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Refractive indices and static permittivities of systems containing n-hexane or n-heptane and isomeric chlorobutanes

J. Benito [a], H. Guerrero [b], H. Artigas [a], M.C. López [a], C. Lafuente [a,*]

[a] Departamento de Química Física, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain
[b] Department of Biotechnology and Chemical Technology, School of Chemical Technology, Aalto University, 02150 Espoo, Finland

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ABSTRACT

Refractive indices and static permittivities at temperatures of (283.15, 298.15, and 313.15) K and at pressure of 99.0 kPa were determined for the binary mixtures formed by n-hexane or n-heptane with isomeric chlorobutanes. Excess properties were obtained from the experimental values and correlated by means of a Redlich–Kister type equation. In addition, these results were used, together with available density values, to estimate at $T = 298.15$ K the Kirkwood correlation factors of the liquid mixtures. The behavior of this magnitude with composition was also discussed.

1. Introduction

The study of optical and electrical properties of liquid mixtures provides complementary information to that given for the measurements of thermodynamic and transport properties. In this sense, refractive index and the dielectric constant are closely related to the molecular structure of the sample [1], so the variation of these properties with composition and temperature gives information on the mixture structure changes [2,3].

Now and following our study on thermodynamic and transport properties of (alkane + chloroalkane) mixtures [4–6], we present experimental results of refractive index and static permittivity for some binary mixtures containing an alkane: n-hexane or n-heptane and an isomeric chlorobutane: 1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane or 2-chloro-2-methylpropane within the temperature range (283.15 to 313.15) K and at pressure of 0.1 MPa. Combining both sets of results with previously reported density values, the Kirkwood correlation factors were also calculated at $T = 298.15$ K.

There are two previous references involving the refractive index of the mixtures studied here. Smyth et al. [7] reported the refractive indices of the mixture (n-heptane + 1-chlorobutane) at $T = 293.14$ K, on the other hand, there is also a previous paper from our laboratory containing the refractive indices of the mixture (n-hexane + 1-chlorobutane) at $T = 298.15$ K [8], but apart from these works there are no more references in the literature about the refractive index or static permittivity for the systems studied here.

2. Experimental

The information about the liquids used in this work is summarized in table 1. No further purification was considered necessary.

Values of refractive index, n_D, corresponding to 589.3 nm sodium D wavelength, were measured using a high precision automatic refractometer Abbemat-HP from Dr. Kernchen. The temperature of the sample was controlled within ±0.002 K by a built-in Peltier device, and a second Peltier thermostat was used to keep constant the temperature of internal refractometer components in order to increase the accuracy of the measurements. The apparatus was calibrated with deionised, twice-distilled water. The uncertainty of the measurements is $\pm 2 \cdot 10^{-5}$.

Values of static permittivity, ε, were obtained at a frequency of 2 MHz using a capacitive measurement method. The capacitances were measured by means of an Agilent 4263BA precision LCR meter connected to a four terminal Agilent 16452A liquid dielectric test fixture through an Agilent 16048A test leads, the capacitor employed has parallel plates. The estimated uncertainty of permittivity measurements is less than 1%. During all measurements, the temperature of the cell was controlled at ±0.01 K by means of a CT52 Schott-Geräte thermostat.

The pure compound properties taken from previous papers [4,9] at working temperatures together with literature values are collected in table 2 [10–24].

* Corresponding author. Tel.: +34 976762295.
E-mail address: celadi@unizar.es (C. Lafuente).

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TABLE 1
Provenance CAS number and mass fraction purity of the samples studied.

Chemical name	Formula	CAS number	Source	Purification method	Final mass fraction purity	Analysis method
n-Hexane	C_6H_{14}	110-54-3	Sigma–Aldrich	None	0.99	GC
n-Heptane	C_7H_{16}	142-82-5	Sigma–Aldrich	None	0.99	GC
1-Chlorobutane	C_4H_9Cl	109-69-3	Sigma–Aldrich	None	0.99	GC
2-Chlorobutane	C_4H_9Cl	78-86-4	Aldrich	None	0.99	GC
1-Chloro-2-methylpropane	C_4H_9Cl	513-36-0	Fluka	None	0.99	GC
2-Chloro-2-methylpropane	C_4H_9Cl	507-20-0	Aldrich	None	0.99	GC

TABLE 2
Refractive indices, n_D, static permittivities, ε, at working temperatures and at p = 99.0 kPa, dipole moments in the gas phase, μ, Kirkwood correlation factors, g, and comparison of refractive indices and static permittivities with literature values.[a]

Compound	T/K	n_D^{exp}	n_D^{lit}	ε^{exp}	ε^{lit}	μ/D	g
n-Hexane	283.15	1.380496 [4]	1.38061 [10] 1.38097 [11]	1.905	1.90128 [18] 1.9010 [19]		
	298.15	1.372227	1.37234 [10] 1.37226 [12]	1.892	1.87882 [18] 1.89 [20]	0 [24]	
	313.15	1.363914 [4]	1.36417 [11] 1.36383 [12]	1.873	1.8562 [19] 1.879 [21]		
n-Heptane	283.15	1.392903 [4]	1.39297 [10]	1.943	1.9349 [19]		
	298.15	1.385204 [4]	1.38515 [10] 1.38512 [12]	1.923	1.9133 [19] 1.93 [22]	0 [24]	
	313.15	1.377350 [4]	1.37726 [12] 1.3776 [13]	1.902	1.8917 [19]		
1-Chlorobutane	283.15	1.407504 [9]		7.552	7.581 [23]		
	298.15	1.399500 [9]	1.399530 [14] 1.39939 [15]	7.157	7.091 [23]	2.05 [24]	0.92
	313.15	1.391309 [9]		6.757	6.583 [23]		
2-Chlorobutane	283.15	1.402257 [9]		9.323	8.929 [23]		
	298.15	1.394036 [9]	1.39405 [15] 1.3941 [16]	8.652	8.393 [23]	2.04 [24]	1.21
	313.15	1.385618 [9]		8.070	7.918 [23]		
1-Chloro-2-methylpropane	283.15	1.403542 [9]		7.472	7.236 [23]		
	298.15	1.395285 [9]	1.3951 [17]	7.074	6.931 [23]	2.00 [24]	0.97
	313.15	1.386827 [9]		6.657	6.636 [23]		
2-Chloro-2-methylpropane	283.15	1.391153 [9]		10.429	10.112 [23]		
	298.15	1.382254 [9]	1.38216 [15] 1.3828 [17]	9.670	9.429 [23]	2.13 [24]	1.34
	313.15	1.373115 [9]		8.952	8.811 [23]		

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.5 kPa, and the combined expanded uncertainties U_c are $U_c(n_D) = 2 \cdot 10^{-5}$ and $U_c(\varepsilon)$ = 1% with 0.95 level of confidence ($k \approx 2$).

As table 2 shows the agreement between experimental and literature refractive index values is good with the average difference lower than 0.00015. On the other hand, the temperature behavior of refractive index observed for n-hexane is similar to that reported by other authors [11,12,25]. Finally, our temperature coefficient for n-heptane is in accordance with the value calculated from refractive indices given in TRC Tables [13]. With respect to permittivity, the average difference between experimental and literature values is around 1%. The accord between our permittivity values for n-hexane and those of Stokes [18] is good, particularly at low temperature. On the other hand, our permittivity results for the n-hexane and n-heptane are also in good agreement, deviations lower than 1%, with those of Scaife and Lyons [19] who measured the permittivity of some n-alkanes over a wide range of temperatures and pressures (see table 3).

3. Results and discussion

Values of the refractive index and static permittivity of the binary mixtures studied at working temperatures can be found in the supplementary material.

Reis et al. [26] have obtained an expression to evaluate the refractive index of thermodynamically ideal liquid mixtures. According to this formulation, it is possible to calculate the excess refractive index, n_D^E, of a given liquid mixture using the following equations:

$$n_D^{id} = \left[\phi_1 \cdot n_{D,1}^2 + \phi_2 \cdot n_{D,2}^2\right]^{1/2}, \quad (1)$$

$$n_D^E = n_D - n_D^{id}, \quad (2)$$

where n_D is the refractive index of the mixture, ϕ_i and $n_{D,i}$ are the volume fraction referred to the unmixed state and the refractive index of component i, respectively. The values of excess refractive indices are graphically represented in figures 1 and 2 and they are also collected in the supplementary material.

On the other hand, it has been demonstrated that the static permittivity of a thermodynamically ideal liquid mixture is given by the values of the volume-fraction-weighted average of the pure component static permittivity [27]. So the excess static permittivity, ε^E, can be estimated by means of the following equations:

$$\varepsilon^E = \varepsilon - \varepsilon^{id}, \quad (3)$$

$$\varepsilon^{id} = \phi_1 \cdot \varepsilon_1 + \phi_2 \cdot \varepsilon_2, \quad (4)$$

where ε is the static permittivity of the mixture, ϕ_i and $\varepsilon_{,i}$ are the volume fraction referred to the unmixed state and the static permittivity of component i, respectively. The values of excess static permittivity are represented in figures 3 and 4 and they are also given in the supplementary material.

Excess properties have been correlated using the Redlich–Kister polynomical expansion [28] in terms of volume fractions:

$$Y^E = \phi_1 \cdot \phi_2 \cdot \sum_{i=0} A_i (\phi_1 - \phi_2)^i \quad (5)$$

where $Y^E = n_D^E$ or ε^E, A_i are adjustable parameters and ϕ_i is volume fractions of component i. Values of the fitting parameters together with standard deviations, σ (Y^E), are gathered in table 2.

Excess refractive indices for all the systems are negative over the entire range of composition. For a given alkane, there are clear differences among the isomeric chlorobutanes, the mixtures