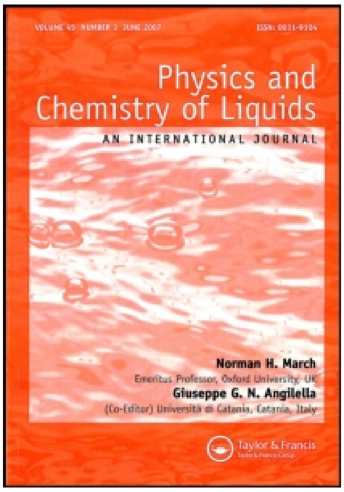

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REFRACTIVE PROPERTIES OF BINARY MIXTURES CONTAINING *N*, *N*-DIMETHYLFORMAMIDE + 2-METHOXYETHANOL OR 1,2-DIMETHOXYETHANE

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Refractive index (n) and related properties such as molar refraction (R) have been investigated for DMF + ME and DMF + DME binary mixtures over the entire composition range, at 15 different temperatures in the range $0 \leq t/°\mathrm{C} \leq 70$. Some relationships have been applied to study the dependence of the measured and derived quantities by temperature and composition. Furthermore, the excess functions n^E, R^E and the excess Kirkwood correlation parameters Δg have been examined, in order to identify the presence of solvent–cosolvent adducts in these binary mixtures. The results obtained have been interpreted on the basis of specific intermolecular interactions between different species.

Keywords: Refractive index; Binary mixtures; *N*, *N*-dimethylformamide; 2-methoxyethanol; 1,2-dimethoxyethane

1. INTRODUCTION

For several decades, some fundamental relationships such as Gladstone–Dale [1] and Lorenz–Lorentz [2] equations have been

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*Corresponding author. Tel.: +39-059-37-8111, Fax: +39-059-37-3543, e-mail: tassi.lorenzo@unimo.it the basis for the most widely used methods to determine and analyse the refractive properties of mixed binary liquid systems. They present the advantage of being simple and rapid estimation methods, based on the knowledge of the properties of the pure species and of the composition of the binary mixtures, and do not require any complex experimental measurements or calculations.

They are very useful and easy methods when rough quantitative determinations are sought. On the other hand, they present inherent drawbacks, which not only limit their usefulness when very precise data are looked for, but make them also unsatisfactory when trying to determine the interpolated values within experimental data gaps, to a precision level close to the experimental uncertainty.

Actually, it has been recognised that the refractive indices of liquids and relevant mixtures can be determined with a maximum accuracy of 5×10^{-5} by employing a critical angle refractometer [3], and an accuracy as good as 3×10^{-6} in the refractive index can be obtained by using a differential refractometer [4], if careful and accurate calibration is performed at all different temperatures. With this respect, it should be considered that the above cited equations re-calculate the experimental data to an average deviation from measured values which is 2 or 3 orders of magnitude lower than the experimental accuracy of commercially available measuring systems [5].

In connection with our previous works dealing with thermophysical properties of binary mixtures containing *N*,*N*-dimethylformamide (DMF) [6–9], we present in this paper the results obtained about refractive properties and related quantities relative to two binary systems formed by DMF (1)+ME (namely 2-methoxyethanol, component 2) and DMF (1)+DME (1,2-dimethoxyethane, component 2).

2. EXPERIMENTAL

2.1. Materials

DMF, ME, and DME solvents [water content lower than 0.10%, 0.05% and 0.10% (w/w), respectively, as found by Karl-Fischer titrations] were high purity grade reagents purchased from Carlo Erba (Milan). DMF and ME were further purified by passing through a neutral alumina column; DME by double fractional distillation over

TABLE I Some physical properties of the selected pure species at 20°C

	Density		*Viscosity*		*Dielectric constant*		*Refractive index*	
Solvent	$\rho/g\,cm^{-3}$	*Ref.*	ν/cSt	*Ref.*	ε	*Ref.*	n	*Ref.*
DMF	0.950252	[8]	0.9121	[33]	38.48	[41]	1.43058	this work
ME	0.964851	[8]	1.769	[40]	17.35	[42]	1.40199	this work
DME	0.866875	[9]	0.5095	[40]	7.70	[42]	1.37944	this work

$LiAlH_4$, in order to eliminate traces of acids and peroxides and to reduce the water content, only retaining the middle fraction (b.p. 83°C) for the measurements. All the purified solvents were preserved for many days over 3 Å molecular sieves before use. The final purity was checked by gas chromatography and resulted of 99.8% for DMF and of 99.7% for both ME and DME, confirming the absence of other significant organic components. Table I lists the data for the pure components that agree satisfactorily with those reported in the literature [10].

2.2. Apparatus and Procedures

All binary mixtures were made up, just before use, by weighting on a Mettler PM 480 Δ-range balance, operating in a dry box to avoid any contact with the atmospheric moisture. The probable error in each mole fraction (X_i) is estimated to be less than 1.5×10^{-4}.

The refractive indexes n_D(Na – D line, at $\lambda = 589\,\text{nm}$) were measured by an automatic refractometer GPR 11-37X Index Instruments, with a resolution of 1×10^{-5} and an accuracy of $\pm 5 \times 10^{-5}$. The instrument operates in the range $0 \leq t/°\text{C} \leq 70$. The measuring cell was calibrated with pure water (from a Milli Q-Plus apparatus, Millipore) at each temperature. A special care was adopted, only keeping the measurement of the n_D value, for each sample and at each temperature, if pre- and post-calibration with water was in the range $n_D = n_D \pm 0.00005$. The temperature was maintained constant within ±0.01°C by an Haake F3C thermostatic bath.

3. RESULTS AND DISCUSSION

The measured refractive index ($n_D \equiv n$, along the text) of the DMF (1)/ME (2) and DMF (1)/DME (2) solvent systems are listed in Tables II and III, respectively, along with the relevant binary composition, expressed on different scales. The temperature (T/K) dependence of these values can be studied by an equation of the type [11]

$$\ln n = \sum_{i=0}^{1} \alpha_i T^i \tag{1}$$

TABLE II Experimental refractive index (n) for the DMF (1) + ME (2) binary system at various temperatures

X_1 =	1	0.9021	0.8038	0.7053	0.6060	0.5063	0.4062	0.3053	0.2044	0.1025	0
$t(°C)^{*}$ $V_1/V_2\%$ =	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90	0/100
0	1.43942	1.43690	1.43433	1.43175	1.42902	1.42616	1.42316	1.42008	1.41674	1.41341	1.40993
5	1.43717	1.43466	1.43216	1.42957	1.42691	1.42403	1.42105	1.41797	1.41470	1.41133	1.40790
10	1.43501	1.43247	1.42995	1.42737	1.42477	1.42191	1.41894	1.41592	1.41264	1.40938	1.40601
15	1.43275	1.43019	1.42769	1.42516	1.42254	1.41977	1.41682	1.41381	1.41060	1.40731	1.40403
20	1.43058	1.42797	1.42552	1.42299	1.42047	1.41763	1.41476	1.41171	1.40857	1.40533	1.40199
25	1.42834	1.42582	1.42329	1.42087	1.41827	1.41554	1.41264	1.40965	1.40651	1.40328	1.40007
30	1.42620	1.42355	1.42110	1.41866	1.41615	1.41338	1.41057	1.40758	1.40447	1.40129	1.39809
35	1.42394	1.42135	1.41890	1.41656	1.41406	1.41127	1.40845	1.40557	1.40244	1.39933	1.39606
40	1.42181	1.41914	1.41672	1.41441	1.41187	1.40919	1.40639	1.40351	1.40041	1.39726	1.39417
45	1.41955	1.41701	1.41454	1.41225	1.40977	1.40709	1.40429	1.40139	1.39839	1.39534	1.39220
50	1.41743	1.41481	1.41242	1.41010	1.40768	1.40499	1.40219	1.39940	1.39637	1.39333	1.39024
55	1.41519	1.41262	1.41024	1.40797	1.40556	1.40291	1.40015	1.39735	1.39435	1.39135	1.38828
60	1.41307	1.41043	1.40806	1.40580	1.40345	1.40080	1.39805	1.39531	1.39234	1.38937	1.38627
65	1.41086	1.40819	1.40588	1.40361	1.40127	1.39870	1.39600	1.39318	1.39027	1.38731	1.38432
70	1.40865	1.40600	1.40369	1.40148	1.39916	1.39658	1.39393	1.39115	1.38826	1.38534	1.38235

* At 20°C.

TABLE III Experimental refractive index (*n*) for the DMF (1) + DME (2) binary system at various temperatures

$X_1 =$ $t(°C)^*$ $V_1/V_2\% =$	1 100/0	0.9252 90/10	0.8422 80/20	0.7575 70/30	0.6702 60/40	0.5744 50/50	0.4742 40/60	0.3704 30/70	0.2527 20/80	0.1291 10/90	0 0/100
0	1.43942	1.43529	1.43074	1.42651	1.42198	1.41701	1.41193	1.40695	1.40102	1.39563	1.38938
5	1.43717	1.43298	1.42847	1.42425	1.41967	1.41467	1.40955	1.40458	1.39861	1.39314	1.38688
10	1.43501	1.43072	1.42614	1.42192	1.41738	1.41235	1.40722	1.40229	1.39622	1.39070	1.38439
15	1.43275	1.42851	1.42386	1.41965	1.41516	1.41007	1.40492	1.39994	1.39383	1.38826	1.38197
20	1.43058	1.42626	1.42165	1.41738	1.41282	1.40774	1.40261	1.39756	1.39141	1.38589	1.37944
25	1.42834	1.42401	1.41934	1.41518	1.41057	1.40543	1.40032	1.39522	1.38908	1.38346	1.37703
30	1.42620	1.42173	1.41713	1.41291	1.40834	1.40318	1.39800	1.39287	1.38669	1.38100	1.37456
35	1.42394	1.41951	1.41486	1.41060	1.40607	1.40086	1.39566	1.39053	1.38430	1.37862	1.37205
40	1.42181	1.41726	1.41254	1.40837	1.40381	1.39861	1.39337	1.38819	1.38187	1.37620	1.36963
45	1.41955	1.41503	1.41029	1.40615	1.40155	1.39630	1.39104	1.38584	1.37951	1.37373	1.36718
50	1.41743	1.41280	1.40811	1.40392	1.39930	1.39407	1.38878	1.38351	1.37717	1.37138	1.36472
55	1.41519	1.41054	1.40586	1.40168	1.39704	1.39177	1.38648	1.38121	1.37481	1.36898	1.36229
60	1.41307	1.40828	1.40362	1.39943	1.39475	1.38950	1.38419	1.37891	1.37238	1.36654	1.35978
65	1.41086	1.40606	1.40132	1.39715	1.39249	1.38721	1.38184	1.37653	1.37001	1.36411	1.35735
70	1.40865	1.40383	1.39908	1.39493	1.39025	1.38497	1.37956	1.37420	1.36765	1.36172	1.35492

* At 20°C.

which reproduces our experimental data with an average uncertainty $\overline{\Delta n}\% = \pm 0.006$ and ± 0.005 for DMF(1)/ME(2) and DMF(1)/DME (2) binary systems, respectively, where

$$\overline{\Delta n}\% = \frac{100}{N}\sum_{N} |n_{\text{calcd}} - n_{\text{exptl}}| \tag{2}$$

and N (165) is the number of experimental data.

Since experimental measurements have been made over the whole composition range for both binary solvent systems, the collected n values have been plotted against the corresponding volume fraction ϕ_2 (densities were taken from our previous papers [8,9]). Since the obtained plots do not suggest a linear dependence of n on the binary composition, the proper relationship was looked for by applying the Eq. [12]

$$\ln n = \sum_{j=0}^{2} \beta_j \phi_1^j \tag{3}$$

to each isothermal set of Tables II and III. Equation (3) reproduces the experimental data with an average uncertainty $\overline{\Delta n}\% = \pm 0.007$ for DMF (1)/ME (2) and ± 0.017 for DMF (1)/DME (2) over all the 165 (N) values of Tables II and III.

It is possible to combine Eqs. (1) and (3) into a single equation:

$$\ln n(T, \phi_1) = \sum_{0}^{i}\sum_{0}^{j} \gamma_{ij} T^i \phi_1^j \tag{4}$$

γ_{ij} coefficients are reported in Table IV for both solvent systems, along with the standard deviations, $\sigma_{(\ln n)}$ of the $\ln n$ dependent variable.

TABLE IV Coefficients γ_{ij} and standard deviations $\sigma(\ln n)$ of model Eq. (4) $n = n(T, \Phi_1)$ for the DMF (1) + ME (2) and DMF (1) + DME (2) binary systems

		γ_{ij}	
ij	*Variable*	*DMF* (1) + *ME* (2)	*DMF* (1) + *DME* (2)
00		4.2053×10^{-1}	4.2673×10^{-1}
01	Φ_1	3.7268×10^{-2}	1.9406×10^{-2}
02	Φ_1^2	-8.9362×10^{-3}	3.2123×10^{-3}
10	T	-2.8183×10^{-4}	-3.5784×10^{-4}
11	$T\Phi_1$	-4.4749×10^{-5}	8.6371×10^{-5}
12	$T\Phi_1^2$	1.6556×10^{-5}	-4.0567×10^{-5}
$\sigma(\ln n)$		6.7×10^{-5}	1.6×10^{-4}

This three-dimensional model allows the calculation of n for any values of T and ϕ, in the investigated ranges, with an average uncertainty equal to ± 0.008 and ± 0.018 for DMF (1)/ME (2) and DMF (1)/DME (2), respectively.

3.1. 'Mixing Rules' Equations

Literature surveys provide for many equations, due to various authors, accounting for the dependence of refractive properties on binary composition of liquid mixtures. With the aim of checking the effectiveness of these equations when applied to the solvent systems here investigated, we have made a stringent test in order to facilitate the speculative comparison on the relative merits, basing the judgement on the average difference between experimental values and those calculated by the selected equation. The 'mixing rules' equations tested are the following:

Arago–Biot equation [13]

$$n = \phi_1 n_1 + \phi_2 n_2 \tag{AB}$$

Gladstone–Dale equation [1]

$$n - 1 = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) \tag{GD}$$

Lorenz–Lorentz equation [2]

$$\frac{n^2 - 1}{n^2 + 2} = \phi_1\left[\frac{n_1^2 - 1}{n_1^2 + 2}\right] + \phi_2\left[\frac{n_2^2 - 1}{n_2^2 + 2}\right] \tag{LL}$$

Wiener equation [14]

$$\frac{n^2 - n_1^2}{n^2 + 2n_1^2} = \phi_2\left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right] \tag{W}$$

Heller equation [15]

$$\frac{n - n_1}{n_1} = \frac{3}{2}\phi_2\left[\frac{(n_2/n_1)^2 - 1}{(n_2/n_1)^2 + 2}\right] \tag{H}$$

SLS-derived equation [16]

$$n = \phi_1^2 n_1 + 2\phi_1\phi_2(n_1 n_2)^{1/2} + \phi_2^2 n_2 \qquad \text{(SLS)}$$

Newton equation [17]

$$n^2 - 1 = \phi_1(n_1^2 - 1) + \phi_2(n_2^2 - 1) \qquad \text{(NW)}$$

Oster equation [18]

$$\frac{(n^2-1)-(2n^2+1)}{n^2} = \sum_{i=1}^{2} \phi_i \left[\frac{(n_i^2-1)-(2n_i^2+1)}{n_i^2}\right] \qquad \text{(OS)}$$

Table V summarises the average differences between the experimental n values and those calculated by Eq. (2) for each Mixing Rule when applied to binary data of Tables II and III on the whole set ($N = 165$). It is evident that all selected relationships can be profitably used if only a rough approximation in predictive calculations is required. However, even if comparable in magnitude for each binary system, $\overline{\Delta n}\%$ average uncertainties are smaller for NW and AB = GD equations, for both solvent systems here investigated. The equations set termed 'Mixing Rules' here investigated is limited to some literature models which can be applied when the preliminary knowledge of liquid mixture density is available. This fact permits their immediate applicability for interpolating procedures in the correspondence of experimental data gaps if binary composition is known, because the mixture property is always extracted and derived in terms of the properties of the pure components. However, for the sake of completeness, it must be remembered that some other equations are available to these purposes (Laplace, Eykman, Rosen and other equations), some of which have been critically reviewed, among other authors, by Parfitt and Wood [19], Munk *et al.* [20, 21], Segré *et al.* [22]. Generally, the applicability of these models needs the *a priori* knowledge of one (or more) empirical parameters (other than density) for each mixed liquid. It should be noticed that this fact has been ignored in the previously examined 'Mixing Rules' set.

As an example. we briefly recognise that Eykman's rule (EYK) is one of the most popular alternative interpolating relationship, which

TABLE V Calculated average percent deviations ($\overline{\Delta n}\%$) for different "Mixing Rules" applied to DMF (1)/ME (2) and DMF (1)/DME (2) binary mixtures at all experimental conditions

System	*AB*	*GD*	*LL*	*W*	*H*	*SLS*	*NEW*	*EYK*	*OST*
DMF+ME	0.069	0.069	0.073	0.070	0.074	0.071	0.065	0.079	0.082
DMF+DME	0.173	0.173	0.187	0.177	0.188	0.180	0.158	0.206	0.216

takes the form [23]

$$\frac{n^2 - 1}{n^2 + 0.4} = k\rho \tag{5}$$

where ρ is the density and k an empirical constant. Equation (5) is valid in particular for pure transparent liquids and for many solvent systems [19, 24], but gives rise to some problems when applied to our selected binary mixtures. Actually, Eq. (5) accounts for a linear trend if the left-hand side term [index function: $f(n)$] is plotted against ρ. Figure 1 reports the plots based on this relationship for the two binary solvent systems here investigated at 20°C. As it can be seen, a linear trend is almost obeyed in the case of DMF (1)/DME (2) binary systems (this observation is valid under all experimental conditions), while this is not true for the DMF (1)/ME (2) solvent system, since a well-pronounced curvature is detectable.

3.2. The Excess Function

It has been outlined in a previous section that the isothermal patterns $n = n(\Phi_1)$ deviate from linearity, which represents the ideal behaviour,

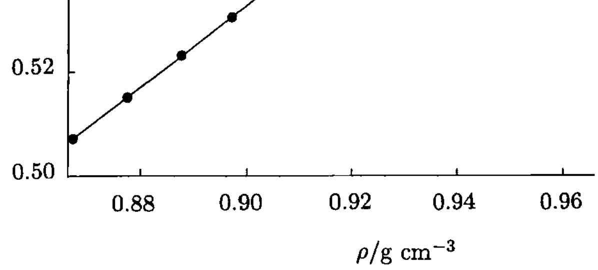

FIGURE 1 Plot of index function $f(n)$ of Eykman Eq. (5) *vs.* $\rho(\mathrm{g\,cm^{-3}})$ for DMF (1)+ME (2) (▲) and DMF (1)+DME (2) (●) binary solvent systems at 20°C.

under all experimental conditions for both DMF/ME and DMF/DME binary mixtures. The ideal dependence on composition of thermodynamic properties like molar volume, molar enthalpy, *etc.*, has been defined within the context of the widely accepted generalisation of Raoult's law. Unfortunately, the ideal mixing "laws" are ambiguously defined and applied for the major part of intensive thermodynamic properties, for which they are not so straightforward derived, as it has been pointed out by Benson *et al.* [25]. When dealing with refractive indices and related properties, *i.e.*, with non-thermodynamic quantities, and with their 'ideal' and 'excess' counterparts, it is necessary to refer to theories and models which either (i) offer an intuitive basis for defining ideality, or (ii) provide a means for translating non-thermodynamic into quasi-thermodynamic quantities. The latter choice seems to be most popular in the literature occurring because, even if it represents a striking forcing to the behaviour of the real systems, it constitutes a very fast and simple way to gain and interpret a variety of chemical and physical pieces of information about 'non-idealities'. Thus, a more suitable way to quantify these deviations is represented by the excess function n^E [26, 27]:

$$Y^E = Y - (Y_1\phi_1 + Y_2\phi_2) \tag{6}$$

which has been plotted in Figure 2 (at 20°C) for DMF(1)/ME(2) and DMF(1)/DME(2) binaries. In this way, we introduce a more common approximation: the mixing ideal behaviour is represented by an additive rule when the composition is expressed in volume fractions, and the addition reaction yielding an heteroaggregated "compound" of the type 1_m2_n is ignored, in order to determine the true average molecular weight of the mixture by the equation:

$$M_{\text{true}} = M_1X_1 + M_2X_2 + M_{1m2n}X_{1m2n} \tag{7}$$

Actually, the application of Eq. (7) is impossible, or at least very difficult, because at the moment no reliable method for determining the mole fraction X_{1m2n} of the additive compound, and hence also X_1 and X_2 of the free species [28], is available. Therefore, instead of the average molecular weight defined by Eq. (7), in physico-chemical analysis it is necessary to simply use the additive molecular weight,

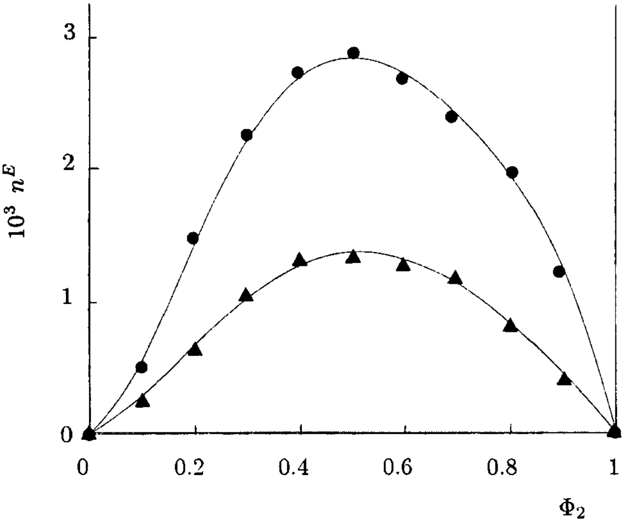

FIGURE 2 Isothermal best fitting curves of excess refractive index (n^E) *vs.* ϕ_2 for the DMF (1)+ME (2) (▲) and DMF (1)+DME (2) (●) binary solvent systems at 20°C.

defined by the equation:

$$M_{\mathrm{add}} = M_1X_1 + M_2X_2 \tag{8}$$

This way permits the evaluation of molar properties, which are obtained under exact form when Eq. (7) can be reasonably applied, as pseudomolar properties by using Eq. (8). The most important difference which originates between true molar and pseudomolar properties in physicochemical analysis of multicomponent systems, is represented by the displacement of the maximum deviations from the abscissa value corresponding to the stoichiometric ratio of the components of the homo- or hetero-aggregated adducts formed in the system; the displacement should be the greater, the greater the equilibrium constant of the aggregation reaction is. On the other hand, within the limits of validity of this approximation, the position of the maximum deviation from additivity of pseudomolar properties is independent of the equilibrium constant value [28, 29]. The n^E values for both the investigated solvent systems are generally positive in all experimental conditions. The curves like those reported in Figure 2 for both solvent systems have been obtained by fitting the initial n^E

data to a Redlich–Kister equation of the type [30]:

$$Y^{\mathrm{E}} = \phi_1\phi_2 \sum_{0}^{K} c_K(\phi_2 - \phi_1)^K \tag{9}$$

The c_K empirical coefficients (for $K = 3$) are listed in Tables VI and VII, along with the standard deviation $\sigma(n^{\mathrm{E}})$ at each temperature. On the whole, regression of experimental n^{E} quantities by Eq. (9) leads to an average deviation $\overline{\Delta n^{\mathrm{E}}}\% = \pm 0.005$ and ± 0.007 for

TABLE VI Coefficients c_k and standard deviations $\sigma(n^{\mathrm{E}})$ of Eq. (9) for the DMF (1) + ME (2) binary system at various temperatures

t(°C)	10^3c_0	10^4c_1	10^3c_2	10^5c_3	$10^5\sigma(n^E)$
0	6.0189	5.3713	− 1.4927	− 22.342	2.0
5	5.8762	5.7870	− 1.6949	4.1027	2.0
10	5.7370	5.0239	− 1.6999	38.263	2.1
15	5.6179	4.7805	− 2.0617	65.982	1.9
20	5.4684	4.2781	− 2.1883	106.16	2.0
25	5.3851	4.7647	− 2.4213	116.63	2.0
30	5.2431	4.3184	− 2.5628	153.84	2.4
35	5.1075	4.5280	− 2.8072	160.68	2.1
40	5.0201	4.5004	− 3.0039	192.42	2.2
45	4.8871	3.4901	− 3.1395	239.31	2.3
50	4.7371	3.6745	− 3.2275	256.40	2.5
55	4.6661	4.5314	− 3.5610	259.17	2.4
60	4.5369	3.1056	− 3.6138	313.56	2.4
65	4.4089	3.6362	− 3.8536	336.30	2.7
70	4.3170	3.5871	− 4.0772	350.37	3.0

TABLE VII Coefficients c_k and standard deviations $\sigma(n^{\mathrm{E}})$ of Eq. (9) for the DMF (1) + DME (2) binary system at various temperatures

t(°C)	10^2c_0	10^5c_1	10^4c_2	10^3c_3	$10^4\sigma(n^E)$
0	1.0413	− 32.109	− 5.1587	6.1863	1.1
5	1.0608	− 32.195	− 9.6267	6.6555	1.1
10	1.0833	− 25.212	− 12.872	6.9452	1.1
15	1.1118	− 12.825	− 17.743	7.1686	1.2
20	1.1321	− 9.4844	− 20.774	7.5515	1.2
25	1.1552	− 1.3966	− 24.334	7.8545	1.2
30	1.1779	13.002	− 27.037	8.2188	1.3
35	1.2045	21.581	− 31.202	8.3454	1.3
40	1.2292	26.430	− 34.683	8.8772	1.3
45	1.2529	29.604	− 38.230	9.3288	1.3
50	1.2806	46.127	− 41.765	9.4184	1.3
55	1.3087	55.064	− 45.719	9.7083	1.3
60	1.3346	59.629	− 49.350	10.183	1.4
65	1.3630	72.838	− 52.905	10.338	1.4
70	1.3847	84.916	− 55.392	10.637	1.4

DMF (1)/ME (2) and DMF (1)/DME (2) binary systems, respectively. It has been outlined in the literature that deviations from ideality in the correspondence to the relative minima or maxima in the plots like those in Figure 2, could be related to the presence of stable solvent–cosolvent adducts in binary solutions [28, 29, 31, 32], whose stoichiometric composition can be fixed on the abscissa in the correspondence to the largest deviations. In the present study, we always observe maxima in the proximity of $\phi_2 \cong 0.5$ for both mixtures, under all experimental conditions, which corresponds to the same values of mole fraction $X_2 \cong 0.5$ for both systems, based on the relation:

$$\Phi_i = \frac{X_i V_i}{\sum_i X_i V_i} \tag{10}$$

In this way, we can confirm that the most stable adducts should be 1DMF • 1ME and 1DMF • 1DME; these findings perfectly agree with all our previous conclusions from investigations on the same binary mixtures by different thermophysical properties [6–9, 33].

3.3. The Molar Refraction

In order to gain further information about the presence of specific intermolecular interactions in these binaries, another property related to refractive index has been investigated, *i.e.*, the molar refraction ($R/\mathrm{cm}^3\,\mathrm{mol}^{-1}$), defined by the equation:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{X_1 M_1 + X_2 M_2}{\rho} \tag{11}$$

where ρ is the density measured under the same experimental conditions [8, 9].

Starting from these data, it is possible to evaluate the excess quantity ($R^E/\mathrm{cm}^3\,\mathrm{mol}^{-1}$) by applying the following equation:

$$R^E = R - (X_1 R_1 + X_2 R_2) \tag{12}$$

and the results for the DMF (1)/ME (2) binaries are shown in Figure 3 where, for clearness reasons, the experimental points have been represented at only one temperature. The curves of this figure have been analytically represented by Eq. (9), the independent variable

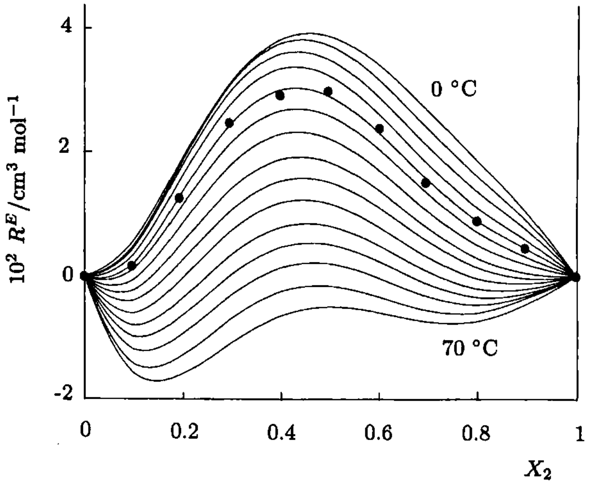

FIGURE 3 Isothermal best fitting curves of excess molar refraction ($R^E/cm^3 mol^{-1}$) *vs.* X_2 for the DMF (1)+ME (2) solvent system at different temperatures ranging from 0°C to 70°C.

being the mole fraction X_i, instead of Φ_i, since the dependence $R^E = R^E(X_i)$ has been already accepted by other authors [29, 34]. The c_K coefficients in Eq. (9) for the trend $R^E = R^E(X_i)$ are listed in Tables VIII and IX for the two binary systems studied.

As it can be seen, DMF/ME shows, in general, positive deviations, with a clear maximum centred at $X_2 \cong 0.5$, which becomes more pronounced as temperature lowers. Furthermore, we still observe the presence of a minimum near to $X_2 \cong 0.1$, that appears in the trend of the plots at temperature $t \cong 30$°C, and becomes progressively more and more marked as temperature increases. In addition, the trend of R^E for the DMF/DME mixtures is quite similar, but with a magnitude which is twofold that observed in DMF/ME solvent system.

The reasons for this behaviour can be ascribed to the quite different patterns of molecular interactions between the common species DMF and the cosolvent ME or DME. In fact, ME is classifiable as an HBDA (Hydrogen Bonding Donor Acceptor) species, while DME shows reduced ability (HBA species) to interact with the amide, and in any case only *via* dipolar (of any kind) and other interactions weaker than hydrogen bonding. However, this fact seems not to be surprising, because it reflects the same situation which has been observed by

TABLE VIII Coefficients c_k and standard deviations $\sigma(R^E/\mathrm{cm}^3\,\mathrm{mol}^{-1})$ of Eq. (9)* for the DMF (1)+ME (2) binary system at various temperatures

$t(°C)$	10^3c_0	10^4c_1	c_2	c_3	$10^3\sigma(R^E)$
0	155.3	− 486.6	− 1.026	1.257	0.9
5	149.3	− 687.6	− 1.119	1.513	1.1
10	139.9	− 799.8	− 1.131	1.568	1.2
15	129.4	− 838.6	− 1.213	1.553	1.2
20	116.1	− 788.6	− 1.251	1.480	1.3
25	103.4	− 706.0	− 1.249	1.306	1.4
30	88.61	− 663.0	− 1.275	1.299	1.4
35	73.39	− 570.9	− 1.309	1.186	1.5
40	60.47	− 489.5	− 1.329	1.153	1.6
45	46.89	− 465.2	− 1.362	1.255	1.6
50	32.47	− 362.8	− 1.392	1.210	1.6
55	20.41	− 291.5	− 1.420	1.215	1.6
60	7.924	− 228.4	− 1.441	1.293	1.6
65	− 6.502	− 153.1	− 1.452	1.398	1.3
70	− 20.09	1.203	− 1.456	1.216	1.1

* $R^E = R^E(X_i)$.

TABLE IX Coefficients c_k and standard deviations $\sigma(R^E/\mathrm{cm}^3\,\mathrm{mol}^{-1})$ of Eq. (9)* for the DMF (1)+DME (2) binary system at various temperatures

$t(°C)$	c_0	$10c_1$	10^2c_2	10^3c_3	$10^2\sigma(R^E)$
0	11.57	− 1.956	294.9	− 10.37	9.6
5	11.22	− 1.683	245.0	− 10.53	9.3
10	10.63	− 1.507	211.4	− 7.333	9.1
15	9.785	− 1.414	175.4	− 1.761	8.8
20	8.576	− 1.429	144.1	6.006	8.5
25	7.356	− 1.488	112.1	14.48	8.1
30	6.266	− 1.544	80.98	22.35	8.0
35	5.301	− 1.592	43.86	27.46	7.8
40	4.524	− 1.675	6.517	33.49	7.6
45	3.816	− 1.734	− 29.91	37.07	7.6
50	3.502	− 1.754	− 67.03	38.65	7.6
55	3.327	− 1.748	− 99.36	39.12	7.6
60	3.284	− 1.739	− 124.4	39.34	7.7
65	3.287	− 1.763	− 134.3	41.02	7.9
70	3.203	− 1.698	− 123.2	42.62	8.1

* $R^E = R^E(X_i)$.

studying the volumetric behaviour of the same binary mixtures [8, 9], where the highest negative deviations were obtained in DMF/DME solvent system. As a final remark, we underline that the intensity of these excess volume functions (R^E) is generally smaller (about one order of magnitude) than that of the corresponding V^E quantities, for both the solvent systems compared here.

3.4. The Kirkwood Correlation Factor

Another important parameter taken into account in this work is the Kirkwood correlation factor (*g*). This parameter provides for useful information regarding the molecular orientation hindrance that, in turn, is indicative of the existence and of the extent of short-range intermolecular interactions in the liquid state. For the systems under study, *g* values have been calculated by means of the equation:

$$g = \frac{\varepsilon_0(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(2 + \varepsilon_\infty)^2} \frac{9KT}{\mathrm{L}\rho} \frac{X_1M_1 + X_2M_2}{(X_1\mu_1 + X_2\mu_2)^2} \qquad (13)$$

where the symbols have their usual meaning [35]. As a very common and accepted approximation, ε_∞ was set to 1.1 n^2, where n is the refractive index of the sample at each temperature. It is also accepted that the dipole moments of pure species are not temperature-dependent throughout the calculations. The obtained *g* values are listed in Tables X and XI for DMF/ME and DMF/DME solvent systems, respectively. A very good agreement can be observed between the *g* values calculated for DMF and those reported in the literature ($g_{\mathrm{DMF}} = 1.03$) [36], while acceptable agreement is obtained for ME ($g_{\mathrm{ME}} = 1.70$) [36]. Finally, our *g* factor value for pure DME seems to be quite far from the literature one ($g_{\mathrm{DME}} = 1.23$) [36].

A very stringent analysis about the structuredness of solvents have been recently conducted by Marcus, by taking into account different physico-chemical parameters, such as the Trouton's constant, *i.e.*, the entropy of vaporisation at constant pressure, and the *g* factor. Hence, it is now understood that for unstructured solvents $g = 1$ by definition (in practice, 1.0 ± 0.3), whereas for structured solvents generally $g > 1$, which implies parallel alignment of molecular dipoles. As a consequence, the three pure species of this work are classified as structured ME, unstructured DMF, while DME probably results unstructured on the basis of other experimental evidence (NMR spectroscopy [37] and thermophysic behaviour [38]). As it can be seen from Tables X and XI, the variation of *g* factor calculated increases at increasing the temperature for DMF and DME, while the opposite happens for ME.

In order to gain further information about these questions, following the literature suggestions [39], we have evaluated an excess

TABLE X Kirkwood correlation factor (g) for the DMF (1)+ME (2) binary mixtures at various temperatures

t(°C)	A	B	C	D	E	F	G	H	I	L	M
0	1.014	1.072	1.112	1.157	1.214	1.252	1.307	1.336	1.316	1.325	1.271
5	1.016	1.074	1.115	1.159	1.216	1.253	1.307	1.333	1.316	1.324	1.271
10	1.019	1.076	1.118	1.161	1.217	1.254	1.306	1.330	1.316	1.323	1.271
15	1.021	1.078	1.120	1.163	1.218	1.254	1.304	1.327	1.316	1.322	1.271
20	1.023	1.080	1.122	1.164	1.219	1.254	1.303	1.323	1.315	1.321	1.270
25	1.025	1.081	1.123	1.164	1.219	1.254	1.301	1.320	1.314	1.319	1.268
30	1.026	1.082	1.124	1.165	1.219	1.253	1.299	1.315	1.313	1.316	1.267
35	1.027	1.083	1.125	1.165	1.218	1.252	1.296	1.311	1.311	1.314	1.265
40	1.028	1.083	1.126	1.165	1.218	1.251	1.293	1.306	1.309	1.311	1.263
45	1.028	1.083	1.126	1.164	1.217	1.249	1.290	1.301	1.307	1.307	1.260
50	1.028	1.083	1.126	1.164	1.215	1.247	1.286	1.295	1.305	1.304	1.257
55	1.028	1.082	1.126	1.162	1.214	1.245	1.282	1.289	1.302	1.300	1.254
60	1.028	1.082	1.125	1.161	1.212	1.243	1.278	1.283	1.299	1.296	1.250
65	1.028	1.081	1.124	1.160	1.210	1.240	1.274	1.277	1.295	1.291	1.247
70	1.028	1.080	1.123	1.158	1.207	1.237	1.269	1.270	1.291	1.286	1.243

TABLE XI Kirkwood correlation factor (g) for the DMF (1)+DME (2) binary mixtures at various temperatures

t(°C)	A	B	C	D	E	F	G	H	I	L	M
0	1.014	1.025	1.132	1.209	1.254	1.369	1.514	1.691	1.944	2.286	2.741
5	1.016	1.028	1.135	1.211	1.258	1.374	1.519	1.697	1.951	2.295	2.753
10	1.019	1.030	1.137	1.213	1.261	1.378	1.524	1.703	1.957	2.303	2.763
15	1.021	1.033	1.140	1.214	1.265	1.382	1.528	1.709	1.962	2.311	2.772
20	1.023	1.034	1.142	1.216	1.268	1.386	1.532	1.713	1.967	2.319	2.781
25	1.025	1.036	1.143	1.217	1.270	1.389	1.535	1.718	1.971	2.325	2.789
30	1.026	1.037	1.144	1.217	1.272	1.392	1.538	1.722	1.975	2.332	2.796
35	1.027	1.039	1.145	1.217	1.274	1.394	1.541	1.725	1.978	2.337	2.802
40	1.028	1.039	1.146	1.217	1.276	1.397	1.543	1.728	1.981	2.342	2.808
45	1.028	1.040	1.147	1.217	1.277	1.399	1.546	1.731	1.983	2.346	2.813
50	1.028	1.041	1.147	1.217	1.278	1.401	1.547	1.733	1.985	2.350	2.817
55	1.028	1.041	1.147	1.217	1.279	1.402	1.549	1.735	1.987	2.353	2.820
60	1.028	1.041	1.147	1.217	1.280	1.403	1.550	1.737	1.988	2.356	2.823
65	1.028	1.041	1.147	1.217	1.280	1.404	1.551	1.739	1.989	2.358	2.825
70	1.028	1.041	1.147	1.217	1.280	1.405	1.552	1.740	1.990	2.360	2.825

correlation factor:

$$\Delta g = g - (X_1 g_1 + X_2 g_2) \tag{14}$$

whose graphical representation is given in Figures 4 and 5 for the two binary systems, respectively. As an evidence, Δg is always positive for DMF/ME mixtures, and negative when DME is the cosolvent. In particular, a sharp maximum is detected in Figure 4 at $X_2 \cong 0.65$ (1DMF • 2ME) under all experimental conditions: this fact is probably enlightening about the highest order degree, which is reached in

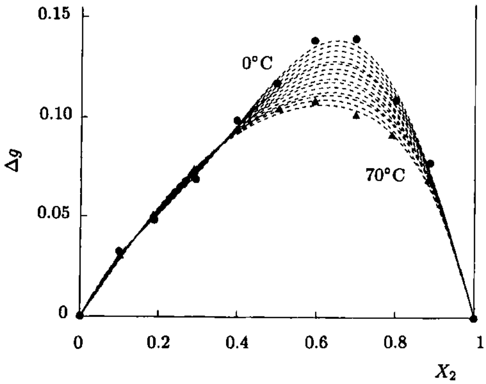

FIGURE 4 Excess Kirkwood correlation factor (Δg) *vs.* X_2 for the DMF (1) + ME (2) binary solvent system at various temperatures: • at 0°C; ▲ at 70°C.

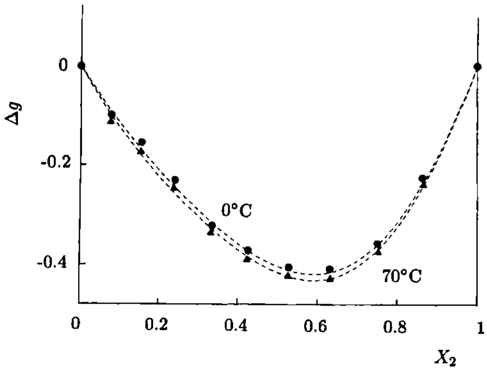

FIGURE 5 Excess Kirkwood correlation factor (Δg) *vs.* X_2 for the DMF (1) + DME (2) binary solvent system at different temperatures: • at 0°C; ▲ at 70°C.

these mixtures at this composition. On the other hand, the minimum centred at $X_2 \cong 0.5$ (Fig. 5) is probably indicative of the reduced order degree in the DMF/DME solutions at all temperatures investigated.

4. CONCLUSIONS

In this paper we have examined the refractive properties of two related binary solvent systems containing DMF as common species, and the two parent cosolvents ME and DME. We have also checked some literature equations for useful correlations concerning the refractive index of the mixed liquids. Furthermore, some empirical relationships accounting for the dependence of n on T, on Φ_i and on both T and Φ_i, have been investigated, and the results obtained seem quite reliable as a whole. All the equations checked along the paper can be safely employed for interpolation purposes, in order to calculate forecasted values in the correspondence to experimental data gaps.

For the binary mixtures studied here, some deviations from ideal refractive behaviour are observed at all the temperatures investigated, which can be ascribed to different tendency of the mixed components to associate to form solvent–cosolvents complexes *via* hydrogen bonding and/or dipolar interactions of any kind. As to the excess refractive mixing quantities, we observe that different related properties here investigated are differently sensitive to various aggregation patterns between different molecules. Maximum deviations have been detected in the correspondence of some stoichiometric ratios of the type DMF • ME, DMF • 2ME, DMF • DME; these adducts seem to be thermostable under the selected experimental conditions.

Acknowledgement

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NOMENCLATURE

c_k	coefficients of Eq. (9)
DME	1,2-dimethoxyethane

DMF	N,N-dimethylformamide
g	Kirkwood correlation factor
L	Avogadro's number
ME	2-methoxyethanol
M_i	molar mass of i-th species (kg mol^{-1})
K	Boltzman constant
k	empirical constant of Eq. (5)
N	number of experimental points
n	refractive index
R	molar refraction (cm^3 mol^{-1})
T	absolute temperature (K)
t	Celsius temperature (°C)
V^E	excess molar volume (cm^3 mol^{-1})
X_i	mole fraction of i-th component
Y	generic property
Y^E	generic excess property

Greek Letters

α_i	coefficients of Eq. (1)
β_j	coefficients of Eq. (3)
γ_{ij}	coefficients of Eq. (4)
Δg	excess correlation factor
ΔY	average uncertainty for a generic property
$\overline{\Delta Y}$	overall average uncertainty for a generic property
ε	static dielectric constant
ε_0	vacuum dielectric constant
Φ_i	volume fraction of i-th component
μ_i	dipole moment of i-th species (D; $1\text{D} \cong 3.335 \times 10^{-12}$ C m)
ρ	density (g cm^{-3})
$\sigma(Y)$	standard deviation of a generic property

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