Viscosities and Densities of Binary Mixtures of Hexane with 1-Chlorohexane between 293.15 K and 333.15 K

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The density and viscosity values of binary mixtures of hexane with 1-chlorohexane have been measured as a function of composition and temperatures between 293.15 K and 333.15 K. The estimated uncertainties are less than $\pm 1 \times 10^{-4}$ g·cm^{-3} for density and ±0.5% for viscosity. Viscosity deviations $\Delta\eta$ were fitted by the Redlich−Kister equation.

Introduction

The thermophysical properties of binary mixtures containing alkanes with 1-chloroalkanes and 1-iodoalkanes with polar molecules of the type (polar group)−$(CH_2)_n$−(CH_3) have been extensively studied with the aim of a better understanding of the intermolecular interactions. A detailed understanding of the effect of the presence of the chlorine (−Cl) or iodine (−I) groups in the mixture on the excess thermodynamic properties and the behavior of haloalkanes in mixtures with alkanes is important from both practical and fundamental viewpoints. On the other hand, a knowledge of the thermophysical properties of nonelectrolyte solutions such as viscosity and density will be helpful for the chemical industry for the design of processes of mass transfer, heat transfer, and fluid flow.

In this work, the viscosity and density of the binary mixtures hexane + 1-chlorohexane were measured at temperatures from 293.15 K to 333.15 K. The excess molar volume of this mixture was found in the literature[3] at 298.15 K. Our literature survey does not include experimental data on the viscosities of the mixture chosen for this study. In works[6,7] on viscosity devoted to study of binary liquid mixtures of *n*-alkanes with 1-chloroalkanes, the mixture researched by us is absent.

Experimental Section

Materials. Hexane, 1-chlorohexane (mole fraction, >0.99) was supplied from Sigma-Aldrich Ltd. All chemicals were partially degassed and dried over Fluka 0.4 nm molecular sieves. The purity of the products was checked by gas chromatography (GC). The purity for hexane and 1-chlorohexane was 99.7 and 99.3 mol %, respectively. The mixtures were prepared by mass, with a precision of $\pm 5 \times 10^{-5}$ g. The uncertainty in the mole fraction is less than 1×10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table (IUPAC, 1986).[4]

Measurements. Densities were measured with a Ostwald−Sprengel type pycnometer, with a capacity of approximately 50 cm^3. The uncertainty of the density measurements was estimated to be $\pm 3 \times 10^{-5}$ g·cm^{-3}. The values of composition reported in Tables 2−4 are approximated up to three digits. The kinematic viscosities of the pure liquids and liquid mixtures were measured between 293.15 K and 333.15 K with a step of 5 K, and atmospheric pressure was determined with a calibrated Ubbelohde suspended level viscometer of 0.56 mm diameter. The accuracy of the flow time measurement was ±0.01 s. Flow time was taken as an average of 10 measurements. The viscometer was always kept in a vertical position in a water thermostat controlled to ±0.01 K. The following equation was used to calculate the viscosities:

$$\frac{\eta}{\rho} = At - \frac{B}{t} \qquad (1)$$

where t is the flow time, η is the absolute viscosity, ρ is the density, and A and B are the viscometer constants, determined by the calibration fluids. The viscometers were calibrated by using high-purity toluene, heptane, and nonane at the working temperatures. The estimated error of the viscosity measurements was ±0.5%. Experimental values of densities and viscosities for the pure liquids at different temperatures were compared with those found in the literature and were in fairly good agreement, as shown in Table 1.

Table 1. Comparison of Experimental Densities, ρ, and Kinematic Viscosities, ν, with Literature Data for Pure Liquids at Different Temperatures

		ρ/(kg·m^{-3})		$10^6 \times \nu$/(m^2·s^{-1})	
liquid	T/K	this work	literature (ref)	this work	literature (ref)
hexane	293.15	659.44	659.40 (8)	0.4796	0.4748 (11)
	298.15	654.93	654.89 (1) 654.8 (12)	0.4635	0.4580 (12)
	303.15	650.36	650.2 (12)	0.4480	0.4523 (10)
	308.15	645.74	645.86 (9)	0.4331	0.4297 (12)
	323.15	631.61	631.5 (12)	0.3930	0.3922 (10)
	333.15	621.95	621.9 (11) 621.8 (12)	0.3711	0.3691 (10)
1-chlorohexane	298.15	873.75	873.38 (2)	0.4213	

Results and Discussion

The measured values of density (ρ) and viscosity (η) along with the values of deviations in viscosity ($\Delta\eta$) calculated as described below for the binary mixtures hexane (1) + 1-chlorohexane (2) as a function of mole fraction x_2 are given in Table 2, for temperatures from 293.15 K to 333.15 K.

The deviations in viscosity are calculated by using the equation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

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Table 2. Experimental Densities, ρ, Viscosities, η, and Excess Viscosities, $\Delta\eta$, of the Binary Mixtures Hexane (1) + 1-Chlorohexane (2) at Different Temperatures

	ρ	η	$\Delta\eta$		ρ	η	$\Delta\eta$
x_2	kg·m^{-3}	mPa·s	mPa·s	x_2	kg·m^{-3}	mPa·s	mPa·s
			293.15 K				
0.000	659.44	0.3163	0.0000	0.500	771.87	0.4691	−0.0742
0.100	683.01	0.3403	−0.0214	0.700	815.39	0.5662	−0.0679
0.150	694.01	0.3532	−0.0312	0.900	856.91	0.6932	−0.0318
0.200	706.37	0.3669	−0.0402	1.000	878.52	0.7704	0.0000
0.300	728.21	0.3965	−0.0560				
			298.15 K				
0.000	654.93	0.3036	0.0000	0.500	767.36	0.4464	−0.0641
0.100	678.51	0.3263	−0.0186	0.700	810.91	0.5367	−0.0566
0.150	689.61	0.3384	−0.0272	0.900	852.37	0.6495	−0.0265
0.200	701.84	0.3520	−0.0343	1.000	873.75	0.7173	0.0000
0.300	723.73	0.3794	−0.0483				
			303.15 K				
0.000	650.36	0.2914	0.0000	0.500	762.82	0.4254	−0.0553
0.100	673.93	0.3130	−0.0162	0.700	806.39	0.5094	−0.0471
0.150	685.15	0.3245	−0.0237	0.900	847.80	0.6103	−0.0220
0.200	697.27	0.3377	−0.0294	1.000	868.98	0.6702	0.0000
0.300	719.21	0.3632	−0.0418				
			308.15 K				
0.000	645.74	0.2797	0.0000	0.500	758.26	0.4061	−0.0479
0.100	669.37	0.2998	−0.0147	0.700	801.83	0.4844	−0.0393
0.150	680.63	0.3107	−0.0213	0.900	843.21	0.5754	−0.0180
0.200	692.67	0.3233	−0.0261	1.000	864.21	0.6283	0.0000
0.300	714.64	0.3475	−0.0368				
			313.15 K				
0.000	641.08	0.2685	0.0000	0.500	753.66	0.3884	−0.0414
0.100	664.73	0.2881	−0.0127	0.700	797.24	0.4614	−0.0329
0.150	676.04	0.2985	−0.0184	0.900	838.59	0.5436	−0.0152
0.200	688.03	0.3109	−0.0222	1.000	859.44	0.5910	0.0000
0.300	710.03	0.3337	−0.0316				
			318.15 K				
0.000	636.37	0.2580	0.0000	0.500	749.03	0.3720	−0.0361
0.100	660.04	0.2765	−0.0115	0.700	792.61	0.4402	−0.0278
0.150	671.39	0.2865	−0.0165	0.900	833.95	0.5152	−0.0128
0.200	683.36	0.2984	−0.0196	1.000	854.67	0.5580	0.0000
0.300	705.37	0.3201	−0.0279				
			323.15 K				
0.000	631.61	0.2482	0.0000	0.500	744.37	0.3569	−0.0315
0.100	655.31	0.2660	−0.0102	0.700	787.95	0.4208	−0.0236
0.150	666.68	0.2755	−0.0148	0.900	829.29	0.4899	−0.0105
0.200	678.65	0.2868	−0.0175	1.000	849.90	0.5285	0.0000
0.300	700.66	0.3076	−0.0247				
			328.15 K				
0.000	626.81	0.2391	0.0000	0.500	739.68	0.3428	−0.0278
0.100	650.53	0.2560	−0.0098	0.700	783.25	0.4027	−0.0203
0.150	661.91	0.2652	−0.0133	0.900	824.61	0.4666	−0.0090
0.200	673.90	0.2759	−0.0158	1.000	845.12	0.5019	0.0000
0.300	695.91	0.2959	−0.0221				
			333.15 K				
0.000	621.95	0.2308	0.0000	0.500	734.96	0.3297	−0.0246
0.100	645.70	0.2468	−0.0087	0.700	778.51	0.3862	−0.0175
0.150	657.07	0.2556	−0.0123	0.900	819.90	0.4455	−0.0076
0.200	669.12	0.2658	−0.0144	1.000	840.35	0.4778	0.0000
0.300	691.11	0.2849	−0.0200				

where x_1 and x_2 are the mole fractions, η is the dynamic viscosity of the mixture, and η_1 and η_2 are the viscosities of components 1 and 2, respectively. The density values were regressed using the polynomial of the second power; because of the value 2 is the minimal degree of the polynomial capable within the limits of error of the measurements of transferring the character of the temperature density dependence in the researched interval of temperatures.

$$\rho = A_0 + A_1T + A_2T^2 \tag{3}$$

Here T is absolute temperature and A_0, A_1, and A_2 are the adjustable parameters. The deviations in viscosity were fitted by a Redlich−Kister type equation,[5]

$$\Delta\eta/\text{mPa·s} = x_1(1 - x_1)\sum_{j=0}^{k} B_j(2x_2 - 1)^j \tag{4}$$

The coefficient A_i in eq 2 and B_j in eq 3 was estimated by the least-squares fit method. The standard deviation $\sigma(Y)$ of ρ and $\Delta\eta$ is defined by

$$\sigma(Y) = [\sum_{i=1}^{n}(Y_{\text{obs}} - Y_{\text{cal}})^2/(n - p)]^{1/2} \tag{5}$$

where Y_{obs} and Y_{cal} are the observed and calculated quantities as defined earlier, n is the total number of experimental points, and p is the number of estimated parameters. The values of parameters A_i of eq 3 and B_j of eq 4 and standard deviation $\sigma(Y)$ are given in Table 3 at all composition interval and Table 4 at temperatures from 293.15 to 333.15 K, respectively.

The viscosity deviations of the hexane + 1-chlorohexane mixtures at 293.15 K, 313.15 K, and 333.15 K are shown in Figure 1. The values of $\Delta\eta$ presented in Figure 1 are negative over the entire range of composition and over the entire range of studied temperatures. An increase in temperature leads to a lower value of $\Delta\eta$.

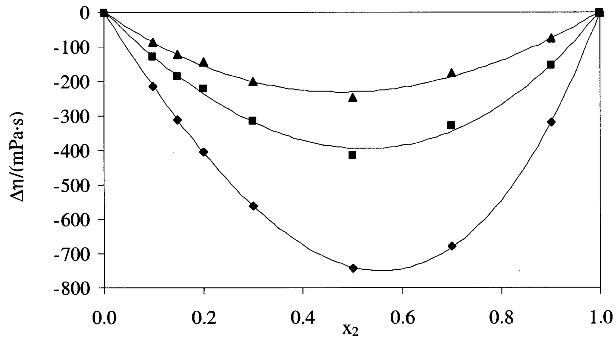

Figure 1. Viscosity deviation for hexane (1) + 1-chlorohexane (2): ◆, 293.15 K; ■, 313.15 K; ▲, 333.15 K.

Table 3. Values of the Parameters A_j of Equation 3 and the Standard Deviation for the Binary Systems Hexane (1) + 1-Chlorohexane (2) from 293.15 K to 333.15 K

x_2	A_0	A_1	A_2	σ/(kg·m^{-3})
0.000	840.651	−0.337	-9.580×10^{-4}	0.010
0.100	866.187	−0.354	-9.234×10^{-4}	0.028
0.150	842.54	−0.140	-1.251×10^{-3}	0.006
0.200	909.305	−0.482	-7.173×10^{-4}	0.006
0.300	910.075	−0.350	-9.216×10^{-4}	0.006
0.500	982.618	−0.540	-6.117×10^{-4}	0.006
0.700	1015	−0.470	-7.221×10^{-4}	0.007
0.900	1083	−0.635	-4.632×10^{-4}	0.009
1.000	1157	−0.945	-1.515×10^{-5}	0.005

Table 4. Values of the Parameters B_j of Equation 4 and the Standard Deviation for the Binary Systems Hexane (1) + 1-Chlorohexane (2) from 293.15 K to 333.15 K

T/K	B_0	B_1	B_2	B_3	σ/(mPa·s)
293.15	−0.298	−0.085	1.384×10^{-3}	0.019	5.655×10^{-4}
298.15	−0.254	−0.05	0.011	-8.332×10^{-3}	1.448×10^{-3}
303.15	−0.217	−0.032	−0.017	−0.014	2.060×10^{-3}
308.15	−0.187	−0.015	0.019	−0.012	2.202×10^{-3}
313.15	−0.161	-8.237×10^{-3}	0.02	−0.015	2.583×10^{-3}
318.15	−0.139	-1.538×10^{-4}	0.019	−0.015	2.629×10^{-3}
323.15	−0.122	6.079×10^{-3}	0.02	−0.013	2.310×10^{-3}
328.15	−0.107	8.909×10^{-3}	0.016	-8.367×10^{-3}	2.280×10^{-3}
333.15	−0.095	0.014	0.016	−0.011	1.992×10^{-3}

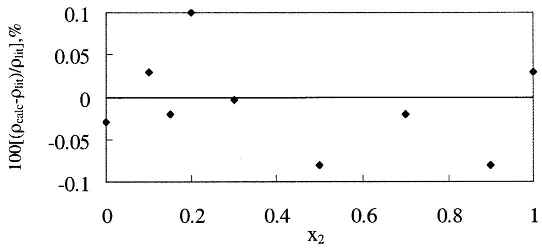

Figure 2. Deviations of literature data for density of hexane (1) + 1-chlorohexane (2) from eq 3: ◆, Kovacs et al. (ref 3) at 293.15 K.

We have compared our results for the density of the researched mixture at 298.15 K with the data reported by Kovacs et al.[3] Kovacs' data for the concentration dependence of density have been processed by a polynomial of the second degree in the form $\rho = 0.0147x^2 - 0.2037x + 0.8735$, where x is the mole composition of 1-chlorohexane. As shown in Figure 2, it was found that their results typically deviated by ±0.05% from the values calculated from eq 3, with a maximum deviation of 0.1% at $x_2 = 0.2$.

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