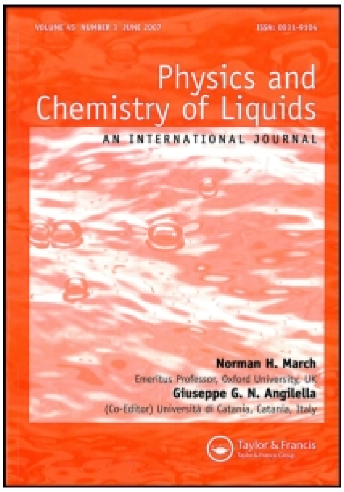

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The Ethane-1,2-diol 2-methoxyethanol 1,2-dimethoxyethane Ternary Solvent System: Density and Volume Properties at Different Temperatures

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THE ETHANE-1,2-DIOL + 2-METHOXYETHANOL + 1,2-DIMETHOXYETHANE TERNARY SOLVENT SYSTEM: DENSITY AND VOLUME PROPERTIES AT DIFFERENT TEMPERATURES

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The density of the ethane-1,2-diol + 2-methoxyethanol + 1,2-dimethoxyethane ternary mixtures has been measured at different temperatures ranging from −10 to 80°C, and over the whole composition range. The experimental data have been used to check the validity of some relationships accounting for the dependence of the density on temperature and composition, useful to evaluate the behaviour of this property in the whole temperature and composition domains.

Starting from the primary data, some derived quantities, such as excess molar volumes, partial molar volumes and partial excess molar volumes, have been obtained. In these mixtures V^E is generally negative at all the experimental conditions, showing the greatest deviations along the binary axes corresponding to the binary subsystems. The results are compared and discussed to get light to the changes in molecular association and structural effects in this solvent system.

Keywords: Ternary solvent systems; Nonelectrolytic liquid mixtures; Density; Ethane-1,2-diol; 2-Methoxyethanol; 1,2-Dimethoxyethane

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1. INTRODUCTION

A literature survey shows that very few studies have been made on thermophysical properties of ternary (and highest) liquid mixtures, in spite of their relative importance as solvent processes in many industrial design or scientific and analytical applications. As an example, let us think to the widespread employment in the field of electroanalytical determinations (conductometric, potentiometric, and all other related techniques which work in solution) and to the separation sciences such as LC and HPLC which need pure, or mixed, or gradient solvents [1].

In particular, a lot of work has been spent from our research group for the evaluation of density and of some related properties of ternary solvent systems containing 1,2-ethanediyl-(—CH_2—CH_2—) derivatives such as ethane-1,2-diol (ED), 2-methoxyethanol (ME), 1,2-dimethoxyethane (DME) and 1,2-dichloroethane (DCE), that mixed one another and with water (W) provide a variety of mixed solvents with different intrinsic characteristics [2, 3].

The volumetric behaviour of a liquid system can be generally expressed in terms of the molecular structural features of its components (*e.g.*, size, shape, dipole moments); therefore, these studies can help in the evaluation of the specific intermolecular interactions by correlating individual structural features with the macroscopic measured quantities [4, 5].

In the present paper, some empirical relationships have been reported, to evaluate the behaviour of the density and of some related quantities for the ternary solvent system {ED (component 1)+ME (2)+DME (3)}. The data were collected employing 12 new three-component mixtures in addition to the density values already obtained for the previously studied binary subsystems ED+ME [6], ED+DME [7] and ME+DME [8], working at 19 different temperatures in the $-10 \leq t/°\mathrm{C} \leq 80$ range, and covering the whole miscibility field, as expressed by the relation $0 \leq x_1, x_2, x_3 \leq 1$.

The density values (and the related quantities) of these mixtures have been represented by some interpolating equations to describe the effects of temperature and composition. An attempt was also made to explain the departure from the ideal behaviour of the calculated excess volumes in terms of specific interactions between the mixture components.

2. EXPERIMENTAL

2.1. Materials

The solvents ED, ME and DME (containing water $< 0.10\%$, $< 0.05\%$ and $< 0.10\%$ by mass, respectively, as found by Karl-Fischer titrations) were high purity grade reagents from Carlo Erba (Milan). ED and ME were stored over 3 Å molecular sieves for many days before use. DME was further purified by double fractional distillation over $LiAlH_4$ to eliminate traces of acids and peroxides and to reduce, as much as possible, the total amount of water, keeping the middle fraction only (bp 83°C) for the measurements. The final purity of the solvents was checked by gas chromatography (mass fraction $= 99.5\%$ for ED and 99.7% for both ME and DME species), confirming the absence of other organic compounds.

2.2. Apparatus and Procedures

All the mixtures were prepared by mixing appropriate volumes of the components and by weight on a Mettler PM 480 Δ-range balance just before use, operating in a dry box to avoid atmospheric contamination. The accuracy for each mole fraction (x_i) is estimated to be less than 1.5×10^{-4}. The density was measured by an oscillating capillary tube, with a sensitivity $\pm 1 \times 10^{-6}$ g cm^{-3}.

The apparatus, procedures and experimental details of the density measurements have been described elsewhere [9].

3. RESULTS AND DISCUSSION

The experimental density values of the twelve {ED (1) + ME (2) + DME (3)} three-component mixtures covering the whole composition range are presented in Table I, along with the corresponding ternary composition. For comparison purposes, Table I also reports the density values for the three pure species.

For each mixture the density values were fitted against temperature (t/°C) by the polynomial equation [10]:

$$\rho(t) = \sum_{0}^{k} a_k t^k \tag{1}$$

TABLE I Ternary composition and experimental densities (ρ/g cm^{-3}) for the {ED (1) + ME (2) + DME (3)} solvent system at various temperatures

x_1	1	0	0	0.3192	0.4727	0.1516	0.1871	0.0770	0.1323	0.3742	0.7191	0.2987	0.8588	0.1237	0.6022
x_2	0	1	0	0.5722	0.5143	0.5299	0.3028	0.6925	0.7890	0.3964	0.1957	0.1963	0.0738	0.0924	0.1539
x_3	0	0	1	0.1086	0.0131	0.3185	0.5101	0.2305	0.0788	0.2294	0.0852	0.5050	0.0675	0.7839	0.2439
t/°C															
−10	1.13363_4	0.99016_9	0.89785_3	1.03138_2	1.05693_7	0.98589_3	0.96633_1	0.98340_1	1.00512_9	1.02638_7	1.08236_7	0.97885_6	1.10346_4	0.92513_5	1.04968_6
−5	1.13045_2	0.98637_7	0.89276_8	1.02669_0	1.05240_3	0.98111_7	0.96161_6	0.97898_2	1.00088_6	1.02144_9	1.07913_8	0.97423_9	1.10056_7	0.92047_9	1.04576_5
0	1.12706_9	0.98234_5	0.88772_3	1.02197_1	1.04792_1	0.97626_8	0.95682_1	0.97438_2	0.99649_3	1.01662_4	1.07577_5	0.96954_1	1.09740_3	0.91573_2	1.04177_8
5	1.12366_4	0.97812_8	0.88258_1	1.01727_9	1.04351_0	0.97138_8	0.95196_9	0.96965_2	0.99198_5	1.01187_8	1.07222_4	0.96479_4	1.09402_3	0.91083_3	1.03770_7
10	1.12029_6	0.97374_1	0.87735_4	1.01255_8	1.03912_4	0.96648_4	0.94707_6	0.96481_8	0.98738_4	1.00715_9	1.06853_1	0.95999_7	1.09045_3	0.90587_9	1.03356_3
15	1.11690_6	0.96925_9	0.87212_5	1.00784_2	1.03475_7	0.96148_0	0.94210_7	0.95982_6	0.98267_5	1.00249_1	1.06469_9	0.95516_4	1.08678_7	0.90082_0	1.02934_6
20	1.11344_0	0.96485_1	0.86687_5	1.00314_6	1.03038_3	0.95648_2	0.93712_8	0.95477_5	0.97787_2	0.99781_1	1.06079_8	0.95027_9	1.08304_7	0.89573_7	1.02506_3
25	1.10991_3	0.96028_8	0.86150_6	0.99840_7	1.02600_1	0.95140_6	0.93213_9	0.94962_3	0.97299_8	0.99312_5	1.05682_2	0.94539_3	1.07924_1	0.89062_9	1.02072_9
30	1.10651_2	0.95574_9	0.85609_7	0.99364_3	1.02160_5	0.94631_5	0.92705_5	0.94439_4	0.96808_5	0.98841_1	1.05280_1	0.94046_5	1.07540_1	0.88547_4	1.01633_8
35	1.10308_9	0.95108_8	0.85068_0	0.98884_0	1.01716_2	0.94115_6	0.92198_7	0.93907_5	0.96312_6	0.98366_6	1.04871_0	0.93551_7	1.07157_6	0.88033_3	1.01189_7
40	1.09974_7	0.94629_2	0.84512_4	0.98407_2	1.01272_7	0.93600_8	0.91689_8	0.93376_5	0.95813_4	0.97886_9	1.04456_8	0.93054_9	1.06772_0	0.87516_2	1.00740_4
45	1.09631_2	0.94162_1	0.83957_5	0.97924_7	1.00827_9	0.93079_9	0.91176_2	0.92840_2	0.95315_8	0.97403_2	1.04037_7	0.92554_6	1.06385_9	0.86997_6	1.00286_8
50	1.09294_6	0.93687_8	0.83395_6	0.97437_8	1.00382_4	0.92554_6	0.90660_1	0.92301_3	0.94815_1	0.96913_8	1.03615_5	0.92053_6	1.05999_8	0.86473_9	0.99828_1
55	1.08947_1	0.93213_3	0.82824_7	0.96951_0	0.99935_5	0.92026_1	0.90140_3	0.91764_6	0.94312_4	0.96420_3	1.03187_1	0.91549_8	1.05611_9	0.85954_5	0.99362_6
60	1.08601_1	0.92738_7	0.82246_8	0.96461_2	0.99490_1	0.91497_1	0.89622_3	0.91227_5	0.93811_6	0.95923_7	1.02756_9	0.91041_5	1.05218_1	0.85425_7	0.98891_1
65	1.08263_4	0.92271_4	0.81667_6	0.95970_7	0.99046_7	0.90967_0	0.89104_7	0.90693_2	0.93309_7	0.95424_4	1.02325_9	0.90530_3	1.04824_8	0.84896_0	0.98416_7
70	1.07900_3	0.91781_1	0.81083_0	0.95474_6	0.98607_2	0.90433_3	0.88585_9	0.90160_9	0.92809_6	0.94921_2	1.01885_5	0.90010_5	1.04418_0	0.84363_3	0.97931_8
75	1.07536_9	0.91308_7	0.80494_7	0.94974_8	0.98172_3	0.89898_7	0.88066_3	0.89631_2	0.92308_3	0.94418_2	1.01440_5	0.89483_7	1.04001_6	0.83823_7	0.97437_9
80	1.07169_9	0.90814_4	0.79906_4	0.94468_9	0.97743_9	0.89359_7	0.87543_0	0.89106_5	0.91806_8	0.93914_9	1.00987_6	0.88943_5	1.03572_9	0.83271_4	0.96931_4

using the least-squares method [11]. The calculated a_k coefficients $(0 \leq k \leq 4)$ are listed in Table II along with the relative standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$, for each studied composition.

Equation (1) represents the experimental data within an uncertainty $\Delta\rho$, as evaluated by

$$\Delta\rho = \frac{1}{N}\sum_{N} |\rho_{\text{calcd}} - \rho_{\text{exptl}}| \tag{2}$$

whose mean value $\overline{\Delta\rho}$, calculated over the set of 285 (N) values in Table I, is equal to $2.1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$.

In order to take into account the dependence of ρ on the composition of the liquid mixtures, the following relationship:

$$\rho(x_1, x_2) = \sum_{0}^{j}\sum_{0}^{h} b_{hj} x_1^j x_2^h \tag{3}$$

was used to fit the experimental data at each temperature. It should be noted that Eq. (3) has been applied taking also into account the previously published binary data on {ED (1)/ME (2)} [6], {ED (1)/DME (2)} [7] and {ME (1)/DME (2)} [8] mixtures (on the whole: 3 pure species, 27 binaries and 12 ternaries). The b_{hj} coefficients, calculated by multilinear regression using the software package TSP [11], are summarised in Table III, together with the relative standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$. The efficiency of this bivariant correlation model seems to be quite acceptable, since it reproduces the experimental data with an average uncertainty $\overline{\Delta\rho} = 1.81 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$, calculated over the entire temperature and composition ranges, and assuming values within the $0 \leq \Delta\rho/\mathrm{g\,cm^{-3}} \leq 2.62 \times 10^{-4}$ interval.

3.1. Excess Molar Volume

The excess molar volumes ($V^{\mathrm{E}}/\mathrm{cm^3\,mol^{-1}}$) of the mixtures were obtained from the measured experimental densities by the usual equation:

$$V^{\mathrm{E}} = \frac{\sum_{i=1}^{3} x_i M_i}{\rho} - \sum_{i=1}^{3} \frac{x_i M_i}{\rho_i} \tag{4}$$

where M_i, are the molar masses of the mixture's components ($M_1 = 62.070$; $M_2 = 76.096$; $M_3 = 90.120\,\mathrm{g\,mol^{-1}}$), and ρ and ρ_i are the densities of the mixtures and of pure species at each temperature,

TABLE II Coefficients a_k and standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$ of Eq. (1) for the ED (1) + ME (2) + DME (3) ternary mixtures

x_1	x_2	x_3	a_0	10^4a_1	10^8a_2	$10^{10}a_3$	$10^{12}a_4$	$10^5\sigma(\rho)$
1	0	0	1.127083	−6.711	−109.7	278.7	−219.2	4.2
0	1	0	0.982296	−8.248	−298.9	350.3	−169.6	5.6
0	0	1	0.887691	−10.230	−76.94	−84.02	59.73	2.2
0.3192	0.5722	0.1086	1.021980	−9.401	−4.129	−42.85	9.477	2.5
0.4727	0.5143	0.0131	1.047937	−8.876	90.14	−252.7	187.7	2.3
0.1516	0.5299	0.3185	0.976277	−9.715	−97.48	18.01	8.969	2.2
0.1871	0.3028	0.5101	0.956813	−9.642	−107.4	58.17	−8.340	2.6
0.0770	0.6925	0.2305	0.974395	−9.315	−292.4	215.1	−26.78	2.3
0.1323	0.7890	0.0788	0.996511	−8.897	−263.9	266.5	−97.86	2.2
0.3742	0.3964	0.2294	1.016627	−9.571	146.4	−366.9	207.8	2.6
0.7191	0.1957	0.0852	1.075761	−6.957	−317.7	335.3	−172.3	2.5
0.2987	0.1963	0.5050	0.969553	−9.442	−127.5	180.4	−137.7	2.3
0.8588	0.0738	0.0675	1.097389	−6.575	−416.4	683.7	−425.4	2.4
0.1237	0.0924	0.7839	0.915714	−9.667	−212.0	312.8	−198.0	2.5
0.6022	0.1539	0.2439	1.041788	−8.070	−170.9	139.7	−100.2	2.2

TABLE IIIa Coefficients b_{kj} and standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$ of Eq. (3) for {ED (1)+ME (2)+DME (3)} ternary solvent system at various temperatures

$t/°C$		-10	-5	0	5	10
kj	*Variable*			$b_{kj}/(g\cdot cm^{-3})$		
00		0.897884	0.892770	0.887634	0.882472	0.877276
01	x_2	8.660×10^{-2}	8.510×10^{-2}	8.277×10^{-2}	7.976×10^{-2}	7.621×10^{-2}
02	x_2^2	-1.394×10^{-2}	-1.133×10^{-3}	1.243×10^{-2}	2.670×10^{-2}	4.176×10^{-2}
03	x_2^3	6.438×10^{-2}	4.085×10^{-2}	1.884×10^{-2}	-2.163×10^{-3}	-2.291×10^{-2}
04	x_2^4	-4.456×10^{-2}	-3.112×10^{-2}	-1.930×10^{-2}	-8.629×10^{-3}	1.450×10^{-3}
10	x_1	0.1169	0.1206	0.1232	0.1249	0.1258
11	x_1x_2	−0.4629	−0.2906	−0.1474	-2.533×10^{-2}	8.259×10^{-2}
12	$x_1x_2^2$	4.3629	3.3551	2.5706	1.9530	1.4506
13	$x_1x_2^3$	−5.8542	−4.1820	−2.9560	−2.0691	−1.4191
14	$x_1x_2^4$	1.7716	0.9271	0.3504	-2.164×10^{-2}	−0.2501
20	x_1^2	0.1675	0.1547	0.1476	0.1453	0.1466
21	$x_1^2x_2$	5.6846	4.6372	3.8016	3.1211	2.5471
22	$x_1^2x_2^2$	−29.6604	−24.3630	−20.4141	−17.4618	−15.1810
23	$x_1^2x_2^3$	25.3430	18.3163	13.7832	11.1062	9.6634
24	$x_1^2x_2^4$	1.4839	4.0944	5.2539	5.3378	4.7233
30	x_1^3	-1.117×10^{-2}	1.452×10^{-2}	3.010×10^{-2}	3.721×10^{-2}	3.757×10^{-2}
31	$x_1^3x_2$	−9.6207	−7.8230	−6.4628	−5.4212	−4.5950
32	$x_1^3x_2^2$	30.9803	23.8633	19.3379	16.6844	15.2310
33	$x_1^3x_2^3$	44.3918	48.4151	47.8927	44.0966	38.2946
34	$x_1^3x_2^4$	−70.0516	−68.7880	−64.8609	−59.0420	−52.1174
40	x_1^4	-3.698×10^{-2}	-5.192×10^{-2}	-6.133×10^{-2}	-6.603×10^{-2}	-6.688×10^{-2}
41	$x_1^4x_2$	4.3594	3.4270	2.7579	2.2797	1.9292
42	$x_1^4x_2^2$	−4.6418	−1.9532	−0.7295	−0.5480	−1.0106
43	$x_1^4x_2^3$	−59.9024	−59.1502	−55.9246	−50.9362	−44.9045
44	$x_1^4x_2^4$	30.2424	30.6332	29.3928	26.9865	23.8707
$10^4\sigma(\rho)$		8.6	7.8	7.4	7.2	7.1

TABLE IIIb Coefficients b_{kj} and standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$ of Eq. (3) for {ED (1)+ME(2)+DME (3)} ternary solvent system at various temperatures

$t/^\circ C$		15	20	25	30	35
kj	*Variable*	$b_{kj}/(g \cdot cm^{-3})$				
00		0.872039	0.856034	0.866756	0.861422	0.850589
01	x_2	7.226×10^{-2}	5.930×10^{-2}	6.806×10^{-2}	6.370×10^{-2}	5.492×10^{-2}
02	x_2^2	5.749×10^{-2}	0.1078	7.380×10^{-2}	9.065×10^{-2}	0.1252
03	x_2^3	-4.378×10^{-2}	−0.1098	-6.506×10^{-2}	-8.708×10^{-2}	−0.1333
04	x_2^4	1.130×10^{-2}	4.212×10^{-2}	2.120×10^{-2}	3.146×10^{-2}	5.337×10^{-2}
10	x_1	0.1263	0.1265	0.1264	0.1264	0.1268
11	x_1x_2	0.1821	0.4671	0.2771	0.3716	0.5654
12	$x_1x_2^2$	1.0228	−0.1135	0.6372	0.2633	−0.5103
13	$x_1x_2^3$	−0.9276	0.2116	−0.5283	−0.1595	0.6228
14	$x_1x_2^4$	−0.3817	−0.5725	−0.4572	−0.5137	−0.6576
20	x_1^2	0.1508	0.1715	0.1569	0.1640	0.1787
21	$x_1^2x_2$	2.0405	0.6422	1.5701	1.1083	0.1571
22	$x_1^2x_2^2$	−13.3268	−8.4085	−11.6873	−10.0783	−6.5650
23	$x_1^2x_2^3$	9.0026	7.9794	8.7119	8.4345	7.1068
24	$x_1^2x_2^4$	3.6791	0.2558	2.4599	1.2768	−0.4577
30	x_1^3	3.240×10^{-2}	-1.617×10^{-3}	2.332×10^{-2}	1.153×10^{-2}	-1.506×10^{-2}
31	$x_1^3x_2$	−3.9011	−2.0104	−3.2724	−2.6518	−1.3164
32	$x_1^3x_2^2$	14.4690	12.4290	13.9638	13.3468	10.9830
33	$x_1^3x_2^3$	31.4124	11.7048	24.2715	17.5725	7.1368
34	$x_1^3x_2^4$	−44.6523	−23.6373	−37.1690	−30.0747	−18.1248
40	x_1^4	-6.451×10^{-2}	-4.559×10^{-2}	-5.973×10^{-2}	-5.320×10^{-2}	-3.750×10^{-2}
41	$x_1^4x_2$	1.6549	0.9210	1.4158	1.1773	0.6276
42	$x_1^4x_2^2$	−1.8138	−3.9735	−2.7012	−3.4596	−4.1101
43	$x_1^4x_2^3$	−38.3540	−19.8007	−31.7560	−25.4913	−14.9449
44	$x_1^4x_2^4$	20.3771	10.3889	16.8327	13.4420	7.8065
$10^4\sigma(\rho)$		7.1	7.0	7.1	7.0	6.9

TABLE IIIc Coefficients b_{kj} and standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$ of Eq. (3) for {ED (1)+ME (2)+DME (3)} ternary solvent system at various temperatures

$t/°C$		40	45	50	55	60
kj	*Variable*			$b_{kj}/(g\cdot cm^{-3})$		
00		0.845088	0.839529	0.833911	0.828240	0.822515
01	x_2	5.064×10^{-2}	4.652×10^{-2}	4.261×10^{-2}	3.892×10^{-2}	3.548×10^{-2}
02	x_2^2	0.1427	0.1601	0.1772	0.1938	0.2096
03	x_2^3	−0.1575	−0.1823	−0.2072	−0.2320	−0.2560
04	x_2^4	6.516×10^{-2}	7.746×10^{-2}	9.006×10^{-2}	0.1028	0.1154
10	x_1	0.1273	0.1283	0.1298	0.1319	0.1348
11	x_1x_2	0.6663	0.7687	0.8698	0.9671	1.0553
12	$x_1x_2^2$	−0.9296	−1.3695	−1.8173	−2.2612	−2.6705
13	$x_1x_2^3$	1.0831	1.5973	2.1485	2.7204	3.2649
14	$x_1x_2^4$	−0.7755	−0.9322	−1.1203	−1.3316	−1.5424
20	x_1^2	0.1848	0.1894	0.1919	0.1920	0.1890
21	$x_1^2x_2$	−0.3469	−0.8664	−1.3850	−1.8889	−2.3455
22	$x_1^2x_2^2$	−4.5445	−2.3443	−0.0502	2.2674	4.4200
23	$x_1^2x_2^3$	5.8004	3.9946	1.8098	−0.6452	−3.1035
24	$x_1^2x_2^4$	−0.8505	−0.8678	−0.5680	-2.031×10^{-2}	0.6476
30	x_1^3	-2.756×10^{-2}	-3.827×10^{-2}	-4.616×10^{-2}	-5.046×10^{-2}	-5.029×10^{-2}
31	$x_1^3x_2$	−0.5716	0.2190	1.0225	1.8073	2.5084
32	$x_1^3x_2^2$	9.0283	6.5502	3.7304	0.7570	−2.0028
33	$x_1^3x_2^3$	3.8453	1.9832	1.3116	1.4845	2.0537
34	$x_1^3x_2^4$	−13.5332	−9.9514	−7.2596	−5.2046	−3.5569
40	x_1^4	-2.957×10^{-2}	-2.230×10^{-2}	-1.624×10^{-2}	-1.186×10^{-2}	-9.647×10^{-3}
41	$x_1^4x_2$	0.2986	-6.332×10^{-2}	−0.4389	−0.8072	−1.1299
42	$x_1^4x_2^2$	−3.8877	−3.2949	−2.4346	−1.4350	−0.5011
43	$x_1^4x_2^3$	−10.9126	−7.7942	−5.4847	−3.7575	−2.4053
44	$x_1^4x_2^4$	5.7122	4.1083	2.9380	2.0401	1.2352
$10^4\sigma(\rho)$		6.9	6.8	6.7	6.7	6.8

TABLE IIId Coefficients b_{kj} and standard deviations $\sigma(\rho)/\mathrm{g\,cm^{-3}}$ of Eq. (3) for {ED (1)+ME (2)+DME (3)} ternary solvent system at various temperatures

t/°C		65	70	75	80
kj	*Variable*	$b_{kj}/(g\cdot cm^{-3})$			
00		0.816740	0.810922	0.805065	0.799176
01	x_2	3.230×10^{-2}	2.933×10^{-2}	2.659×10^{-2}	2.402×10^{-2}
02	x_2^2	0.2243	0.2378	0.2496	0.2594
03	x_2^3	−0.2785	−0.2991	−0.3166	−0.3303
04	x_2^4	0.1273	0.1383	0.1477	0.1549
10	x_1	0.1383	0.1426	0.1476	0.1534
11	x_1x_2	1.1292	1.1821	1.2057	1.1916
12	$x_1x_2^2$	−3.0155	−3.2570	−3.3466	−3.2324
13	$x_1x_2^3$	3.7326	4.0588	4.1632	3.9557
14	$x_1x_2^4$	−1.7254	−1.8462	−1.8615	−1.7213
20	x_1^2	0.1829	0.1732	0.1598	0.1426
21	$x_1^2x_2$	−2.7216	−2.9762	−3.0566	−2.9094
22	$x_1^2x_2^2$	6.2200	7.4285	7.7457	6.8477
23	$x_1^2x_2^3$	−5.2431	−6.6875	−6.9562	−5.4979
24	$x_1^2x_2^4$	1.2452	1.5614	1.3311	0.2351
30	x_1^3	-4.511×10^{-2}	-3.417×10^{-2}	-1.701×10^{-2}	6.715×10^{-3}
31	$x_1^3x_2$	3.0543	3.3595	3.3149	2.8055
32	$x_1^3x_2^2$	−4.1277	−5.1121	−4.3305	−1.0737
33	$x_1^3x_2^3$	2.2660	1.3389	−1.7120	−8.0932
34	$x_1^3x_2^4$	−1.8435	0.4291	3.8488	9.1629
40	x_1^4	-9.975×10^{-3}	-1.329×10^{-2}	-1.991×10^{-2}	-3.012×10^{-2}
41	$x_1^4x_2$	−1.3627	−1.4531	−1.3350	−0.9369
42	$x_1^4x_2^2$	0.1093	9.388×10^{-2}	−0.9161	−3.3510
43	$x_1^4x_2^3$	−0.9990	0.8993	3.8267	8.4607
44	$x_1^4x_2^4$	0.2716	−1.1979	−3.5400	−7.2029
$10^4\sigma(\rho)$		7.1	7.6	8.4	9.8

respectively. The V^E data for all the mixtures were isothermally fitted by the method of least-squares to the equation [12]:

$$V^E = d_1x_1x_2 + d_2x_2x_3 + d_3x_1x_3 + d_4x_1x_2(x_2 - x_1) + d_5x_2x_3(x_3 - x_2) + d_6x_1x_3(x_1 - x_3) + d_7x_1x_2x_3 \quad (5)$$

A similar equation has been successfully used by other authors and by us in some previous papers to fit different excess mixing properties for different three-component liquid systems [3]. The d_k parameters are collected in Table IV together with the standard deviation $\sigma(V^E)/\mathrm{cm^3\,mol^{-1}}$ of the different fits calculated at each temperature. This relationships reproduces the V^E quantities within $\overline{\Delta V^E} = \pm 0.053\,\mathrm{cm^3\,mol^{-1}}$ over all the 798 starting points, and assuming values in the $0.000 \leq |\Delta V^E|(\mathrm{cm^3\,mol^{-1}}) \leq 0.121$ range. The fitting Eq. (5) has been chosen between a set of other similar relationships in view of the fact that it is simple in structure and that it provides good results inspite of the low number of empirical coefficients to be determined.

Equation (5) formally derives from the Redlich-Kister one [13]:

$$V_{ij}^E = x_ix_j \sum_0^h c_h(x_j - x_i)^h \quad (6)$$

when applied to the three binary subsystems ($V_{12}^E, V_{13}^E, V_{23}^E$) and truncating each polynomial in correspondence of the first power term.

For comparison purposes, Figure 1 shows the trend of V^E *vs.* x_2 for the three binary subsystems {ED (1)+ME (2)}, {ED (1)+DME (2)} and {ME (1)+DME (2)} at 25°C. It is evident that the V^E values are generally negative, with a sharp minimum centred at $x_2 \cong 0.35$ for the ED+DME (2ED : 1DME) and ME+DME (2ME : 1DME) binaries, and at $x_2 \cong 0.5$ in the case of the ED+ME (1ED : 1ME) system. This minimum is deeper in the sequence {ME+DME} < {ED+ME} < {ED+DME} and this observation is generally true at all the experimental conditions. Furthermore we mention that for the {ED+ME} and {ED+DME} binary systems, an increasing temperature provides more negative values of V^E, while, on the contrary, an inversion of this trend is observed for the {ME+DME} liquid mixtures.

The negative values of V^E indicate that the packing degree is enhanced in these mixed liquids with respect to the pure species and to their ideal mixtures, suggesting that specific intermolecular

TABLE IV Coefficients d_k and standard deviations $\sigma(V^E)/\mathrm{cm^3\,mol^{-1}}$ of Eq. (5) for {ED (1)+ME (2)+DME (3)} ternary solvent system at various temperatures

$t/°C$	d_1	$10^2 d_2$	d_3	$10 d_4$	d_5	d_6	d_7	$10^2\sigma(V^E)$
−10	−2.244	−203.5	−3.963	−8.318	1.633	−4.676	−24.63	8.5
−5	−2.088	−195.7	−4.167	−7.079	1.520	−4.822	−24.68	7.8
0	−1.972	−185.3	−4.351	−5.992	1.467	−4.943	−24.85	7.3
5	−1.889	−172.6	−4.516	−5.063	1.468	−5.049	−25.15	7.0
10	−1.833	−158.3	−4.668	−4.299	1.503	−5.126	−25.55	6.8
15	−1.795	−142.5	−4.806	−3.699	1.559	−5.180	−26.04	6.6
20	−1.772	−125.7	−4.936	−3.248	1.621	−5.205	−26.61	6.5
25	−1.761	−107.9	−5.061	−2.971	1.680	−5.201	−27.21	6.4
30	−1.755	−89.83	−5.183	−2.832	1.730	−5.168	−27.89	6.5
35	−1.755	−71.41	−5.306	−2.862	1.761	−5.105	−28.58	6.6
40	−1.758	−52.68	−5.435	−3.016	1.773	−5.012	−29.27	6.8
45	−1.764	−33.90	−5.569	−3.261	1.762	−4.892	−29.97	7.1
50	−1.773	−15.13	−5.717	−3.614	1.723	−4.746	−30.65	7.6
55	−1.790	3.964	−5.877	−4.029	1.664	−4.579	−31.30	8.1
60	−1.815	23.25	−6.058	−4.514	1.586	−4.390	−31.90	8.8
65	−1.852	43.10	−6.260	−5.017	1.500	−4.185	−32.46	9.6
70	−1.906	63.74	−6.485	−5.497	1.416	−3.972	−32.96	10
75	−1.987	85.49	−6.742	−5.957	1.342	−3.748	−33.36	12
80	−2.100	109.0	−7.030	−6.282	1.307	−3.525	−33.70	13

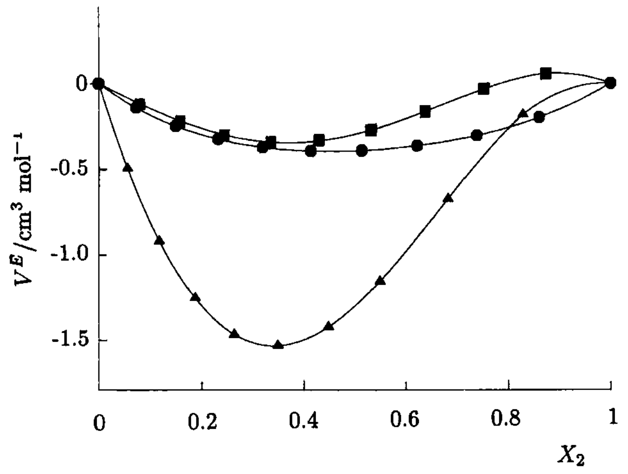

FIGURE 1 Excess molar volumes V^E against x_2 for the three binary subsystems at 25°C: ● ED (1)+ME (2); ▲ ED (1)+DME (2); ■ ME (1)+DME (2).

interactions such as hydrogen bonding and dipolar interactions of any kind between the component molecules are more effective and operative. Therefore, the attractive interactions (which are generally responsible for structure-making effects) seem to be the prevailing forces in the liquid structure [14] of these mixed nonelectrolytic solutions, with respect to repulsive phenomena due to sterical hindrances and unfavourable interactions between polar and apolar groups (structure-breaking effects). These considerations agree with the literature suggestions about the molecular dynamics of the selected species ED [15], ME [16] and DME [17]. In fact, it has been demonstrated that all these molecules can exist in different rotameric conformers, *i.e.*, *anti* and *gauche*. The *gauche* conformers of ED and ME are strongly stabilised by the presence of an intramolecular hydrogen bond (whose energy is about 24 kJ mol^{-1} at ordinary conditions) [18, 19], and this skeletal arrangement resembles the molecules to a pseudo-cyclic form, having density and entropy values higher than the more or less linear *anti* conformers. Obviously the molecular arrangement is quite different for the DME units, because of the total absence of HBD (Hydrogen Bonding Donor) sites, and in presence of 2HBA (Hydrogen Bonding Acceptor) sites. In this respect, one should remember that ED shows parity in HBDA active sites, while disparity is observed in the ME species (1HBD : 2HBA), this fact being responsible for a possible interactive competition between hydrophilic and hydrophobic substituent groups in order to provide an heterocooperative network able to sustain the liquid structure and the most common local density fluctuations.

In order to check the presence of three-component adducts in these liquid mixtures, we have plotted the V^E quantity at each investigated temperature in the ternary composition domain $\{x_1, x_2, x_3\}$ and, as an example, the results at 25°C are shown in Figure 2. An accurate examination of these plots does not furnish any evidence of stable three-component adducts in this ternary solvent system, relative minima being absent in the ternary domain other than those detected along the binary axes of the three binary subsystems. Similar trends as described in Figure 2 have been obtained at all the temperatures in the investigated range $-10 \leq t/°\mathrm{C} \leq 80$, presenting only slight deformations of the surface $V^E = V^E\{x_1, x_2, x_3\}$ and of the corresponding isolines in the ternary domain. The presence of an absolute minimum at all the temperatures in correspondence of the binary composition 2ED : 1DME probably suggests that the corresponding termolecular solvent-cosolvent adduct is the most stable one in these ternary mixtures.

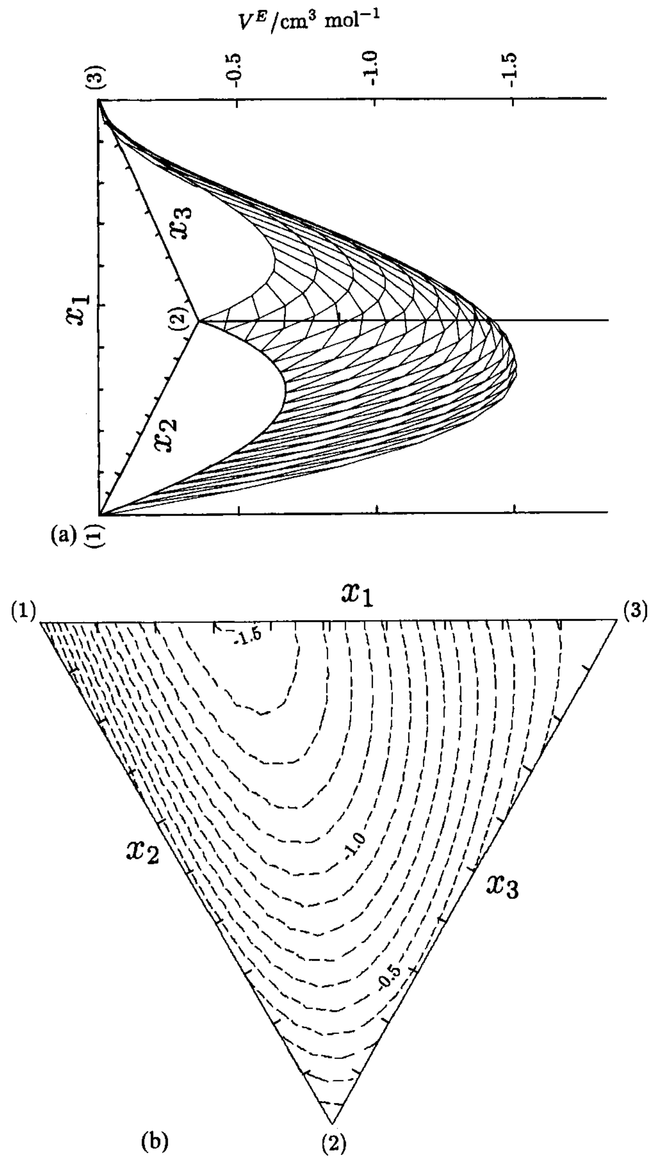

FIGURE 2 (a) Pictorial view of V^E against composition x_i surface for {ED (1) + ME (2) + DME (3)} ternary system at 25°C; (b) isolines at constant V^E.

From a theoretical point of view, an examination of the partial derivatives of the excess properties seems to be of particular interest. The partial molar excess volume $\bar{V}_i^E$ of the i-th species in a multi-component mixture can be determined from the excess molar volume by the equation [20]:

$$\bar{V}_i^{\mathrm{E}} = V^{\mathrm{E}} + (1 - x_i)\frac{\partial V^{\mathrm{E}}}{\partial x_i} \tag{7}$$

from which the partial molar volume $\bar{V}_i$ can be evaluated as follows:

$$\bar{V}_i = V_i^0 + \bar{V}_i^{\mathrm{E}} \tag{8}$$

where V_i^0 is the molar volume of the i-th pure component at each temperature. Considering the relationship (5), and making use of the d_k fitting coefficients reported in Table IV, the quantity $\partial V^{\mathrm{E}}/\partial x_i$ is calculated at each temperature and then, using Eqs. (7) and (8), the $\bar{V}_i^{\mathrm{E}}$ and $\bar{V}_i$ values are determined.

As far as $\bar{V}_i^{\mathrm{E}}$, is concerned, the trends for the three species at 25°C are reported in Figure 3. The greatest evidence for these surfaces $\bar{V}_i^{\mathrm{E}} = \bar{V}_i^{\mathrm{E}}\{x_1, x_2, x_3\}$ consists in the generally negative trends for all the three species. However, $\bar{V}_i^{\mathrm{E}}$ becomes slightly > 0 for ED and ME at infinite dilution in the DME species. This behaviour seems to be perfectly coherent with the above mentioned features of these components: the intramolecular hydrogen bonds, characteristic for the *gauche*

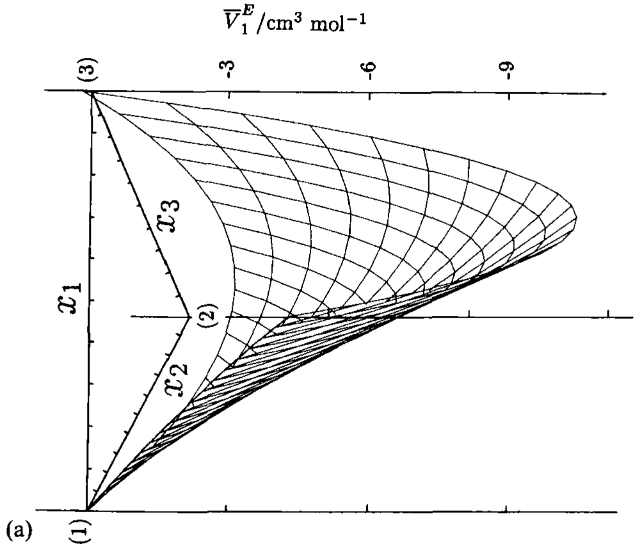

FIGURE 3 Show view of partial excess molar volumes ($\bar{V}_i^{\mathrm{E}}$) surfaces for {ED (1)+ME (2)+DME (3)} ternary system at 25°C: (a) ED (1); (b) ME (2); (c) DME (3).

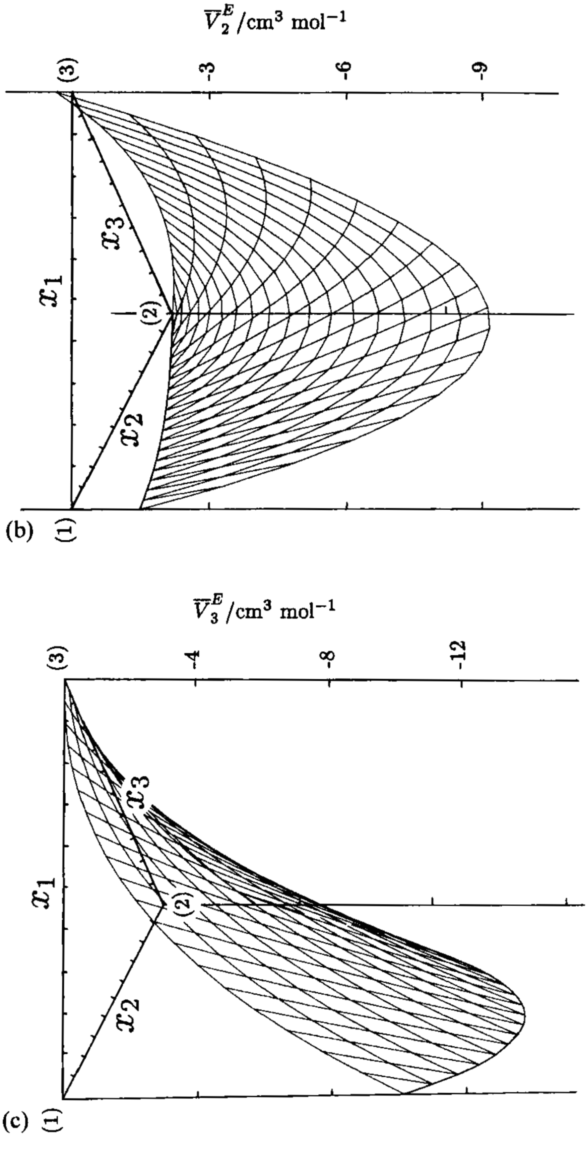

FIGURE 3 (Continued).

conformers, probably break down in dilute region (near pure DME), this fact providing a volumic expansion of the components ED and ME rearranged as *anti* conformers (low density-low entropy). On the contrary, $\bar{V}_3^E$ values are always negative in both the cosolvents and the greatest molecular deformation of DME is detected in ED, while ME compresses DME of about 30% only with respect to ED species.

4. CONCLUSIONS

The theories, models and empirical treatments used here to analyse the experimental density data of {ED (1) + ME (2) + DME (3)} three-component mixtures appear to be sufficiently simple in structure but very effective. In connection with our previous works, we have tried to justify some experimental evidences considering the probable formation of binary adducts, whose presence may be revealed only by means of derived quantities such as V^E. Moreover, the absence of singular points (maxima deviations from ideality) in the ternary domain $\{x_1, x_2, x_3\}$ allows to exclude the formation of three-component adducts at each experimental condition. Further information has been gained by studying the excess partial molar quantities. It seems very likely that by mixing the selected three components, DME acts as the major structure breaker with respect to the other two cosolvents. The consequent change in intermolecular forces on passing from pure to mixed species, has an appreciable effect on the properties of the molecules and, therefore, on the macroscopic behaviour of the system.

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