Densities and Refractive Indices of 1-Hexanol + n-Pentadecane Binary System at Temperatures from (293.15 to 323.15) K

ADRIAN CRISCIU[1], CATINCA SECUIANU[1,2]*, VIOREL FEROIU[1]*

[1] University Politehnica of Bucharest, Department of Inorganic Chemistry, Physical Chemistry & Electrochemistry,1-7 Gh. Polizu Str., 011061, Bucharest, Romania

[2]Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ London, United Kingdom

Densities and refractive indices of the 1-hexanol + n-pentadecane binary system have been measured at T = (293.15, 298.15, 303.15, 313.15, and 323.15 K) and atmospheric pressure, over the whole composition range. Different theoretical (n-ρ) mixing rules were tested for the system studied. The excess molar volumes (V^E), the molar refraction (R), and the corresponding deviations of the 1-hexanol + n-pentadecane system have been calculated. The deviations of the respective excess properties have been also evaluated and correlated with the consistent 3-parameters Redlich-Kister equation with good results.

Keywords: densities, refractive indices, n-ρ mixing rules, excess volumes, 1-hexanol, n-pentadecane

Recently, the thermodynamics of alcohol + alkane mixtures have been investigated extensively, due to their application as additives for biofuels, in modified rectification processes for binary azeotropes, to estimate the composition of the animal complex diet, different chemical processes such as separation units for recovering industrial solvents, food engineering, or pharmacological applications [1-6]. 1-Alkanol + n-alkane binary mixtures are also used as model systems for studying interrelations between various physicochemical properties and intermolecular interactions in solutions of nonelectrolytes [7]. Density (ρ), surface tension (σ), viscosity (η) and refractive index (n_D) are the physicochemical properties which provide important information, useful for different problems in chemical engineering in order to develop industrial processes, as well as for database applications and model formulations.

In this work, our attention is focused on the measurement of the density and refractive index data for pure 1-hexanol and n-pentadecane, as well as for the binary systems constituted by the aforementioned components in the whole mole fraction range at temperatures between (293.15 and 323.15) K and atmospheric pressure. A literature study was made [8, 9] and it reveals that there are no such data on this system, the components of which have wide applicability in chemical analyses and industry. From these experimental results, excess molar volumes (V^E), excess molar refractions (R^E), and refractive index (Δn_D) deviations from ideal behaviour were calculated. The excess and deviation properties were fitted to a Redlich–Kister-type [10] equation using least-squares to obtain their dependencies on compositions and temperature.

Prediction of refractive indices of binary liquid mixtures is essential for the determination of composition of binary liquid mixtures. Therefore, different refractive index mixing rules (Arago-Biot, Gladstone-Dale, Edwards, Eykman, Eyring and John, Heller, Lorenz-Lorentz, Newton, Oster, and Weiner [11-14]) were studied for the binary system investigated. The relative reliability of each of these rules has been assessed by comparing with experimental data.

To the best of the authors' knowledge, this paper is the first to report refractive index and density data for the aforementioned mixture.

Experimental part
Materials equipment and methods

Both 1-hexanol (mass fraction purity > 0.99) and n-pentadecane (mass fraction purity >0.99) were Sigma-Aldrich products. The chemicals were used without further purification.

All 1-hexanol + n-pentadecane binary mixtures were prepared, just before use, in airtight glass bottles by weighing the components on a precision balance (A&D Instruments Ltd., type HM-200, Tokyo, Japan) with an accuracy of ± 0.0001 g.

The densities of pure substances, as well as those of the binary mixtures were measured at (293.15, 298.15, 303.15, 313.15, and 323.15) K, over the entire range of compositions, using a two stem pycnometer made of Borosil glass with a bulb capacity 25 cm³. One of the stems has graduated marks and a well fitted glass cap, the other one has a thermometer. The marks on the stem were calibrated using double distilled water. The pycnometer containing test solution was kept for about 1 h in an electronically controlled thermostatic water bath (LAUDA, Model E100, Germany) having precision of ± 0.1 K, in order to minimize the thermal fluctuations.

Refractive indices were measured with an automatic digital refractometer (ATAGO, Model RX 9000α) with built-in thermo-module, after calibrating it with double distilled water at known temperature. The instrument operates in the temperature range of (273.15 to 343.15) K. The measurement uncertainty of the refractometer is ± 0.00004 for refractive index. The refractometer required only 0.1 cm³ of the sample. A procedure called "zero setting" was always performed before the actual measurements of the sample's refractive index, to ensure that the refractometer is working properly. Double distilled and deionized liquid water was used in performing the "zero setting" procedure. The measurements were done in 5

replicate runs. The estimated error in the mole fractions is ± 0.0001 and the errors in the measurement of ρ and n_D were found to be ± 0.0001 g·cm^{-3} and ± 0.00004, respectively.

Results and discussions

Densities and refractive indexes for the 1-hexanol (1) + n-pentadecane (2) mixture were measured in this paper at 293.15, 298.15, 303.15, 313.15 and 323.15 K and the data are presented in table 1 and plotted in figure 1.
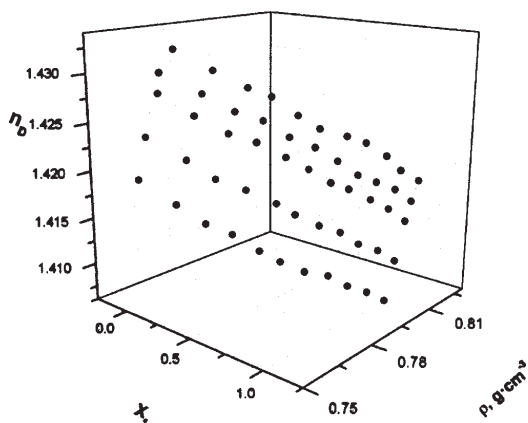

Fig. 1. Refractive index as function of composition and density at different temperatures for the 1-hexanol + n-pentadecane system

The molar refraction (R) is defined based on the refractive index (n_D) and molar volume (V) of the mixture as:

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot V \tag{1}$$

From the measured densities and refractive indices, the excess properties were computed applying the equations (2)-(4):

$$R^E = R - \sum_{i=1}^{2} X_i R_i \tag{2}$$

$$V^E = \sum_{i=1}^{2} X_i M_i \left(\rho^{-1} - \rho_i^{-1} \right) \tag{3}$$

$$n_D^E = n_D - \sum_{i=1}^{2} X_i n_{D,i} \tag{4}$$

where R, ρ, n_D are the molar refractivity, density, and the refractive index of the mixture, R_i, ρ_i, and $n_{D,i}$ are the properties of pure substances, X_i are the mole fractions and M_i are the molar masses of the pure components. The calculated excess properties for the 1-hexanol + n-pentadecane binary mixtures are shown in table 2.

The values of the excess molar volumes, excess molar refractions, and the changes of refractive indexes on mixing were fitted by the Redlich–Kister [10] polynomial equation for the 1-hexanol + n-pentadecane binary mixture, according to the following form:

$$R^E \text{ or } V^E \text{ or } n_D^E = X_1 \left(1 - X_1\right) \sum_{i=0}^{n} A_i \left(2X_1 - 1\right)^i \tag{5}$$

where X_1 is the mole fraction of the pure component 1 and A_i are the polynomial coefficients evaluated by fitting the equation to the experimental result with a least squares regression method. The standard deviations, σ, were calculated using the expression:

$$\sigma = \left[\sum_{i=0}^{n} \left(Y_{exp}^E - Y_{calc}^E\right)^2 \Big/ \left(n - p\right) \right]^{1/2} \tag{6}$$

where n is the number of measurements and p is the number of coefficients. The values of coefficients, A_i and the standard deviations, σ are presented in table 3. The n_D^E are positive for all temperatures, while R^E and V^E have both positive and negative values.

X_1	ρ, g/cm^3	n_D	X_1	ρ, g/cm^3	n_D
		$T/K = 293.15$			
0.0000	0.7713	1.43211	0.7695	0.8019	1.42349
0.1994	0.7769	1.43014	0.8366	0.8035	1.42270
0.3628	0.7822	1.42849	0.9011	0.8125	1.42110
0.4919	0.7849	1.42776	0.9535	0.8164	1.41944
0.5960	0.7902	1.42583	1.0000	0.8227	1.41800
0.6871	0.7943	1.42450			
		$T/K = 298.15$			
0.0000	0.7657	1.42997	0.7695	0.7974	1.42119
0.1994	0.7724	1.42797	0.8366	0.8027	1.41953
0.3628	0.7768	1.42635	0.9011	0.8073	1.41867
0.4919	0.7811	1.42553	0.9535	0.8136	1.41759
0.5960	0.7863	1.42385	1.0000	0.8189	1.41603
0.6871	0.7923	1.42270			
		$T/K = 303.15$			
0.0000	0.7650	1.42787	0.7695	0.7942	1.41913
0.1994	0.7691	1.42590	0.8366	0.7983	1.41839
0.3628	0.7740	1.42428	0.9011	0.8046	1.41700
0.4919	0.7784	1.42351	0.9535	0.8103	1.41573
0.5960	0.7848	1.42188	1.0000	0.8158	1.41409
0.6871	0.7892	1.42061			
		$T/K = 313.15$			
0.0000	0.7599	1.42371	0.7695	0.7890	1.41505
0.1994	0.7656	1.42162	0.8366	0.7946	1.41408
0.3628	0.7686	1.42002	0.9011	0.7991	1.41268
0.4919	0.7737	1.41897	0.9535	0.8053	1.41158
0.5960	0.7806	1.41740	1.0000	0.8108	1.41005
0.6871	0.7833	1.41638			
		$T/K = 323.15$			
0.0000	0.7567	1.41951	0.7695	0.7823	1.41072
0.1994	0.7612	1.41733	0.8366	0.7890	1.40990
0.3628	0.7643	1.41575	0.9011	0.7940	1.40856
0.4919	0.7679	1.41488	0.9535	0.8001	1.40745
0.5960	0.7732	1.41306	1.0000	0.8060	1.40608
0.6871	0.7767	1.41201			1.41072

Table 1
DENSITIES AND REFRACTIVE INDICES FOR THE
1-HEXANOL + n-PENTADECANE SYSTEM AT
DIFFERENT TEMPERATURES AND
COMPOSITIONS

Table 2

EXCESS MOLAR REFRACTION, R^E, EXCESS MOLAR VOLUMES, V^E, AND DEVIATIONS OF REFRACTIVE INDICES, $n_D{}^E$, OF THE 1-HEXANOL + n-PENTADECANE SYSTEM AT DIFFERENT TEMPERATURES

X_1	R^E, cm^3/mol	V^E, cm^3/mol	$n_D{}^E$	X_1	R^E, cm^3/mol	V^E, cm^3/mol	$n_D{}^E$
				$T/K = 293.15$			
0.0000	0.0000	0.0000	0.0000	0.7695	0.0037	0.0546	0.0022
0.1994	-0.0969	-0.1091	0.0008	0.8366	0.0661	0.1206	0.0024
0.3628	-0.1122	-0.1117	0.0015	0.9011	0.0300	0.0178	0.0017
0.4919	0.1308	0.5268	0.0026	0.9535	0.0576	0.2084	0.0008
0.5960	0.0392	0.3897	0.0021	1.0000	0.0000	0.0000	0.0000
0.6871	0.0913	0.5580	0.0021				
				$T/K = 298.15$			
0.0000	0.2118	0.0000	0.0000	0.7695	0.0414	0.0619	0.0020
0.1994	-0.0086	-0.4058	0.0008	0.8366	-0.0067	0.0139	0.0012
0.3628	0.0360	-0.0557	0.0014	0.9011	0.0766	0.1992	0.0013
0.4919	0.1423	0.1925	0.0024	0.9535	0.0428	0.0264	0.0009
0.5960	0.0768	0.1456	0.0022	1.0000	0.0128	0.0000	0.0000
0.6871	0.0397	-0.0227	0.0023				
				$T/K = 303.15$			
0.0000	-0.0232	0.0000	0.0000	0.7695	0.0280	0.2705	0.0019
0.1994	-0.0097	0.3224	0.0008	0.8366	0.1130	0.4070	0.0021
0.3628	-0.0046	0.3852	0.0014	0.9011	0.0745	0.2297	0.0016
0.4919	0.1086	0.5327	0.0024	0.9535	0.0471	0.0974	0.0010
0.5960	-0.0248	0.1128	0.0022	1.0000	0.0025	0.0000	0.0000
0.6871	0.0189	0.2333	0.0022				
				$T/K = 313.15$			
0.0000	-0.1529	0.0000	0.0000	0.7695	-0.0515	0.3126	0.0018
0.1994	-0.2815	-0.2043	0.0006	0.8366	-0.0551	0.1561	0.0018
0.3628	-0.1055	0.4889	0.0013	0.9011	-0.0060	0.3163	0.0013
0.4919	-0.0686	0.4251	0.0020	0.9535	-0.0409	0.0922	0.0009
0.5960	-0.2123	-0.0911	0.0018	1.0000	-0.0743	0.0000	0.0000
0.6871	-0.0380	0.4325	0.0021				
				$T/K = 323.15$			
0.0000	-0.4736	0.0000	0.0000	0.7695	-0.0837	0.8235	0.0015
0.1994	-0.4816	0.1435	0.0005	0.8366	-0.1249	0.4013	0.0016
0.3628	-0.2961	1.0174	0.0011	0.9011	-0.0951	0.4088	0.0012
0.4919	-0.1234	1.0014	0.0020	0.9535	-0.1202	-0.1399	0.0007
0.5960	-0.1964	0.6467	0.0016	1.0000	-0.1543	0.0000	0.0000
0.6871	-0.0727	1.0248	0.0017				

Table 3

PARAMETERS, A_i, AND STANDARD DEVIATION, σ, OF EXCESS FUNCTIONS FOR 1-HEXANOL +n-PENTADECANE BINARY SYSTEM AT DIFFERENT TEMPERATURES

Excess Function	T/K	A_0	A_1	A_2	σ
R^E, cm^3/mol		0.1509	0.9121	-0.9282	$3.20 \cdot 10^{-1}$
V^E, cm^3/mol	293.15	1.4774	2.2436	-4.1373	$1.66 \cdot 10^{-1}$
$n_D{}^E$		0.0083	0.0068	0.0051	$2.93 \cdot 10^{-4}$
R^E, cm^3/mol		0.3325	0.2203	-0.5336	$3.78 \cdot 10^{-1}$
V^E, cm^3/mol	298.15	0.3326	2.0653	-3.0683	$1.09 \cdot 10^{-1}$
$n_D{}^E$		0.0086	0.0055	-0.0015	$2.34 \cdot 10^{-4}$
R^E, cm^3/mol		0.0622	0.2849	0.4925	$4.36 \cdot 10^{-1}$
V^E, cm^3/mol	303.15	1.2745	-0.5094	2.3312	$1.18 \cdot 10^{-1}$
$n_D{}^E$		0.0082	0.0065	0.0030	$2.42 \cdot 10^{-4}$
R^E, cm^3/mol		-0.4617	0.8591	-1.1649	$4.94 \cdot 10^{-1}$
V^E, cm^3/mol	313.15	1.1951	1.2410	-0.9115	$2.21 \cdot 10^{-1}$
$n_D{}^E$		0.0070	0.0062	0.0032	$1.49 \cdot 10^{-4}$
R^E, cm^3/mol		-0.6471	1.7806	-3.2376	$5.53 \cdot 10^{-1}$
V^E, cm^3/mol	323.15	4.0128	1.5777	-3.6003	$2.07 \cdot 10^{-1}$
$n_D{}^E$		0.0063	0.0054	0.0018	$2.11 \cdot 10^{-4}$

For the excess molar refractions, the deviations from ideality are negative in the n-pentadecane rich-region and positive in the 1-hexanol rich-region, while for the excess molar volumes this behavior changes with increasing temperature. In the n-alkanes mixtures, the strong effect of 1-hexanol molecules on the partial excess magnitude could be observed [4,15].

The refractive indices were also compared with the predicted results from the mixing rules proposed by Arago–Biot (A-B), Gladstone–Dale (G-D), Eykman (E), Edwards (ED), Eyring and John (E-J), Heller (H), Lorentz–Lorenz (L-L), Newton (N), Oster (O), and Weiner (W) [11-14]:

Mixing rules	T/K				
	293.15	298.15	303.15	313.15	323.15
A-B	0.00032	0.00035	0.00032	0.00040	0.00050
G-D	0.00032	0.00035	0.00032	0.00040	0.00050
L-L	0.00032	0.00034	0.00031	0.00039	0.00049
E	0.00032	0.00035	0.00032	0.00040	0.00049
ED	0.00031	0.00033	0.00031	0.00038	0.00048
E-J	0.00032	0.00035	0.00032	0.00039	0.00049
H	0.00032	0.00034	0.00031	0.00039	0.00049
N	0.00033	0.00036	0.00032	0.00041	0.00050
O	0.00032	0.00036	0.00032	0.00040	0.00050
W	0.00039	0.00043	0.00039	0.00048	0.00058

Table 4
AVERAGE DEVIATIONS IN THE REFRACTIVE INDICES FROM n_D-ρ MIXING RULES FOR THE 1-HEXANOL (1) + nN-PENTADECANE (2) BINARY SYSTEM AT DIFFERENT TEMPERATURES

Arago-Biot: $n_D = n_{D,1}\phi_1 + n_{D,2}\phi_2$ (7)

Gladstone-Dale: $n_D - 1 = (n_{D,1} - 1)\phi_1 + (n_{D,2} - 1)\phi_2$ (8)

Eykman: $\dfrac{n_D^2 - 1}{n_D + 0.4} = \left(\dfrac{n_{D,1}^2 - 1}{n_{D,1} + 0.4}\right)\phi_1 + \left(\dfrac{n_{D,2}^2 - 1}{n_{D,2} + 0.4}\right)\phi_2$ (9)

Edwards: $\dfrac{n_D - 1}{n_D} = \left(\dfrac{n_{D,1} - 1}{n_{D,1}}\right)\phi_1 + \left(\dfrac{n_{D,2} - 1}{n_{D,2}}\right)\phi_2$ (10)

Eyring & John: $n_D = n_{D,1}\phi_1^2 + 2(n_{D,1}n_{D,2})^{1/2}\phi_1\phi_2 + n_{D,2}\phi_2^2$ (11)

Heller: $\dfrac{n_D - n_{D,1}}{n_{D,1}} = \dfrac{3}{2}\left[\dfrac{(n_{D,2}/n_{D,1})^2 - 1}{(n_{D,2}/n_{D,1})^2 + 2}\right]\phi_2$ (12)

Lorentz-Lorenz: $\dfrac{n_D^2 - 1}{n_D^2 + 2} = \left(\dfrac{n_{D,1}^2 - 1}{n_{D,1}^2 + 2}\right)\phi_1 + \left(\dfrac{n_{D,2}^2 - 1}{n_{D,2}^2 + 2}\right)\phi_2$ (13)

Newton: $n_D^2 - 1 = (n_{D,1}^2 - 1)\phi_1 + (n_{D,2}^2 - 1)\phi_2$ (14)

Oster: $\dfrac{(n_D^2 - 1)(2n_D^2 + 1)}{n_D^2} = \dfrac{(n_{D,1}^2 - 1)(2n_{D,1}^2 + 1)}{n_{D,1}^2}\phi_1 + \dfrac{(n_{D,2}^2 - 1)(2n_{D,2}^2 + 1)}{n_{D,2}^2}\phi_2$ (15)

Weiner: $\dfrac{n_D^2 - n_{D,1}^2}{n_D^2 + 2n_{D,2}^2} = \dfrac{n_{D,2}^2 - n_{D,1}^2}{n_{D,2}^2 + 2n_{D,1}^2}\phi_2$ (16)

The average deviations of the experimental results from those estimated for refractive indices are shown in table 4 and are calculated by:

$$AD = \dfrac{\sum\limits_{i=1}^{N} \left| n_{D,i}^{\exp} - n_{D,i}^{calc} \right|}{N}$$ (17)

As can be seen in table 4, the refractive index predicted by Edwards has shown excellent agreement with the experimental values at all temperatures, followed by Lorentz-Lorenz and Heller relations. The other mixing rules show a good agreement with the experimental values, except for the Weiner relation where deviations from theoretical values are bigger.

Conclusions

For the first time, the refractive indices and densities of the 1-hexanol + n-pentadecane binary mixture were measured at (293.15, 298.15, 303.15, 313.15, and 323.15) K and atmospheric pressure, over the entire range of compositions. From the experimental refractive indices and densities, the excess molar refraction, excess molar volumes, and the change of refractive indices were calculated. The excess molar refraction, excess molar volumes, and the change of refractive indices were satisfactorily correlated with the composition data by means of the Redlich-Kister polynomial. Ten mixing rules equations were used for the quantitative determination of the refractive indices of the 1-hexanol (1) + n-pentadecane (2) mixture.

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