Refractive Indices, Densities and Excess Molar Volumes of Monoalcohols + Water

Jose V. Herráez · R. Belda

Abstract The refractive index, n_D, and density, ρ, of binary mixtures of monoalcohols + water, have been measured at a temperature of 298.15 K and atmospheric pressure. The variation of the refractive indices of these solutions has also been determined with temperature in the range $T = (278.15 \text{ to } 338.15)$ K and atmospheric pressure. A comparative study has been made of the refractive indices obtained experimentally and those calculated by means of the Lorentz-Lorenz [Theory of Electrons, Dover Phoenix (1952)] and Gladstone-Dale relations [Trans. R. Soc. London **148**:887–902 (1858)]; in all cases, the Gladstone–Dale equation was seen to afford values similar to those obtained experimentally. Calculations have been made of the excess molar volumes, V^E, and the molar refraction deviations, ΔR, of these mixtures and the differences between the experimental values for refractive index and those obtained by means of the Gladstone–Dale equation. Values of V^E were compared with others in the literature. In all cases the V^E values were negative, and in all cases, except in the methanol + water system, ΔR showed a maximum for $x = 0.8$.

1. Introduction

Alcohols, either pure or mixed with water, are widely used in the pharmaceutical industry, in cosmetics, enology and as a source of energy [1–3].

The density, refractive index, viscosity, surface tension, *etc*., of these binary systems are very useful analytical information for industrial purposes [4–7].

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The most widely used theoretical method for predicting the refractive index of binary mixtures of liquids is the Lorentz–Lorenz relation [8]

$$\frac{n_L^2 - 1}{n_L^2 + 2} = \Phi_1 \frac{n_{D1}^2 - 1}{n_{D1}^2 + 2} + \Phi_2 \frac{n_{D2}^2 - 1}{n_{D2}^2 + 2} \tag{1}$$

where n_L is the refractive index of the mixture according to the Lorentz–Lorenz formula; Φ_1 and Φ_2 are the volume fractions of alcohol and water, calculated from volume determinations based on the mass and density measurements, and n_{D1} and n_{D2} are the refractive indices of the alcohol and of water, respectively.

Empirical equations have also been developed to determine refractive indices of binary systems of liquids, including that proposed by Gladstone-Dale [9]:

$$\frac{n_G - 1}{\rho} = w_1 \left(\frac{n_{D1} - 1}{\rho_1} \right) + w_2 \left(\frac{n_{D2} - 1}{\rho_2} \right) \tag{2}$$

where n_G is the refractive index of the mixture according to the Gladstone–Dale formula; ρ is the experimental density of the mixture; w_1 and w_2 are the mass fractions of alcohol and water; and n_{D1} and n_{D2} are the refractive indices of the alcohol and water, respectively.

The validity of the Lorentz–Lorenz and Gladstone–Dale relations in application to different types of mixtures has been confirmed by a number of investigators [10–13].

In order to add new data for the properties of the monoalcohol-water mixtures reported earlier [14], we have measured the refractive indices and densities of these mixtures at a temperature of 298.15 K and at atmospheric pressure, and comparisons have been made with the values obtained from Eqs. (1) and (2) for the purpose of determining the formula that best predicts the refractive indices of these mixtures.

Likewise, calculations have been made of the excess molar volume, V^E, by means of the following equation [15]:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{3}$$

where ρ is the density of the mixture; ρ_1 and ρ_2 are the densities of the components; x_1 and x_2 are the respective mole fractions; and M_1 and M_2 are the molar masses of the pure components.

The molar refraction deviations, ΔR, have been calculated from the following expressions [4, 16]:

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{4}$$

$$\Delta R = R_m - (x_1 R_1 + x_2 R_2) \tag{5}$$

where n_D is the refractive index of the mixture.

On the other hand, calculations have also been made of the differences between the refractive index obtained experimentally, n_D, and that calculated from the equation of Gladstone–Dale, n_G, i.e., $\Delta n_G = n_D - n_G$.

Finally a study was done of the variations in the refractive index of these solutions with temperature.

Table 1 Comparison of the values of density, ρ, and refractive index, n_D, measured in our laboratory and reported in the literature, at a temperature of 298.15 K and atmospheric pressure for the indicated pure monoalcohols

Component	ρ (kg·m^{-3})	ρ_{lit} (kg·m^{-3})	n_D	$n_{D\ lit}$
Water	997.02	997.0 [20]	1.3326	1.3324 [20]
		997.04 [18]		1.33250 [18]
		997.048 [21]		
Methanol	786.62	787.2 [17]	1.3264	1.326 [17]
		786.6 [20]		1.3264 [20]
		786.64 [18]		1.32652 [18]
		786.350 [21]		1.32645 [21]
Ethanol	785.08	787.3 [17]	1.3593	1.359 [17]
		784.93 [18]		1.35941 [18]
		785.1 [20]		1.3592 [20]
		784.962 [21]		1.35925 [21]
1-Propanol	799.68	802.0 [17]	1.3836	1.383 [17]
		799.353 [21]		1.38314 [21]
2-Propanol	784.98	785.0 [17]	1.3761	1.375 [17]
1-Butanol	801.04	810.0 [17]	1.3973	1.397 [17]
		805.75 [18]		1.39741 [18]
2-Butanol	803.24	805.0 [17]	1.3948	1.395 [17]
1-Pentanol	809.42	811.0 [17, 19]	1.4087	1.408 [17]
				1.4095 [19]
2-Pentanol	811.03	812.0 [17]	1.4065	1.416 [17]
3-Pentanol	814.26	815.0 [17]	1.4073	–

2. Experimental method

The alcohols used were methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol, with purity >99%, supplied by Aldrich, without further purification. Alcohols containing more than four carbon atoms have not been used, since they are practically insoluble in water.

Table 1 shows the values of the densities and refractive indices of the pure alcohols as measured in our laboratory and reported in the literature [17–21].

Considering that alcohols containing up to three carbon atoms are completely soluble in water, whereas butanols are only partially soluble, we have proceeded as follows:

In all cases mixtures of alcohol(1) and water(2) were prepared based on the mole fraction of the alcohol (x). The masses were recorded on an electronic balance (Mettler AE 163) with an uncertainty of 0.01 mg. The possible uncertainty in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. Each preparation was distributed into three containers to ensure that all measurements were made in triplicate—thereby allowing assessment of the possible dispersion of the results obtained.

For the partially soluble alcohols we were only able to obtain measurements up to the point of water saturation, which at a temperature of 298.15 K corresponded to the following proportions: 1-butanol: $x = 0.5$; 2-butanol: $x = 0.333$.

The index of refraction for the sodium D-Line was measured using the Abbe-3L refractometer thermostatted to within ± 0.02 K at atmospheric pressure. The uncertainty in the measurements was within ± 0.0001 units.

Determination of the density of the mixture was made using a vibrating tube digital densimeter (Density/Specific Gravity Meter DA 505) with an uncertainty of 10^{-2} kg·m^{-3}.

Table 2 Experimental measurements of density, ρ, and refractive index, n_D, for methanol-water mixtures, along with the values obtained for n_G, n_L, Δn_G, ΔR and V^E at a temperature of 298.15 K

x	ρ (kg·m^{-3})	n_D	n_G	n_L	Δn_G	ΔR (m^3·mol^{-1}) $\times 10^{-6}$	V^E (m^3·mol^{-1}) $\times 10^{-6}$
0.0000	997.02	1.3326	1.33260	1.33260	0.00000	0.00000	0.00000
0.1010	971.66	1.3364	1.33693	1.33134	−0.00053	−0.01705	−0.35947
0.1995	948.15	1.3387	1.33943	1.33037	−0.00073	−0.02823	−0.63911
0.3102	922.64	1.3395	1.34051	1.32948	−0.00101	−0.03896	−0.85815
0.3330	917.74	1.3396	1.34063	1.32931	−0.00103	−0.04050	−0.89700
0.4054	901.76	1.3394	1.34040	1.32884	−0.00100	−0.04270	−0.97369
0.5006	881.50	1.3389	1.33944	1.32830	−0.00054	−0.03760	−1.01260
0.5998	861.17	1.3379	1.33775	1.32781	0.00015	−0.02476	−0.97445
0.7035	840.72	1.3360	1.33538	1.32737	0.00062	−0.01115	−0.84819
0.8122	820.14	1.3331	1.33240	1.32698	0.00070	−0.00323	−0.62060
0.9002	804.10	1.3302	1.32969	1.32669	0.00051	0.00080	−0.36469
1.0000	786.62	1.3264	1.32637	1.32640	0.00000	0.00000	0.00000

3. Results and discussion

Based on the present protocol, and as a function of the mole fraction of the mixture (x), Tables 2–7 show the values of the experimental refractive indices, n_D, and the expected values according to the equations of Gladstone-Dale, n_G, and Lorentz-Lorenz, n_L.

These tables allow us to represent graphically (Fig. 1) the values of the refractive indices of all the mixtures. In two cases a peak refractive index is observed: for methanol at a mole fraction of 0.333; and for ethanol at a mole fraction of 0.666. The rest of the alcohols studied showed no such maxima.

On the other hand, and for each alcohol, Figs. 2–8 likewise represent as a function of mole fraction the experimental values of the refractive indices, along with the values calculated according to the Gladstone–Dale and Lorentz–Lorenz equations. In all cases a very good correlation is observed between the experimental values and the values obtained

Table 3 Experimental measurements of density, ρ, and refractive index, n_D, for ethanol-water mixtures, along with the values obtained for n_G, n_L, Δn_G, ΔR and V^E at a temperature of 298.15 K

x	ρ (kg·m^{-3})	n_D	n_G	n_L	Δn_G	ΔR (m^3·mol^{-1}) $\times 10^{-6}$	V^E (m^3·mol^{-1}) $\times 10^{-6}$
0.0000	997.02	1.3326	1.33260	1.33261	0.00000	0.00000	0.00000
0.1010	960.05	1.3457	1.34679	1.33968	−0.00109	−0.02260	−0.45476
0.2001	930.02	1.3535	1.35517	1.34452	−0.00167	−0.04039	−0.78770
0.2987	903.49	1.3574	1.35976	1.34801	−0.00236	−0.06021	−0.98588
0.3332	894.81	1.3582	1.36071	1.34914	−0.00251	−0.06492	−1.02180
0.4087	876.73	1.3595	1.36187	1.35102	−0.00237	−0.06727	−1.04150
0.5051	855.63	1.3604	1.36212	1.35309	−0.00172	−0.05721	−0.96649
0.6030	836.60	1.3614	1.36158	1.35484	−0.00018	−0.02147	−0.80368
0.6664	825.77	1.3618	1.36111	1.35685	0.00069	0.00134	−0.67725
0.7032	820.06	1.3617	1.36086	1.35623	0.00084	0.00740	−0.60328
0.7956	807.52	1.3614	1.36040	1.35731	0.00100	0.01798	−0.43115
0.9075	795.40	1.3609	1.36023	1.35850	0.00067	0.01397	−0.26738
1.0000	785.08	1.3593	1.35930	1.35892	0.00000	0.00000	0.00000

Table 4 Experimental measurements of density, ρ, and refractive index, n_D, for 1-propanol-water mixtures, along with the values obtained for n_G, n_L, Δn_G, ΔR and V^E at a temperature of 298.15 K

x	ρ (kg·m^{-3})	n_D	n_G	n_L	Δn_G	ΔR (m^3·mol^{-1}) $\times 10^{-6}$	V^E (m^3·mol^{-1}) $\times 10^{-6}$
0.0000	997.02	1.3326	1.33260	1.33260	0.00000	0.00000	0.00000
0.0452	974.30	1.3451	1.34439	1.34087	0.00071	0.00447	−0.20663
0.0770	959.68	1.3516	1.35060	1.34557	0.00100	0.00633	−0.31598
0.1006	949.61	1.3554	1.35441	1.34861	0.00099	0.00666	−0.38267
0.1242	940.18	1.3587	1.35767	1.35132	0.00103	0.00629	−0.43832
0.1431	933.04	1.3609	1.35994	1.35330	0.00096	0.00565	−0.47573
0.1668	924.60	1.3634	1.36244	1.35556	0.00096	0.00462	−0.51454
0.2031	912.65	1.3665	1.36564	1.35863	0.00086	0.00299	−0.55856
0.2498	898.88	1.3696	1.36888	1.36201	0.00072	0.00177	−0.59228
0.3330	878.13	1.3738	1.37302	1.36683	0.00078	0.00430	−0.60454
0.5003	847.35	1.3792	1.37788	1.37359	0.00132	0.02257	−0.52072
0.6671	826.31	1.3820	1.38063	1.37805	0.00137	0.03373	−0.37345
0.7980	814.10	1.3833	1.38211	1.38063	0.00119	0.03565	−0.24210
0.9035	806.09	1.3839	1.38301	1.38230	0.00089	0.03180	−0.12694
1.0000	799.68	1.3836	1.38360	1.38360	0.00000	0.00000	0.00000

from the Gladstone–Dale equation. In contrast, the values obtained with the Lorentz–Lorenz expression differ greatly from the experimental values.

This observation could be explained by taking into account that the volume contraction occurs in mixtures of alcohols and water, and the density of the mixture is considered in the Gladstone–Dale equation. In fact, the discrepancy between the experimental values and those obtained from the Lorentz–Lorenz expression decreases and the number of carbon

Table 5 Experimental measurements of density, ρ, and refractive index, n_D, for 2-propanol-water mixtures, along with the values obtained for n_G, n_L, Δn_G, ΔR and V^E at a temperature of 298.15 K

| x	ρ (kg·m^{-3})	n_D	n_G	n_L	Δn_G	ΔR (m^3·mol^{-1}) $\times 10^{-6}$	V^E (m^3·mol^{-1}) $\times 10^{-6}$
0.0000	997.02	1.3326	1.33260	1.33260	0.00000	0.00000	0.00000
0.0150	988.34	1.3373	1.33667	1.33521	0.00063	0.00572	−0.08091
0.0386	975.68	1.3437	1.34219	1.33884	0.00151	0.01287	−0.19694
0.0602	965.16	1.3485	1.34664	1.34178	0.00186	0.01617	−0.29986
0.0850	954.12	1.3530	1.35107	1.34476	0.00193	0.01685	−0.41060
0.1125	942.87	1.3571	1.35524	1.34766	0.00186	0.01483	−0.52148
0.1250	938.05	1.3587	1.35688	1.34885	0.00182	0.01329	−0.56680
0.1431	931.24	1.3607	1.35906	1.35047	0.00164	0.01065	−0.62726
0.1662	922.96	1.3629	1.36145	1.35236	0.00145	0.00702	−0.69352
0.2100	908.21	1.3661	1.36500	1.35549	0.00110	0.00091	−0.78597
0.2501	895.70	1.3683	1.36736	1.35792	0.00094	−0.00245	−0.83450
0.3329	872.81	1.3713	1.37043	1.36200	0.00087	−0.00117	−0.84959
0.5050	837.40	1.3747	1.37348	1.36783	0.00122	0.01549	−0.71569
0.6664	814.27	1.3761	1.37463	1.37144	0.00147	0.03384	−0.48266
0.8010	799.58	1.3762	1.37501	1.37366	0.00119	0.03654	−0.23199
0.9022	790.87	1.3760	1.37529	1.37500	0.00071	0.02610	−0.05390
1.0000	784.98	1.3761	1.37610	1.37610	0.00000	0.00000	0.00000

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Table 6 Experimental measurements of density, ρ, and refractive index, n_D, for 1-butanol-water mixtures, along with the values obtained for n_G, n_L, Δn_G, ΔR and V^E at a temperature of 298.15 K

x	ρ (kg·m^{-3})	n_D	n_G	n_L	Δn_G	ΔR (m^3·mol^{-1}) $\times\ 10^{-6}$	V^E (m^3·mol^{-1}) $\times\ 10^{-6}$
0.0000	997.02	1.3326	1.33260	1.33260	0.00000	0.00000	0.00000
0.5000	842.13	1.3920	1.39095	1.38654	0.00105	0.02121	−0.59651
0.5703	833.30	1.3937	1.39236	1.38884	0.00134	0.03510	−0.51780
0.6659	823.75	1.3953	1.39403	1.39141	0.00127	0.03726	−0.42887
0.8040	813.08	1.3968	1.39589	1.39430	0.00091	0.03230	−0.30080
1.0000	801.04	1.3973	1.39730	1.39730	0.00000	0.00000	0.00000

Table 7 Experimental measurements of density, ρ, and refractive index, n_D, for 2-butanol-water mixtures, along with the values obtained for n_G, n_L, Δn_G, ΔR and V^E at a temperature of 298.15 K

| x	ρ (kg·m^{-3})	n_D	n_G	n_L	Δn_G	ΔR (m^3·mol^{-1}) $\times\ 10^{-6}$	V^E (m^3·mol^{-1}) $\times\ 10^{-6}$
0.0000	997.02	1.3326	1.33260	1.33260	0.00000	0.00000	0.00000
0.3330	869.95	1.3831	1.38262	1.37701	0.00048	0.00197	−0.59646
0.4000	858.28	1.3863	1.38565	1.38045	0.00065	0.00715	−0.61505
0.5000	843.48	1.3895	1.38854	1.38443	0.00096	0.01991	−0.55692
0.5714	834.62	1.3912	1.38991	1.38669	0.00129	0.03462	−0.47610
0.6660	825.28	1.3931	1.39148	1.38913	0.00162	0.05212	−0.38576
0.8000	814.39	1.3943	1.39292	1.39184	0.00138	0.05460	−0.20055
1.0000	803.24	1.3948	1.39480	1.39480	0.00000	0.00000	0.00000
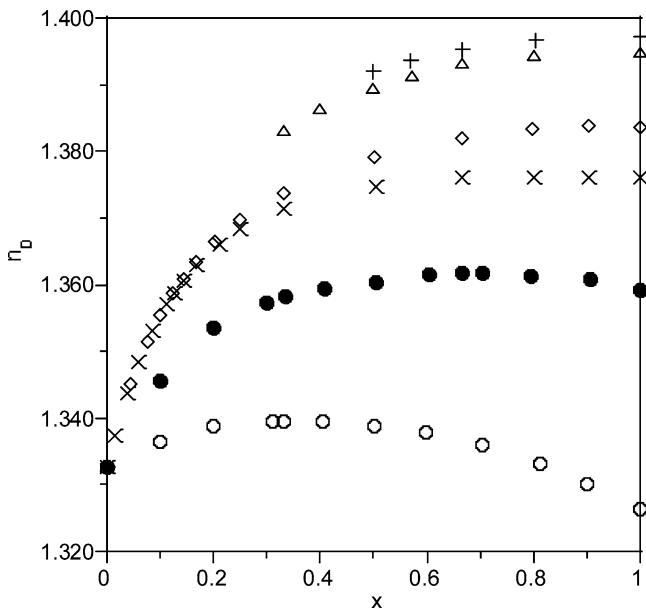
Fig. 1 Refractive indices, n_D, for monoalcohols-water mixtures *versus* mole fraction, x, of monoalcohols, (○) methanol, (●) ethanol, (◇) 1-propanol, (×) 2-propanol, (+) 1-butanol and (△) 2-butanol at 298.15 K
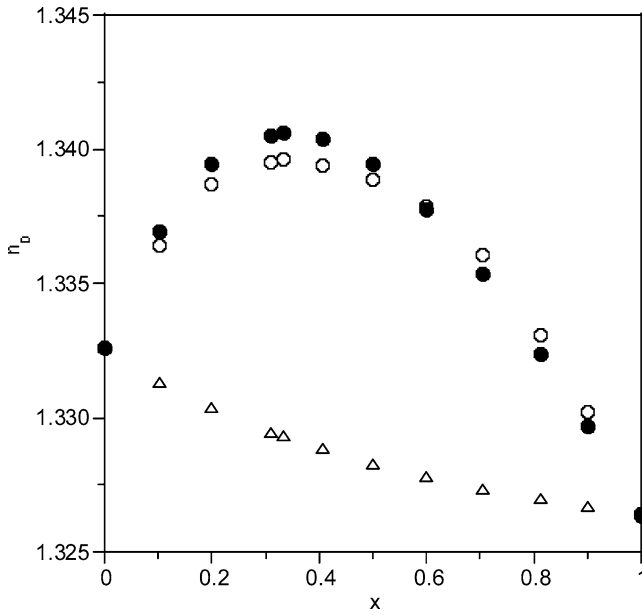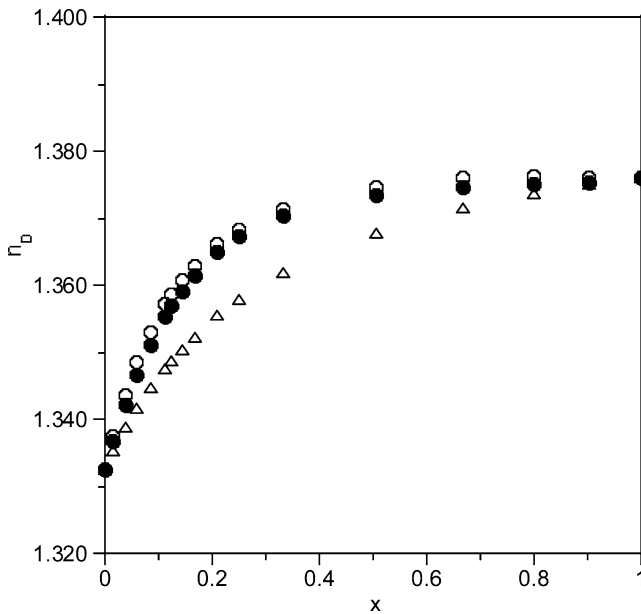
Fig. 2 Refractive indices for methanol-water mixtures *versus* mole fraction, x, ($\circ$) n_D, ($\bullet$) n_G and ($\triangle$) n_L at 298.15 K
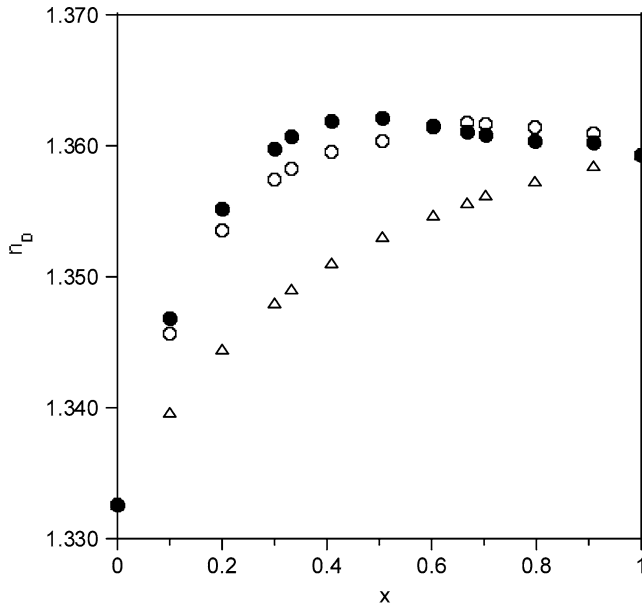
Fig. 3 Refractive indices for ethanol-water mixtures *versus* mole fraction, x, ($\circ$) n_D, ($\bullet$) n_G and ($\triangle$) n_L at 298.15 K
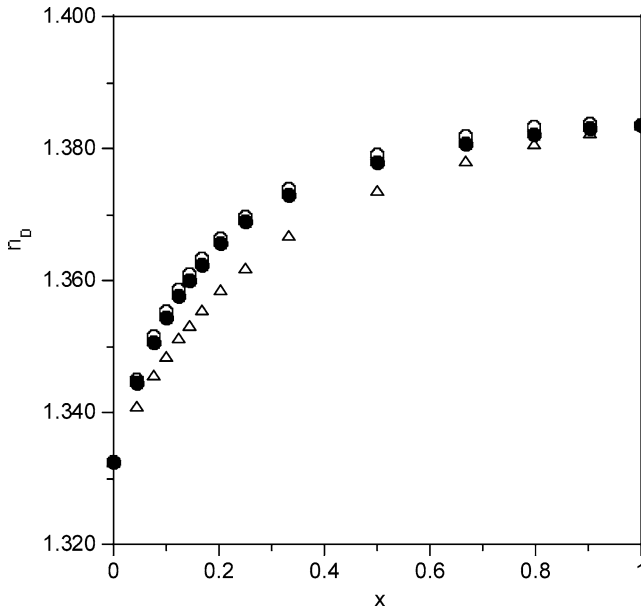
Fig. 4 Refractive indices for 1-propanol-water mixtures *versus* mole fraction, x, ($\circ$) n_D, ($\bullet$) n_G and ($\triangle$) n_L at 298.15 K

Fig. 5 Refractive indices for 2-propanol-water mixtures *versus* mole fraction, x, ($\circ$) n_D, ($\bullet$) n_G and ($\triangle$) n_L at 298.15 K

Fig. 6 Refractive indices for 1-butanol-water mixtures *versus* mole fraction, *x*, (○) n_D, (●) n_G and (△) n at 298.15 K
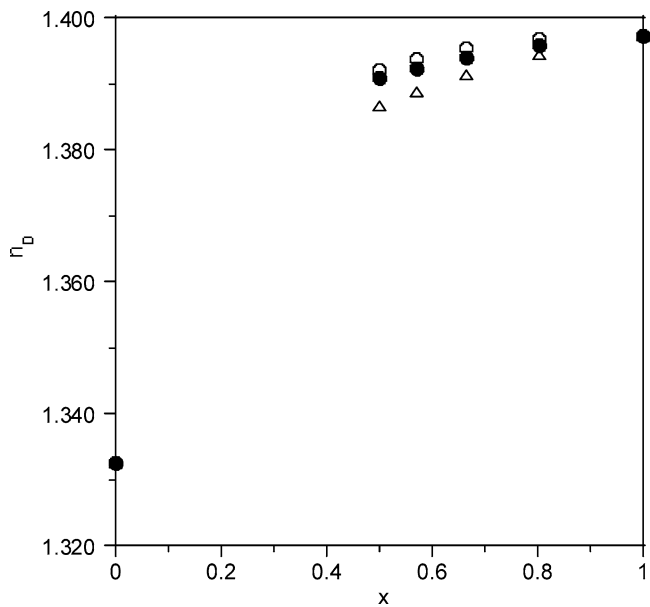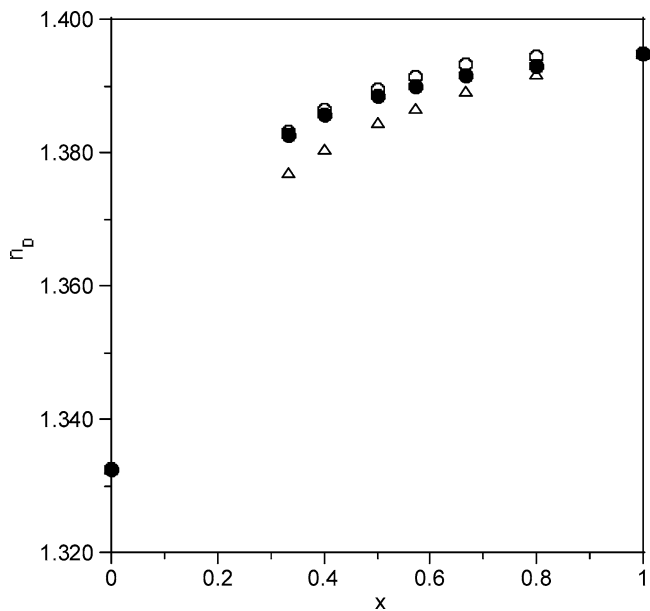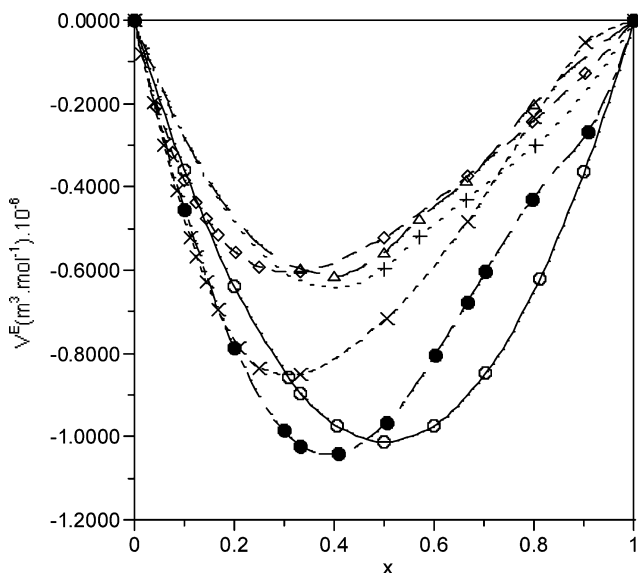

Fig. 7 Refractive indices for 2-butanol-water mixtures *versus* mole fraction, *x*, (○) n_D, (●) n_G and (△) n_L at 298.15 K

Fig. 8 Excess molar volume, V^E, for monoalcohols-water mixtures *versus* mole fraction, x, of monoalcohols, (○) methanol, (●) ethanol, (◇) 1-propanol, (×) 2-propanol, (+) 1-butanol and (△) 2-butanol at 298.15 K

atoms in the alcohol molecule increases—because in these cases volume contraction is less significant.

Accordingly, and taking into account that the Gladstone–Dale relation is the refractive index-predicting equation that best reproduces the experimental values, we have also calculated the differences, Δn_G, between the experimental refractive index values, n_D, and the values obtained with the Gladstone–Dale equation, n_G, i.e.:
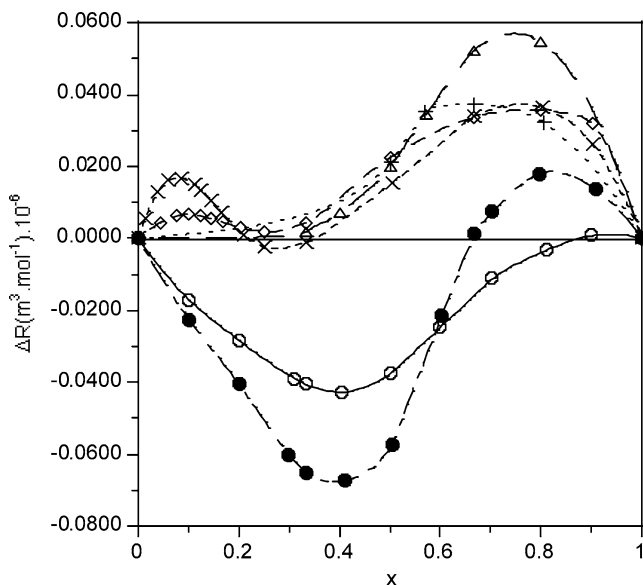
$$\Delta n_G = n_D - n_G \qquad (6)$$

which are also shown in Tables 2–7.

The experimental data have allowed us to calculate the excess molar volume, V^E, for all cases, as well as the molar refraction deviations, ΔR, likewise included in the aforementioned tables.

Figures 8–10 reflect the excess molar volume, V^E, the molar refraction deviations, ΔR, and Δn_G, respectively, as a function of the mole fraction (x).

Table 8 Comparison of the values of V^E_{min} measured and reported in the literature at a temperature of 298.15 K and atmospheric pressure for the indicated mixtures

| Ref.	(x) Methanol + water		(x) Ethanol + water		(x) 1-Propanol + water	
	x	V^E_{min} (m^3·mol^{-1}) × 10^{-6}	x	V^E_{min} (m^3·mol^{-1}) × 10^{-6}	x	V^E_{min} (m^3·mol^{-1}) × 10^{-6}
Exptl	0.5006	−0.97369	0.4087	−1.04150	0.3330	−0.60454
[20]	0.5057	−1.028	0.3906	−1.096	–	–
[21]	0.47727	−1.0014	0.44162	−1.0872	0.39953	−0.6673
[22] (293.15) K	0.5000	−0.97	0.4	−1.13	–	–

Fig. 9 Molar refraction deviations, ΔR, for monoalcohols-water mixtures *versus* mole fraction, x, of monoal-cohols, ($\circ$) methanol, ($\bullet$) ethanol, ($\diamond$) 1-propanol, ($\times$) 2-propanol, ($+$) 1-butanol and ($\triangle$) 2-butanol at 298.15 K

From Fig. 8 it is deduced that for all alcohols the excess molar volume, V^{E}, is always negative. These values in turn decrease in absolute terms as the number of carbon atoms in the chain increases.

Table 9 Variations with temperature of the refractive indices, n_D, of the indicated soluble monoalcohols for each of the specified mole fractions, x

	(x) Methanol + water			(x) Ethanol + water			(x) 1-Propanol + water			(x) 2-Propanol + water		
						x						
	1	0.666	0.333	1	0.666	0.333	1	0.800	0.167	1	0.800	0.167
T/K						n_D						
278.15	1.3326	1.3425	1.3446	1.3670	1.3696	1.3653	1.3906	1.3902	1.3681	1.3836	1.3838	1.3683
283.15	1.3312	1.3411	1.3438	1.3648	1.3675	1.3630	1.3885	1.3880	1.3668	1.3822	1.3815	1.3672
288.15	1.3293	1.3403	1.3419	1.3627	1.3661	1.3618	1.3876	1.3869	1.3662	1.3798	1.3803	1.3666
293.15	1.3281	1.3379	1.3410	1.3612	1.3640	1.3597	1.3853	1.3848	1.3649	1.3782	1.3779	1.3645
298.15	1.3264	1.3368	1.3396	1.3593	1.3618	1.3582	1.3836	1.3833	1.3634	1.3761	1.3762	1.3629
303.15	1.3250	1.3356	1.3382	1.3572	1.3600	1.3564	1.3821	1.3817	1.3621	1.3739	1.3747	1.3613
308.15	1.3231	1.3337	1.3371	1.3559	1.3582	1.3549	1.3793	1.3800	1.3614	1.3726	1.3724	1.3604
313.15	1.3216	1.3329	1.3363	1.3538	1.3561	1.3528	1.3784	1.3776	1.3597	1.3706	1.3701	1.3590
318.15	1.3203	1.3306	1.3344	1.3520	1.3536	1.3511	1.3760	1.3762	1.3590	1.3688	1.3689	1.3576
323.15	1.3185	1.3299	1.3334	1.3500	1.3518	1.3496	1.3745	1.3748	1.3573	1.3666	1.3668	1.3563
328.15	1.3169	1.3279	1.3321	1.3484	1.3502	1.3471	1.3726	1.3731	1.3562	1.3650	1.3647	1.3548
333.15	1.3156	1.3270	1.3308	1.3463	1.3478	1.3465	1.3710	1.3713	1.3551	1.3629	1.3629	1.3534
338.15	1.3129	1.3251	1.3290	1.3446	1.3460	1.3442	1.3690	1.3693	1.3539	1.3610	1.3612	1.3519
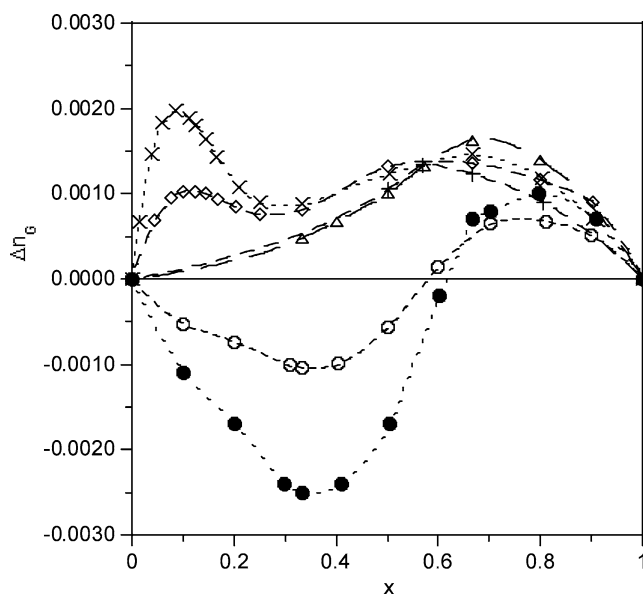
Fig. 10 Deviations in refractive index, Δn_G, for monoalcohols-water mixtures *versus* mole fraction, x, of monoalcohols, (○) methanol, (●) ethanol, (◇) 1-propanol, (×) 2-propanol, (+) 1-butanol and (△) 2-butanol at 298.15 K

The minimum values of V^E (V^E_{min}) are in concordance with those referred to in the literature [20–22] as it can be observe in Table 8.

In Fig. 9, it is particularly significant that all alcohols show a maximum in the molar refraction deviations, ΔR, at $x = 0.8$, except for methanol.

When the minimum values of ΔR obtained in this work were compared with those obtained by [20], the differences observed between them were less than 5%.

Of note in Fig. 10 is the qualitative similarity of the variations in ΔR and Δn_G with respect to the mole fraction.

4. Variation in refractive index with temperature

To study the variation in refractive index with temperature, we have proceeded as follows: for the totally soluble alcohols, measurements were made of the pure alcohol and of two aqueous solutions of each alcohol at different mole fractions which were: $x = 0.33$ and $x = 0.66$ for methanol and ethanol, respectively, and $x = 0.167$ and $x = 0.8$ for 1-propanol and 2-propanol, respectively. For the partially soluble alcohols (1-butanol and 2-butanol) we analyzed the pure alcohol and the mole fraction $x = 0.5$. Finally, since the pentanols are practically insoluble in water, they have been studied in their pure form. The results obtained are shown in Tables 9 and 10.

These results have allowed us to obtain graphic representations of the variations in refractive index with temperature for both pure alcohols and their aqueous solutions. In all cases a linear decrease in refractive index with temperature is observed with a correlation that in all cases exceeds 0.99.

Table 10 Variations with temperature of the refractive indices, n_D, of the indicated partially soluble monoalcohols for each of the specified mole fractions, x

	(x) 1-Butanol + water		(x) 2-Butanol + water		(x) 1-Pent	(x) 2-Pent	(x) 3-Pent
				x			
	1	0.5	1	0.5	1	1	1
T/K				n_D			
278.15	1.4039	1.3984	1.4020	1.3961	1.4156	1.4135	1.4145
283.15	1.4023	1.3969	1.4003	1.3943	1.4141	1.4119	1.4125
288.15	1.4006	1.3955	1.3979	1.3931	1.4119	1.4097	1.4104
293.15	1.3994	1.3934	1.3960	1.3909	1.4107	1.4084	1.4092
298.15	1.3973	1.3920	1.3948	1.3895	1.4087	1.4065	1.4073
303.15	1.3954	1.3904	1.3928	1.3881	1.4067	1.4045	1.4054
308.15	1.3940	1.3886	1.3913	1.3860	1.4055	1.4030	1.4039
313.15	1.3920	1.3874	1.3893	1.3837	1.4033	1.4015	1.4023
318.15	1.3909	1.3851	1.3879	1.3820	1.4018	1.3995	1.4003
323.15	1.3891	1.3837	1.3858	1.3804	1.4002	1.3974	1.3990
328.15	1.3872	1.3825	1.3841	1.3797	1.3983	1.3961	1.3966
333.15	1.3859	1.3802	1.3824	1.3777	1.3967	1.3941	1.3953
338.15	1.3841	1.3789	1.3803	1.3763	1.3949	1.3925	1.3936

5. Conclusions

Determinations of the refractive indices of aqueous mixtures of water$(1 - x)$ + soluble alcohols(x) have shown that in the case of methanol, a peak refractive index is recorded for a mole fraction of $x = 0.333$. Ethanol presents a peak with $x = 0.666$ and 2-propanol has one at $x = 0.8$. In all cases the Gladstone–Dale formula is the refractive index-predicting equation that affords the best results.

Determinations of the excess molar volume, V^E, of these mixtures yielded negative results in all cases—ethanol being the alcohol showing the greatest absolute value for a mole fraction of $x = 0.4$.

Maximum molar refraction deviations, ΔR, were found to correspond to a mole fraction of $x = 0.8$ for all alcohols, except for methanol.

Likewise, calculations have been made of the deviations of the experimental refractive indices with respect to the values calculated from Eq. (6)—excellent qualitative similarity being observed with the molar refraction deviations.

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