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Effect of Temperature on the Refractive Index of Aliphatic Hydroxilic Mixtures (C_2–C_3)

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The refractive indices of mixtures of ethanol + (1-propanol, 2-propanol, 1,2-propanediol, and 1,3-propanediol) have been measured at temperatures of 288.15, 293.15, 298.15, and 303.15 K at atmospheric pressure. In this work, an analysis of the mixing properties gives valuable information on packing trends, showing the interactions of ethanol in a hydroxilic environment. From the measured refractive indices on mixing, the parameters of a set of analytical expressions, which represent the composition and temperature dependences of the derived property, are reported. The excess molar volumes are estimated using derivations of the Heller equation, which are dependent on the refractive indices on mixing; accurate values are obtained for the alcohol mixtures, using literature data. The effect of temperature on the mixing and derived properties is analyzed in terms of the relative position of hydroxyl groups, the alkyl chain length, and the available hydrogen-bond interactions between solute and solvent molecules.

KEY WORDS: ethanol; excess molar volume; hydroxilic mixture; 1,2-propanediol; 1,3-propanediol; 1-propanol; 2-propanol; refractive index.

1. INTRODUCTION

As a part of our research program on the thermodynamics of chemical processes, we have conducted studies on the properties of binary and multicomponent mixtures that are involved in separation units for recovering industrial solvents, food engineering, or pharmacological applications [1–3]. In the latter application, the important role of hydroxilic compounds (sugars,

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alcohols, or polyols) as protein protectors against loss of solubility during drying and inhibitors of heat coagulation has been reported earlier [4–6]. Hydrophobic interactions and hydrogen bonding are generally considered to be the major factors in stabilizing the three-dimensional structure of proteins, increasing their transition temperatures in aqueous solutions, and inducing a decreased hydrogen bond rupture potency [7]. However, the use of cosolvents to reinforce the stability effect introduces highly nonideal new interactions; for these systems, experimental data are needed, along with adequate and accurate estimation procedures. It is the purpose of this study to analyze these factors in mixtures of short aliphatic solvents by measurement of the refractive index, due to its relation with other thermodynamic properties, and sensitivity to structure molecular effects.

In the last few years ethanol has been used as a distillation entrainer or extractive solvent in the chemical industry, as a carrier or additive in food and pharmaceutical processes, and in antimicrobial applications for medical uses. This molecule contains a hydrophilic hydroxyl group which is available to hydrogen-bond to similar compounds and a residual end conferring a degree of hydrophobicity on the molecule. The mixing properties and behavior of ethanol vary with the nature of the chemical environment, the operation conditions, and, also, its steric hindrance molecular effects. These factors are clearly demonstrated by the unusual packing characteristics of ethanol in hydroxilic mixtures, its behavior in the biological environment, and its common azeotropic tendencies. Solution property measurements have proved useful in understanding solute + solvent interactions and packing effects of solutes among solvent molecules. Experimental values of the changes of refractive indices provide information about ethanol + hydroxilic mixture interactions as the mole fraction of ethanol is increased, as well as the packing efficiency.

In this work, we present a study of the effect of temperature on this property to analyze the influence of the molecular chain residues, as well as the progressive occultation, and relative position of hydroxyl groups toward hydrogen bond formation, and mixing thermodynamics. To this end, the refractive index on mixing of ethanol + (1-propanol, 2-propanol, 1,2-propanediol, or 1,3-propanediol) in the temperature range 288.15 to 303.15 K at atmospheric pressure, was experimentally determined. A corresponding derived property was computed, and correlated by application of a modified temperature dependent Redlich–Kister [8] equation.

Values of the refractive index on mixing were compared with those estimated using different mixing rules [9], which are dependent on pure compound values. Because the refractive index and the density are among the most relevant solvent properties, the excess molar volumes of the mixtures were estimated from the experimental measurements using the Heller equation [10], which is dependent on the refractive indices on mixing; accurate results are obtained for the alcohol mixtures, using literature data. The temperature influence on the mixing, and the derived property, was analyzed in terms of the relative position of the hydroxyl groups in the molecules, the chain molecular residues, and available hydrogen-bond interactions.

2. EXPERIMENTAL

The substances employed were supplied by Merck (Lichrosolv quality). Their mole-fraction purities were better than 0.995 for the compounds used, as determined by means of gas–liquid chromatography, in accordance with vendor specifications. Values of the measured property were in agreement with those published in the open literature as shown in Table I. Normal purification procedure for chemicals was applied using molecular sieves (4 Å) to dehydrate, ultrasonic treatment for degassing solvents, and injection of argon in solvent bottles (better than 2 ppmv in water). The chemicals were recently acquired, and stored under sun- and humidity-protection conditions. Precautions were taken, such as cooling chemicals before sample preparation and minimizing empty space in the vessels, to avoid evaporation losses during handling or errors in compositions.

The measured property, the index of refraction, is the ratio of the velocity of light in vacuum, usually taken as the velocity in air, to that in a substance saturated with air. The refractive index is useful in characterizing molecular interactions and for estimating other physicochemical properties. The refractive index is a function of both temperature and the wavelength of the incident sodium D light. An automated refractometer (ABBEMAT-HP Dr. Kernchen) with a precision of $\pm 10^{-5}$ was used; it was thermostated by a controlled bath (PolyScience Model 9510), with a temperature stability of

Table I. Comparison of Experimental Refractive Indices with Literature Data for Pure Liquids at 298.15 K

	n_D	
Component	Exptl.	Lit.
Ethanol	1.35922	1.35941 [11] 1.35931 [13]
1-Propanol	1.38283	1.38370 [11]
2-Propanol	1.37474	1.3752 [12]
1,2-Propanediol	1.43100	1.4314 [12]
1,3-Propanediol	1.43794	1.439 [12]

$\pm 10^{-2}$ K. The refractometer is used to determine the experimental values by placing the sample to be measured on the polished surface of a prism made of synthetic sapphire, where a cone-shaped yellow light beam of sodium D wavelength illuminates the sample from its bottom side at different angles of reflection. The measuring prism is water-jacketed to maintain a constant temperature during the measurement, as mentioned above. Sample preparation was made by weight using a Mettler AT-261 Delta Range balance with a precision of $\pm 10^{-5}$ g, covering the complete composition range of the mixtures. The uncertainty for both changes of refractive indices, on mixing and mole fractions, was estimated as better than 10^{-4}. Each sample remained in the thermostat for at least 30 min, while three measurements of refractive index were performed. Besides daily testing, the instruments were calibrated in accordance with instructions before every series of measurements (Millipore quality water and ambient air were used for calibration).

3. DATA CORRELATION

The refractive indices of the binary mixtures are given in Table II, applying Eq. (1) to compute the corresponding derived property:

$$\delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{1}$$

Table II. Refractive Indices and Changes of Refractive Indices on Mixing for the Binary Mixtures Ethanol (1) + (1-Propanol, 2-Propanol, 1,2-Propanediol, or 1,3-Propanediol) (2) in the Temperature Range 288.15 to 303.15 K

	n_D				δn_D			
x_1	288.15 K	293.15 K	298.15 K	303.15 K	288.15 K	293.15 K	298.15 K	303.15 K
				Ethanol (1) + 1-propanol (2)				
0.0000	1.38720	1.38512	1.38283	1.38067	0.00000	0.00000	0.00000	0.00000
0.1008	1.38514	1.38309	1.38089	1.37888	0.00034	0.00038	0.00046	0.00060
0.2250	1.38261	1.38060	1.37839	1.37634	0.00077	0.00084	0.00091	0.00102
0.3221	1.38057	1.37858	1.37645	1.37449	0.00104	0.00114	0.00128	0.00147
0.4561	1.37770	1.37568	1.37358	1.37155	0.00136	0.00143	0.00161	0.00172
0.5265	1.37611	1.37413	1.37196	1.36994	0.00145	0.00155	0.00166	0.00178
0.6558	1.37306	1.37103	1.36888	1.36681	0.00148	0.00154	0.00166	0.00173
0.7189	1.37148	1.36945	1.36724	1.36515	0.00140	0.00146	0.00152	0.00157
0.8304	1.36845	1.36644	1.36425	1.36221	0.00103	0.00111	0.00118	0.00128
0.9205	1.36585	1.36380	1.36156	1.35949	0.00058	0.00061	0.00064	0.00070
1.0000	1.36338	1.36129	1.35903	1.35690	0.00000	0.00000	0.00000	0.00000

Table II. *(Continued)*

	n_D				δn_D			
x_1	288.15 K	293.15 K	298.15 K	303.15 K	288.15 K	293.15 K	298.15 K	303.15 K
				Ethanol (1) + 2-propanol (2)				
0.0000	1.37927	1.37694	1.37474	1.37253	0.00000	0.00000	0.00000	0.00000
0.1112	1.37780	1.37555	1.37339	1.37125	0.00030	0.00035	0.00040	0.00045
0.2504	1.37593	1.37373	1.37156	1.36937	0.00064	0.00071	0.00075	0.00075
0.3202	1.37497	1.37276	1.37058	1.36843	0.00079	0.00083	0.00087	0.00091
0.4646	1.37281	1.37062	1.36844	1.36632	0.00092	0.00096	0.00100	0.00105
0.5511	1.37146	1.36928	1.36709	1.36499	0.00095	0.00096	0.00100	0.00107
0.6556	1.36976	1.36760	1.36539	1.36327	0.00091	0.00092	0.00095	0.00099
0.7019	1.36894	1.36683	1.36461	1.36248	0.00083	0.00088	0.00090	0.00092
0.8451	1.36640	1.36433	1.36210	1.35993	0.00056	0.00062	0.00064	0.00061
0.9278	1.36482	1.36277	1.36053	1.35838	0.00029	0.00035	0.00037	0.00035
				Ethanol (1) + 1,2-propanediol (2)				
0.0000	1.43471	1.43297	1.43100	1.42931	0.00000	0.00000	0.00000	0.00000
0.0809	1.43004	1.42864	1.42684	1.42513	0.00110	0.00146	0.00166	0.00168
0.2306	1.42200	1.42029	1.41886	1.41700	0.00364	0.00385	0.00426	0.00439
0.3192	1.41689	1.41527	1.41345	1.41185	0.00495	0.00519	0.00542	0.00566
0.4541	1.40842	1.40662	1.40480	1.40315	0.00610	0.00620	0.00648	0.00672
0.5003	1.40527	1.40349	1.40158	1.39996	0.00624	0.00638	0.00659	0.00688
0.6562	1.39385	1.39197	1.39003	1.38829	0.00595	0.00604	0.00626	0.00650
0.7144	1.38928	1.38736	1.38535	1.38359	0.00552	0.00560	0.00576	0.00601
0.8432	1.37848	1.37646	1.37421	1.37242	0.00392	0.00393	0.00390	0.00417
0.9181	1.37165	1.36948	1.36726	1.36531	0.00243	0.00232	0.00234	0.00248
				Ethanol (1) + 1,3-propanediol (2)				
0.0000	1.44087	1.43941	1.43794	1.43678	0.00000	0.00000	0.00000	0.00000
0.1537	1.43250	1.43147	1.43009	1.42867	0.00354	0.00407	0.00428	0.00417
0.3038	1.42365	1.42243	1.42079	1.41942	0.00632	0.00675	0.00682	0.00691
0.3785	1.41895	1.41749	1.41587	1.41438	0.00741	0.00765	0.00779	0.00783
0.4512	1.41405	1.41261	1.41071	1.40925	0.00814	0.00845	0.00837	0.00851
0.5437	1.40709	1.40539	1.40359	1.40198	0.00835	0.00846	0.00855	0.00864
0.6528	1.39805	1.39620	1.39452	1.39270	0.00777	0.00779	0.00809	0.00807
0.7741	1.38706	1.38544	1.38350	1.38170	0.00617	0.00650	0.00665	0.00676
0.8316	1.38135	1.38023	1.37754	1.37595	0.00492	0.00518	0.00522	0.00560
0.9248	1.37168	1.36993	1.36784	1.36571	0.00247	0.00276	0.00288	0.00280

In these equations, n_D is the refractive index of the mixture, n_{D_i} is the refractive index of pure component i, x_i is the mole fraction of component i in the mixture, N is the number of components, and δ means the variation of the property. The changes in refractive index on mixing at the measurement temperature are included in the same table. A modified Redlich–

Kister-type equation was used to correlate the values of the changes of refractive index on mixing as a function of temperature for the corresponding binary mixtures. The parameters of these fits are those corresponding to the equations which are expressed as

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^{m} A_p (x_i - x_j)^p \tag{2}$$

$$A_p = \sum_{q=0}^{2} B_{pq} T^q \tag{3}$$

where m is the limit of the expansion according to the Bevington test [14], B_{pq} are the fitting parameters, and T is the temperature in K. The parameters were determined by the method of least squares, with all points weighted equally using a routine developed in accordance with the Marquardt algorithm [15]. The parameters are reported for the mixtures of this study in Table III. The root-mean-square deviation for each system is also given in Table III. The root-mean-square deviation, where the value

Table III. Fitting Parameters of Eq. (3) and Root-Mean-Square Deviations (σ)

		Ethanol (1) + 1-propanol (2)		
δn_D	$B_{00} = 0.059714$	$B_{01} = -0.000451$	$B_{02} = 9.137 \times 10^{-7}$	$\sigma = 0.00002$
	$B_{10} = -0.343990$	$B_{11} = 0.002412$	$B_{12} = -4.196 \times 10^{-6}$	
	$B_{20} = 0.538600$	$B_{21} = -0.003699$	$B_{22} = 6.354 \times 10^{-6}$	
	$B_{30} = 0.086414$	$B_{31} = -0.000661$	$B_{32} = 1.249 \times 10^{-6}$	
		Ethanol (1) + 2-propanol (2)		
δn_D	$B_{00} = 0.103756$	$B_{01} = -0.000703$	$B_{02} = 1.240 \times 10^{-6}$	$\sigma = 0.00001$
	$B_{10} = 0.362818$	$B_{11} = -0.002445$	$B_{12} = 4.120 \times 10^{-6}$	
	$B_{20} = -1.063886$	$B_{21} = 0.007153$	$B_{22} = -1.201 \times 10^{-5}$	
	$B_{30} = -1.369067$	$B_{31} = 0.009311$	$B_{32} = -1.582 \times 10^{-5}$	
		Ethanol (1) + 1,2-propanediol (2)		
δn_D	$B_{00} = 0.500206$	$B_{01} = -0.003378$	$B_{02} = 6.000 \times 10^{-6}$	$\sigma = 0.00003$
	$B_{10} = -0.103657$	$B_{11} = 0.000757$	$B_{12} = -1.336 \times 10^{-6}$	
	$B_{20} = -1.248949$	$B_{21} = 0.008278$	$B_{22} = -1.371 \times 10^{-5}$	
	$B_{30} = 5.881248$	$B_{31} = -0.039399$	$B_{32} = 6.601 \times 10^{-5}$	
		Ethanol (1) + 1,3-propanediol (2)		
δn_D	$B_{00} = -0.147208$	$B_{01} = 0.001145$	$B_{02} = -1.803 \times 10^{-6}$	$\sigma = 0.00007$
	$B_{10} = 1.751899$	$B_{11} = -0.011795$	$B_{12} = 1.990 \times 10^{-5}$	
	$B_{20} = -5.155038$	$B_{21} = 0.034408$	$B_{22} = -5.737 \times 10^{-5}$	
	$B_{30} = 0.710781$	$B_{31} = -0.004794$	$B_{32} = 8.092 \times 10^{-6}$	

of the property and the number of experimental data are represented by z and n, respectively, is given by

$$\sigma = \sqrt{\frac{\sum_i^n (z_{\text{exp}} - z_{\text{pred}})^2}{n}} \tag{4}$$

In currently available literature, only values of the derived property for the system ethanol + 2-propanol have been published earlier. Figures 1a–d shows the derived property for the binary mixtures plotted against the mole fraction as well as the fitted curves at each temperature (288.15, 293.15, 298.15, and 303.15 K).

4. REFRACTIVE INDEX ON MIXING

The experimental refractive indices were compared with predicted results by the mixing rules proposed by Lorentz–Lorenz, Dale–Gladstone, and Eykman [9], which are expressed by the following equations, respectively:

$$\frac{n_{\text{D}}^2 - 1}{n_{\text{D}}^2 + 2} = \sum_{i=1}^{N} \left[\phi_i \left(\frac{n_{\text{D}i}^2 - 1}{n_{\text{D}i}^2 + 2} \right) \right] \tag{5}$$

$$n_{\text{D}} - 1 = \sum_{i=1}^{N} \left[\phi_i (n_{\text{D}i} - 1) \right] \tag{6}$$

$$\frac{n_{\text{D}}^2 - 1}{n_{\text{D}}^2 + 0.4} = \sum_{i=1}^{N} \left[\phi_i \left(\frac{n_{\text{D}i}^2 - 1}{n_{\text{D}i}^2 + 0.4} \right) \right] \tag{7}$$

where n_{D} and $n_{\text{D}i}$ stand for the same meaning reported above. The ϕ term is the volumetric fraction, which can be expressed as a function of volume additivity. In Table IV; the root-mean-square deviations of refractive index estimations are reported, good accuracy is observed due to the linearity of this property, and its slight dependence on temperature. As could be observed, the best results were obtained for alcohol mixtures, although, in general, small deviations were observed in all cases. In Fig. 2, literature data [16] for the ethanol + 2-propanol system were analyzed in terms of deviations from the experimental values measured in this work. As noted, small differences between both sets of data were obtained; only at the highest temperature were deviations as large as 3%. In the same figure, the deviations corresponding to the different rules at 298.15 K were analyzed. These estimated values were accurate with maximum deviations of about 7% at high ethanol mole fractions.

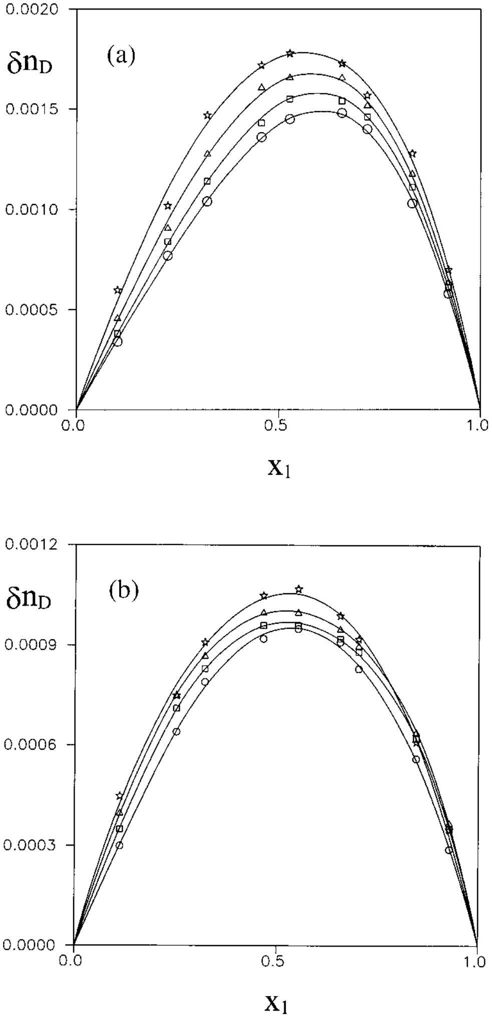

Fig. 1. Curves of constant changes of refractive index on mixing as a function of temperature for (a) ethanol (1) + 1-propanol (2), (b) ethanol (1) + 2-propanol (2), (c) ethanol (1) + 1,2-propanediol (2), and (d) ethanol (1) + 1,3-propanediol (2) at (○) 288.15, (□) 293.15, (△) 298.15, and (☆) 303.15 K.

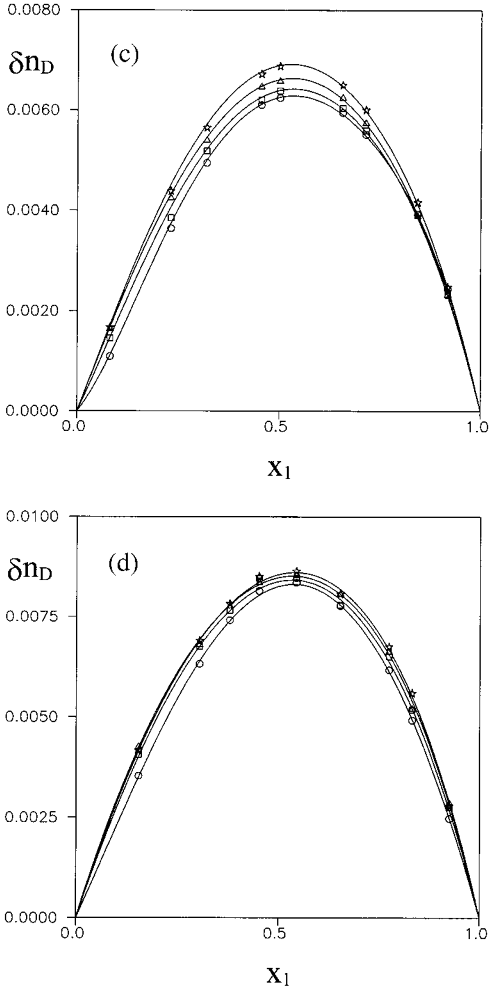

Fig. 1. *(Continued)*

5. EXCESS MOLAR VOLUME ESTIMATION

For many practical purposes it is necessary to show the capability of predicting the nonideality of binary or multicomponent liquid mixtures from other mixing properties or by means of pure component properties. The methods applied to these mixtures can be used to evaluate the excess molar volume from refractive indices on mixing, based on different applications of the Heller equation [10], and different rules for the refractive

Table IV. Root-Mean-Square Deviations of the Experimental Refractive Indices from the Estimated Results by the Lorentz–Lorenz (LL), Dale–Gladstone (DG), and Eykman (Ey) Rules

	288.15 K	293.15 K	298.15 K	303.15 K
		Ethanol (1) + 1-propanol (2)		
LL	0.00012	0.00014	0.00020	0.00029
DG	0.00012	0.00012	0.00017	0.00025
Ey	0.00012	0.00013	0.00018	0.00026
		Ethanol (1) + 2-propanol (2)		
LL	0.00048	0.00089	0.00003	0.00004
DG	0.00048	0.00089	0.00003	0.00003
Ey	0.00048	0.00089	0.00003	0.00003
		Ethanol (1) + 1,2-propanediol (2)		
LL	0.00148	0.00187	0.00208	0.00226
DG	0.00178	0.00157	0.00177	0.00195
Ey	0.00158	0.00167	0.00187	0.00205
		Ethanol (1) + 1,3-propanediol (2)		
LL	0.00324	0.00352	0.00357	0.00364
DG	0.00287	0.00314	0.00318	0.00324
Ey	0.00299	0.00326	0.00331	0.00337

indices on mixing. In the last few years, the prediction of excess molar volumes from refractive index mixing rules, and the relation of excess molar volumes with the density of pure components was suggested for binary mixtures by some authors. In an earlier study [17], we have tested various relations for binary and ternary self-associative mixtures. The generalized expression, which is a function of the mixture density and those of the pure components, can be written

$$\frac{f(n_{\mathrm{D}})}{\rho} = \sum_{i=1}^{N} \frac{w_i f(n_{\mathrm{D}i})}{\rho_i} \tag{8}$$

where w_i is the weight fraction, and f is a function of the refractive index of the mixture (n_{D}) and the refractive index of each component ($n_{\mathrm{D}i}$). Expressing this equation in terms of excess molar volumes by means of some algebra,

$$V^{\mathrm{E}} = \frac{(\sum_{i=1}^{N} x_i M_i)(\sum_{i=1}^{N} \frac{W_i f(n_{\mathrm{D}i})}{\rho_i})}{f(n_{\mathrm{D}})} - \sum_{i=1}^{N} \frac{x_i M_i}{\rho_i} \tag{9}$$

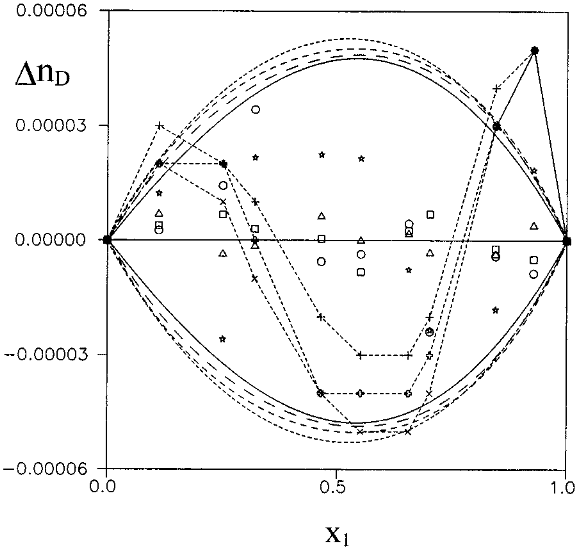

Fig. 2. Deviations ($\Delta n_{\mathrm{D,\ EXPERIMENTAL}} - n_{\mathrm{D,\ LITERATURE\ OR\ ESTIMATED\ BY\ MODELS}}$, 5%, at (——) 288.15, (— — —) 293.15, (- - -) 298.15, and (··· ···) 303.15 K) from computed changes of refractive index on mixing by application of (+) Eq. (5), (×) Eq. 6, and (✙) Eq. (7) at 298.15 K, and literature data [16] for ethanol (1)+2-propanol (2) at (○) 288.15, (□) 293.15, (△) 298.15, and (☆) 303.15 K. The experimental values of this work at each temperature are shown by the solid line at zero value.

From this equation, considering the relation between the weight fractions and the mole fractions, the equation can be transformed so that

$$V^{\mathrm{E}} = \frac{\left(\sum_{i=1}^{N} \left(M_i x_i f(n_{\mathrm{D}i})/\rho_i\right)\right)}{f(n_{\mathrm{D}})} - \sum_{i=1}^{N} \frac{x_i M_i}{\rho_i} \tag{10}$$

Expressed in another way, the relation of the excess molar volumes to the function of refractive indices would be

$$V^{\mathrm{E}} = \sum_{i=1}^{N} \left[\left(f(n_{\mathrm{D}i}) - f(n_{\mathrm{D}})\right) \left(\frac{x_i M_i}{f(n_{\mathrm{D}})\, \rho_i} \right) \right] \tag{11}$$

In another way, Nakata and Sakurai [18] have proposed expressions to relate excess molar volumes by means of expansions in powers to first order, taking into account different mixing rules:

$$f(n_{\mathrm{D}})|_{n_{\mathrm{D1}}} = \sum_{n=0}^{\infty}\left[\frac{f^{\mathrm{a}}(n_{\mathrm{D1}})}{n_{\mathrm{D}}!}(n_{\mathrm{D}}-n_{\mathrm{D1}})^{n}\right] = f(n_{\mathrm{D1}})+f'(n_{\mathrm{D1}})(n_{\mathrm{D}}-n_{\mathrm{D1}})+\cdots \quad (12)$$

$$f(n_{\mathrm{D2}})|_{n_{\mathrm{D1}}} = \sum_{n=0}^{\infty}\left[\frac{f^{\mathrm{a}}(n_{\mathrm{D1}})}{n_{\mathrm{D}}!}(n_{\mathrm{D2}}-n_{\mathrm{D1}})^{n}\right] = f(n_{\mathrm{D1}})+f'(n_{\mathrm{D1}})(n_{\mathrm{D2}}-n_{\mathrm{D1}})+\cdots \quad (13)$$

then we obtain

$$V^{\mathrm{E}} = -\left(\frac{f'(n_{\mathrm{D1}})}{f(n_{\mathrm{D1}})}\right)\sum_{i=1}^{N}\left[\left(\frac{x_i M_i}{\rho_i}\right)\left(n_{\mathrm{D}}-\sum_{i=1}^{N} n_{\mathrm{D}i}\phi_i\right)\right] \quad (14)$$

where f' means the first derivative of the mathematical function f. In this paper, the experimental and estimated values of excess molar volumes using Eqs. (11) and (14) are compared for the binary mixtures, while using the Lorentz–Lorenz, Dale–Gladstone, and Eykman mixing rules for the function f. Figure 3 shows the excess molar volumes at an equimolar

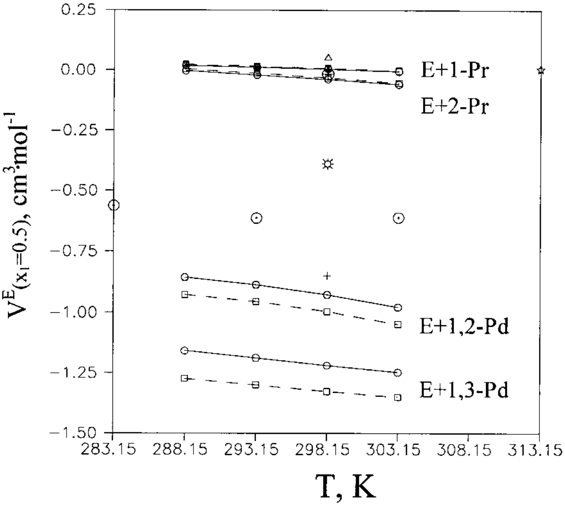

Fig. 3. Estimations of excess molar volumes [V^{E} (cm^3·mol^{-1})] at equimolar composition by Eq. (11) (solid line) and Eq. (14) (dashed line) for the binary mixtures over a range of temperatures (K), and literature data. (+) Ethanol + 1,2-ethanediol [13]; (∗, ⊕, △) ethanol + 2-propanol [16, 21, 23]; (╪, ☆) ethanol + 1-propanol [19, 22]; (☼) ethanol + 1,2-propanediol [20]; (⊙) methanol + 1,2-propanediol [24].

composition ($x_1 = 0.5$) estimated by means of these equations at different temperatures, where a similar capability for this property is obtained, although the Lorentz–Lorenz mixing rule shows slightly better results. In the same figure, the values corresponding to previously published data of excess molar volumes of the systems ethanol + (1-propanol, 2-propanol, and 1,2-propanediol) [19–23] and aliphatic alcohols + diols [13, 24] are shown for comparison. Although the observed trend of equimolar excess molar volumes is consistent with that from literature data for alcohols, a slight decreasing tendency is observed that is different from the experimental results. This result is negligible for ethanol + aliphatic alcohol mixtures, where a surprising accuracy for estimated excess volumes is obtained at each temperature for both theoretical procedures [Eqs. (11) and (14)]. The estimated values for ethanol + diol compounds show two characteristics: a greater negative value with a strong decreasing trend for higher temperatures and a large difference between the results for both procedures. In any case, an overview of experimental data related to these mixtures reveals the exaggerated associative behavior assigned to these compounds. This fact is probably due to the inaccuracy of the mixing rules used in the equations, which are not able to estimate the associative behavior and the steric hindrance for these mixtures. These equations give an adequate accuracy for moderate excess molar volumes (slight nonlinear trend for the refractive index for mixture), although the components of these mixtures are polar or weakly self-associative.

6. RESULTS AND DISCUSSION

As observed, all cases studied show positive values of change of refractive index on mixing, due to two opposing factors: (a) the hydrogen-bond interaction between solute and solvent for each mixture and (b) the steric hindrance of aliphatic residues. Two tendencies could be observed related to the molecular structure of the chemicals studied; at first, the alcohol isomers show a moderate change of refractive index by cross-interactions among different molecules. These systems are sensitive to temperature; the small expansion effect is reduced at higher temperatures by a better packing of the aliphatic residues among the highly polar functional groups. The contraction effect of breaking pure solvent bonds and creating hydrogen bonds of ethanol and propanol isomers is decreased when the alkanol shows a linear chain (1-propanol) by steric hindrance or interaction between aliphatic residues. As a consequence of the similarity of structures of the employed alcohols, the observed nonideality is almost negligible. Second, the alkanediol compounds in the mixture give higher values and a lower dependence on temperature due to the strong hydroxyl-bond interactions. This fact is due to the less important role played by the aliphatic ends. The coupling of hydroxilic group compounds leads to an important contraction trend, which is stronger for 1,3-propanediol by the higher association of the two exposed hydroxyl groups. The influence of the temperature provides larger contraction at higher temperatures. The lower contraction of 1,2-propanediol could be a result of the self-association of hydroxyl groups for each molecule, with a reduction of hydrogen bond potency. As for the 2-propanol, the aliphatic end makes it more difficult to accommodate itself among polar groups. The observed synergistic contraction trend in the diol mixtures could be used to obtain a stronger effect of protein protection, by means of the compaction of solvent layers around the solute, due to the intense hydrogen bond relation, and the interaction among residues. The ethanol + 1,3-propanediol mixture behaves differently from the other cases. To bring its behavior in line, it must be assumed that this alkanediol represents a considerable occultation of the aliphatic chain. This behavior between ethanol and 1,3-propanediol explains the interest in these compounds as solvent and cosolvent agents for drying protein processes, the addition of slightly polar compounds such as 1,2-propanediol or alkanol isomers possibly being used to obtain an adequate temperature transition in aqueous solution.

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