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Dielectric and refractive index measurements for the systems 1-pentanol + octane, or + dibutyl ether or for dibutyl ether + octane at different temperatures

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ABSTRACT

Relative permittivities, ε_r and refractive indices, n_D, have been measured at (288.15–308.15) K and (293.15–303.15) K, respectively, for the mixtures 1-pentanol + octane, or + dibutyl ether and dibutyl ether + octane. These data have been used, together with density measurements available in the literature, to determine the correlation factor, g_k, for the studied systems according to the Kirkwood–Fröhlich equations. Results show that the existence of cyclic species of 1-pentanol is predominant at low concentrations of this alkanol when is mixed with octane. These species are broken in large extent by the more active molecules of oxaalkane in the dibutyl ether mixture, which is in agreement with calorimetric data. The dibutyl ether + octane system does not show meaningful structure. These conclusions are confirmed by values of the molar polarization and by the temperature dependence of ε_r. The empirical expressions of Lorentz–Lorenz, Wiener, Heller, Gladstone–Dale and Newton correlate well the n_D data.

1. Introduction

Interactions and structural effects in liquid mixtures of non-electrolytes have a marked effect on their thermodynamic properties such as phase equilibria, or excess molar functions, enthalpies (H_m^E), isobaric heat capacities (C_{pm}^E) or volumes (V_m^E). This type of data may be used to investigate orientational and structural effects by means of the application of different theories. The Flory model [1] allows the characterization of deviations from random mixing by studying the concentration dependence of the interaction parameter, X_{12} [2–4]. The Kirkwood–Buff formalism [5,6] is concerned with the study of fluctuations in the number of molecules of each mixture component, and of crossed fluctuations [3,4]. The ERAS model [7] is a useful tool to characterize self-association and solvation effects [8]. The purely physical model DISQUAC [9,10] can describe accurately a whole set of thermodynamic properties such those mentioned above (except V_m^E, as it is a rigid lattice model and $V_m^E = 0$ it is assumed) [8,11], the Kirkwood–Buff integrals [11,12], or concentration–concentration structure factor [13]. Other physical properties which are also important to gain insight into interactional effects and those related to molecular size and shape are viscosity [14,15], refractive index [16,17] or permittivity. Measurements of this magnitude together with n_D and density data can be used to determine the Kirkwood correlation factor, g_k, [18–21] which provides useful information on the mixture structure (see below) [18–21]. In this work, we report ε_r data at (288.15–308.15) K for the systems 1-pentanol + octane, + dibutyl ether, or for dibutyl ether + octane. Data on n_D at (293.15–303.15) K are also given for the mentioned systems. These measurements together with those available in the literature for the density of the systems [22–24] are used to calculate g_k. Derived quantities as polarizability volume [25], or molar refraction [26,27] are also considered to a better understanding of the interactional and structural effects present in the investigated solutions. Data on ε_r and n_D 298.15 K for the 1-pentanol systems are already available in the literature [28–30]. The n_D measurements have been correlated using the following empirical equations: Lorentz–Lorenz, Weiner, Heller, Gladstone–Dale and Newton [31,32].

2. Experimental

2.1. Materials

1-Pentanol and octane were supplied by Fluka, and dibutyl ether by Sigma–Aldrich and were used without further purification. Their purity in mass fractions was ≥0.99, ≥0.99 and ≥0.995, respectively. Values of the physical properties of pure compounds, density, ρ (measured with an Anton Paar DMA 602 vibrating-tube densimeter; uncertainty 5 g cm^{-3}) relative permittivity, ε_r, and refractive

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Table 1
Properties of pure compounds at temperature, T, density, ρ, dielectric permittivity, ε_r, and refractive index, n_D.

Compound	T/K	ρ/cm^3 mol^{-1}		ε_r		n_D	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1-Pentanol	288.15	0.81849	0.8189 [56]	16.334			
	293.15	0.81482	0.8147 [57]	15.736		1.41001	
	298.15	0.81119	0.81083 [29] 0.810883 [40] 0.81090 [30] 0.8116 [56] 0.8107 [58]	15.144	15.04 [28] 15.558 [58]	1.4084	1.40767 [28] 1.4080 [29] 1.49790 [40] 1.4077 [30] 1.4075 [58]
	303.15	0.80750	0.8073 [57]	14.565		1.4065	
	308.15	0.80386	0.8039 [56]	13.998	13.590 [59]		
Dibutyl ether	288.15	0.77260		3.186			
	293.15	0.76827		3.145		1.3991	
	298.15	0.76397	0.76395 [30] 0.764067 [60]	3.106	3.040 [60]	1.3967	1.3965 [30] 1.3969[60]
	303.15	0.75962		3.068		1.3945	
	308.15	0.75531	0.755469 [60]	3.031	2.964 [60]		
Octane	288.15	0.70681		1.975			
	293.15	0.70277	0.70262 [61]	1.968		1.3978	
	298.15	0.69873	0.69850 [29]	1.961	1.96 [28] 1.95 [62]	1.3958	1.3951 [29]
	303.15	0.69470		1.954		1.3930	
	308.15	0.69067		1.947			

indices, n_D, are listed in Table 1. They are in good agreement with the literature values (Table 1).

2.2. Apparatus and procedures

Binary mixtures were prepared by mass in small flasks of about 10 cm^3. All weighings were corrected for buoyancy effects. The error on the final mole fraction is estimated to be lower than ±0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1995 issued by I.U.P.A.C. [33]. All the measurements of the thermophysical properties were carried out under static conditions and atmospheric pressure.

Permittivity measurements were carried out using the Agilent 16452A cell, connected to a precision impedance analyzer model 4294A through a 16048G test lead, both also from Agilent. The frequency range of the impedance analyzer is from 40 Hz to 110 MHz, and that for the measuring cell is from 20 Hz to 30 MHz. Temperature is controlled within ±0.02 K by means of a thermostatic bath LAUDA RE304. Different spaces for the cell can be selected in order to vary the separation between electrodes and, consequently, the volume of the dielectric under study. The calibration procedure led to use a separation of 3 mm, which corresponds to a total volume of the dielectric of 6.8 cm^3. A scheme of the measuring cell and of the experimental arrangement are shown in Fig. 1. Measurements were taken, for all the samples, at the frequencies: 1, 10, 100 kHz and 1, 10 MHz. Calculations were carried out at 1 MHz, as the results are less scattered. In addition, according to specifications from the manufacturer, the relative error is smaller. This configuration leads to an estimated error in the electric capacity of the cell of 0.1% and to an accuracy for the relative permittivity of 3% or less. Calibration was developed with the following pure liquids: water, benzene, cyclohexane, hexane, nonane, decane, dimethyl carbonate, diethyl carbonate, methanol, 1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol in the temperature range (288.15–333.15) K. From the differences between our data and values available in the literature, the uncertainty of ε_r is estimated to be l% or less.

Refractive indices were measured with a refractometer model RMF970 from Bellingham–Stanley. The accuracy of the apparatus is ±0.00002. The measurement method is based on the optical detection of the critical angle at the wavelength of the sodium D line (586.9 nm). The temperature is controlled by Peltier modulus and the temperature stability is ±0.05 K. Prior to the measurement at each temperature, the apparatus must be calibrated with a known reference, usually distilled and deionised water or toluene. The uncertainty of the n_D measurements is 0.02% or better, as it is shown by the differences between our n_D results and those reported in the literature for recommended liquids [34] (methylcyclohexane, *iso*-octane, octane and hexadecane).

3. Results

Table 2 lists, in the temperature range (288.15–308.15) K, values of ε_r and of deviations of this magnitude from the ideal state vs x_1, the mole fraction of the first component for 1-pentanol + octane, or +dibutyl ether, or for dibutyl ether + octane systems. For an ideal

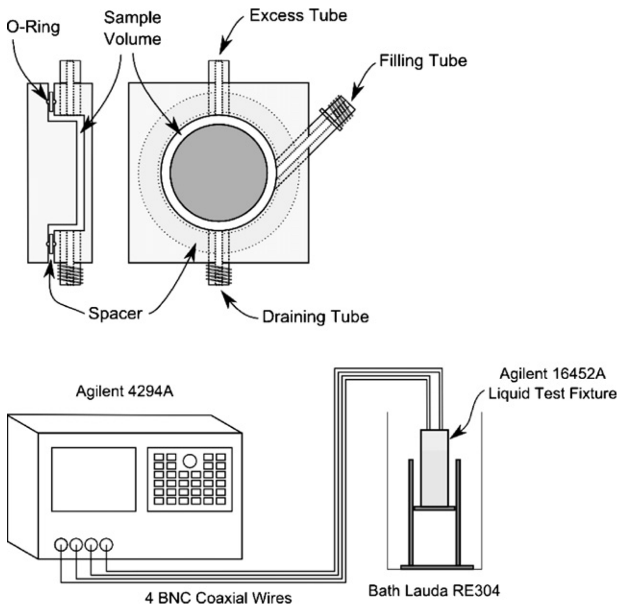

Fig. 1. (a) Scheme of the measuring cell Agilent 16452A. (b) Scheme of the experimental arrangement.