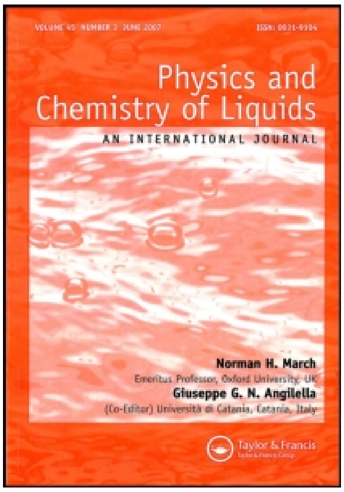

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Density and Volume Properties of the 2-Methoxyethanol 1,2-Dimethoxyethane Water Ternary Solvent System at Various Temperatures

Marina Cocchi[a]; Andrea Marchetti[a]; Laura Pigani[a]; Lorenzo Tassi[a]; Alessandro Ulrici[a]; Giulia Vaccari[a]; Chiara Zanardi[a]
[a] Department of Chemistry, University of Modena, Modena, Italy

To cite this Article Cocchi, Marina , Marchetti, Andrea , Pigani, Laura , Tassi, Lorenzo , Ulrici, Alessandro , Vaccari, Giulia and Zanardi, Chiara(2001) 'Density and Volume Properties of the 2-Methoxyethanol 1,2-Dimethoxyethane Water Ternary Solvent System at Various Temperatures', Physics and Chemistry of Liquids, 39: 2, 151 — 168

To link to this Article: DOI: 10.1080/00319100108030336

URL: http://dx.doi.org/10.1080/00319100108030336

Phys. Chem. Liq., 2001, Vol. 39, pp. 151–168
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

DENSITY AND VOLUME PROPERTIES OF THE 2-METHOXYETHANOL + 1,2-DIMETHOXYETHANE + WATER TERNARY SOLVENT SYSTEM AT VARIOUS TEMPERATURES

MARINA COCCHI, ANDREA MARCHETTI, LAURA PIGANI,
LORENZO TASSI*, ALESSANDRO ULRICI,
GIULIA VACCARI and CHIARA ZANARDI

Department of Chemistry, University of Modena, via G. Campi, 183,
41100 Modena, Italy

(Received 10 October 1999)

Densities (ρ) of the ternary mixtures 2-methoxyethanol + 1,2-dimethoxyethane + water have been measured at 19 temperatures in the range $-263.15 \leq T/K \leq 353.15$. The experimental data were processed by empirical relations accounting for the dependence of ρ on temperature and ternary composition expressed as mole fraction of the components ($0 \leq x_i \leq 1$). All checked equations seem to be suitable for correlation purposes, in order to obtain interpolated values in correspondence to experimental data gaps. Furthermore, the excess molar volume (V^E) has been investigated to make evident the possibility of forming stable solvent-cosolvent adducts. The excess property has been interpreted on the basis of specific intermolecular interactions between the components.

Keywords: Density; Ternary mixtures; 2-methoxyethanol; Water

1. INTRODUCTION

In our efforts to establish some meaningful procedures for analysing and interpreting the temperature and composition dependence of volumetric properties of multicomponent hydroorganic liquids, our

---

*Corresponding author.

interest has focused on examining a number of binary [1–3] and ternary aquo-mixed solvent systems [4].

Though we have been in the past primarily interested in electroanalytical and conductometric studies of electrolytic solutes in binary mixtures of associated (structured) liquids [5, 6], we could more recently realise the necessity of starting with further investigations about thermophysical properties of such mixed solvents, whose knowledge is essential for many applications in different research areas. We paid hence attention to elaboration and application of procedures that can be used to extract, from the dependence on composition of macroscopic properties of mixed solvents, information as about the nature of dynamic and structural characteristics of the homo- and for hetero-molecular aggregation patterns and about the structural organisation within hydro-organic mixtures.

The solvent system chosen for the present study consists of 2-methoxyethanol (ME, component 1) + 1,2-dimethoxyethane (DME, 2) + water (W, 3); densities were accurately measured at 19 different temperatures in the $263.15 \leq T/\mathrm{K} \leq 353.15$ range, employing 12 three-component mixtures covering the whole miscibility $[0 \leq x_i \leq 1 (i = 1, 2, 3)]$. To complete this study, we have re-analysed the whole of the previously published data on {ME(1) + DME(2)} [1], {ME(1) + W(2)} [2] and {DME(1) + W(2)} [3] binary subsystems, which were separately investigated in our previous works.

2. EXPERIMENTAL

2.1. Materials

The solvents ME and DME (water content < 0.05% and < 0.10%, respectively, as found by Karl–Fischer titration) were high-purity grade reagents from Carlo Erba (Milan). ME was purified by passing it through a neutral alumina column. DME was further purified by double fractional distillation over $LiAlH_4$ to eliminate traces of acids and peroxides and to reduce the total amount of water, only retaining the middle fraction (b.p. 356.15 K) for the measurements. The purified solvents were preserved over 0.3 nm type molecular sieves for many days before use. The final purity was checked by gas chromatography

(99.7% mass for both solvents), confirming the absence of other organic components to significant amount. The water used for the preparation of the mixtures was deionized by a Milli-Q-Plus apparatus (Millipore) up to a specific conductance $\leq 0.70\,\mu\mathrm{S}\cdot\mathrm{cm}^{-1}$ at 298.15 K.

2.2. Apparatus and Procedures

All ternary mixtures were prepared, just before use, by weighting on a Mettler PM 480Δ-range balance, operating in a dry box to avoid any contact with the atmospheric moisture. The error in each mole fraction x_i is estimated to be lower than 1.5×10^{-4}.

Apparatus, procedures and experimental details for the density measurements have been described elsewhere [2].

3. RESULTS AND DISCUSSION

Experimental values of ρ as a function of temperature and ternary composition for 12 new {ME(1) + DME(2) + W(3)} mixtures and the three pure species are listed in Table I. Because pure water was used as calibrating fluid for the instrumental equipment, the corresponding densities were taken from the literature [7, 8] and are reported in italic characters, for comparison purposes, in the same table. These data were fitted at each composition to the polynomial expansion

$$\rho(T) = \sum_{0}^{4} a_h T^h \; T/\mathrm{K}. \tag{1}$$

The a_h adjustment coefficients are listed in Table II, along with the standard deviations $\sigma(\rho)/\mathrm{g}\cdot\mathrm{cm}^{-3}$. The recognition ability of Eq. (1) is established on the basis of an average uncertainty $\overline{\Delta\rho\%}$

$$\overline{\Delta\rho\%} = \frac{100}{N}\sum |\rho_{\mathrm{exptl}} - \rho_{\mathrm{calcd}}| \tag{2}$$

where N (283) is the number of experimental points (see Tab. I). $\overline{\Delta\rho\%}$ results equal to $\pm 0.0019\,\mathrm{g}\cdot\mathrm{cm}^{-3}$, and the single $\Delta\rho\%$ values always fall within the range $0.0000 \leq \Delta\rho\% \leq 0.0029$.

TABLE I Ternary composition and experimental density values ρ for {ME(1) + DME(2) + W(3)}

x_1	1	0	0	0.1491	0.8222	0.0228	0.6063	0.5468	0.4517	0.3518	0.3627	0.2111	0.266	0.0706	0.1461
x_2	0	1	0	0.8073	0.0992	0.0851	0.3057	0.1424	0.2986	0.489	0.0998	0.5976	0.4051	0.5359	0.2304
x_3	0	0	1	0.0436	0.0786	0.8921	0.0880	0.3108	0.2497	0.1592	0.5375	0.1913	0.3289	0.3935	0.6235
T/K	$\rho/(g \cdot cm^{-3})$														
263.15	0.990191	0.897853	–	0.925519	0.982753	1.007206	0.960339	0.984651	0.963203	0.941511	1.000083	0.930314	0.951416	0.934751	0.981983
268.15	0.986369	0.892768	–	0.921095	0.978477	1.004503	0.955819	0.980417	0.958713	0.936888	0.996017	0.925450	0.946796	0.930013	0.977709
273.15	0.982354	0.887723	*0.999834*	0.916521	0.974078	1.001608	0.951190	0.976055	0.954105	0.932152	0.991813	0.920477	0.942055	0.925159	0.973298
278.15	0.978147	0.882581	*0.999964*	0.911855	0.969617	0.998583	0.946513	0.971628	0.949441	0.927362	0.987537	0.915453	0.937253	0.920249	0.968813
283.15	0.973732	0.877354	*0.999700*	0.906989	0.965084	0.995419	0.941829	0.967126	0.944709	0.922592	0.983166	0.910351	0.932329	0.915317	0.964227
288.15	0.969266	0.872125	*0.999100*	0.902291	0.960562	0.992193	0.937066	0.962626	0.939992	0.917667	0.978815	0.905301	0.927516	0.910307	0.959669
293.15	0.964843	0.866875	*0.998204*	0.897446	0.955998	0.988869	0.932317	0.958084	0.935248	0.912748	0.974410	0.900252	0.922648	0.905314	0.955048
298.15	0.960290	0.861506	*0.997045*	0.892468	0.951378	0.985403	0.927541	0.953477	0.930429	0.907867	0.969919	0.895057	0.917648	0.900251	0.950342
303.15	0.955745	0.856097	*0.995647*	0.887702	0.946773	0.981873	0.922667	0.948882	0.925656	0.902837	0.965449	0.889955	0.912756	0.895138	0.945666
308.15	0.951088	0.850680	*0.994032*	0.882378	0.942058	0.978205	0.917932	0.944176	0.920747	0.897954	0.960840	0.884714	0.907642	0.890073	0.940826
313.15	0.946292	0.845124	*0.992216*	0.877308	0.937334	0.974435	0.913091	0.939449	0.915820	0.892892	0.956231	0.879439	0.902608	0.884807	0.935996
318.15	0.941621	0.839575	*0.990213*	0.871997	0.932574	0.970571	0.908212	0.934694	0.910919	0.887903	0.951553	0.874246	0.897472	0.879748	0.931094
323.15	0.936878	0.833956	*0.988036*	0.866386	0.927769	0.966584	0.903313	0.929845	0.905830	0.882889	0.946805	0.868752	0.892252	0.874553	0.926122
328.15	0.932133	0.828247	*0.985695*	0.861321	0.922921	0.962498	0.898375	0.925026	0.900939	0.877709	0.942051	0.863647	0.887134	0.869270	0.921142
333.15	0.927387	0.822468	*0.983199*	0.855802	0.917972	0.958278	0.893529	0.920136	0.896038	0.872734	0.937157	0.858593	0.881771	0.864201	0.916056
338.15	0.922714	0.816676	*0.980555*	0.850380	0.913130	0.954016	0.888450	0.915203	0.890836	0.867400	0.932366	0.852947	0.876656	0.858668	0.911011
343.15	0.917811	0.810830	*0.977770*	0.844971	0.908245	0.949664	0.883403	0.910265	0.885716	0.862100	0.927527	0.847478	0.871491	0.853210	0.905942
348.15	0.913087	0.804947	*0.974899*	0.839281	0.903317	0.945250	0.878550	0.905343	0.880725	0.857086	0.922617	0.842254	0.866150	0.848052	0.900784
353.15	0.908144	0.799064	*0.971798*	0.833626	0.898351	0.940708	0.873560	0.900347	0.875617	0.851879	0.917667	0.836861	0.860838	0.842690	0.895598

TABLE II Compositions x_i, coefficients a_h and standard deviations $\sigma(\rho)$ of Eq. (1) for {ME(1) + DME(2) + W(3)}

			$10 \cdot a_0$	$10^4 \cdot a_1$	$10^6 \cdot a_2$	$10^9 \cdot a_3$	$10^{12} \cdot a_4$	$10^5 \cdot \sigma(\rho)$
x_1	x_2	x_3	$g \cdot cm^{-3}$	$g \cdot cm^{-3} \cdot K^{-1}$	$g \cdot cm^{-3} \cdot K^{-2}$	$g \cdot cm^{-3} \cdot K^{-3}$	$g \cdot cm^{-3} \cdot K^{-4}$	$g \cdot cm^{-3}$
1	0	0	−6.61748	223.33	−106.98	219.05	−168.64	5.5
0	1	0	16.1327	−73.493	32.837	−73.624	59.698	2.2
0	0	1	−17.1382	313.88	−135.14	259.26	−190.53	1.3
0.1491	0.8073	0.0436	14.9236	−60.647	29.015	−69.275	58.864	1.1
0.8222	0.0992	0.0786	12.9798	−24.952	10.205	−26.128	23.118	3.3
0.0228	0.0851	0.8921	11.0670	−9.7839	6.5279	−21.185	19.187	2.7
0.6063	0.3057	0.0880	10.4537	8.0882	−6.9584	12.385	−8.6875	5.1
0.5468	0.1424	0.3108	12.2691	−15.872	5.9084	−16.934	15.619	2.6
0.4517	0.2986	0.2497	11.2057	−2.6635	−1.1680	−1.0223	2.5583	5.5
0.3518	0.4890	0.1592	9.01281	24.777	−15.169	30.242	−23.442	7.3
0.3627	0.0998	0.5375	13.1325	−26.752	11.734	−30.115	26.493	3.5
0.2111	0.5976	0.1913	9.90016	12.529	−9.2226	16.861	−12.090	1.0
0.2660	0.4051	0.3289	14.3597	−45.861	20.300	−48.428	41.513	5.9
0.0706	0.5359	0.3935	8.66286	28.731	−17.080	34.149	−26.497	8.0
0.1461	0.2304	0.6235	12.4564	−19.200	7.7929	−21.427	19.277	3.2

The dependence of isothermal densities on ternary composition has been fitted by the relationship

$$\rho(x_1, x_2) = \sum_{K=0}^{4}\sum_{J=0}^{4} b_{KJ} x_1^K x_2^J. \tag{3}$$

b_{KJ} empirical coefficients are summarised in Table III, together with the standard deviation $\sigma(\rho)$ at each fitting temperature. Equation (3) has been applied for the whole ternary solvent system, taking into account also the previously published data on the {ME + DME} [1], {ME + W} [2] and {DME + W} [3] binary systems.

Equation (3) recalculates the initial ρ values within $\overline{\Delta\rho\%} = \pm 0.0124\ \mathrm{g \cdot cm^{-3}}$, and the same uncertainty level is reasonably supposed to affect also the interpolated data, in the correspondence of the experimental data gaps. Obviously, the use of these model equations must be avoided in the correspondence of the experimental data gaps in the Water-rich region, where phase separation occurs, in order to avoid extrapolated values without physical meaning.

3.1. Excess Molar Volume

When dealing with completely miscible multicomponent systems, it seems very useful to examine how their excess properties depend on the composition of the liquid mixtures. Therefore, the densities were converted into the excess molar volumes ($V^E/\mathrm{cm^3\,mol^{-1}}$) by applying the relationship:

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

where M_i are the molar masses ($M_1 = 76.096$; $M_2 = 90.120$; $M_3 = 18.015\ \mathrm{g \cdot mol^{-1}}$), and ρ_i are the densities of the pure species at the different temperatures. The calculations performed with Eq. (4) provide for V^E values which results, in general, negative under experimental conditions.

TABLE III(a) Coefficients b_{KJ} and standard deviations σ of Eq. (3) for {ME(1) + DME(2) + W(3)} at various temperatures T

T/K		263.15	268.15	273.15	278.15	283.15
KJ	*Variable*	$b_{KJ}/(g \cdot cm^{-3})$				
00		0.996465	0.997814	0.998542	0.998739	0.998483
01	x_2	$1.46561 \cdot 10^{-1}$	$1.01486 \cdot 10^{-1}$	$6.33260 \cdot 10^{-2}$	$3.07970 \cdot 10^{-2}$	$2.76900 \cdot 10^{-3}$
02	x_2^2	$-8.87675 \cdot 10^{-1}$	$-7.57139 \cdot 10^{-1}$	$-6.53058 \cdot 10^{-1}$	$-5.70703 \cdot 10^{-1}$	$-5.05862 \cdot 10^{-1}$
03	x_2^3	$9.97562 \cdot 10^{-1}$	$8.29758 \cdot 10^{-1}$	$6.98972 \cdot 10^{-1}$	$5.99153 \cdot 10^{-1}$	$5.24843 \cdot 10^{-1}$
04	x_2^4	$-3.55059 \cdot 10^{-1}$	$-2.79133 \cdot 10^{-1}$	$-2.20096 \cdot 10^{-1}$	$-1.75435 \cdot 10^{-1}$	$-1.42862 \cdot 10^{-1}$
10	x_1	$3.59444 \cdot 10^{-1}$	$3.12650 \cdot 10^{-1}$	$2.74040 \cdot 10^{-1}$	$2.41950 \cdot 10^{-1}$	$2.14985 \cdot 10^{-1}$
11	x_1x_2	$-8.09822 \cdot 10^{-1}$	$-3.77610 \cdot 10^{-1}$	$-3.87870 \cdot 10^{-2}$	$2.26607 \cdot 10^{-1}$	$4.35694 \cdot 10^{-1}$
12	$x_1x_2^2$	−13.5336	−15.2773	−16.6802	−17.8076	−18.7163
13	$x_1x_2^3$	36.4910	39.4457	41.9633	44.1140	45.9599
14	$x_1x_2^4$	−22.6732	−24.2811	−25.7112	−26.9853	−28.1223
20	x_1^2	−1.20614	−1.06202	$-9.50270 \cdot 10^{-1}$	$-8.63665 \cdot 10^{-1}$	$-7.96247 \cdot 10^{-1}$
21	$x_1^2x_2$	−4.32395	−5.82244	−6.97199	−7.85132	−8.52847
22	$x_1^2x_2^2$	96.4868	103.879	110.075	115.291	119.724
23	$x_1^2x_2^3$	−206.585	−220.772	−233.669	−245.413	−256.133
24	$x_1^2x_2^4$	110.759	118.668	126.204	133.339	140.046
30	x_1^3	1.42978	1.24493	1.10801	1.00781	$9.35179 \cdot 10^{-1}$
31	$x_1^3x_2$	11.1748	13.3551	15.0562	16.3876	17.4438
32	$x_1^3x_2^2$	−161.849	−174.375	−185.467	−195.333	−204.162
33	$x_1^3x_2^3$	292.317	317.653	342.186	365.766	388.240
34	$x_1^3x_2^4$	−123.476	−136.216	−149.290	−162.361	−175.104
40	x_1^4	$-5.89309 \cdot 10^{-1}$	$-5.07000 \cdot 10^{-1}$	$-4.47990 \cdot 10^{-1}$	$-4.06693 \cdot 10^{-1}$	$-3.78575 \cdot 10^{-1}$
41	$x_1^4x_2$	−6.50625	−7.57954	−8.44202	−9.14082	−9.71697
42	$x_1^4x_2^2$	81.0113	87.6385	93.7686	99.4305	104.652
43	$x_1^4x_2^3$	−119.524	−131.855	−144.425	−156.952	−169.164
44	$x_1^4x_2^4$	40.6122	43.4367	46.7700	50.3042	53.750
$\sigma(\rho)/(g \cdot cm^{-3})$		$1.9 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$

TABLE III(b) Coefficients b_{KJ} and standard deviations σ of Eq. (3) for {ME(1) + DME(2) + W(3)} at various temperatures T

T/K		288.15	293.15	298.15	303.15	308.15
KJ	*Variable*			$b_{KJ}/(g \cdot cm^{-3})$		
00		0.997845	0.996886	0.995657	0.994200	0.992549
01	x_2	$-2.17900 \cdot 10^{-2}$	$-4.37280 \cdot 10^{-2}$	$-6.37830 \cdot 10^{-2}$	$-8.25310 \cdot 10^{-2}$	$-1.00469 \cdot 10^{-1}$
02	x_2^2	$-4.54622 \cdot 10^{-1}$	$-4.13742 \cdot 10^{-1}$	$-3.80253 \cdot 10^{-1}$	$-3.51883 \cdot 10^{-1}$	$-3.26406 \cdot 10^{-1}$
03	x_2^3	$4.70868 \cdot 10^{-1}$	$4.32876 \cdot 10^{-1}$	$4.06716 \cdot 10^{-1}$	$3.89217 \cdot 10^{-1}$	$3.76930 \cdot 10^{-1}$
04	x_2^4	$-1.20157 \cdot 10^{-1}$	$-1.05427 \cdot 10^{-1}$	$-9.68090 \cdot 10^{-2}$	$-9.28720 \cdot 10^{-2}$	$-9.19320 \cdot 10^{-2}$
10	x_1	$1.91868 \cdot 10^{-1}$	$1.71530 \cdot 10^{-1}$	$1.53103 \cdot 10^{-1}$	$1.35883 \cdot 10^{-1}$	$1.19336 \cdot 10^{-1}$
11	$x_1 x_2$	$6.04703 \cdot 10^{-1}$	$7.45290 \cdot 10^{-1}$	$8.68948 \cdot 10^{-1}$	$9.83134 \cdot 10^{-1}$	1.09492
12	$x_1 x_2^2$	−19.4619	−20.0814	−20.6163	−21.0913	−21.5330
13	$x_1 x_2^3$	47.5647	48.9659	50.2140	51.3362	52.3663
14	$x_1 x_2^4$	−29.1442	−30.0614	−30.8923	−31.6462	−32.3366
20	x_1^2	$-7.42527 \cdot 10^{-1}$	$-6.97966 \cdot 10^{-1}$	$-6.58915 \cdot 10^{-1}$	$-6.22462 \cdot 10^{-1}$	$-5.86449 \cdot 10^{-1}$
21	$x_1^2 x_2$	−9.06644	−9.510641	−9.90531	−10.2782	−10.6558
22	$x_1^2 x_2^2$	123.557	126.910	129.923	132.675	135.250
23	$x_1^2 x_2^3$	−265.964	−274.967	−283.265	−290.910	−297.977
24	$x_1^2 x_2^4$	146.322	152.138	157.507	162.430	166.921
30	x_1^3	$8.81668 \cdot 10^{-1}$	$8.40316 \cdot 10^{-1}$	$8.05583 \cdot 10^{-1}$	$7.73067 \cdot 10^{-1}$	$7.39540 \cdot 10^{-1}$
31	$x_1^3 x_2$	18.3118	19.0545	19.7324	20.3842	21.0457
32	$x_1^3 x_2^2$	−212.137	−219.370	−226.009	−232.135	−237.834
33	$x_1^3 x_2^3$	409.537	429.530	448.207	465.552	481.545
34	$x_1^3 x_2^4$	−187.298	−198.735	−209.277	−218.864	−227.439
40	x_1^4	$-3.59451 \cdot 10^{-1}$	$-3.45870 \cdot 10^{-1}$	$-3.35103 \cdot 10^{-1}$	$-3.24984 \cdot 10^{-1}$	$-3.13931 \cdot 10^{-1}$
41	$x_1^4 x_2$	−10.2079	−10.6410	−11.0423	−11.4293	−11.8175
42	$x_1^4 x_2^2$	109.467	113.890	117.956	121.688	125.107
43	$x_1^4 x_2^3$	−180.874	−191.906	−202.140	−211.529	−220.010
44	$x_1^4 x_2^4$	56.9050	59.6078	61.7126	63.1858	63.9977
$\sigma(\rho)/(g \cdot cm^{-3})$		$2.3 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$

TABLE III(c) Coefficients b_{KJ} and standard deviations σ of Eq. (3) for {ME(1) + DME(2) + W(3)} at various temperatures T

T/K		313.15	318.15	323.15	328.15	333.15
KJ	*Variable*			$b_{KJ}/(g\cdot cm^{-3})$		
00		0.990727	0.988750	0.986622	0.984341	0.981892
01	x_2	$-1.17876\cdot10^{-1}$	$-1.34919\cdot10^{-1}$	$-1.51659\cdot10^{-1}$	$-1.68010\cdot10^{-1}$	$-1.83700\cdot10^{-1}$
02	x_2^2	$-3.02506\cdot10^{-1}$	$-2.79257\cdot10^{-1}$	$-2.55939\cdot10^{-1}$	$-2.32340\cdot10^{-1}$	$-2.09090\cdot10^{-1}$
03	x_2^3	$3.67719\cdot10^{-1}$	$3.59892\cdot10^{-1}$	$3.51777\cdot10^{-1}$	$3.42320\cdot10^{-1}$	$3.31630\cdot10^{-1}$
04	x_2^4	$-9.2911\cdot10^{-2}$	$-9.4893\cdot10^{-2}$	$-9.68670\cdot10^{-2}$	$-9.80620\cdot10^{-2}$	$-9.82370\cdot10^{-2}$
10	x_1	$1.03165\cdot10^{-1}$	$8.7214\cdot10^{-2}$	$7.15250\cdot10^{-2}$	$5.63300\cdot10^{-2}$	$4.20290\cdot10^{-2}$
11	x_1x_2	1.20673	1.32007	1.43469	1.54700	1.65140
12	$x_1x_2^2$	−21.9503	−22.3523	−22.7418	−23.1121	−23.4484
13	$x_1x_2^3$	53.3161	54.2024	55.0337	55.8115	56.5263
14	$x_1x_2^4$	−32.9687	−33.5526	−34.0939	−34.5992	−35.0702
20	x_1^2	$-5.49774\cdot10^{-1}$	$-5.11948\cdot10^{-1}$	$-4.73394\cdot10^{-1}$	$-4.35340\cdot10^{-1}$	$-3.99850\cdot10^{-1}$
21	$x_1^2x_2$	−11.0456	−11.4531	−11.8733	−12.2912	−12.6813
22	$x_1^2x_2^2$	137.675	139.997	142.204	144.289	146.197
23	$x_1^2x_2^3$	−304.503	−310.588	−316.230	−321.506	−326.422
24	$x_1^2x_2^4$	171.005	174.751	178.176	181.368	184.395
30	x_1^3	$7.03451\cdot10^{-1}$	$6.64179\cdot10^{-1}$	$6.22556\cdot10^{-1}$	$5.80690\cdot10^{-1}$	$5.41969\cdot10^{-1}$
31	$x_1^3x_2$	21.7284	22.4413	23.1754	23.9120	24.6149
32	$x_1^3x_2^2$	−243.160	−248.201	−252.942	−257.435	−261.652
33	$x_1^3x_2^3$	496.289	509.969	522.636	534.569	545.982
34	$x_1^3x_2^4$	−235.075	−241.921	−248.085	−253.832	−259.467
40	x_1^4	$-3.01210\cdot10^{-1}$	$-2.86542\cdot10^{-1}$	$-2.70379\cdot10^{-1}$	$-2.53820\cdot10^{-1}$	$-2.38570\cdot10^{-1}$
41	$x_1^4x_2$	−12.2132	−12.6216	−13.0391	−13.4595	−13.8684
42	$x_1^4x_2^2$	128.248	131.166	133.868	136.415	138.838
43	$x_1^4x_2^3$	−227.646	−234.555	−240.827	−246.675	−252.346
44	$x_1^4x_2^4$	64.1864	63.8603	63.1553	62.2556	61.4395
$\sigma(\rho)/(g\cdot cm^{-3})$		$2.9\cdot10^{-4}$	$3.0\cdot10^{-4}$	$3.1\cdot10^{-4}$	$3.2\cdot10^{-4}$	$3.3\cdot10^{-4}$

TABLE III(d) Coefficients b_{KJ} and standard deviations σ of Eq. (3) for {ME(1) + DME(2) + W(3)} at various temperatures T

T/K		338.15	343.15	348.15	353.15
KJ	*Variable*		$b_{KJ}/(g \cdot cm^{-3})$		
00		0.979255	0.976397	0.973277	0.969847
01	x_2	$-1.98392 \cdot 10^{-1}$	$-2.11534 \cdot 10^{-1}$	$-2.22489 \cdot 10^{-1}$	$-2.30474 \cdot 10^{-1}$
02	x_2^2	$-1.86775 \cdot 10^{-1}$	$-1.66875 \cdot 10^{-1}$	$-1.51026 \cdot 10^{-1}$	$-1.41439 \cdot 10^{-1}$
03	x_2^3	$3.19477 \cdot 10^{-1}$	$3.06928 \cdot 10^{-1}$	$2.94951 \cdot 10^{-1}$	$2.85288 \cdot 10^{-1}$
04	x_2^4	$-9.68710 \cdot 10^{-2}$	$-9.40620 \cdot 10^{-2}$	$-8.97370 \cdot 10^{-2}$	$-8.41510 \cdot 10^{-2}$
10	x_1	$2.92130 \cdot 10^{-2}$	$1.86960 \cdot 10^{-2}$	$1.14240 \cdot 10^{-2}$	$8.53600 \cdot 10^{-3}$
11	x_1x_2	1.73954	1.80226	1.82582	1.79642
12	$x_1x_2^2$	−23.7239	−23.9203	−23.9929	−23.9042
13	$x_1x_2^3$	57.1506	57.6844	58.0799	58.3106
14	$x_1x_2^4$	−35.4999	−35.9003	−36.2584	−36.5748
20	x_1^2	$-3.69715 \cdot 10^{-1}$	$-3.48819 \cdot 10^{-1}$	$-3.41545 \cdot 10^{-1}$	$-3.53243 \cdot 10^{-1}$
21	$x_1^2x_2$	−13.0061	−13.2295	−13.2918	−13.1358
22	$x_1^2x_2^2$	147.822	149.133	149.956	150.175
23	$x_1^2x_2^3$	−330.912	−335.118	−338.916	−342.339
24	$x_1^2x_2^4$	187.287	190.211	193.205	196.401
30	x_1^3	$5.10907 \cdot 10^{-1}$	$4.93806 \cdot 10^{-1}$	$4.97640 \cdot 10^{-1}$	$5.31019 \cdot 10^{-1}$
31	$x_1^3x_2$	25.2322	25.7166	25.9841	25.9563
32	$x_1^3x_2^2$	−265.504	−269.061	−272.155	−274.741
33	$x_1^3x_2^3$	557.007	568.189	579.670	591.915
34	$x_1^3x_2^4$	−265.267	−271.740	−279.280	−288.433
40	x_1^4	$-2.26989 \cdot 10^{-1}$	$-2.22203 \cdot 10^{-1}$	$-2.27747 \cdot 10^{-1}$	$-2.47984 \cdot 10^{-1}$
41	$x_1^4x_2$	−14.2445	−14.5702	−14.8105	−14.9334
42	$x_1^4x_2^2$	141.144	143.435	145.704	148.011
43	$x_1^4x_2^3$	−258.060	−264.254	−271.233	−279.449
44	$x_1^4x_2^4$	60.9881	61.2498	62.6568	65.6138
$\sigma(\rho)/(g \cdot cm^{-3})$		$3.4 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	$3.7 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$

The obtained V^E data were smoothed by a least-squares methods by using the equation:

$$V^E = c_1x_1x_2 + c_2x_2x_3 + c_3x_1x_3 + c_4x_1x_2(x_2 - x_1) + c_5x_2x_3(x_3 - x_2) + c_6x_1x_3(x_1 - x_3) + c_7x_1x_2x_3 \quad (5)$$

which has been applied to each isothermal set of 42 values, *i.e.*, by also taking into account the data previously published [1–3] (3 pure species, 27 binaries and 12 ternaries).

An equation like (5) has been used by Katz *et al.* [7]. It should be noticed that Eq. (5) formally derives from the Redlich-Kister equation, generally applied for binary mixtures:

$$Y^E = x_1x_2\sum_0^K c_K(x_2 - x_1)^K \quad (6)$$

with the polynomial degree truncated for $K = 1$. This procedure permits the evaluation of the V^E values for a ternary solvent system mainly as a sum of contributions due to the three binary subsystems:

$$V^E_{123} = V^E_{12} + V^E_{23} + V^E_{13} + \delta_{123} \quad (5.1)$$

the overall ternary mixture effects (δ_{123}) being explicitly accounted for be c_7 term of Eq. (5) alone. The fitting coefficients of Eq. (5) are given in Table IV, together with the relevant standard deviations $\sigma(V^E)/\text{cm}^3\,\text{mol}^{-1}$ at each investigated temperature in the $263.15 \leq T/\text{K} \leq 353.15$ range.

Equation (5) recalculates the V^E values with an average uncertainty $\overline{\Delta V^E} = \pm 0.014\ \text{cm}^3\,\text{mol}^{-1}$ (all ΔV^E values in the range 0.000 to 0.022) over all the 714 input data related the whole set of ternary and binary systems together with the pure solvent [1–3]. The trend of Eq. (5) is shown in Figure 1, where the V^E quantity is plotted in the ternary composition domain $\{x_1, x_2, x_3\}$ at 298.15 K.

First of all it should be noticed that the trend of the $V^E = V^E(x_i)$ plots is only slightly sensitive to temperature, so that the plots in the figure are well representative of the situation in any experimental conditions.

TABLE IV Coefficients c_K and standard deviations σ of Eq. (5) of {ME(1) + DME(2) + W(3)} at various temperatures T

T/K	$\frac{c_1}{cm^3 \cdot mol^{-1}}$	$\frac{c_2}{cm^3 \cdot mol^{-1}}$	$\frac{c_3}{cm^3 \cdot mol^{-1}}$	$\frac{c_4}{cm^3 \cdot mol^{-1}}$	$\frac{c_5}{cm^3 \cdot mol^{-1}}$	$\frac{c_6}{cm^3 \cdot mol^{-1}}$	$\frac{c_7}{cm^3 \cdot mol^{-1}}$	$\frac{10^2 \cdot \sigma(V^E)}{cm^3 \cdot mol^{-1}}$
273.15	−2.2957	−8.8394	−4.6172	−0.8715	−5.0622	1.7860	18.7996	2.4
278.15	−2.1904	−8.7529	−4.4881	−0.9610	−5.1092	1.6540	17.9980	2.5
283.15	−2.0736	−8.6687	−4.3878	−1.0142	−5.1771	1.5259	17.0937	2.6
288.15	−1.9481	−8.5891	−4.3116	−1.0388	−5.2559	1.4055	16.1002	2.7
293.15	−1.8154	−8.5169	−4.2526	−1.0494	−5.3390	1.2879	15.0298	2.9
298.15	−1.6768	−8.4531	−4.2067	−1.0551	−5.4278	1.1785	13.9010	3.0
303.15	−1.5350	−8.4014	−4.1698	−1.0595	−5.5057	1.0737	12.7355	3.1
308.15	−1.3908	−8.3615	−4.1394	−1.0738	−5.5780	0.9754	11.5212	3.3
313.15	−1.2442	−8.3354	−4.1116	−1.0944	−5.6353	0.8789	10.2733	3.4
318.15	−1.0969	−8.3233	−4.0853	−1.1330	−5.6850	0.7839	8.9977	3.5
323.15	−0.9478	−8.3256	−4.0578	−1.1907	−5.7233	0.6926	7.6936	3.6
328.15	−0.7952	−8.3418	−4.0299	−1.2677	−5.7568	0.6041	6.3445	3.8
333.15	−0.6389	−8.3727	−4.0043	−1.3638	−5.7847	0.5090	4.9662	3.9
338.15	−0.4755	−8.4182	−3.9763	−1.4730	−5.8174	0.4186	3.5134	4.0
343.15	−0.3031	−8.4715	−3.9535	−1.5939	−5.8607	0.3227	1.9795	4.2
348.15	−0.1189	−8.5372	−3.9385	−1.7203	−5.9224	0.2170	0.3663	4.4
353.15	−0.0835	−8.6080	−3.9309	−1.8381	−6.0149	0.1102	−1.4008	4.5

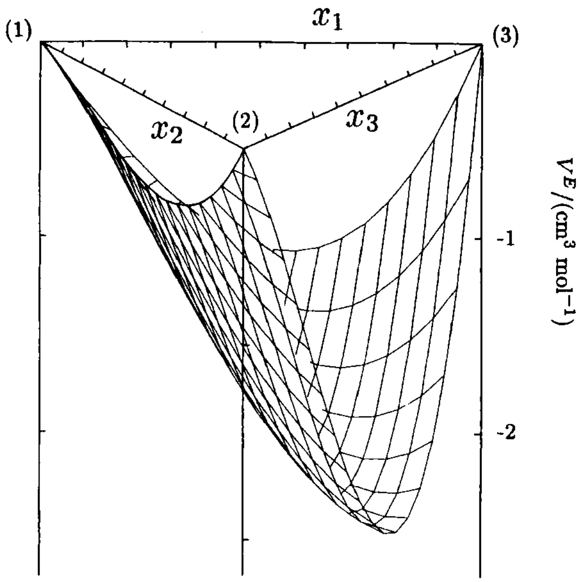

FIGURE 1a Pictorial view of the V^E – composition surface for {ME(1) + DME(2) + W(3)} ternary solvent system at 298.15 K.

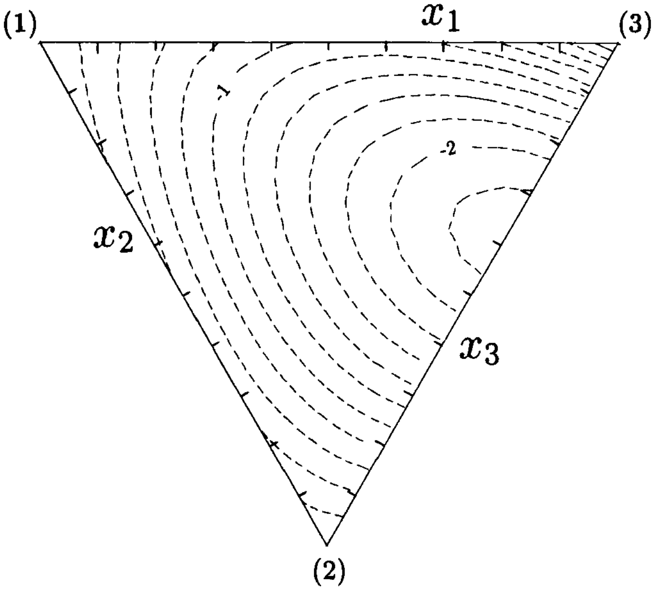

FIGURE 1b Computer generated contour diagram showing lines of constant V^E on a liquid mole fraction grid {ME(1) + DME(2) + W(3)} at 298.15 K.

In the literature, negative excess molar volumes have been attributed to the presence of attractive specific intermolecular interactions between different units, such as hydrogen bonding and dipolar network of any kind (structure making effects). In addition to this effect, on according to Horta *et al.* [10], the V^E quantity can be interpreted in terms of different effects such as: (i) dissociation of self-associated hydroxilated pure species (structured breaking effects); (ii) increase in dipolar hetero association of the components when mixing species of relatively high dipole moment ($\mu_{\mathrm{ME}} = 2.36\,\mathrm{D}$; $\mu_{\mathrm{DME}} = 1.17\,\mathrm{D}$; $\mu_{\mathrm{W}} = 1.85\,\mathrm{D}$); (iii) differences in molecular size and shape (geometrical effects) of the components, which favour the reciprocal interstitial accommodation of the species. Generally, the two factors (i) and (ii) should contribute to volume expansion ($V^E > 0$), while structure making effects and factor (iii) may lead to a volume contraction ($V^E < 0$).

For this ternary solvent system, the obtained values of the excess molar volumes indicate that the factors responsible for contraction in the mixing process prevail in all the experimental conditions. Turning now to Figure 1, a careful examination of these plots does not provide for any evidence of stable three-component adducts in this ternary solvent system, singular points (related to the maxima deviations) other than those observed along the binary axis being absent in the graphs. For comparison purposes, Figure 2 shows the plots of V^E against the binary composition of {ME(1) + DME(2)}, {ME(1) + W(2)} and {DME(1) + W(2)} subsystems, respectively, at 298.15 K. In the present case, the V^E *vs.* x_i curves exhibit a well defined minimum, which becomes deeper and deeper along the sequence (ME + DME) < (ME + W) < (DME + W). Furthermore, the minimum seems to be centred at $x_i \cong 0.35$ for ME + DME (2ME : 1DME), and at $x_i \cong 0.65$ for the two aquomixed solvent systems, indicating the probable existence of stable complexes [11, 12] at stoichiometric ratios 1ME : 2W and 1DME : 2W, respectively. Therefore, in cases similar to this one, we can assert that no particularly stable three-component aggregate is present in these mixtures. However, the presence of the upper limit of the V^E function suggests that the most stable solvent-cosolvent adduct is represented by the 1DME :2W species, observed under all experimental conditions.

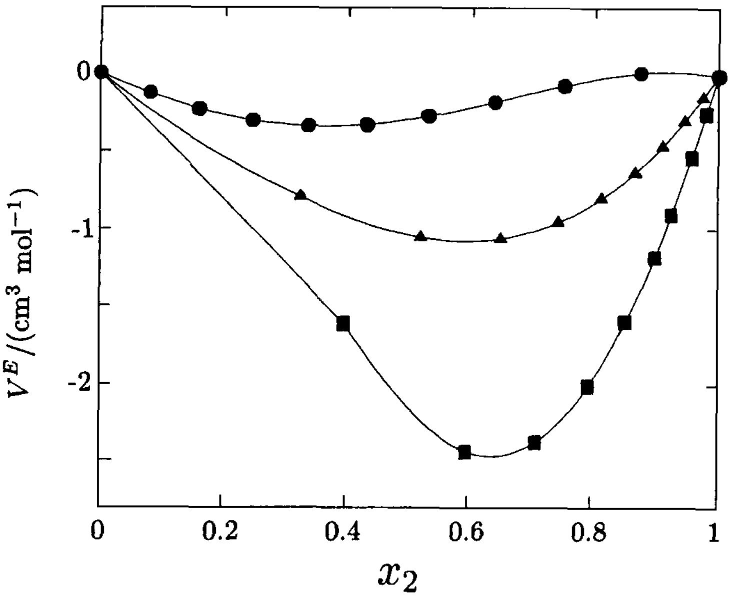

FIGURE 2 Plots of the excess property V^E with changing mole fraction x_i of binary subsystems at 298.15 K: ●{ME(1) + DME(2)}; ▲{ME(1) + W(2)}; ■{DME(1) + W(2)}.

A very intriguing strategy to gain further insight about the behaviour of various mixtures involves the generation of plots of partial excess molar volumes of the relevant components, $\overline{V_i^E}$. These quantities have been calculated by applying the relationship [13]:

$$\overline{V_i^E} = V^E + (1 - x_i)\frac{\partial V^E}{\partial x_i} \tag{7}$$

from which:

$$\overline{V_i} = V_i^0 + \overline{V_i^E} \tag{8}$$

where V_i^0 is the molar volume of the pure i-th component at each temperature. From the Eq. (5) and using the coefficients in Table IV at 298.15 K for the ternary system, $((\partial V^E)/(\partial x_i))$ is calculated and by using the Eq. (7) the partial molar volumes are determined. Figure 3 shows these trends for the three components. The values of $\overline{V_i^E}$ are always negative at the chosen temperature. However, as it is evident

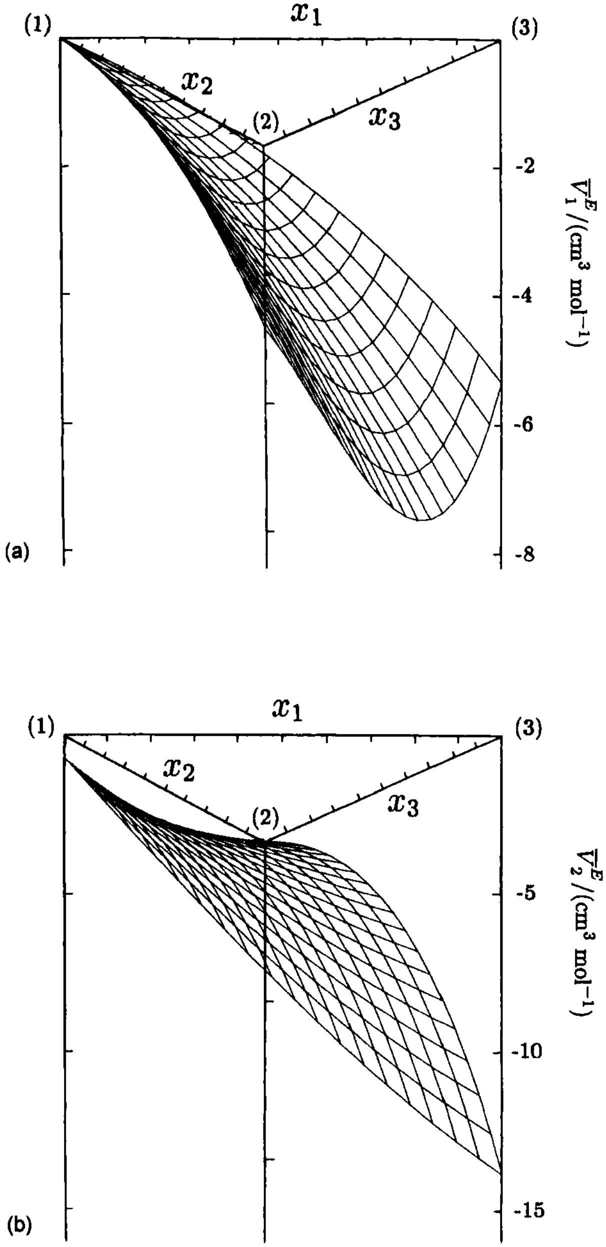

FIGURE 3 Partial excess molar volumes ($\overline{V_i^E}$) for {ME(1) + DME(2) + W(3)} ternary mixtures at 298.15 K: (a) ME(1); (b) DME(2); (c) W(3).

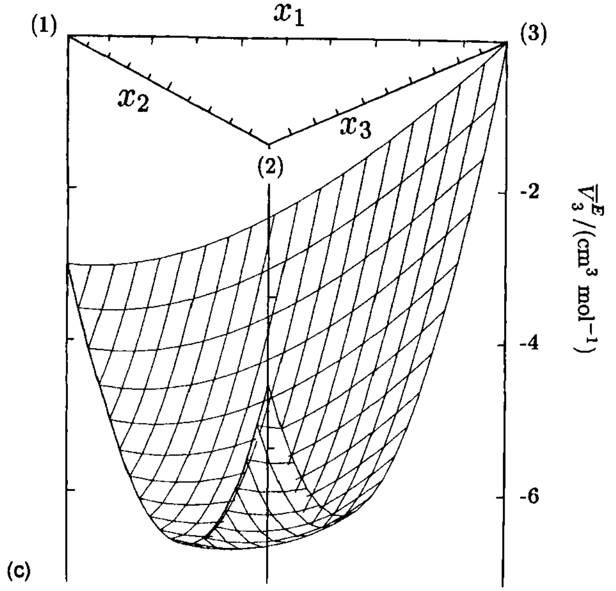

FIGURE 3 (Continued).

from Figure 3(b), the greatest values have been detected for DME component, while increasingly negative $\overline{V_i^E}$ values are found for the cosolvents, according to the sequence W < ME < DME.

Acknowledgments

The authors express their thanks to Prof. R. Seeber for many helpful discussions during the progress of this work. The MURST of Italy is gratefully acknowledged for the financial support.

References

[1] Corradini, F., Marchetti, A., Tagliazucchi, M., Tassi, L. and Tosi, G. (1994). *Aust. J. Chem.*, **47**, 415.
[2] Corradini, F., Franchini, G. C., Marcheselli, L., Tassi, L. and Tosi, G. (1992). *Aust. J. Chem.*, **45**, 1109.
[3] Marchetti, A., Tassi, L. and Ulrici, A. (1997). *Bull. Chem. Soc. Jpn.*, **70**, 987.
[4] Marchetti, A., Martignani, A. and Tassi, L. (1998). *J. Chem. Thermodyn.*, **30**, 653.
[5] Marchetti, A., Picchioni, E., Tassi, L. and Tosi, G. (1989). *Anal. Chem.*, **61**, 1971.
[6] Franchini, G. C., Marchetti, A., Tassi, L. and Tosi, G. (1990). *Anal. Chem.*, **62**, 1004.

[7] Weast, R. C., *Handbook of Chemistry and Physics*: 66th edition. Chemical Rubber Co.: Cleveland, OH, 1985.
[8] Paar Digital Densymeter, Instruction Manual, Graz, Austria, 1984.
[9] Pedrosa, G. C., Salas, J. A. and Katz, M. (1990). *Thermochim. Acta*, **160**, 243.
[10] Prolongo, M. G., Masegosa, R. M., Hernandez Fuentes, I. and Horta, A. (1984). *J. Phys. Chem.*, **88**, 2163.
[11] Fort, R. J. and Moore, W. R. (1966). *Trans. Faraday Soc.*, **62**, 1112.
[12] Fialkov, Yu. Ya. (1963). *Zh. Fiz. Khim.*, **37**, 1051.
[13] Koga, Y. and Westh, P. (1996). *Bull. Chem. Soc. Jpn.*, **69**, 1505.