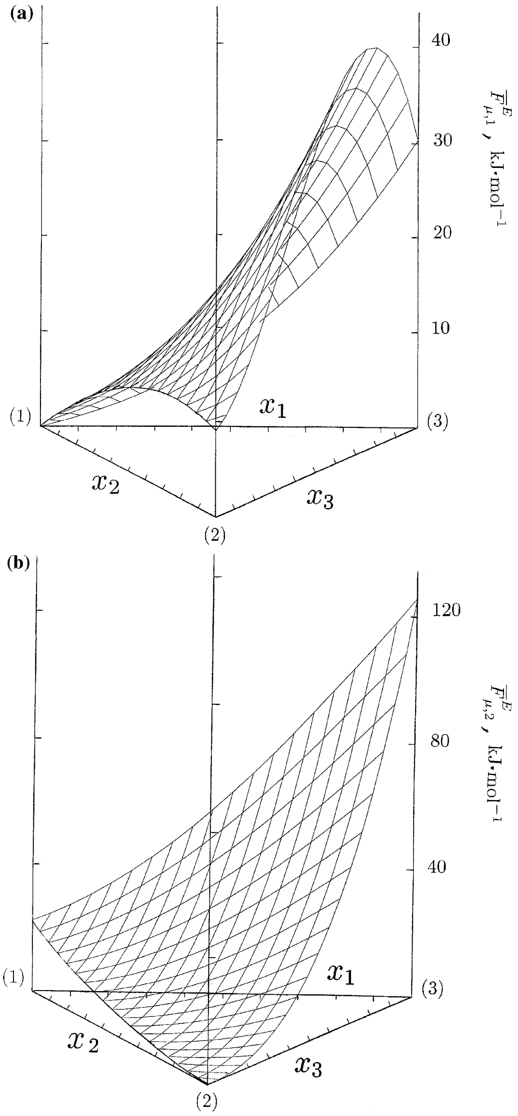

Fig. 2. View of the partial molar excess interaction free energy, $\overline{F}^{E}_{\mu,i}$(kJ · mol^{-1})— composition, x_i, surfaces for {ED(1) + DME(2) + W(3)} ternary mixtures at 298.15 K: (a) ED(1); (b) DME(2); and (c) W(3).

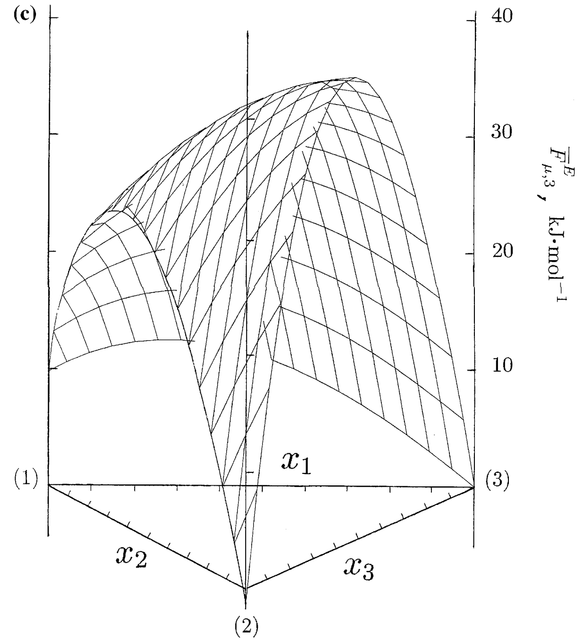

Fig. 2. Continued.

4. CONCLUSIONS

In this paper we have investigated some well known and widely accepted correlation methods for dielectric constant data analysis and other relevant properties, such as the molar dipolar interaction free energies, applied to a selected polar ternary solvent system. Even though good accuracy has been obtained by applying different semi-empirical or theoretical models, it is understood that new reliable and consistent experimental information is needed to provide a more comprehensive database for better assessment of modeling efforts.

In particular, working with the {ED(1) + DME(2) + W(3)} ternary solvent system, and in a complementary fashion with previous studies, we have shed some light on the structural behavior reached in these nonelectrolyte solutions. However, the most outstanding experimental evidence coming out from the present work is that specific intermolecular interactions are very effective at the binary level among ED, DME, and W components, but they are not clearly demonstrated in the ternary system, where no large (singular maximum) deviation is exhibited over the whole composition domain.

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