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Viscosities of Binary Liquid Mixtures of Butanol + Pentane, + Hexane, + Heptane, and + Octane at $T = 298.15$ K

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Kinematic viscosities ν have been measured for binary liquid mixtures of butanol (n-C_4H_9OH) + pentane (n-C_5H_{12}), + hexane (n-C_6H_{14}), + heptane (n-C_7H_{16}), and + octane (n-C_8H_{18}) at $T = 298.15$ K. Values of ν have been used to calculate dynamic viscosities η, using available density data. The values of the quantity $\Delta\eta$, which refers to the deviations of η of mixtures from those arising from a mole fraction average, have also been calculated. The values of ν, η, and $\Delta\eta$ have been fitted in appropriate equations using a least-squares method. The analysis has shown that McAllister's approach correlates the liquid-mixture viscosity data of the present systems throughout the entire composition range to a significantly high degree of accuracy, whereas Lobe's approach predicts ν of mixtures to a lower degree of accuracy.

Introduction

Binary (alkane + alkanol) mixtures are interesting from the theoretical viewpoint of the models of the hydrogen-bonded systems. Systematic studies of their properties provide important information concerning the deeper understanding of the molecular liquid structure and the intermolecular interactions predominated by the self-association of the alkanol molecules due to hydrogen bonding. These studies are also important from the viewpoint of the prediction of properties of (alkanol + alkane) mixtures of components having varying numbers of $-CH_2-$ units in the alkyl chain or varying numbers of $-CH_3$ substituents attached to the alkyl chain in the alkanol or alkane molecules. With this viewpoint, Wagner and Heintz (1986) and Heintz et al. (1986) measured excess molar volumes, V_m^E, of binary mixtures of nonane and hexane with five different 1-alkanols at various temperatures. Fuente et al. (1992) measured V_m^E of (nonan-1-ol + decane or tetradecane) at $T = 298.15$ K, 308.15 K, and 318.15 K. Franjo et al. (1994) have determined V_m^E of $xCH_3(CH_2)_5OH + (1 - x)CH_3(CH_2)_4CH_3$ at $T = 298.15$ K. Zielkiewicz (1994a,b) has measured total vapor pressures and V_m^E of (heptane + propan-2-ol or butan-1-ol or 2-methylpropan-1-ol or 2-methylpropan-2-ol or pentan-1-ol) at $T = 313.15$ K. Nath and Pandey (1997a,b) have recently measured V_m^E and refractive indexes, n_D, of binary mixtures of butanol (n-C_4H_9OH) and heptanol (n-$C_7H_{15}OH$) with pentane (n-C_5H_{12}), hexane (n-C_6H_{14}), heptane (n-C_7H_{16}), octane (n-C_8H_{18}), and 2,2,4-trimethylpentane (2,2,4-TMP). Since the viscosity data of binary liquid mixtures are known (Fort and Moore, 1966; Nath and Dubey, 1981; Nath and Dixit, 1984; Nath and Tripathi, 1986; Nath and Rashmi, 1990; Matos et al., 1996) to shed light on the molecular liquid structure and intermolecular interactions between the components, it was thought worthwhile to get information concerning the effect of concentration on the self-association of alkanol molecules and intermolecular forces between the components, in (alkanol + alkane) mixtures, from viscosity data. The measurements of viscosities have, therefore, been made in this work for binary mixtures of n-C_4H_9OH with n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, and n-C_8H_{18} at $T = 298.15$, and the results obtained are reported and interpreted in this paper.

Experimental Section

Materials. Pentane, hexane, heptane, octane, and butanol used in this work were of the same quality and were purified; their purity was checked as described earlier (Nath and Pandey, 1997a,b; Nath, 1997).

Table 1. Experimental Kinematic Viscosities, ν, and Dynamic Viscosities, η, of Pure Liquids at $T = 298.15$ K

	ν/mm^2·s^{-1}	η/mPa·s	
liquid	this work	this work	lit.[a]
butanol	3.224	2.598	2.60
pentane	0.349	0.217	0.215
hexane	0.447	0.293	0.292
heptane	0.574	0.390	0.390
octane	0.734	0.513	0.514

[a] Riddick and Bunger (1970).

Method. The viscosities of the various pure liquids and binary mixtures were measured at (298.15 ± 0.01) K, by using the kinematic viscometer described by Taun and Fuoss (1963) and by following the procedure described by Nath and Dubey (1981). The measured values of the kinematic viscosities, ν, were converted to dynamic viscosities, η, by using the densities which for pure liquids were those reported by Riddick and Bunger (1970). The densities of mixtures were obtained from the densities of the pure components and measurements (Nath and Pandey, 1997a) on V_m^E for their binary mixtures. The values of the densities ρ of the mixtures thus obtained are given in Table 2. The values of η are accurate to ±0.002 mPa·s.

Results and Discussion

The values of ν and η of the pure components pentane, hexane, heptane, octane, and butanol at $T = 298.15$ are given in Table 1, whereas the values of ν and η of binary mixtures of butanol with pentane, hexane, heptane, and octane at $T = 298.15$ K are given in Table 2, where x refers to the mole fraction of butanol in the mixture. x has an uncertainty of ±0.0001. The values of η of the various mixtures have been plotted against the mole fraction of butanol, x, in Figure 1. The experimental values of dynamic viscosities η of the mixtures have been used to calculate the quantity from the relation

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i\eta_i \qquad (1)$$

where η_i refers to the dynamic viscosity of the pure component i for which the mole fraction in the mixture is x_i. The values of $\Delta\eta$ for the various mixtures have been

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Table 2. Kinematic Viscosities, ν, Densities, ϱ, Dynamic Viscosities, η, and Viscosity Deviations, $\Delta\eta$, for the Various Mixtures at T = 298.15 K

x	ν/mm^2·s^{-1}	ρ/g·cm^{-3}	η/mPa·s	$\Delta\eta$/mPa·s
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_5H_{12}$				
0.0549	0.370	0.629 31	0.233	−0.1147
0.1224	0.396	0.639 59	0.253	−0.2554
0.2107	0.456	0.653 71	0.298	−0.4207
0.2475	0.486	0.659 80	0.321	−0.4853
0.2799	0.522	0.665 25	0.347	−0.5364
0.3431	0.592	0.676 13	0.400	−0.6339
0.3956	0.668	0.685 40	0.458	−0.7009
0.4401	0.743	0.693 41	0.515	−0.7499
0.4799	0.823	0.700 70	0.577	−0.7826
0.5300	0.937	0.710 03	0.665	−0.8139
0.5708	1.046	0.717 76	0.751	−0.8251
0.6150	1.177	0.726 25	0.855	−0.8263
0.6666	1.355	0.736 32	0.998	−0.8062
0.7124	1.529	0.745 40	1.140	−0.7732
0.7621	1.751	0.755 40	1.323	−0.7086
0.8177	2.021	0.766 79	1.550	−0.6139
0.8778	2.375	0.779 35	1.851	−0.4560
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_6H_{14}$				
0.0744	0.474	0.662 24	0.314	−0.1505
0.1835	0.531	0.674 48	0.358	−0.3580
0.2346	0.566	0.680 64	0.385	−0.4487
0.2750	0.604	0.685 69	0.414	−0.5129
0.3169	0.644	0.691 11	0.445	−0.5784
0.3758	0.715	0.699 01	0.500	−0.6592
0.4329	0.806	0.707 01	0.570	−0.7208
0.4800	0.889	0.713 85	0.635	−0.7644
0.5209	0.981	0.719 99	0.706	−0.7877
0.5662	1.085	0.726 94	0.789	−0.8091
0.6288	1.263	0.736 93	0.931	−0.8114
0.6740	1.402	0.744 40	1.044	−0.8026
0.7376	1.648	0.755 30	1.245	−0.7482
0.7844	1.854	0.763 62	1.416	−0.6850
0.8369	2.119	0.773 28	1.639	−0.5830
0.9012	2.491	0.785 61	1.957	−0.4133
0.9636	2.932	0.798 19	2.340	−0.1741
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_7H_{16}$				
0.0852	0.621	0.685 71	0.426	−0.1521
0.1620	0.672	0.692 16	0.465	−0.2827
0.2260	0.722	0.697 85	0.504	−0.3850
0.2844	0.773	0.703 41	0.544	−0.4739
0.3309	0.828	0.708 08	0.586	−0.5346
0.3751	0.875	0.712 71	0.624	−0.5942
0.4338	0.964	0.719 18	0.693	−0.6548
0.4868	1.052	0.725 34	0.763	−0.7018
0.5482	1.171	0.732 90	0.858	−0.7424
0.5924	1.266	0.738 63	0.935	−0.7630
0.6412	1.394	0.745 26	1.039	−0.7668
0.6828	1.523	0.751 17	1.144	−0.7536
0.7617	1.800	0.763 10	1.374	−0.6978
0.8070	1.996	0.770 41	1.538	−0.6339
0.8493	2.208	0.777 56	1.717	−0.5482
0.9682	2.968	0.799 48	2.373	−0.1548
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_8H_{18}$				
0.0820	0.738	0.702 82	0.519	−0.1650
0.1692	0.755	0.708 37	0.536	−0.3298
0.2380	0.796	0.713 21	0.568	−0.4412
0.2906	0.841	0.717 18	0.603	−0.5159
0.3508	0.911	0.722 04	0.658	−0.5864
0.3857	0.957	0.725 02	0.694	−0.6232
0.4229	1.010	0.728 33	0.736	−0.6587
0.4621	1.079	0.731 98	0.790	−0.6865
0.5020	1.158	0.735 88	0.852	−0.7077
0.5489	1.266	0.740 70	0.938	−0.7195
0.5905	1.375	0.745 22	1.025	−0.7192
0.6257	1.488	0.749 23	1.115	−0.7026
0.7000	1.739	0.758 30	1.319	−0.6535
0.7432	1.908	0.763 99	1.458	−0.6046
0.7829	2.079	0.769 51	1.600	−0.5453
0.8639	2.466	0.781 76	1.928	−0.3862
0.9655	3.024	0.799 26	2.417	−0.1091

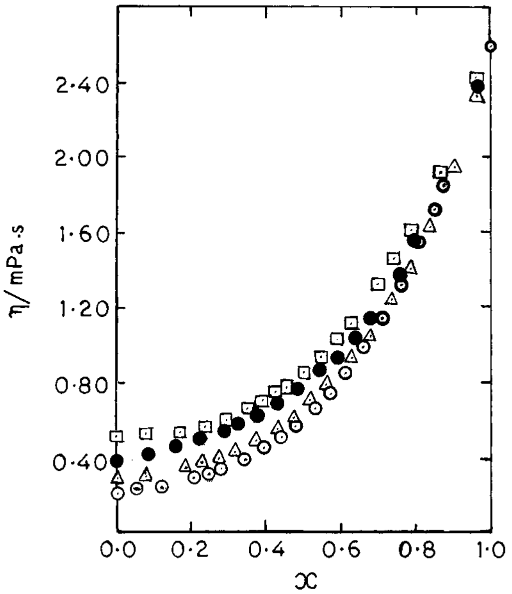

Figure 1. η plotted versus x for the following systems at T = 298.15 K: (⊙) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_5H_{12}$; (△) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_6H_{14}$; (●) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_7H_{16}$; (⊡) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_8H_{18}$.

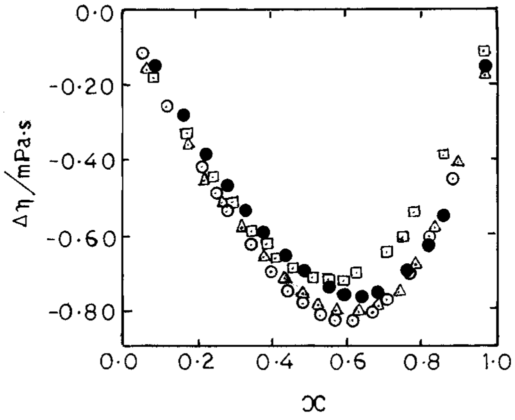

Figure 2. $\Delta\eta$ plotted versus x for the following systems at T = 298.15 K: (⊙) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_5H_{12}$; (△) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_6H_{14}$; (●) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_7H_{16}$; (⊡) $(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_8H_{18}$.

Table 3. Values of the Parameters B_k of Eq 2 and the Standard Deviations, δ, for the Various Mixtures

property	B_0	B_1	B_2	B_3	δ
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_5H_{12}$					
ν/mm^2·s^{-1}	0.3557	0.2120	1.7580	0.9044	0.0051
η/mPa·s	0.2201	0.2266	0.9767	1.1776	0.0028
$\Delta\eta$/mPa·s	−3.2938	−0.5209	0.0999	0.0163	0.0021
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_6H_{14}$					
ν/mm^2·s^{-1}	0.4502	0.3061	1.8598	0.6066	0.0032
η/mPa·s	0.2941	0.2815	1.1825	0.8375	0.0024
$\Delta\eta$/mPa·s	−3.2570	−0.2552	−0.0394	−0.0977	0.0020
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_7H_{16}$					
ν/mm^2·s^{-1}	0.5752	0.7583	1.0994	0.7922	0.0025
η/mPa·s	0.3900	0.6044	0.7362	0.8676	0.0016
$\Delta\eta$/mPa·s	−3.0619	−0.1956	−0.0446	0.0184	0.0018
$(x)n\text{-}C_4H_9OH + (1-x)n\text{-}C_8H_{18}$					
ν/mm^2·s^{-1}	0.7373	−0.2582	4.6377	−1.8907	0.0036
η/mPa·s	0.5172	−0.1581	3.4622	−1.2201	0.0034
$\Delta\eta$/mPa·s	−2.7948	0.9572	0.0144	−0.0021	0.0022

plotted against the mole fraction of butanol, x, in Figure 2, which shows that $\Delta\eta$ is negative throughout the entire range of composition for all the present mixtures. The values of ν, η, and $\Delta\eta$ have been fitted by the method of least squares to the equation

Table 4. Values of the Parameters ν_{AB} and ν_{BA} of Eq 3, the Standard Deviations, $\delta(\nu)$, Average Percent Deviations, $(\Delta\%)_{av}$, and the Maximum Percent Deviations, $(\Delta\%)_{max}$, for the Various Mixtures at T = 298.15 K

				$(\Delta\%)_{av}$		$(\Delta\%)_{max}$	
mixture	ν_{AB}/mm^2·s^{-1}	ν_{BA}/mm^2·s^{-1}	$\delta(\nu)$/mm^2·s^{-1}	eq 3	eq 5	eq 3	eq 5
$(x)n$-$C_4H_9OH + (1 - x)n$-C_5H_{12}	1.4551	0.4520	0.0042	0.41	14.2	0.82	25.6
$(x)n$-$C_4H_9OH + (1 - x)n$-C_6H_{14}	1.3705	0.5374	0.0055	0.45	10.4	1.12	20.5
$(x)n$-$C_4H_9OH + (1 - x)n$-C_7H_{16}	1.3318	0.7545	0.0039	0.26	9.36	0.80	15.9
$(x)n$-$C_4H_9OH + (1 - x)n$-C_8H_{18}	1.7435	0.6619	0.0081	0.53	8.15	1.22	16.2

$$Y = a\sum_{k=0}^{n} B_k Z^k \tag{2}$$

using $a = 1$, $z = \phi_A$ when $Y = \nu$ or η and $a = \phi_A\phi_B$, $Z = (\phi_A - \phi_B)$ when $Y = \Delta\eta$. Here ϕ_A and ϕ_B refer to the volume fractions of the components A (butanol) and B (alkane) respectively. The values of the parameters B_k of eq 2, along with the standard deviation, δ, are given in Table 3.

The viscosity data of the various mixtures can be analyzed in light of the various theories of liquid-mixture viscosity. The various theories for prediction of viscosities of liquid mixtures have been discussed by Reid et al. (1977). One of the approaches for estimation of liquid-mixture viscosity is that due to McAllister (1960), who has adopted the Eyring approach (Bloomfield and Dewan, 1971; Glasstone et al., 1941) and has considered the interaction between layers of molecules in the velocity gradient to involve activated jumps of molecules between layers. In this picture, the motion of the molecule has been treated as if the molecule were undergoing a chemical reaction and has to overcome a potential barrier in this process. For a binary mixture of A and B in which case molecular interactions of A−A−A, B−B−B, A−B−A, B−A−B, A−A−B, and A−B−B types can be visualized, McAllister's approach yields the relation

$$\ln \nu = x_A^3 \ln \nu_A + 3x_A^2 x_B \ln \nu_{AB} + 3x_A x_B^2 \ln \nu_{BA} + x_B^3 \ln \nu_B + R^\circ \tag{3}$$

where

$$R^\circ = x_B^3 \ln \frac{M_B}{M_A} + 3x_A x_B^2 \ln \frac{1 + 2\frac{M_B}{M_A}}{3} + 3x_A^2 x_B \ln \frac{2 + M_B/M_A}{3} - \ln(x_A + x_B M_B/M_A) \tag{4}$$

In eq 3, ν refers to the kinematic viscosity of the mixture of components A and B having mole fractions x_A and x_B, respectively, in the mixture, and ν_A and ν_B are the kinematic viscosities of pure components A and B, respectively. ν_{AB} and ν_{BA} are the two undetermined parameters that are characteristic of a system. In eq 4, M_A and M_B are the molecular weights of the components A and B, respectively. Taking A for butanol and B for the alkane component in the various mixtures, the values of the parameters ν_{AB} and ν_{BA} have been determined from eq 3 using the viscosity data for the present mixtures. The values of the parameters ν_{AB} and ν_{BA}, along with those of the standard deviations, δ (ν), for the various systems are given in Table 4. The values of the average percent deviations, $(\Delta\%)_{av}$, and the maximum percent deviations, $(\Delta\%)_{max}$, of the experimental values of kinematic viscosities from those estimated for the various mixtures from eq 3 are given in Table 4 which shows that McAllister's eq 3 correlates the liquid-mixture viscosity to a significantly high degree of accuracy in the case of all the present mixtures.

According to Lobe's approach (Lobe, 1973), the kinematic viscosity, ν, of a binary mixture of components A and B is given by the equation

$$\nu = \phi_A \nu_A\, e^{\nu_B \alpha_B^*} + \phi_B \nu_B\, e^{\nu_A \alpha_A^*} \tag{5}$$

where ϕ_A and ϕ_B refer to the volume fractions of the components A and B, respectively, in the mixture. Lobe has suggested that if A is chosen as the component with lesser pure-liquid viscosity and if the kinematic viscosity of the mixture varies monotonically with composition, then the values of α_A^* and α_B^* are given by the equations

$$\alpha_A^* = -1.7 \ln \frac{\nu_B}{\nu_A} \tag{6}$$

$$\alpha_B^* = 0.27 \ln \frac{\nu_B}{\nu_A} + \left(1.3 \ln \frac{\nu_B}{\nu_A}\right)^{1/2} \tag{7}$$

The values of the average percent deviations, $(\Delta\%)_{av}$, and the maximum percent deviations, $(\Delta\%)_{max}$, of the experimental values of kinematic viscosities from those estimated for the various mixtures from eq 5 are given in Table 4. It is seen that Lobe's eq 5 estimates liquid mixture viscosities to a much lesser degree of accuracy, which may be ascribed to the fact that eq 5 has no adjustable parameter.

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