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Refractive indices and their related properties for several binary mixtures containing cyclic ketones and chloroalkanes

Dana Dragoescu

"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202, 060021 Bucharest, Romania

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ABSTRACT

Experimental refractive index data for eleven binary systems of cyclopentanone + 1,2-dichloroethane, +1,3-dichloropropane, +1,4-dichlorobutane, +trichloromethane, +1,1,1-trichloroethane and cyclohexanone + 1-chlorobutane, +1,2-dichloroethane, +1,3-dichloropropane, +1,4-dichlorobutane, +trichloromethane, and +1,1,1-trichloroethane, at $T = 298.15$ K and atmospheric pressure, over the entire mole fraction range are reported. The excess refractive index, n_D^E, molar refraction, R, and excess molar refraction, R^E, were calculated from the experimental data. The ability of different theoretical (n_D, ρ) mixing rules (Lorentz–Lorenz, Gladstone–Dale, Arago–Biot, Edwards and Eykman) to predict the refractive indices are evaluated. The experimental density data of the studied mixtures, previously measured, were used to calculate the partial and apparent volumetric properties at infinite dilution. Moreover, from these density data, the surface tensions and the surface tension deviations for mixtures were predicted. The excess molar quantities have evidenced intermolecular interactions between the components of mixtures.

1. Introduction

Knowledge of thermophysical properties of organic binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in the design process (flow, mass transfer, or heat transfer calculations) of many chemical and industrial processes.

The information about thermodynamic properties of liquid mixtures containing ketones and chloroalkanes, and their dependence on compositions and temperature are important data for their applications in the separation fields.

The cyclic ketones and chloroalkanes have important applications in the chemical industry as intermediates or as final products, being used in the synthesis of pharmaceuticals, in agricultural chemistry, and as solvents for polymers. The mixtures of cycloketones and chloroalkanes are interesting also from the theoretical point of view, because of the inter- and intra-molecular effects, since they present important deviations from ideal behavior.

As a continuation of our previous research on thermodynamic and optical behavior of linear and cyclic ketone + chloroalkane binary mixtures [1–3], this paper presents new refractive index experimental data for eleven binary systems of cyclopentanone + 1,2-dichloroethane, +1,3-dichloropropane, +1,4-dichlorobutane, +trichloromethane, +1,1,1-trichloroethane and cyclohexanone + 1-chlorobutane, +1,2-dichloroethane, +1,3-dichloropropane, +1,4-dichlorobutane, +trichloromethane, and +1,1,1-trichloroethane, at $T = 298.15$ K and atmospheric pressure, over the entire mole fraction range.

Refractive index and density measurements are expected to enlighten both solvent–solvent and solute–solvent interactions. The excess properties of binary liquid mixtures are of considerable importance in the fundamental understanding and interpreting of nature of the interactions between unlike molecules.

A survey of the specific literature indicates that for the studied mixtures, no refractive index data have been reported at the working temperature. Instead, there are available some data for other systems from the same classes. Refractive property measurements for (cyclopentanone + 1-chlorobutane and cyclopentanone/cyclohexanone + 1,1,2,2-tetrachloroethane) mixtures have been recently reported [4]. The experimental data of volumetric properties for (cyclohexanone + 1,2-dichloroethane and +1,1,2,2-tetrachloroethane) mixtures at different temperatures have been presented by some authors [5]. Also, for binary mixtures of cyclohexanone with (dichloromethane, trichloromethane, 1,2-dichloroethane, trichloroethene and cyclohexane), data on refractive indices and relative permittivities, at $T = 303.15$ K were published [6].

The refractive index of a liquid at the sodium D line light, n_D, being a property comfortable to measure with proper accuracy, it has been often associated with other electrical and thermophysical properties, as dielectric permittivity, surface tension and density [7,8]. Some details concerning this aspect are developed further in Section 3, Results and discussions.

The measurements of refractive indices provide precious information on the interactions determined only by dispersive forces [9,10] as

E-mail address: ddragoescu@chimfiz.icf.ro.

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the refractive index values are closer associated to the mean polarizability, P, of the liquid, by the molar refraction, R:

$$R = V_m\left(n_D{}^2-1\right)/\left(n_D{}^2+2\right) \quad (1)$$

$$R = N_A P/3\varepsilon_0 \quad (2)$$

where: N_A is Avogadro's number, ε_0 is the vacuum permittivity, and V_m is the molar volume.

The polarizability represents the relative tendency of a system of electric charges to become polarized in the presence of an external electric field (such as the field generated by sodium D line light in optical region). Polarizability allows understanding better the interactions between non-polar atoms or molecules and other electrically charged species, such as ions or polar molecules with dipole moments.

From the measured data of refractive index, the excess refractive indices, n_D^E, were calculated. Also, using the values of refractive index, molar refractions, R, and excess molar refractions, R^E was calculated with Lorentz–Lorenz equation [11].

For calculation of the excess refractive indices n_D^E, succeeding the formulation of Reis et al. [12] we used the following equations:

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

$$n_D{}^{id} = \left[\phi_1 n^2_{D,1} + \phi_2 n^2_{D,2}\right]^{1/2} = \left[\phi_1 n^2_{D,1} + (1-\phi_1) n^2_{D,2}\right]^{1/2} \quad (4)$$

where: n_D is the refractive index of the mixture, and $n_{D,1}$ is the refractive index of component i, respectively; ϕ_i is the volume fractions of the pure component i, calculated as: $\phi_i = \omega_i\rho_{ij}/\rho_i$, in which $\omega_i = \frac{x_i M_i}{\sum x_i M_i}$.

Thus, the excess refractive indices n_D^E was calculated as:

$$n_D{}^E = n_D - \left[\phi_1 n^2{}_{D,1} + \phi_2 n^2{}_{D,2}\right]^{1/2}. \quad (5)$$

Taking into account Eq. (1), the molar refraction was evaluated by the expression:

$$R = \frac{n_D^2-1}{n_D^2+1}\cdot\frac{x_1M_1 + x_2M_2}{\rho} \quad (6)$$

and the excess molar refraction was calculated by:

$$R^E = R - x_1R_1 - x_2R_2. \quad (7)$$

Consequently, the excess molar refraction, R^E, was estimated using the relation:

$$R^E = \frac{\sum_i x_iM_i}{\rho}\frac{n_D{}^2-1}{n_D{}^2+2} - \sum_i x_i\frac{M_i}{\rho_i}\frac{n_{D,i}^2-1}{n_{D,i}^2+2} \quad (8)$$

where: M_i represents the molar mass, x_i represents the mole fraction, ρ_i and $n_{D,i}$ represent the density and the refractive index of pure component i, ρ and n_D represent the density and the refractive index of the mixtures and R_1 and R_2 are the molar refractions of the two pure components.

In the present paper, from the experimental density data and the excess molar volume, V^E, and the molar volumes of pure compounds, V_1^* and V_2^* taken from [2,3], the partial molar volumes at infinite dilution, were calculated. The partial properties at infinite dilution are of interest since at the limit of infinite dilution, the solute–solute interaction disappears and only the solute–solvent interactions are present. In literature [5], the volumetric properties of cyclohexanone + 1,2-dichloroethane mixtures have been recently reported at different temperatures from 288.15 to 313.15 K.

Additionally, on the base of our previously measured density data, the surface tension and the surface tension deviations were predicted using well-known equations [13,14].

Table 1
Material description.

Chemical name	Source	Mass fraction purity	Purification method
Cyclopentanone	Aldrich	>0.99	None
Cyclohexanone	Aldrich	>0.998	None
1-Chlorobutane	Aldrich	≥0.996	None
1,2-Dichloroethane	Aldrich	≥0.998	None
1,3-Dichloropropane	Aldrich	>0.998	None
1,4-Dichlorobutane	Merck	≥0.98	None
Trichloromethane	Aldrich	≥0.99	None
1,1,1-Trichloroethane	Merck	≥0.99	None

2. Experimental

2.1. Materials

The substances were commercial products from Aldrich and Merck, of the first grade purity. The quality of the compounds was verified by gas chromatography and it was better than declared. The commercial sources and purity levels of the compounds used in this work are shown in Table 1. The liquids were store over 4A molecular sieves, therefore dried by water traces and used without other further purification procedure.

2.2. Apparatus and procedure

The binary mixtures were prepared by mixing the known masses of the pure liquids in airtight narrow-mouth grounded glass stopped bottle, taking the precaution to minimize the evaporation losses, and weighed using a GH-252 (A&D Japan) electronic balance with a precision of $\pm 10^{-7}$ kg. The experimental uncertainty in mole fractions was estimated to be less than ± 0.0002.

The refractive indices of the pure compounds and their mixtures were carried out at the 589.3 nm wavelength of the sodium D line, using a digital automatic refractometer Abbemat RXA 170 (Anton Paar-Austria) with uncertainty of ± 0.00001 for refractive index. The temperature of the Safire prism was controlled by a Peltier element to within ± 0.01 K. The apparatus was calibrated with dry air and distilled and deionized ultra pure water at atmospheric pressure, according to the instrument operating instructions.

For each measurement of refractive index, we made at least three independent readings for the same sample at working temperature, to obtain the reproducibility of the measurements; hence, its averaged value as one experimental point is reported in the paper.

The density measurements of the pure solvents and of the mixtures previously reported [2,3] were performed by means of an Anton Paar DMA 4500 densimeter with a precision of ± 0.05 kg·m^{-3}. The DMA cell was calibrated with dry air and ultra pure water at atmospheric pressure. The sample thermostating was controlled to ± 0.01 K.

Table 2
Comparison of measured refractive index with literature values for pure components at $T = 298.15$ K.[a]

Component	n_D	
	Experimental	Literature
Cyclopentanone	1.43471	1.4349 [4]; 1.4347 [15]
Cyclohexanone	1.44822	1.4481 [4]; 1.4480 [16]
1-Chlorobutane	1.39962	1.3999 [17]; 1.39950 [18]; 1.39953 [19]
1,2-Dichloroethane	1.44204	1.44206 [19];1.44216 [20]
1,3-Dichloropropane	1.44612	1.4459 [1]; 1.44617 [19]; 1.4460 [21]
1,4-Dichlorobutane	1.45213	1.4520 [1]; 1.45224 [19]; 1.4518 [21]
Trichloromethane	1.44207	1.44293 [18]; 1.44209 [19]; 1.4430 [22]
1,1,1-Trichloroethane	1.43455	1.43492 [19];1.4357 [23]; 1.43588 [24]

[a] $u(T) = \pm 0.01$ K and $u(n_D) = \pm 0.00001$.