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RELATIVE PERMITTIVITIES OF BINARY MIXTURES OF 1-BUTANOL + *n*-ALKANE AT 298.15 K

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Abstract

A previous study on the physical properties of 1-alkanol + *n*-alkane has establised a correlation between dielectric permittivity at 1 GHz and excess molar volumes for all binary systems that were studied. In order to determine whether this behaviour is similar at lower frequencies, relative permittivity was measured at 100 kHz. The refractive index was measured to explore the effects at higher frequencies. Mixtures under study are in particular the systems (1-butanol + *n*-hexane, or *n*-octane, or *n*-decane) at the temperature of 298.15 K and atmospheric pressure, over the entire composition range.

Keywords: 1-alkanol, dielectric permittivity, *n*-alkane

Introduction

The termodynamic properties of alcohol–alkane mixtures have been studied extensively in recent years, due to their application as additives to gasolines and alternative entrainers and coentrainers in modified rectification processes for binary azeotropes distillation.

The aim of this work is to complete our studies on physical properties of binary mixtures of 1-alkanol + *n*-alkane [1–4].

This communication reports relative permittivities at 100 kHz of the mixtures 1-butanol + *n*-alkane at the temperature of 298.15 K and atmospheric pressure, over the entire composition range. From the experimental values, the corresponding increments of relative permittivity were computed. Variable-degree polynomials were fitted to the results. The main aim of this work is to study the permittivity, its deviation from the behaviour defined as ideally (usually called increment) and its relation to other magnitudes, in particular to excess molar volumes and refractive index. In previous works were presented excess molar volumes and refractive index of the mixtures of 1-butanol + *n*-hexane [1] and 1-butanol + *n*-octane [2]; the excess molar volume of 1-butanol + *n*-decane [5] and the dielectric permittivity at 1GHz of the mixtures of 1-butanol + *n*-hexane [6] and 1-butanol + *n*-octane [7].

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Experimental

The *n*-hexane and *n*-octane employed was supplied by Fluka, *n*-decane by Sigma and the 1-butanol by Merck. Their mole fraction purities were: *n*-hexane (>0.995), *n*-octane (>0.995), *n*-decane (>0.99) and 1-butanol (>0.995). The substances were kept in argon (N-55) atmosphere, degassed and stored over molecular sieves (Union Carbide, type 0.4 nm). Mixtures were prepared by mass using a Mettler AE-240 balance, with an accuracy of $\pm 5\cdot 10^{-5}$ g. Precautions were taken during samples preparation, such as weighting liquids in increasing order of volatility and reducing to a minimum the vapour space in the vessels, to avoid losses by evaporation during manipulation and possible errors in mole fraction calculations. A digital controller bath with a temperature stability of $\pm 10^{-2}$ K was used to thermostatize the samples, that remained at the measuring temperature at least thirty minutes.

Relative dielectric permittivity at low frequencies (100 kHz) was determined using a HP4284A precision LCR Meter together the measuring cell HP16452A. A HP16452/60601 test lead cable was used to connect the liquid test fixture and the LCR Meter. This is a 4-terminal BNC cable for the temperature range 253 to 398 K. The cell was thermostatted with a temperature stability of ±0.01 K. The equipment is fully automated and computer controlled through a HP-IB. The technique was described previously [8].

Results and discussion

Density, ρ, refractive index, n_D, and relative permittivity at 100 kHz, ε, of the pure components liquids are listed in Table 1 together with literature values. Relative permittivity, ε, of 1-butanol (1) + *n*-alkane (2) at 298.15 K are presented in Table 2.

The experimental relative permittivity increments $\Delta\varepsilon$ were calculated using the following equation:

$$\Delta Q = Q - \sum_{i=1}^{2} x_i Q_i \qquad (1)$$

where Q is the property under study, ε, ΔQ is the increment $\Delta\varepsilon$, and the corresponding quantities with subscript *i* refer to pure chemicals.

Relative permittivity increments were correlated by means of the Redlich–Kister expression [12] for every binary mixture:

$$\Delta Q = x(1-x)\sum_{p=0}^{M} A_p\,(2x-1)^p \qquad (2)$$

where x is the molar fraction of 1-butanol, A_p a parameter and M the degree of the polynomial expansion. An unweighted least-squares method was used to fit the data [13].

The precision of the dielectric permittivity depends on the magnitude of ε, as indicated by the supplier. However the quality of measurements can be checked in Table 1 where values for pure liquids are shown together with those in the literature. Measurements were also performed for 1-butanol and 1-pentanol between 293 K and 303 K; the results differ from those in the literature by less than 1 per cent in all cases.

Table 1 Comparison of the density ρ, the refractive index n_D, the relative permittivity at 100 kHz, ε, of the pure liquids with the available literature data at 298.15 K

Liquid	ρ/g cm^{-3}		n_D		ε	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1-butanol	0.8058	0.80580[a]	1.39719	1.39716[b]	17.15	17.2[c]
n-hexane	0.6552	0.65510[a]	1.37207	1.37226[d]	1.89	1.8799[d]
n-octane	0.6985	0.69847[a]	1.39510	1.39505[d]	1.95	1.948[d] (20°C)
n-decane	0.72609	0.72606[d]	1.40962	1.40967[d]	2.00	1.989[d] (20°C)

[a][6–7], [b][9], [c][10], [d][11]

Table 2 Relative permittivity at 100 kHz, ε, of 1-butanol (1) + *n*-alkane (2) at 298.15 K

x_1	ε	x_1	ε	x_1	ε
1-butanol (1) + *n*-hexane (2)		1-butanol (1) + *n*-octane (2)		1-butanol (1) + *n*-decane (2)	
0.0690	15.46	0.0489	16.03	0.04912	2.06
0.1467	13.56	0.0994	14.49	0.98350	2.11
0.2706	10.77	0.1997	11.65	0.19649	2.29
0.3243	9.42	0.3000	9.09	0.29728	2.65
0.3531	8.76	0.4045	6.75	0.39987	3.37
0.4160	7.40	0.5088	4.89	0.49833	4.40
0.5141	5.47	0.6044	3.64	0.59617	6.07
0.5290	5.25	0.7102	2.77	0.69821	8.12
0.5554	4.78	0.8076	2.33	0.79992	10.80
0.6819	3.16	0.9046	2.08	0.89841	13.87
0.7284	2.76	0.9359	2.04	0.95031	15.69
0.7797	2.44				
0.8472	2.17				
0.9233	1.99				

Figure 1 shows relative permittivity increments, Δε, for 1-butanol + *n*-hexane, *n*-octane and *n*-decane *vs.* mole fraction of 1-butanol as well as the smoothed curves at the temperature of 298.15 K

Figures 2 and 3 show the experimental values of V_m^E and Δn_D for 1-butanol + *n*-hexane, *n*-octane and *n*-decane, *vs.* mole fraction of 1-butanol as well as the smoothed curves at the temperature of 298.15 K. Values of Δε are negative, while those of Δn_D are negative for 1-butanol + *n*-hexane, *n*-octane and positive with *n*-decane. Values V_m^E and Δn_D show a similar behaviour, both increase with the length of the alkyl chain in the alkane. The values of Δε are negative for all the binary mixtures at all the molar fraction, and the trend is regular, decreasing with the length of the alkyl chain in the alkane.

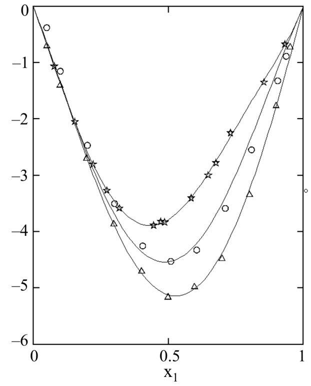

Fig. 1 Relative permittivity increments Δε for ☆ – 1-butanol + *n*-hexane, o – *n*-octane and △ – *n*-decane, *vs.* mole fraction of 1-butanol as well as the smoothed curves at the temperature of 298.15 K

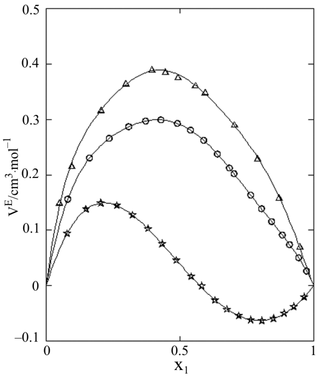

Fig. 2 Excess molar volumes V_m^E for ☆– 1-butanol + *n*-hexane, o – *n*-octane and △ – *n*-decane, *vs.* mole fraction of 1-butanol as well as the smoothed curves at the temperature of 298.15 K

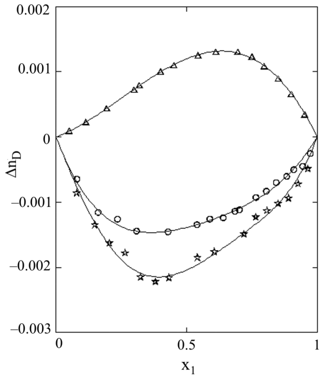

Fig. 3 Changes of refractive index on mixing Δn_D for ☆– 1-butanol + *n*-hexane, o – *n*-octane and △ – *n*-decane, *vs.* mole fraction of 1-butanol as well as the smoothed curves at the temperature of 298.15 K.

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