Refractive Properties of Binary Mixtures Formed by an Isomer of Chlorobutane and Butyl Ethyl Ether

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Abstract: Refractive indices of the binary mixtures containing an isomer of chlorobutane (1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane, or 2-methyl-2-chloropropane) and butyl ethyl ether have been measured at seven temperatures from T = 283.15 to 313.15 K From these data refractive index deviations were calculated and correlated with a Redlich-Kister polynomial expansion. The refractive index deviations were found positive. Finally, from these refractive indices both densities and surface tensions of the studied systems were predicted and compared with previously reported values.

Keywords: Butyl ethyl ether, Isomeric chlorobutane, Predicted properties, Refractive index.

1. INTRODUCTION

The density together with the refractive index are the thermophysical properties of liquid mixtures more closely related with the structural changes that take place in the mixing process. So, the study of refractive index is adequate to obtain this kind of information [1-4].

Here, we present refractive indices for the mixtures containing an isomeric chlorobutane (1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane, or 2-methyl-2-chloropropane) and butyl ethyl ether in the temperature range 283.15 K - 313.15 K along with the calculated refractive index deviations. As far as we know there are no references for refractive index studies on the systems involved in this work.

Moreover, we have used these experimental results together with previously reported density and surface tension results [5,6] to check some relations between thermophysical properties like refractive index, density and surface tension.

2. EXPERIMENTAL

The chemicals used were 1-chlorobutane, 2-chlorobutane, 2-methyl-2-chloropropane and butyl ethyll ether (> 0.99 in mass fraction) purchased from Aldrich and 2-methyl-1-chloropropane (> 0.99 in mass fraction) obtained from Fluka. The liquids were used without additional purification.

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The refractive indices at 589.3 nm were measured using a high precision automatic refractometer Abbemat-HP from Dr. Kernchen. The liquid sample was placed on the polished surface of a prism made of synthetic sapphire. A cone shaped yellow light beam of sodium D wavelength illuminated the sample from its bottom side under different angles of reflection. This reflected light has the advantage that both colour and cloudiness of the sample do not significantly influence the measurement. The temperature of both the sample and the prism was controlled within ± 0.002 K by a built-in Peltier device. On the other hand, a second Peltier thermostat is used to keep constant the temperature of internal components of refractometer in order to increase the accuracy of the measurements. The apparatus was calibrated with deionized double-distilled water. The corresponding uncertainty is ± 5×10^{-6}.

All the mixtures were prepared by mass, making use of a Mettler H20T balance. The uncertainty of mass determinations is ± $1\cdot10^{-5}$ g. The maximum estimated error in the volume fraction is ± 1×10^{-4}.

In Table **1** the experimental refractive indices of pure compounds at working temperatures together with literature values at T = 298.15K [7-9] are collected.

3. RESULTS AND DISCUSSION

The measured refractive indices of the binary mixtures at working temperatures can be found in the supplementary material. Refractive index deviations, Δn_D, were calculated form refractive indices following the suggestions of Fialkov and Fenerly [10] and Fialkov [11] by using the equation:

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Table 1: Refractive Indices of Pure Compounds at Working Temperatures and Comparison with Literature Values at *T* = 298.15 K

T / K	n_D^{exp}	n_D^{lit}	*T* / K	n_D^{exp}	n_D^{lit}
1-Chlorobutane			2-Chlorobutane		
283.15	1.407504		283.15	1.402257	
288.15	1.404813		288.15	1.399533	
293.15	1.402123		293.15	1.396800	
298.15	1.399500	1.399300[a]	298.15	1.394036	1.3941[b]
303.15	1.396716		303.15	1.391249	
308.15	1.393949		308.15	1.388444	
313.15	1.391309		313.15	1.385618	
1-Chloro-2-methylpropane			2-Chloro-2-methylpropane		
283.15	1.403542		283.15	1.391153	
288.15	1.400797		288.15	1.388209	
293.15	1.398017		293.15	1.385217	
298.15	1.395285	1.3951[c]	298.15	1.382254	1.3828[c]
303.15	1.392451		303.15	1.379211	
308.15	1.389626		308.15	1.376189	
313.15	1.386827		313.15	1.373115	
Butyl ethyl ether					
283.15	1.387223				
288.15	1.384638				
293.15	1.382037				
298.15	1.379431	1.3793[c]			
303.15	1.376761				
308.15	1.374063				
313.15	1.371409				

[a]Reference [7]; [b]reference [8]; [c]reference [9].

$$\Delta n_D = n_D - \sum_i \phi_i n_{D,i} \quad (1)$$

where n_D is the refractive index of the mixture, ϕ_i and $n_{D,i}$ are respectively the volume fraction referred to the unmixed state and the refractive index of component *i*. The calculated values of refractive index deviations are graphically represented in Figures **1-4** and they are also collected in the supplementary material.

Refractive index deviations were satisfactorily correlated using the Redlich-Kister equation [12] in terms of volume fractions:

$$\Delta n_D = \phi_1 \phi_2 \sum_{i=0}^{m} A_i (\phi_1 - \phi_2)^i \quad (2)$$

where A_i are adjustable parameters and ϕ_i is the volume fractions of component *i*. Values of the fitting parameters along with standard deviations, $\sigma(\Delta n_D)$, are collected in Table **2**.

The refractive index deviations for all the investigated systems are positive over the whole composition and temperature ranges. Δn_D values are very small for all the systems, the corresponding maximum values are located around a volume fraction $\phi_1 \approx 0.5$, except for the system containing 2-chloro-2-methylpropane where the maxima are located at lower chloroalkane concentrations ($\phi_1 \approx 0.4$). The refractive index deviations become less positive when temperature rises in all the systems, except again for the mixture containing 2-chloro-2-methylpropane where the temperature effect is opposite and more relevant being the Δn_D values more positive at higher temperatures. At *T* = 298.15 K, refractive index deviations increase following the sequence: 2-chloro-2-

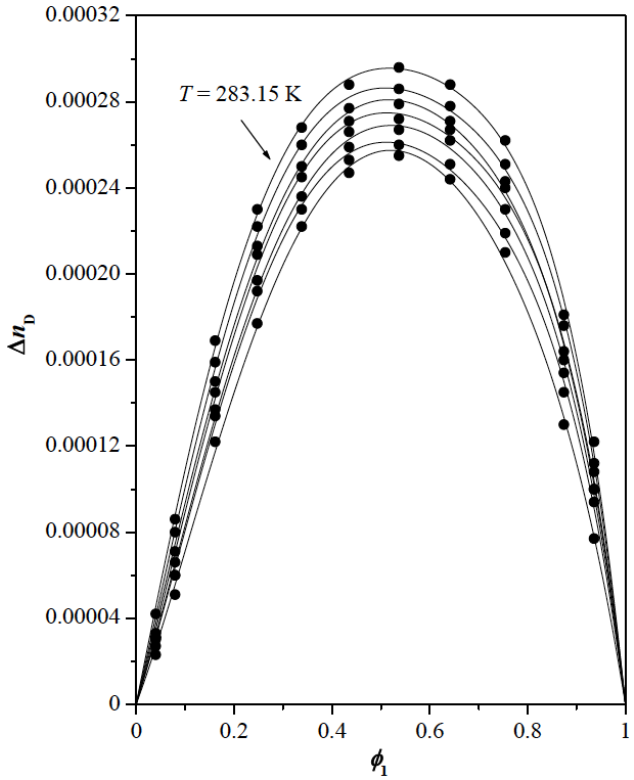

Figure 1: Refractive index deviations, Δn_D, for the binary mixture 1-Chlorobutane (1) + butyl ethyl ether (2) as a function of volume fraction, ϕ_1: (●) experimental data; (——) correlation equation.

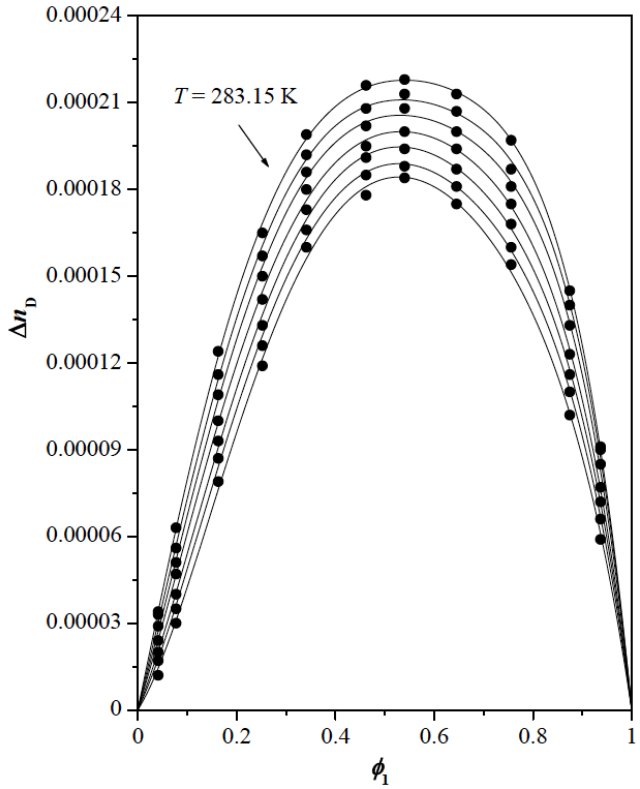

Figure 2: Refractive index deviations, Δn_D, for the binary mixture 2-Chlorobutane (1) + butyl ethyl ether (2) as a function of volume fraction, ϕ_1: (●) experimental data; (——) correlation equation.

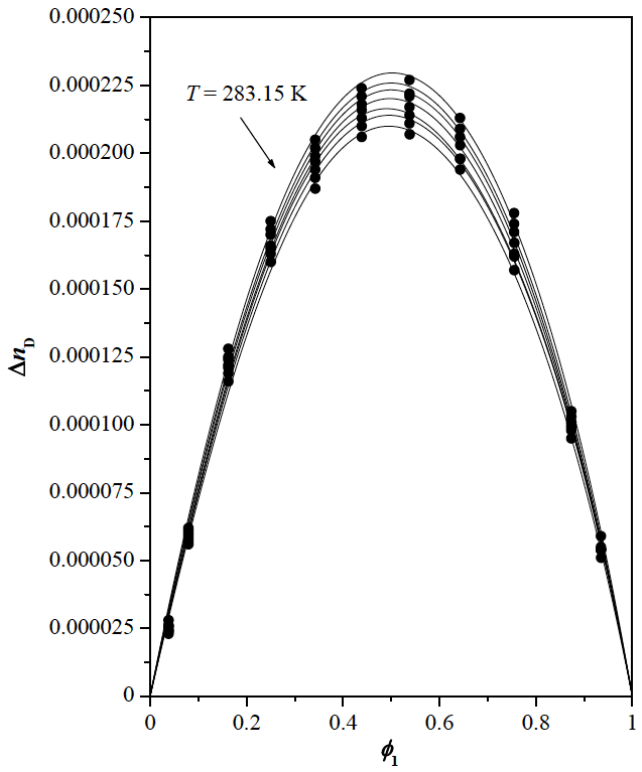

Figure 3: Refractive index deviations, Δn_D, for the binary mixture 1-Chloro-2-methylpropane (1) + butyl ethyl ether (2) as a function of volume fraction, ϕ_1: (●) experimental data; (——) correlation equation.

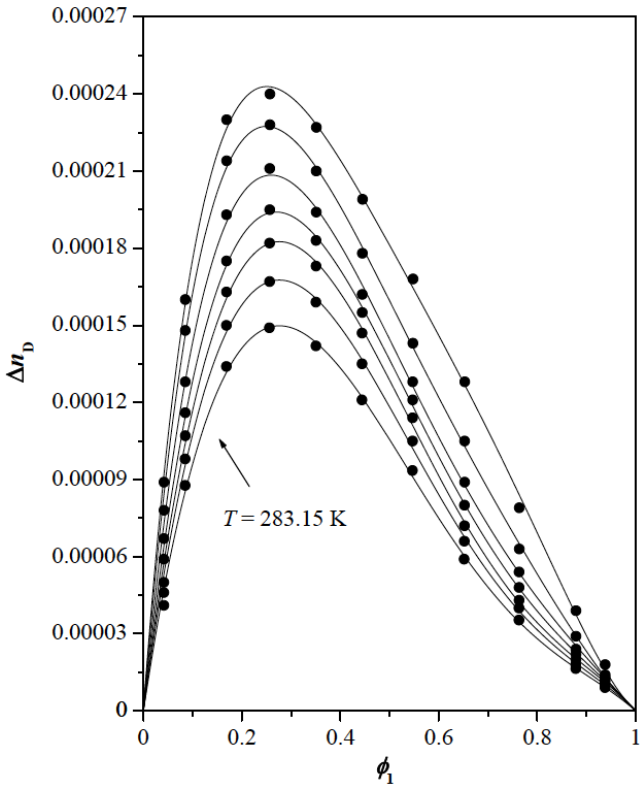

Figure 4: Refractive index deviations, Δn_D, for the binary mixture 2-Chloro-2-methylpropane (1) + butyl ethyl ether (2) as a function of volume fraction, ϕ_1: (●) experimental data; (——) correlation equation.

Table 2: Parameters and Standard Deviations of the Redlich Kister Equation

T / K	A_0	A_1	A_2	A_3	$\sigma(\Delta n_D)$
1-Chlorobutane (1) + butyl ethyl ether (2)					
283.15	0.001182	0.000046	0.000505	0.000502	0.000004
288.15	0.001145	0.000028	0.000428	0.000543	0.000004
293.15	0.001123	0.000063	0.000297	0.000442	0.000005
298.15	0.001095	0.000050	0.000419	0.000651	0.000004
303.15	0.001071	0.000070	0.000298	0.000567	0.000005
308.15	0.001045	0.000040	0.000180	0.000454	0.000004
313.15	0.001028	0.000084	-0.000016	0.000314	0.000004
2-Chlorobutane (1) + butyl ethyl ether (2)					
283.15	0.000869	0.000065	0.000428	0.000402	0.000002
288.15	0.000842	0.000059	0.000375	0.000436	0.000003
293.15	0.000821	0.000060	0.000305	0.000435	0.000002
298.15	0.000798	0.000073	0.000215	0.000388	0.000002
303.15	0.000777	0.000072	0.000131	0.000399	0.000002
308.15	0.000754	0.000075	0.000067	0.000382	0.000002
313.15	0.000735	0.000085	-0.000021	0.000354	0.000003
1-Chloro-2-methylpropane (1) + butyl ethyl ether (2)					
283.15	0.000918	0.000007	0.000038	0.000067	0.000004
288.15	0.000904	0.000001	0.000019	0.000069	0.000004
293.15	0.000894	0.000002	0.000011	0.000056	0.000004
298.15	0.000881	-0.000008	0.000006	0.000083	0.000003
303.15	0.000866	-0.000030	0.000013	0.000121	0.000004
308.15	0.000856	-0.000014	0.000015	0.000101	0.000004
313.15	0.000840	-0.000016	-0.000003	0.000088	0.000004
2-Chloro-2-methylpropane (1) + butyl ethyl ether (2)					
283.15	0.000422	-0.000611	0.000296	0.000063	0.000003
288.15	0.000473	-0.000682	0.000330	0.000065	0.000003
293.15	0.000515	-0.000744	0.000360	0.000077	0.000004
298.15	0.000546	-0.000757	0.000422	-0.000008	0.000003
303.15	0.000578	-0.000775	0.000520	-0.000119	0.000003
308.15	0.000638	-0.000762	0.000614	-0.000322	0.000003
313.15	0.000725	-0.000691	0.000646	-0.000508	0.000003

methylpropane < 2-chlorobutane < 1-chloro-2-methyl-propane < 1-chlorobutane, although at lower chloroalkane volume fractions the Δn_D values for 2-chloro-2-methylpropane are the biggest. It can be underlined that the behaviour of refractive index deviation is opposite to that of the excess volumes [5,13].

It is well known that the refractive index behaviour is mainly related with structural effects. For our systems the small increase of refractive index, slightly positive Δn_D values, can be due to a decrease of the intermolecular distance caused by the interstitial accommodation.

4. DENSITY AND SURFACE TENSION PREDICTION

The density and refractive index of a liquid mixture can be linked through a refractive index mixing rule, which for a binary mixture is:

$$\left(\frac{1}{\rho}\right) f\left(n_D\right) = \left(\frac{w_1}{\rho_1}\right) f\left(n_{D,1}\right) + \left(\frac{w_2}{\rho_2}\right) f\left(n_{D,2}\right) \quad (3)$$

where w_i is the weight fraction of component *i* and $f\left(n_D\right)$ denotes a particular function of the refractive index.

We have employed the Gladstone-Dale mixing rule [15]:

$$f\left(n_D\right) = n_D - 1 \quad (4)$$

Taking into account these last equations, the densities can be obtained from refractive index values:

$$\rho = \frac{\left(n_D - 1\right)}{\left(\frac{w_1}{\rho_1}\right)\left(n_{D,1} - 1\right) + \left(\frac{w_2}{\rho_2}\right)\left(n_{D,2} - 1\right)} \quad (5)$$

The relative root mean square deviations, *RMSDr*, between experimental and predicted density values are given in Table **3**, the definition for *RMSDr* of a given property *Y* is:

$$RMSDr\ (\%) = 100\left(\frac{1}{n}\sum_{i=1}^{n}\left(\frac{Y_i^{\exp} - Y_i^{pred}}{Y_i^{\exp}}\right)^2\right)^{1/2} \quad (6)$$

being *n* the number of experimental data.

Table 3: Relative Root Mean Square Deviations, $RMSD_r$, for the Prediction of Densities, ρ, and Surface Tensions, σ, from Refractive Indices, n_D

T / K	$RMSD_r$ (ρ) / %	$RMSD_r$ (σ) / %
1-Chlorobutane (1) + butyl ethyl ether (2)		
283.15	0.028	0.59
288.15	0.028	0.52
293.15	0.028	0.45
298.15	0.027	0.36
303.15	0.028	0.32
308.15	0.028	0.24
313.15	0.028	0.22
2-Chlorobutane (1) + butyl ethyl ether (2)		
283.15	0.044	0.19
288.15	0.044	0.21
293.15	0.043	0.23
298.15	0.043	0.15
303.15	0.043	0.16
308.15	0.043	0.18
313.15	0.042	0.27
1-Chloro-2-methylpropane (1) + butyl ethyl ether (2)		
283.15	0.020	0.35
288.15	0.024	0.50
293.15	0.019	0.34
298.15	0.018	0.29
303.15	0.017	0.55
308.15	0.016	0.59
313.15	0.015	0.46
2-Chloro-2-methylpropane (1) + butyl ethyl ether (2)		
283.15	0.021	0.11
288.15	0.021	0.12
293.15	0.022	0.20
298.15	0.023	0.26
303.15	0.022	0.26
308.15	0.021	0.30
313.15	0.020	0.32

Taking into account the *RMSDr* values the prediction of densities from refractive indices can be considered satisfactory. The best predictions are for the densities of the mixtures containing 1-chloro-2-methylpropane or 2-chloro-2-methylpropane

On the other hand, the surface tension can be calculated from refractive index [16,17] combining the Sudgen equation [18] that relates surface tension and density of a liquid trough the parachor with the concept of molar refractivity [19] that is defined from refractive index, molar mass and density.

Sudgen equation:

$$\sigma_i^{1/4} = \frac{P_i \rho_i}{M_i} \tag{7}$$

where σ_i, ρ_i, and M_i are, respectively, surface tension, density, and molar mass of the liquid, while constant P_i is the parachor.

Molar refractivity:

$$R_i = \left(\frac{n_{D,i}^2 - 1}{n_{D,i}^2 + 2} \right) \cdot \frac{M_i}{\rho_i} \tag{8}$$

Finally, assuming the additivity rules for parachor, *P*, and molar refractivity, *R*, of the liquid mixture:

$$\sigma^{1/4} = \left(\frac{\sum_i x_i P_i}{\sum_i x_i R_i} \right) \cdot \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \tag{9}$$

In Table **3** the relative root mean square deviations, *RMSDr*, between experimental and predicted surface tension values are also shown.

With respect to surface tension predictions form refractive indices, they can also be considered satisfactory. The best results are obtained for the mixtures containing 2-chlorobutane and 2-chloro-2-methylpropane. For these mixtures the deviation between experimental and predicted values are near to the uncertainty of the surface tension measurements.

5. CONCLUSIONS

This work reports the measurement of the refractive indices of the binary mixtures containing: 1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane, or 2-methyl-2-chloropropane and butyl ethyl ether, over the entire composition range within the temperature interval (283.15 to 313.15) K. From these experimental data refractive index deviations of the mixtures were calculated and correlated using a Redlich-Kister polynomial expansion. The refractive index deviation values were positive for all the systems investigated. Furthermore, both the densities and surface tensions were satisfactorily predicted form refractive index.

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SUPPLEMENTAL MATERIALS

The supplemental materials can be downloaded from the journal website along with the article.

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