Densities, Viscosities, and Refractive Indices of Binary Liquid Mixtures of Hexane, Decane, Hexadecane, and Squalane with Benzene at 298.15 K

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Densities, ρ, viscosities, η, and refractive indices, n_D, for binary mixtures of hexane, decane, hexadecane, and squalane with benzene were measured over the whole composition range at 298.15 K and atmospheric pressure. The excess molar volumes, V_m^E, and viscosity deviations, $\delta\eta$, were calculated from experimental measurements. These result were further fitted to the Redlich−Kister equation to estimate the binary coefficients and standard errors. The effects of chain length and branching of alkanes on V_m^E and $\delta\eta$ values have been discussed.

Introduction

Density, viscosity, and refractive index data for liquid mixtures are important from practical and theoretical points of view. Experimental measurements of these properties for binary mixtures have gained much importance in many chemical industries and engineering disciplines. In the present study, density, ρ, and viscosity, η, were measured for the binary mixtures of hexane, decane, hexadecane, and squalane (2,6,10,15,19,23-hexamethyltetracosane) with benzene at the temperature 298.15 K. Refractive index, n_D, was also measured for all the above-mentioned systems except hexane + benzene.

From the experimental results, excess molar volume, V_m^E, and viscosity deviations, $\delta\eta$, have been evaluated to provide additional information on molecular interactions, whereas refractive index data are given as such. Components for this study were chosen with the intent of considering mixtures with molecules of significantly different size and flow behavior. The five components may be put into two groups: hexadecane and squalane, with molar volumes greater than 294 $cm^3 \cdot mol^{-1}$, and the others, with molar volumes of 195 $cm^3 \cdot mol^{-1}$ or less.

Excess molar volumes and viscosities of binary liquid mixtures have been studied by several workers.[1−12] From the search of the literature, we find that almost no data are available on the viscosity of squalane at 298.15 K, even though Croucher and Patterson[13] studied excess enthalpies in higher alkanes such as hexdecane and squalane.

The excess molar volumes and viscosity deviations have been fitted to the Redlich−Kister equations[14] to estimate the regression coefficients and the standard errors between the experimentally calculated and fitted quantities. The sign and magnitude of these deviations have been used to study the type of thermodynamic interactions between the mixture components.

Experimental Section

Materials. The chemicals used were of analytical grade. Benzene and hexane were Ranbaxy products; decane and hexadecane were supplied by S. D. Fine Chemicals Ltd., whereas squalane was obtained from E. Merck chemical company. All reagents were used after purification by fractional distillation. Squalane was used without further purification. The experimentally measured values of densities, viscosities, and refractive indices of all the pure components, except the viscosity of squalane, at the temperature 298.15 K were compared with the literature values and are presented in Table 1.

Apparatus and Procedure. Densities, viscosities, and refractive indices were measured at 298.15 K. The temperature was maintained constant by a thermostatically controlled water bath. The densities of all the pure components and their binary mixtures were measured by a bicapillary pycnometer with a bulb of 12 cm^3 and a capillary of an internal diameter of about 1 mm.[3,15] The pycnometer was calibrated with deionized double-distilled water with 0.9970 $g \cdot cm^{-3}$ as its density at 298.15 K. The pycnometer, filled with the desired liquid, was kept in a transparent-walled water bath with a thermal stability of ±0.01 °C, as checked by means of a calibrated thermometer, to attain thermal equilibrium. The relative error in the density measurement was within ±0.0003 $g \cdot cm^{-3}$.

The kinematic viscosities, ν, of the binary liquid mixtures as well as their pure components were measured using a modified suspended level Ubbelohde viscometer.[16] The viscometer was calibrated with doubly distilled water and toluene. Care was taken to reduce evaporation during the measurements. A thoroughly cleaned and dried viscometer filled with experimental liquid was placed vertically in a glass-fronted, well-stirred water bath. After thermal stability was attained, the flow times of the liquids were recorded with an accurate stopwatch correct to ±0.01 s. The present values of kinematic viscosity for the various liquids agree with the literature values within a deviation of the order of ±0.005 $mm^2 \cdot s^{-1}$.

Refractive indices were measured with a thermostated Abbe refractometer (Erma, A-302 A) with an error of less than ±0.0001 unit. Water was circulated into the prims of the refractometer by using a circulation pump, connected from a constant temperature water bath. Calibration of the instrument was done by measuring the refractive indices of doubly distilled water, cyclohexane, toluene, and carbon tetrachloride at known temperatures.[17] The sample mix-

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Table 1. Properties of Pure Liquids at 298.15 K

liquid	ρ/g·cm^3		η/mPa·s		ν/mm^2·s^{-1}		n_D	
	exptl	lit.	exptl	lit.	exptl	lit.[a]	exptl	lit.
benzene	0.8734	0.873 70[17] 0.654 89[18]	0.599	0.6028[17] 0.6010[18]	0.686	0.6899	1.5035	1.4979[17]
hexane	0.6548	0.654 89[18] 0.654 89[17]	0.294	0.2968[18] 0.2985[17]	0.449	0.4532	1.3745	1.3723[17] 1.3732[10]
decane	0.7262	0.726 25[17] 0.726 14[18]	0.859	0.8614[17] 0.8406[18]	1.183	1.1861	1.4125	1.4125[2] 1.4097[17]
hexadecane	0.7706	0.769 94[18] 0.770 79[20]	3.039	3.0320[19] 3.0520[18]	3.944	3.9379	1.4340	1.4327[20] 1.4345[19]
squalane	0.8054	0.806 00[18]	31.123	–	38.643	–	1.4474	1.4509[18]

[a] Values of ν were obtained from the relation $\nu = \eta/\rho$ using the values of the dynamic viscosities, η, and densities, ρ, of the pure liquids available in the literature.

Table 2. Densities, Viscosities, Refractive Indices, Excess Molar Volumes, and Viscosity Deviations for Binary Mixtures at the Temperature 298.15 K

x_1	ρ/g·cm^3	η/mPa·s	ν/mm^2·s^{-1}	n_D	V_m^E/cm^3·mol^{-1}	$\delta\eta$/mPa·s	x_1	ρ/g·cm^3	η/mPa·s	ν/mm^2·s^{-1}	n_D	V_m^E/cm^3·mol^{-1}	$\delta\eta$/mPa·s
Hexane (1) + Benzene (2)													
0.0000	0.8734	0.599	0.686		–	–	0.6162	0.7175	0.333	0.464		0.3708	−0.0785
0.0932	0.8434	0.532	0.631		0.1450	−0.0385	0.6899	0.7039	0.323	0.459		0.3407	−0.0660
0.1599	0.8236	0.487	0.591		0.2298	−0.0627	0.7811	0.6882	0.313	0.455		0.2835	−0.0482
0.2174	0.8076	0.453	0.561		0.2873	−0.0796	0.8733	0.6734	0.303	0.450		0.2000	−0.0295
0.2798	0.7913	0.425	0.537		0.3350	−0.0883	0.9378	0.6637	0.299	0.451		0.1085	−0.0145
0.3458	0.7751	0.395	0.510		0.3620	−0.0983	0.9845	0.6570	0.295	0.449		0.0339	−0.0039
0.4331	0.7549	0.373	0.494		0.3961	−0.0941	0.9943	0.6555	0.294	0.449		0.0200	−0.0015
0.5070	0.7391	0.354	0.479		0.4002	−0.0902	1.0000	0.6548	0.294	0.449		–	–
Decane (1) + Benzene (2)													
0.0000	0.8734	0.599	0.686	1.5035	–	–	0.4113	0.7776	0.630	0.810	1.4416	1.1643	−0.0762
0.0233	0.8645	0.593	0.686	1.4970	0.1699	−0.0118	0.4441	0.7731	0.639	0.827	1.4370	1.1725	−0.0750
0.0521	0.8545	0.589	0.689	1.4800	0.3392	−0.0234	0.5715	0.7581	0.678	0.894	1.4270	1.1331	−0.0691
0.1058	0.8422	0.583	0.692	1.4735	0.5970	−0.0432	0.6335	0.7520	0.702	0.934	1.4245	1.0502	−0.0619
0.1317	0.8312	0.583	0.701	1.4706	0.6864	−0.0505	0.7949	0.7391	0.757	1.024	1.4186	0.6303	−0.0487
0.1658	0.8227	0.583	0.709	1.4680	0.7903	−0.0586	0.8927	0.7328	0.803	1.096	1.4160	0.2882	−0.0283
0.2426	0.8060	0.594	0.737	1.4580	0.9632	−0.0677	0.9460	0.7295	0.830	1.138	1.4142	0.1187	−0.0149
0.3232	0.7912	0.606	0.766	1.4478	1.0856	−0.0774	1.0000	0.7262	0.859	1.183	1.4125	–	–
Hexadecane (1) + Benzene (2)													
0.0000	0.8734	0.599	0.686	1.5035	–	–	0.3692	0.7995	1.287	1.610	1.4490	1.2883	−0.2129
0.0102	0.8692	0.616	0.709	1.4995	0.0912	−0.0081	0.4886	0.7897	1.570	1.988	1.4440	1.3725	−0.2207
0.0156	0.8669	0.626	0.722	1.4962	0.1466	−0.0109	0.5886	0.7838	1.831	2.336	1.4398	1.2906	−0.2039
0.0611	0.8513	0.696	0.818	1.4845	0.4835	−0.0522	0.8532	0.7749	2.588	3.340	1.4368	0.2707	−0.0923
0.1012	0.8403	0.756	0.900	1.4740	0.6982	−0.0895	0.9143	0.7733	2.766	3.577	1.4352	0.0373	−0.0641
0.1640	0.8269	0.862	1.042	1.4674	0.9164	−0.1373	0.9784	0.7713	2.972	3.853	1.4348	−0.0402	−0.0143
0.2047	0.8200	0.949	1.157	1.4610	1.0126	−0.1498	0.9943	0.7708	3.021	3.919	1.4344	−0.0145	−0.0042
0.2688	0.8107	1.064	1.312	1.4565	1.1510	−0.1903	1.0000	0.7705	3.039	3.944	1.4340	–	–
Squalane (1) + Benzene (2)													
0.0000	0.8734	0.599	0.686	1.5035	–	–	0.4018	0.8178	5.869	7.177	1.4524	0.4252	−6.9944
0.0147	0.8667	0.748	0.863	1.4886	0.1367	−0.3001	0.5045	0.8153	8.286	10.163	1.4500	−0.0747	−7.7114
0.0354	0.8588	0.970	1.129	1.4832	0.3073	−0.7087	0.8238	0.8094	23.110	28.552	1.4470	−0.8820	−2.6357
0.0590	0.8516	1.249	1.467	1.4779	0.4730	−1.1521	0.8635	0.8085	25.352	31.357	1.4460	−0.7861	−1.6050
0.0972	0.8427	1.716	2.036	1.4694	0.6810	−1.8513	0.9007	0.8077	27.314	33.817	1.4463	−0.6431	−0.7780
0.1609	0.8328	2.498	3.000	1.4629	0.8778	−3.0120	0.9801	0.8059	30.691	38.083	1.4468	−0.1618	–
0.2082	0.8279	3.070	3.708	1.4588	0.9275	−3.8833	1.0000	0.8054	31.123	38.643	1.4474	–	–
0.3314	0.8203	4.684	5.710	1.4542	0.7069	−6.0306							

Table 3. Parameters and Standard Deviations, σ, of Eqs 3 and 4 for Binary Mixtures at 298.15 K

	A_1	A_2	A_3	A_4	σ
Hexane (1) + Benzene (2)					
V_m^E/cm^3·mol^{-1}	1.5815	−0.1031	0.2952	0.2760	0.0050
$\delta\eta$/mPa·s	−0.3687	0.1828	−0.0028	−0.0839	0.0016
Decane (1) + Benzene (2)					
V_m^E/cm^3·mol^{-1}	4.7036	−0.4359	−0.1238	−2.6448	0.0029
$\delta\eta$/mPa·s	−0.2920	0.1007	−0.1404	−0.0082	0.0016
Hexadecane (1) + Benzene (2)					
V_m^E/cm^3·mol^{-1}	5.4806	−0.3132	−1.8865	−6.0953	0.0046
$\delta\eta$/mPa·s	−0.8749	0.2055	0.0232	−0.1302	0.0043
Squalane (1) + Benzene (2)					
V_m^E/cm^3·mol^{-1}	−0.2019	−9.8861	0.7072	0.8914	0.0038
$\delta\eta$/mPa·s	−30.8082	−4.5269	24.7520	19.1795	0.0037

tures were directly injected into the prism assembly of the instrument by means of an airtight hypodermic syringe. When the liquid mixtures attained the constant temperature, the refractive index values were noted. An average of four or five measurements was taken for a sample mixture. The experimental and literature values of density, viscosity, and refractive index for all the pure components have been given in Table 1.

Results and Discussion

The experimental densities, viscosities (dynamic and kinematic), refractive indices, excess molar volumes, and viscosity deviations of the different binary mixtures at 298.15 K are summarized in Table 2. The experimental values of density are used to calculate the excess molar volumes, V_m^E, of the mixture as

$$V_m^E/\text{cm}^3\ \text{mol}^{-1} = \frac{M_1x_1 + M_2x_2}{\rho_m} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2}\right) \quad (1)$$

where M_i, x_i, and ρ_i (i = 1, 2) are the molecular weights, the mole fractions, and the densities of the pure components, respectively. ρ_m is the density of the mixture. The

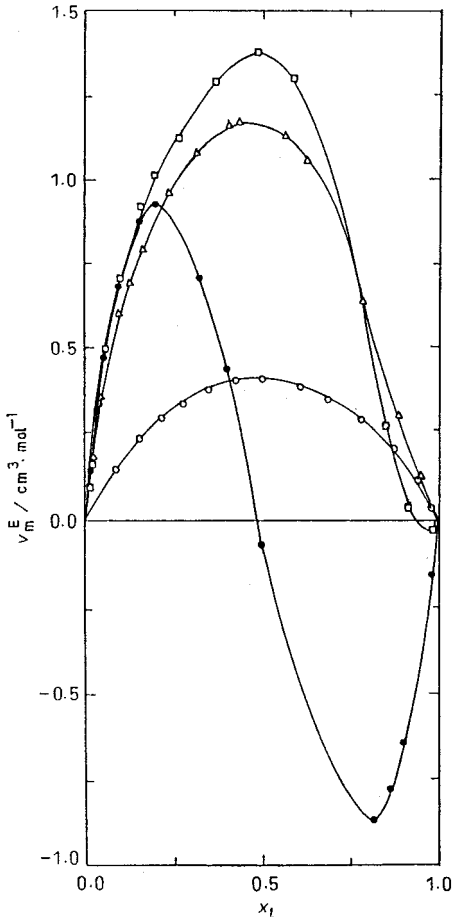

Figure 1. Excess molar volume, V_m^E, for (○) hexane (1); (△) decane (1); (□) hexadecane (1); and (●) squalane (1) + benzene (2) at 298.15 K. The curves have been drawn from eq 3.

viscosity deviation, $\delta\eta$, was calculated using the equation

$$\delta\eta/\text{mPa·s} = \eta_m - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

where η_m is the viscosity of the mixture and η_i represents that for the ith component. The composition dependence of either the V_m^E or the $\delta\eta$ isotherm was represented by a Redlich−Kister type equation.[14]

$$Y = x_1x_2\sum_{i=1}^{k} A_i(x_1 - x_2)^{i-1} \qquad (3)$$

where A_i are the polynomial coefficients, which were obtained by fitting the equation to the experimental result with a least-squares regression method. The correlated results are given in Table 3, in which the tabulated standard deviation, σ, was defined as

$$\sigma = [\sum(Y_{exp} - Y_{cal})^2/(n - k)]^{1/2} \qquad (4)$$

where n is the number of measurements and k is the number of estimated parameters. For all mixtures $\sigma(V_m^E) \leq 0.005$ cm^3·mol^{-1}, whereas $\sigma(\delta\eta) \leq 0.004$ mPa·s.

The values of the excess molar volumes and the viscosity deviations varying with the mole fraction of the first component for the investigated binary mixtures are presented in Figures 1 and 2, respectively. Figure 1 shows that V_m^E values for binary mixtures of hexane and decane with benzene are positive over the whole composition range. However, V_m^E values for hexadecane and squalane with benzene mixtures do not follow the trend and become negative when the concentration of the alkanes increases. For the mixture of squalane + benzene, V_m^E is about eight times more negative than that observed for hexadecane + benzene.

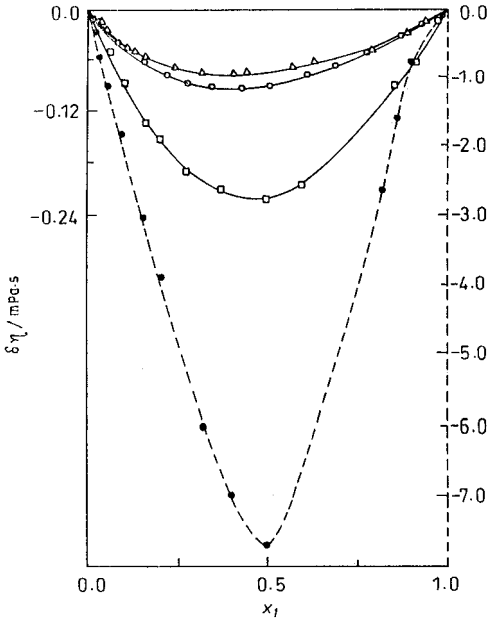

Figure 2. Viscosity deviation, $\delta\eta$, for (○) hexane (1); (△) decane (1); (□) hexadecane (1); and (●) squalane (1) + benzene (2) at 298.15 K. The curves have been drawn from eq 3.

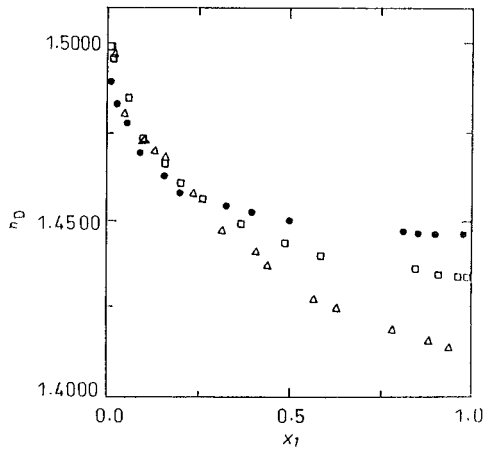

Figure 3. Refractive index, n_D, for (△) decane (1); (□) hexadecane (1); and (●) squalane (1) + benzene (2) at 298.15 K.

Figure 2 illustrates that $\delta\eta$ values are negative for all the four binary mixtures, over the whole range of mole fractions, and become more negative with an increase in chain length and branching of alkanes. The viscosity deviation for the mixture squalane + benzene shows maximum negative values. Squalane is similar in chemical nature to hexadecane. However, squalane is branched in molecular structure, and the pure liquid shows little orientational order.[13] The viscosity of pure squalane is found to be much higher (≈31 mPa·s) than that of hexadecane (≈3 mPa·s).

The dependence of n_D on the mole fractions of alkane for all the binary mixtures, except hexane + benzene, at 298.15 K is displayed in Figure 3, wherein we observe that n_D values for different components of the mixtures vary in the sequence squalane + benzene > hexadecane + benzene > decane + benzene. It again shows an increasing trend

with the increasing size and molar masses of alkane molecules.

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