The Relative Permittivity of the Ternary 1,2-Ethanediol+2-Methoxyethanol+Water Solvent System

Fulvio CORRADINI, Luigi MARCHESELLI, Andrea MARCHETTI, Mara TAGLIAZUCCHI, Lorenzo TASSI, and Giuseppe TOSI*
Department of Chemistry, University of Modena, via G. Campi, 183 41100 Modena, Italy

(Received May 10, 1993)

For many multicomponent cosolvent systems which can be important in electrochemical studies as far as in practical applications, the relative permittivity (ε) is a continuous but nonlinear function of the solvent composition. Rational functions were applied to the 1,2-ethanediol (1)+2-methoxyethanol (2)+water (3) ternary mixtures data at various temperatures ($50 \leq t/°C \leq 80$) instead of the more conventional polynomial regressions for $\varepsilon = \varepsilon(X_i)$. These rational functions seem to be more adequate than the other polynomials, being reduced the number of required adjustable coefficients; in fact only a first power dependence on mole fraction (X_i) is necessary, and a computational simplicity in reproducing reliable ε values over the total mole fraction $0 \leq X_1/X_2/X_3 \leq 1$ range is achieved. Furthermore, the calculated excess function (ε^E) is always negative, confirming the existence of rather strong interaction between components, probably via hydrogen bonding networks. Changes with temperature in ε^E for these ternary mixtures seem to be very useful in order to depict and differentiate the experimental trend in three well distincted regions (namely M_I,M_{II},M_{III}) which are likely characterized by different specific interactions between like and/or unlike species. Nevertheless, no evidence for a three component adduct was obtained.

The relative permittivity represents a noticeable target of the material chemistry because it is a measure of the polarization character of the constituting units. In particular, working with polar liquids, this property can provide many valuable informations about the local structure due to the molecular orientation and to specific interactions between neighboring species.

Furthermore, the availability of the relative permittivity data of pure liquids, or complex mixtures, employed as solvents for practical applications or electroanalytial studies, is necessary to estimate the electrostatic solute–solvent interactions on the basis of the electrostriction theory for ionic solutions, for the Debye–Hückel law coefficients, and other thermodynamic and thermomechanical properties of the systems.$^{1)}$

Although the relative permittivity as a function of the temperature and composition of binary mixtures has been so far measured for a lot of solvent systems, there are very few available experimental data in the literature about the ternary liquid mixtures. Therefore, the present work was designed to extend our knowledge on the dielectric behavior of 1,2-ethanediol (ED, component 1)+2-methoxyethanol (ME, component 2) +water (W, component 3) ternary mixtures in the $50 \leq t/°C \leq 80$ temperature range, and covering the whole miscibility field expressed by the mole fractions $0 \leq X_1/X_2/X_3 \leq 1$.

All these species may be classified as dipolar amphiprotic solvents.

1,2-Ethanediol is the simplest homologue of the diol series, largely utilized as thermoregulator fluid, as a controlling agent of density/viscosity reaction baths, and as emulsion coating owing to its unusual physico-chemical properties such as the high autoprotolysis constant (pK_{autoprot}=15.8 at 25 °C)$^{2)}$ and the high dipole moment (μ_{ED}=2.28 D) (1 D=3.3356×10^{-30} C m).

2-Methoxyethanol is a potentially acidic medium with a low autoprotolysis constant (pK_{autoprot}=20.5 at 20 °C)$^{3)}$ and low relative permittivity, resulting scarcely dissociating solvent$^{4)}$ either for ionogen and ionophore solutes (μ_{ME}=2.36 D).

Furthermore, the uncommon properties of liquid water and aqueous solutions derive from distinctive features of the water molecule, as its small size, large dipole moment (μ_{W}=1.85 D), quadrupolar charge distribution and equal proton donor and acceptor sites. Owing to the latter two features, strong directional forces occur between molecules in the liquid water, which can propagate into three-dimensional networks substantially larger than in the other organic solvents.

In this light, the peculiar properties of this ternary solvent system can be examined rather systematically, taking into account that we can consider a series of mixtures whose components are ranging from a very three-dimensional structure solvent (pure W)$^{5)}$ to a solvent where the bi-dimensional network interactions are prevailing (pure ED)$^{6)}$ and, finally, to a species where the molecular interaction should be of linear type (pure ME)$^{6)}$. Generally, the trend of the thermomechanical properties vs. solvent composition of strongly interacting real systems is not linear; therefore the ε values calculated for the mixtures corresponding to the experimental data gaps could be subject to substantial interpolating errors. In this paper, we report some investigations about the functions $\varepsilon = \varepsilon(T)$, $\varepsilon = \varepsilon(X_1, X_2)$, and $\varepsilon = \varepsilon(T, X_1, X_2)$ in order to check their validity for the ternary mixtures too.

Experimental

Materials. The solvents 1,2-ethanediol and 2-methoxyethanol (containing water<0.10% and <0.05% by mass, respectively, as found by Karl–Fischer titrations) were high-purity grade reagents from Carlo Erba (Milan). These solvents were preserved over 3 Å molecular sieves for many days before use, and the final purity was checked by gas chromatography (99.5% ED and 99.7% ME), confirming the absence of other significant organic components. Water for mixture preparation was deionized by a MilliQ-Plus apparatus (Millipore) and has a specific conductance ≤ 0.70 μS cm^{-1} at 25 °C.

Apparatus and Procedures. The mixtures were prepared just before use by weight on a Mettler PM 4800 Δ-range balance, operating in a dry box to avoid atmospheric moisture. The binaries without water were stored on 3 Å molecular sieves. The probable error on each mole fraction X_1, X_2, X_3 is estimated to be less than 1.5×10^{-4}.

The apparatus and procedures for the relative permittivity measurements and for the temperature control have been described elsewhere.[7]

In all the cases, the experiments were generally performed at least for 10 replicate runs for each composition and at each temperature, and the results were averaged. Reproducibility of the measurements [standard deviation $\sigma(\varepsilon)$] was approximately equal to ±0.2%, and the accuracy was $\pm2\times10^{-3}$ with a 95% confidence interval.

Results and Discussion

The experimental measurements of relative permittivity were carried out on the three pure solvents and on 63 ternary mixtures in the whole miscibility field expressed by the mole fraction of the three components ($0 \leq X_1/X_2/X_3 \leq 1$), and collecting the data at various temperatures in the $50 \leq t/°\text{C} \leq 80$ range, at 5 °C intervals. The experimental data are given in Table 1, along with the ternary composition. As one can see, a few values are absent in Table 1 because the high conductivity of the two corresponding ME/W binary mixtures makes unavailable the experimental measurement technique employed (heterodyne beat method). For example, Fig. 1 shows the representation of the experimental data at 70 °C in the ternary composition domain.

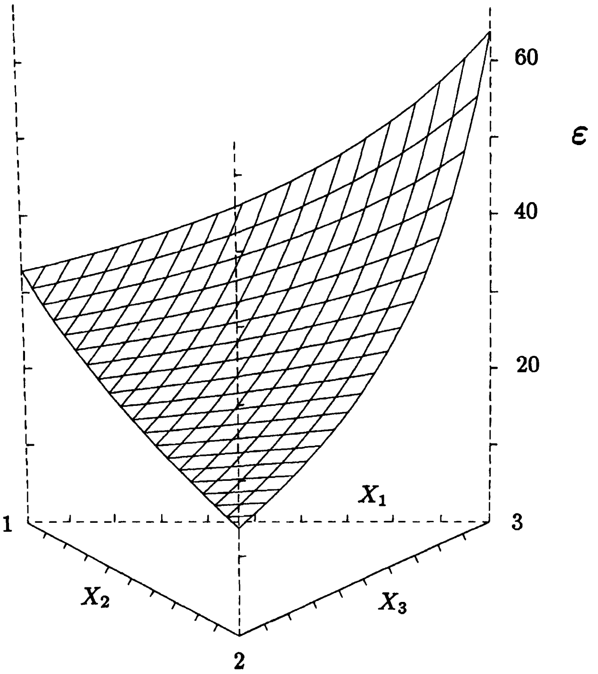

Fig. 1. Computer generated ε–X_i surface for ED(1)/ME(2)/W(3) ternary solvent system at 70 °C.

The dependence on temperature was investigated by the equation:[8]

$$\ln \varepsilon = \sum_{i=0}^{1} \alpha_i T^i \quad T/\text{K} \tag{1}$$

This correlation procedure provides the α_i values and the standard deviation σ ($\ln \varepsilon$) at each composition which have been deposited as Document No. 67008 at the Office of the Editor of Bull. Chem. Soc. Jpn. The fitting adequacy of Eq. 1 is ascertained by an average uncertainty $\overline{\Delta\varepsilon}$, evaluated as following

$$\overline{\Delta\varepsilon} = \frac{1}{N}\sum_{N} \mid \varepsilon_{\text{calcd}} - \varepsilon_{\text{exptl}} \mid \tag{2}$$

where N is the number of experimental data, equal to ± 0.03. All the calculations were performed by using a TSP[9] computer package.

Equation 1 may represent the dielectric behavior of various liquids (including polar, apolar, protic, aprotic, amphiprotic species) within experimental error, over a wide temperature range (from −100 to +150 °C approximately), compatibly with the physico-chemical properties of the systems.[10]

The coefficient α_1 in Eq. 1 represents a very important factor in the theory for heats of dilution of ionized solutes. In fact, this property is strongly affected by the factor $[1+\frac{T}{\varepsilon}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}]$, which is characteristic of the selected solvent.[11]

By simple algebraic manipulation, Eq. 1 provides immediately the quantity

$$\frac{T}{\varepsilon}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T} = \alpha_1 T \tag{3}$$

Working with binary or more complex solvent systems, Eq. 3 allows us to evaluate the dependence of the integral heat of dilution of the composition of the solvent mixtures.

One of the early attempts for the $\varepsilon=\varepsilon(X_1)$ correlation for binary liquid mixtures was a polynomial.equation of the type

$$\ln \varepsilon = \beta_0 + \beta_1 X_1 + \beta_2 X_1^2 \cdots + \beta_n X_1^n \tag{4}$$

but in the literature[12] it has been suggested that rational functions are more adequate in best fitting procedures of phisico-chemical experimental data rather than polynomial ones. In the case of relative permittivity values for binary mixtures, the generally employed rational equation is the reciprocal Padé approximant[12] in the form

$$\ln \varepsilon = \frac{a_0 + a_1 X_1}{b_0 + b_1 X_1} \tag{5}$$

Table 1. Composition and Relative Permittivities of 1,2-Ethanediol(1)/2-Methoxyethanol(2)/Water(3) Ternary Mixtures at Different Temperatures from 50 to 80 °C

X_1	X_2	ε_{50}	ε_{55}	ε_{60}	ε_{65}	ε_{70}	ε_{75}	ε_{80}
1.0000	0.0000	36.07	35.14	34.30	33.44	32.68	31.84	31.00
0.9272	0.0728	33.76	32.99	32.14	31.34	30.58	29.90	28.99
0.7442	0.0000	40.62	39.53	38.58	37.66	36.67	35.78	34.88
0.8499	0.1501	31.65	30.93	30.16	29.41	28.65	27.98	27.21
0.6760	0.0601	38.47	37.61	36.57	35.63	34.81	33.96	33.08
0.5638	0.0000	44.79	43.77	42.58	41.51	40.62	39.55	38.56
0.7676	0.2324	29.41	28.78	27.92	27.30	26.47	25.89	25.09
0.6053	0.1243	36.42	35.46	34.62	33.77	32.89	32.06	31.25
0.4952	0.0589	42.38	41.34	40.36	39.38	38.37	37.41	36.38
0.4274	0.0000	48.73	47.67	46.44	45.36	44.12	43.03	42.00
0.6798	0.3202	27.34	26.64	25.99	25.34	24.50	24.08	23.30
0.5296	0.1903	34.35	33.43	32.63	31.83	31.01	30.17	29.34
0.4422	0.1044	40.62	39.64	38.65	37.65	36.74	35.91	34.96
0.3756	0.0447	46.65	45.63	44.54	43.31	42.29	41.21	40.25
0.3267	0.0000	52.34	51.16	49.87	48.68	47.36	46.39	45.19
0.5860	0.4140	25.20	24.50	23.89	23.32	22.67	22.20	21.50
0.4554	0.2595	32.29	31.39	30.59	29.87	29.02	28.40	27.61
0.3692	0.1647	38.55	37.67	36.64	35.70	34.89	33.97	33.01
0.3198	0.0850	45.32	44.07	43.06	41.99	40.85	39.88	38.93
0.2755	0.0405	50.42	49.09	47.92	46.78	45.57	44.47	43.31
0.2432	0.0000	55.73	54.33	53.04	51.85	50.61	49.43	48.10
0.4855	0.5145	22.96	22.33	21.68	21.04	20.61	20.00	19.48
0.3688	0.3273	30.41	29.60	28.91	28.15	27.41	26.72	25.99
0.3038	0.2193	36.81	35.94	35.00	34.15	33.35	32.55	31.73
0.2583	0.1388	42.80	41.71	40.54	39.63	38.62	37.56	36.69
0.2220	0.0816	48.45	47.32	46.19	44.99	43.82	42.77	41.61
0.1956	0.0360	53.79	52.55	51.39	50.09	48.90	47.72	46.43
0.1775	0.0000	58.97	57.43	56.21	54.80	53.47	52.09	50.88
0.3776	0.6224	20.45	19.76	19.29	18.60	18.20	17.64	17.03
0.2889	0.4101	27.94	27.18	26.47	25.75	25.12	24.45	23.74
0.2367	0.2797	34.50	33.61	32.83	31.99	31.10	30.34	29.47
0.1970	0.1873	40.77	39.84	38.68	37.74	36.85	35.93	34.92
0.1694	0.1189	46.84	45.60	44.47	43.46	42.37	41.19	40.30
0.1513	0.0705	51.99	50.58	49.45	48.20	46.89	45.73	44.70
0.1342	0.0312	57.09	55.55	54.36	52.99	51.57	50.29	49.15
0.1213	0.0000	62.30	60.85	59.34	58.05	56.73	55.29	54.09
0.2614	0.7386	18.29	17.71	17.16	16.60	16.12	15.66	15.29
0.1916	0.4634	26.87	26.15	25.47	24.85	24.18	23.49	22.81
0.1618	0.3411	32.51	31.61	30.85	30.07	29.18	28.45	27.77
0.1362	0.2394	38.67	37.54	36.63	35.76	34.76	33.94	33.10
0.1208	0.1635	44.51	43.50	42.41	41.21	40.20	39.12	38.26
0.1018	0.1071	50.03	48.81	47.69	46.50	45.37	44.16	43.01
0.0959	0.0634	55.01	53.60	52.29	50.96	49.56	48.31	47.16
0.0822	0.0285	58.96	57.52	56.19	54.61	53.13	51.81	50.51
0.0749	0.0000	64.19	62.63	61.25	59.72	58.19	56.79	55.57
0.1359	0.8641	16.82	16.35	15.97	15.50	15.16	14.80	14.39
0.1138	0.5655	23.94	23.23	22.63	22.05	21.38	20.75	20.26
0.0871	0.4011	30.77	29.98	29.13	28.31	27.59	26.85	26.19
0.0732	0.2915	36.74	35.68	34.73	33.72	32.93	31.91	31.10
0.0599	0.2083	42.59	41.33	40.38	39.20	38.30	37.13	36.31
0.0549	0.1459	47.99	46.62	45.55	44.35	43.08	41.94	40.92
0.0457	0.0971	53.19	51.95	50.76	49.41	48.28	46.99	45.83
0.0393	0.0590	57.48	56.13	54.53	53.26	51.76	50.62	49.21
0.0366	0.0265	62.09	60.64	59.27	57.71	56.42	54.88	53.68
0.0346	0.0000	66.56	65.00	63.55	61.83	60.46	58.86	57.63
0.0000	1.0000	15.02	14.68	14.32	14.04	13.71	13.34	13.01
0.0000	0.6756	20.77	20.18	19.56	19.02	18.52	17.80	17.24
0.0000	0.4792	28.81	28.12	27.40	26.58	25.76	25.14	24.43
0.0000	0.3494	34.23	33.49	32.43	31.59	30.92	30.10	29.15
0.0000	0.2564	40.22	39.34	38.19	37.13	36.12	35.34	34.45
0.0000	0.1865	45.36	44.29	42.96	41.79	40.83	39.56	38.49
0.0000	0.1327	51.56	50.20	49.00	47.75	46.49	45.34	44.30
0.0000	0.0892	—	—	—	—	—	—	—
0.0000	0.0545	—	—	—	—	—	—	—
0.0000	0.0249	63.55	61.82	60.15	58.55	56.87	55.33	53.84
0.0000	0.0000	70.00	68.45	66.85	65.42	63.87	62.47	61.10

where some conditions, such as $a_0=1$ and $b_0=(\ln \varepsilon_2)^{-1}$, are imposed.

It should be noted that only the first power term of X_1 appears into Eq. 5, and that only two adjustable coefficients, a_1 and b_1, must be determined. In this investigation, the use of the best fitting Eq. 5 has been extended to the ternary mixtures, too, in the form

$$\ln \varepsilon = \frac{1 + a_1X_1 + a_2X_2}{(\sum_{i=1}^{3} X_i \ln \varepsilon_i)^{-1} + b_1X_1 + b_2X_2} \tag{6}$$

where ε_i are the relative permittivities of the pure components at each temperature, and X_i are their mole fractions, respectively.

The isothermal fitting coefficients a_i and b_i of Eq. 6 are summarized in Table 2, along with the average uncertainty at each temperature. The overall average deviation $\overline{\Delta\varepsilon}$ for this correlation procedure is equal to ±0.30.

Now two equations are available, $\varepsilon=\varepsilon(T)$ and $\varepsilon=\varepsilon(X_1,X_2)$. In an attempt to provide a comprehensive $\varepsilon=\varepsilon(T,X_1,X_2)$ model equation, we can combine Eqs. 1 and 6, and after algebraic manipulation we can write

$$\ln \varepsilon\ (T,X_1,X_2) = \frac{\sum_{h=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1} \gamma_{hkl}T^hX_1^kX_2^l}{(\sum_{i=1}^{3} X_i \ln \varepsilon_i)^{-1} + \sum_{i=1}^{2}\delta_iX_i} \tag{7}$$

where $(k+l)=0,1$ is the only required condition. The fitting coefficients of Eq. 7, evaluated by the least squares method employing the above cited TSP computer package, are listed in Table 3. This model equation provides calculated ε values which match very well the experimental ones, with an average uncertainty $\overline{\Delta\varepsilon}=\pm0.26$.

Even though the easy availability of Eqs. 6 and 7, more careful attention should be made in their forecasting employment in order to avoid meaningless ε interpolated values in the very narrow $0.0545\leq X_2\leq0.0892$ mole fraction range for the ME(2)/W(3) binary mixtures (see Tables). However, in our opinion, this range is so narrow that the unavailability of the corresponding experimental data should not affect the physical significance of the present curve-fitting procedures.

Table 2. Coefficients and Average Deviations, $\overline{\Delta\varepsilon}$ of Eq. 6 for 1,2-Ethanediol(1)/2-Methoxyethanol(2)/Water(3) Solvent System at Various Temperatures

t/°C	$a_1\times10$	$a_2\times10$	$b_1\times10$	$b_2\times10$	$\overline{\Delta\varepsilon}$
50	5.61766	3.90476	1.56193	1.47769	0.26
55	5.63868	3.92579	1.57826	1.50694	0.27
60	5.67581	3.99626	1.59934	1.55163	0.28
65	5.72754	4.06956	1.62437	1.60012	0.31
70	5.79907	4.15820	1.65718	1.65106	0.32
75	6.04398	4.17241	1.73628	1.68582	0.34
80	5.93343	4.20392	1.72071	1.72054	0.35

Table 3. Coefficients of Eq. 7 for 1,2-Ethanediol(1)/2-Methoxyethanol(2)/Water(3) Ternary Solvent System

Variable quantity	Coefficient	
	γ_{000}	1.04293
X_1	γ_{010}	6.61453×10^{-1}
X_2	γ_{001}	7.41346×10^{-1}
T	γ_{100}	-1.41682×10^{-4}
TX_1	γ_{110}	-5.10232×10^{-4}
TX_2	γ_{101}	-1.10099×10^{-3}
X_1	δ_1	1.37015×10^{-1}
X_2	δ_2	1.43830×10^{-1}

Excess Function. Generally, the dielectric behavior of the real mixtures shifts from ideality and, accordingly with the literature suggestions,[13] the deviations were evaluated by supposing a linear dependence of ε on composition for ideal mixtures. The following relationship was used:

$$\varepsilon = \varepsilon^{\mathrm{E}} + \sum_{i=1}^{3} X_i\varepsilon_i \tag{8}$$

where ε^{E} is the excess function. These quantities have been evaluated starting from the best fitting values provided by Eq. 1 in order to avoid excessive experimental data point scattering; the obtained values have been summarized in Table 2 available as supplementary material. To provide the best understanding about this function, some considerations about the three binary sub-systems are now necessary.

At first, one should note that ε^{E} is always negative at all the selected experimental conditions. Figure 2 shows the plot of ε^{E} vs. binary composition of ED+ME, ED+W, and ME+W binaries at 70 °C. In all these cases, the ε^{E} vs. X_i curves exhibit a minimum that becomes deeper as the difference in the dipole moment of the constitutive species is greater.

This minimum seems to be located at $X_i\simeq0.65$ for ED+ME and ME+W binaries, and slightly shifted to-

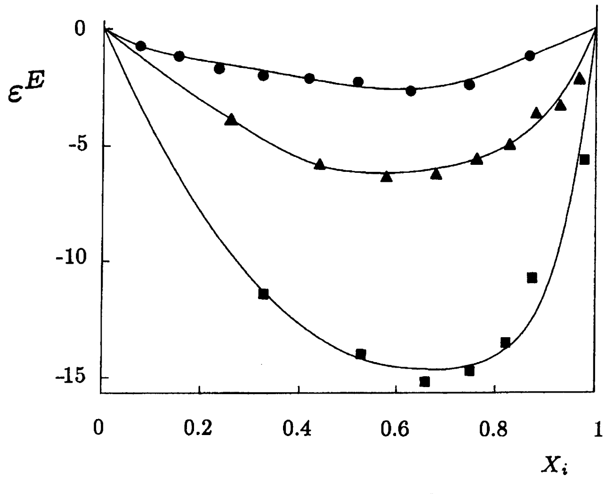

Fig. 2. Trend in the excess function ε^{E} at 70 °C with changing mole fraction X_i of binary systems: (●) ED/ME vs. X_{ME}; (▲) ED/W vs. X_{w}; (■) ME/W vs. X_{w}.

ward the ED rich region for ED+W ($X_i \simeq 0.6$).[14] Furthermore, the two aqueous binary systems show that ε^E tends to become less negative as temperature increases, while the contrary is true, even if slightly, for ED+ME binaries.

These evidences can be partly accounted for by the assumption that small negative ε^E values ($|\varepsilon^E| \leq 5$) are a consequence of weak specific interactions (of any kind, such as dipole–dipole, dipole–dipole induced, hydrogen bonding, etc.) which take place between unlike molecules.[13] In this light, one may hypothesize that specific interactions, and hydrogen bonding network in particular, become stronger in the binaries sequence ED+ME<ED+W<ME+W.

According to the literature suggestions,[15,16] the study of the thermomechanical properties of binary liquid mixtures could be a complementary tool (in addition to spectroscopic IR and NMR techniques) to investigate the formation of solvent–cosolvent complexes, and could provide a valuable help to determine their stoichiometry as well as their relative thermostability. On these bases, we can suggest the composition ratios for the complexes as follows: 1ED·2ME, 1ME·2W, and 2ED·3W for the corresponding binary mixtures. In the case of ED/W solvent system, we are obliged to mention that many authors disagree with the hypothesis of complex formation because they suggest that ED appears to be unable to form a clathrate or other well defined hydrates in aqueous solution.[17] These inferences are consistent with the observations previously reported in the literature[18,19] and with our argumentations presented in a recent paper.[14]

The relative permittivity excess data for binary mixtures generally are isothermally fitted by an equation of the type:[20]

$$\varepsilon^E = X_1 X_2 \sum_0^k a_k (X_2 - X_1)^k \tag{9}$$

which allows us to recalculate the ε^E quantity, for a suitable k value, in the limits of the experimental error at each composition.

For ternary mixtures, the literature is very poor in providing reliable equations to fit the excess thermomechanical properties, so that we have used the relationship

$$\begin{aligned}\varepsilon^E &= c_0 X_1 X_2 + c_1 X_2 X_3 + c_2 X_1 X_3 + c_3 X_1 X_2 (X_2 - X_1) \\ &+ c_4 X_2 X_3 (X_3 - X_2) + c_5 X_1 X_3 (X_3 - X_1) + c_6 X_1 X_2 X_3\end{aligned} \tag{10}$$

whose c_i adjustment parameters are summarized in Table 3 of supplementary material, together with the standard deviation $\sigma(\varepsilon^E)$ at each temperature. Equation 10 reproduces the experimental ε^E values with an average uncertainty $\overline{\Delta\varepsilon^E} = \pm 0.40$.

It is noteworthy that Eq. 10, formally deriving from the Redlich–Kister one[20] with $k=1$, reproduces the ε^E values for a ternary liquid mixture mainly as sum of contributions due to the three binary sub-systems, being the overall ternary mixture effect explicitly contained into the c_6 term only.

To evidentiate the presence of three components stable adducts in these ternary mixtures, we have plotted the ε^E quantity at each temperature in the ternary composition domain $[X_1, X_2, X_3]$ and the results are displayed in Figs. 3 and 4.

By examining these plots, one may deduce that no stable three components complex is present in these ternary mixtures, being absent any relative minimum in the graphs. Moreover, these latter figures tend to

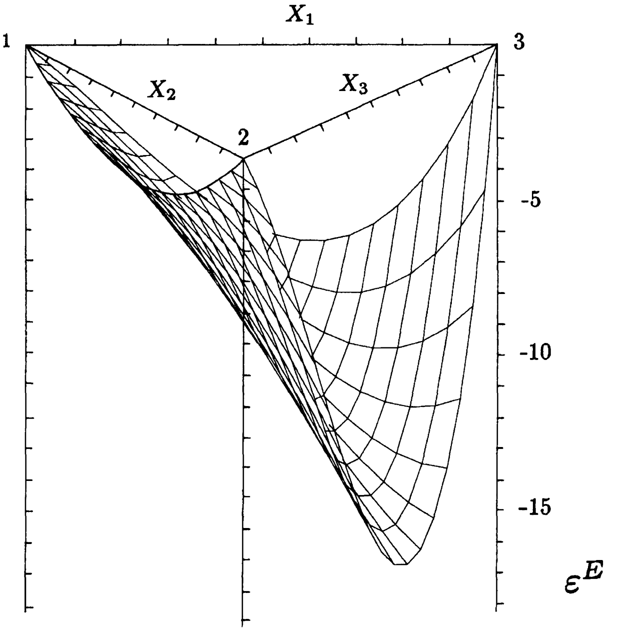

Fig. 3. View of the ε^E-composition surface for the ED(1)/ME(2)/W(3) ternary system at 70 °C.

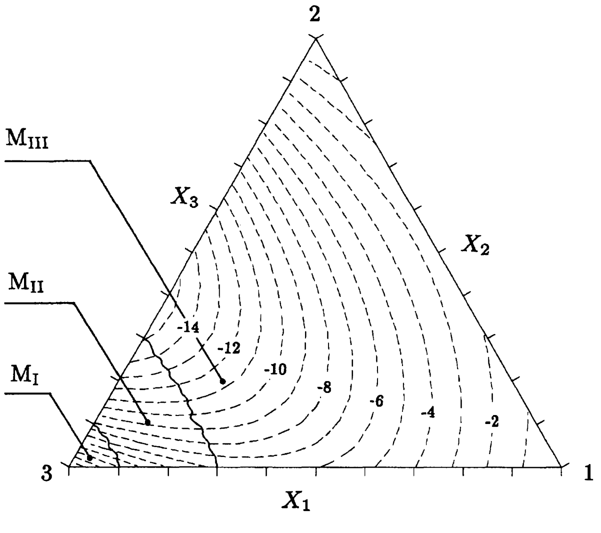

Fig. 4. Computer generated contour diagram showing lines of constant ε^E on a liquid-mole fraction grid ED(1)/ME(2)/W(3) at 70 °C, and regions M_I,M_{II}, M_{III}.

show that the more stable two components adduct is provided by ME and W at all the experimental conditions, confirming the observations previously reported about Fig. 2.

Now, some interesting and remarkable conclusions may be tried about these ternary mixtures containing water and "water-like" cosolvents. As discussed previously by Lumry et al.[21] about binary aqueous mixtures, the addition to water of a "water-like" cosolvent progressively inhibits the homocooperative fluctuations of the W–W hydrogen bond connetivities, and this network is progressively replaced by water–cosolvent mixed connectivities. Changes in the thermodynamic and thermomechanical properties of such mixtures make evident these microstructural variations, and the binary solutions could then be depicted in three distinct regions. Now, the same evidences have been obtained in the present investigations, working with a ternary ED+ME+W solvent system. In fact, examination of the excess relative permittivity vs. temperature trend leds to the following description being evidentiated three well distincted composition zones in the ternary domain.

1) Region $M_I : 1 > X_3 \simeq 0.9$. In this region, solution properties exhibit a sharp concentration dependence reflecting disruption of the homocooperative fluctuation units. Furthermore, the changes in the thermodynamic and thermomechanical properties as a function of composition appear strongly influenced by the hydrophobic character of both organic cosolvents. An explanation of the hydrophobic character of both ED and ME is that, working in very dilute aqueous solutions, ED and ME may exist in the predominant *gauche* cyclic conformation.[22,23] In this rotameric form, a strong intramolecular hydrogen bond would reduce ED–W and ME–W hydrogen bonding and increase the hydrophobicity of the organic species. In this light, it can be concluded that ED and ME do not undergo highly heterocooperative ED–W and ME–W interactions in the M_I region. This behavior could be inferred by the fact that the curves ε^E vs. temperature show a temperature coefficient $\frac{d\varepsilon^E}{dT} < 0$ in this composition region, as one can note from Table 2 of supplementary material. An increase in temperature should promote the upper energetic *anti*-rotameric conformations of ED and ME, with a disruption of the intramolecular hydrogen bonding and favorishing the heteroconnectivities with water molecules. Therefore, an increase in temperature provides a deviation from ideality and shifts the behavior of the ternary mixtures towards the real systems where strong interactions between components are observed. In terms of structural models, the M_I lower boundary would correspond to the cosolvents concentration beyond which clathrate-like hydrophobic hydration structures cannot exist. In fact, it should be noted that for ED+ME+W ternary mixtures, the temperature dependence of ε^E is negative for $X_3 > 0.9$ and positive at higher content of nonaqueous components. Now, following the Endo suggestions,[24] we propose that the composition of the zero temperature coefficient of ε^E could be taken as the limiting composition under which clathrate structures of organic species can exist. Therefore, the M_I composition range seems to be characterized by a progressive loss of the unique homocooperative fluctuations of liquid water. In the case of these ternary mixtures with ED and ME as cosolvents, this could be evidentiated through the hydrophobic hydration effects of both nonaqueous components. The lower water concentration limit of the M_I range will thus correspond to that which allows the statistically significant existence of the minimal $(H_2O)_n$ homocooperative units, with $n=5$ as previously suggested by other authors.[21]

2) Region $M_{II} : 0.9 > X_3 \simeq 0.7$. In this composition range, the properties vary smoothly with concentration reflecting the progressive loss of W–W hydrogen bonding connectivities. In view of the preceding remarks about the M_I composition range, we envisage a suitable intermolecular dynamic in the M_{II} region as follows. At the upper concentration of the M_{II} range the organic species, and ME in particular, should have eliminated the homocooperative $(H_2O)_n$ fluctuating units. Moreover, the dielectric behavior of the mixtures seems to be yet dominated by the W–W hydrogen bonding interactions; a further decrease in the X_3 mole fraction will reduce the intermolecular interactions in the homonucleated $(H_2O)_n$ clusters, which may be replaced by mixed W–cosolvents heteroconnectivities. In this picture, the lower X_3 concentration limit of the M_{II} region is represented as that where the hydrogen bond network between cosolvent species becomes dominant. This condition begins when the thermomechanical properties of the mixtures appear invariable with composition.

3) Region $M_{III} : 0.7 \simeq X_3 > 0$. In this composition domain, the properties rapidly approach to those of pure nonaqueous species, the water mixed hydrogen bonding connectivities closely resembling those occurring in the pure and mixed organic cosolvents. Mainly, the dielectric behavior, and probably other relevant properties, of ED+ME+W mixtures examined in this study should indicate a pseudo ideality in this composition range. In fact, the smooth variations in the investigated property may be depicted as resulting from the almost-ideal mixing of three liquids, i. e. ED, ME and the more stable adduct ME·2W directly formed in these nonelectrolytic solutions. These ME·2W heteronucleated clusters should be immersed and scattered in the bulk which should be constituted by slightly interacting ED·ME species, up to the pure components in the extreme composition limits of the ternary domain.

It is a pleasure to thank Professor C. Preti for helpful discussion and constructive suggestions on this paper. One of us (L. M.) wishes to gratefully thank Hospal-

Dasco s. p. a. (Modena, Italy) for awarding a junior research fellowship. The Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica (M. U. R. S. T.) of Italy is gratefully acknowledged for the financial support.

References

1) D. J. Bradley and K. S. Pitzer, *J. Phys. Chem.*, **83**, 1599 (1979).

2) K. Bose and K. K. Kundu, *Can. J. Chem.*, **57**, 2470 (1979).

3) A. P. Kreshkov, N. T. Smolova, A. Veveris, and B. Spince, *Zh. Fiz. Khim.*, **51**, 1827 (1977).

4) G. C. Franchini, A. Marchetti, L. Tassi, and G. Tosi, *Anal. Chem.*, **62**, 1004 (1990).

5) H. S. Frank, in "Water, a Comprehensive Treatise," ed by F. Franks, Plenum Press, New York (1972).

6) V. Viti and P. Zampetti, *Chem. Phys.*, **2**, 233 (1973).

7) L. Marcheselli, G. Pistoni, M. Tagliazucchi, L. Tassi, and G. Tosi, *J. Chem. Eng. Data*, **38**, 204 (1993).

8) A. A. Maryott and E. R. Smith, "Table of Dielectric Constant of Pure Liquids, Natl. Bur. Stand. Circ. No. 514," U. S. Government Printing Office, Washington, DC (1951).

9) "Time Series Processor-TSP-User's Guide," ed by Bronwyn H. Hall, TSP International, Standford, California, 94305, July 1987.

10) C. P. Smyth and S. O. Morgan, *J. Am. Chem. Soc.*, **50**, 1547 (1928).

11) E. Lange and A. L. Robinson, *J. Am. Chem. Soc.*, **52**, 2811 (1930).

12) M. King and N. Queen, *J. Chem. Eng. Data*, **24**, 178 (1979).

13) R. Payne and I. Theodorou, *J. Phys. Chem.*, **76**, 2892 (1972).

14) F. Corradini, L. Marcheselli, L. Tassi, and G. Tosi, *J. Chem. Soc., Faraday Trans.*, **89**, 123 (1993).

15) R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).

16) Yu. Ya. Fialkov, *Zh. Fiz. Khim.*, **37**, 1051 (1963).

17) J. B. Ott, J. R. Goates, and D. J. Lamb, *J. Chem. Termodyn.*, **4**, 123 (1972).

18) N. Takenaka and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **47**, 566 (1974).

19) S. Nishikawa, M. Tanaka, and M. Mashima, *J. Phys. Chem.*, **85**, 686 (1981).

20) O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 341 (1948).

21) R. Lumry, E. Battistel, and C. Jolicoeur, *Faraday Symp. Chem. Soc.*, **17**, 93 (1982).

22) P. Buckley and P. A. Giguere, *Can. J. Chem.*, **45**, 397 (1987).

23) L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

24) H. Endo, *Bull. Chem. Soc. Jpn.*, **46**, 1106 (1973).