Density and Viscosity Measurement of *n*-Butylamine with Hexyl Alcohol Isomer Binary Systems

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Densities and viscosities were measured for the binary mixtures of *n*-butylamine with 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 2-methyl-2-pentanol, and 4-methyl-2-pentanol at 303.15 K, 313.15 K, and 323.15 K over the entire composition range. Excess volumes and viscosity deviations were calculated at various temperatures. Both excess molar volumes and viscosity deviations are negative for all investigated systems. A Redlich−Kister-type equation was fit to the isothermal excess molar volumes and viscosity deviations, and McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities.

Introduction

A series of density and viscosity measurements have been made recently for mixtures containing highly polar compounds.[1−5] Density and viscosity measurements for binary mixtures of anisole, *n*-butylamine, and benzylamine organic compounds with 1-alkanols or alcohol isomers are of major interest in our laboratory. As a part of this continuing work, the experimental results are reported in this paper for the binary systems of *n*-butylamine with 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 2-methyl-2-pentanol, and 4-methyl-2-pentanol at temperatures from 303.15 K to 323.15 K. Although several similar studies have been published,[6−10] no available data were found in the literature for the binary mixtures of this study. These results not only reveal the effects of the self-association of the hexyl alcohols and the steric hindrance of methyl groups on both viscosities and densities but also add the availability of the physical property data, which are useful for model developments and engineering application.

Experimental Section

n-Butylamine (99 mass %), 2-hexanol (99 mass %), 3-hexanol (98 mass %), 2-methyl-1-pentanol (98 mass %), 2-methyl-2-pentanol (99 mass %), and 4-methyl-2-pentanol (99 mass %) were supplied by Fluka Chemie AG. The purities of these substances were checked with gas chromatography. All reagents were used without further purification. The measured densities of these pure substances at 313.15 K were compared with literature values in Table 1.

An Anton Paar densimeter (DMA 60/602H) was employed to measure the density (ρ). Each sample mixture was prepared by mass with an uncertainty of ±0.0001 mole fraction. The temperature of the measuring cell in the densimeter was controlled to within ±0.03 K by circulating thermostated water. A precision digital thermometer (model 1560, Hart Scientific) with a thermistor probe was used to read the cell temperature to an uncertainty of ±0.015 K. The oscillation period (τ) in the vibrating U-tube of the densimeter was converted to density by the following equation:

$$\rho = A(\tau^2 - B) \tag{1}$$

where A and B are apparatus constants determined by literature density data of pure water[11] and dry air[12] at temperatures of interest. The uncertainty of the density measurements is estimated to be less than $\pm 1 \times 10^{-4}$ g·cm^{-3}. The composition of the mixture sample was checked frequently by gas chromatography after the measurement, and the variation was found to be minimal.

Table 1. Densities (ρ) for Pure Components at 313.15 K

component	ρ/g·cm^{-3} exptl	lit
n-butylamine	0.7229	0.7243[a]
		0.7232[b]
2-hexanol	0.7984	0.7984[a]
3-hexanol	0.8017	0.8016[a]
2-methyl-1-pentanol	0.8095	0.8094[a]
2-methyl-2-pentanol	0.8024	0.7967[a]
4-methyl-2-pentanol	0.7907	0.7908[a]

[a] TRC Thermodynamic Tables (1994).[15] [b] Lee et al. (1993).[5]

The kinematic viscosities (ν) were measured by using a Cannon-Fenske routine viscometer (size 75, supplied by Cannon Instrument Co.). The detailed procedure of the viscosity measurements was described elsewhere.[1] The kinematic viscosities were obtained from the following equation:

$$\nu = kt \tag{2}$$

where k is the capillary constant of the viscometer and t is the flow time. The absolute viscosities, η, were calculated from $\eta = \rho\nu$. The uncertainty of the reported viscosities is within ±1.0%.

Results and Discussion

Experimental results for the five binary systems of *n*-butylamine with the hexyl alcohols are listed in Tables 2 to 6, respectively.

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Table 2. Densities (ρ) and Viscosities (η) of *n*-Butylamine (1) + 2-Hexanol (2)

	303.15 K		313.15 K		323.15 K	
x_1	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s
0.0000	0.8064	3.23	0.7984	2.29	0.7901	1.64
0.1000	0.8020	2.67	0.7942	1.97	0.7860	1.45
0.2000	0.7967	2.19	0.7889	1.68	0.7806	1.26
0.3000	0.7915	1.78	0.7837	1.40	0.7753	1.10
0.4000	0.7850	1.47	0.7769	1.17	0.7685	0.93
0.5000	0.7777	1.20	0.7694	0.98	0.7608	0.79
0.6000	0.7698	0.97	0.7614	0.81	0.7511	0.67
0.6999	0.7607	0.79	0.7521	0.68	0.7416	0.57
0.8000	0.7513	0.65	0.7427	0.56	0.7324	0.47
0.9000	0.7421	0.53	0.7329	0.47	0.7229	0.40
1.0000	0.7321	0.46	0.7229	0.40	0.7127	0.36

Table 3. Densities (ρ) and Viscosities (η) of *n*-Butylamine (1) + 3-Hexanol (2)

	303.15 K		313.15 K		323.15 K	
x_1	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s
0.0000	0.8102	3.52	0.8017	2.34	0.7928	1.58
0.1000	0.8064	2.85	0.7984	2.20	0.7898	1.44
0.2000	0.8014	2.26	0.7935	1.79	0.7850	1.24
0.3000	0.7956	1.78	0.7875	1.39	0.7769	1.07
0.3999	0.7886	1.41	0.7805	1.09	0.7700	0.91
0.5000	0.7804	1.13	0.7720	0.89	0.7632	0.76
0.5999	0.7720	0.92	0.7635	0.78	0.7545	0.65
0.7000	0.7629	0.76	0.7541	0.68	0.7452	0.55
0.7999	0.7530	0.65	0.7436	0.58	0.7344	0.48
0.9000	0.7420	0.54	0.7327	0.46	0.7232	0.40
1.0000	0.7321	0.46	0.7229	0.40	0.7127	0.36

Table 4. Densities (ρ) and Viscosities (η) of *n*-Butylamine (1) + 2-Methyl-1-pentanol (2)

	303.15 K		313.15 K		323.15 K	
x_1	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s
0.0000	0.8168	4.55	0.8095	3.18	0.8015	2.25
0.1000	0.8103	3.38	0.8030	2.51	0.7953	1.85
0.2000	0.8048	2.67	0.7974	2.06	0.7896	1.57
0.2999	0.7982	2.10	0.7906	1.65	0.7826	1.32
0.4000	0.7910	1.67	0.7832	1.35	0.7750	1.08
0.5000	0.7836	1.37	0.7757	1.11	0.7672	0.91
0.6000	0.7745	1.10	0.7663	0.90	0.7577	0.75
0.6999	0.7647	0.89	0.7562	0.72	0.7474	0.60
0.8000	0.7539	0.69	0.7452	0.59	0.7361	0.50
0.8999	0.7429	0.54	0.7345	0.48	0.7243	0.42
1.0000	0.7321	0.46	0.7229	0.40	0.7127	0.36

Table 5. Densities (ρ) and Viscosities (η) of *n*-Butylamine (1) + 2-Methyl-2-pentanol (2)

	303.15 K		313.15 K		323.15 K	
x_1	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s
0.0000	0.8108	2.93	0.8024	2.06	0.7935	1.46
0.1000	0.8067	2.62	0.7982	1.88	0.7892	1.34
0.2000	0.8015	2.25	0.7931	1.66	0.7840	1.20
0.3000	0.7957	1.86	0.7872	1.41	0.7782	1.04
0.4000	0.7888	1.55	0.7802	1.20	0.7712	0.92
0.4999	0.7814	1.26	0.7728	1.00	0.7637	0.79
0.5999	0.7729	1.01	0.7642	0.83	0.7547	0.67
0.7000	0.7638	0.82	0.7550	0.69	0.7451	0.57
0.8000	0.7534	0.66	0.7443	0.57	0.7343	0.48
0.9000	0.7424	0.54	0.7333	0.47	0.7236	0.41
1.0000	0.7321	0.46	0.7229	0.40	0.7127	0.36

Excess volumes (V^E) and viscosity deviations ($\delta\eta$) were calculated from the experimental results by the following equations, respectively.

$$V^E = V_M - (x_1V_1 + x_2V_2) \quad (3)$$

$$\delta\eta = \eta_M - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

where x_i, V_i, and η_i are the mole fraction, molar volume, and viscosity of the pure component i, respectively. The subscript M represents mixture properties. The composition dependence of either the V^E or $\delta\eta$ isotherm was represented by a Redlich−Kister-type equation:[13]

$$Y = x_1x_2\sum_{i=0}^{P} a_i(x_1 - x_2)^i \quad (5)$$

where Y refers to V^E/cm^3·mol^{-3} or $\delta\eta$/mPa·s and x_1 and x_2 are the mole fractions of *n*-butylamine and the hexyl

Table 6. Densities (ρ) and Viscosities (η) of *n*-Butylamine (1) + 4-Methyl-2-pentanol (2)

	303.15 K		313.15 K		323.15 K	
x_1	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s	ρ/g·cm^{-3}	η/mPa·s
0.0000	0.7993	3.23	0.7907	2.24	0.7820	1.55
0.1000	0.7948	2.61	0.7870	1.91	0.7786	1.40
0.2000	0.7907	2.06	0.7829	1.57	0.7745	1.21
0.3000	0.7852	1.66	0.7773	1.31	0.7689	1.02
0.3999	0.7796	1.35	0.7715	1.09	0.7630	0.87
0.5000	0.7728	1.09	0.7646	0.91	0.7559	0.75
0.6000	0.7660	0.92	0.7575	0.77	0.7486	0.64
0.6999	0.7580	0.77	0.7494	0.65	0.7403	0.54
0.7999	0.7497	0.64	0.7409	0.55	0.7311	0.47
0.9000	0.7408	0.56	0.7317	0.48	0.7217	0.41
1.0000	0.7321	0.46	0.7229	0.40	0.7127	0.36

Table 7. Correlated Results for the Excess Molar Volume (V^E)

system	T/K	a_0	a_1	a_2	a_3	$\sigma \times 10^3$ cm^3·mol^{-1}
n-butylamine + 2-hexanol	303.15	−2.3133	1.4113	0.7228	−0.9043	0.5592
	313.15	−2.6048	1.3593	0.6973	0.0155	0.4601
	323.15	−2.6164	2.9835	0.4076	−2.0710	0.9463
n-butylamine + 3-hexanol	303.15	−2.9768	1.3398	0.8060	1.5731	0.7585
	313.15	−3.3344	1.9227	0.8300	1.9407	0.6063
	323.15	−3.3371	0.0891	−0.6766	5.0250	1.1442
n-butylamine + 2-methyl-1-pentanol	303.15	−2.4452	0.3130	2.6156	−0.3380	0.5668
	313.15	−2.5529	0.7131	1.8548	−1.5531	0.6900
	323.15	−2.0985	0.3003	2.0504	0.1325	0.4953
n-butylamine + 2-methyl-2-pentanol	303.15	−3.1624	0.5449	1.0317	1.8271	0.3080
	313.15	−3.3551	0.6213	1.2686	1.9392	0.3225
	323.15	−3.5430	1.1927	1.2151	0.6414	0.3412
n-butylamine + 4-methyl-2-pentanol	303.15	−1.9525	0.9651	1.2670	−0.5120	0.5261
	313.15	−2.3602	1.2563	0.6322	0.4107	0.4729
	323.15	−2.8708	1.3010	0.7473	1.3425	0.4104

Table 8. Correlated Results for the Viscosity Deviation ($\delta\eta$)

system	T/K	a_0	a_1	a_2	a_3	$\sigma \times 10^2$ mPa·s
n-butylamine + 2-hexanol	303.15	−2.6068	0.6701	−0.2038	−0.2638	0.57
	313.15	−1.4777	0.2112	0.1456	−0.2490	0.27
	323.15	−0.8217	−0.0728	0.0633	−0.1371	0.48
n-butylamine + 3-hexanol	303.15	−3.4632	1.3579	0.2540	−0.6773	0.34
	313.15	−1.9338	1.0058	2.3201	−3.5463	0.80
	323.15	−0.8217	−0.0146	0.5055	−0.6471	0.68
n-butylamine + 2-methyl-1-pentanol	303.15	−4.5034	2.2131	−2.2333	1.1092	2.19
	313.15	−2.7097	0.9286	−0.7790	0.5875	1.23
	323.15	−1.5642	0.1634	−0.4626	0.6166	0.98
n-butylamine + 2-methyl-2-pentanol	303.15	−1.7890	−0.2883	0.7058	−0.6875	0.68
	313.15	−0.9243	−0.3342	0.5556	−0.3463	0.40
	323.15	−0.4855	−0.2005	0.1758	−0.2595	0.63
n-butylamine + 4-methyl-2-pentanol	303.15	−3.0356	1.3887	0.0479	−0.4221	1.15
	313.15	−1.6597	0.4470	0.3743	−0.1078	0.57
	323.15	−0.8668	0.0877	0.4743	−0.5207	0.66

Table 9. Correlated Results of McAllister's Models

		three-body model			four-body model			
system	*T*/K	ν_{12}	ν_{21}	AAD%[a]	ν_{1112}	ν_{1122}	ν_{2221}	AAD%[a]
n-butylamine + 2-hexanol	303.15	1.0275	2.2200	0.55	0.8569	1.6309	2.5036	0.41
	313.15	0.8991	1.8243	0.36	0.7908	1.2846	2.0362	0.35
	323.15	0.7646	1.4583	0.76	0.6312	1.1503	1.5406	0.58
n-butylamine + 3-hexanol	303.15	0.9592	2.1011	0.94	0.9418	1.2131	2.7140	0.28
	313.15	0.8474	1.7707	4.45	1.1241	0.6079	3.0118	2.14
	323.15	0.7069	1.4716	0.72	0.6856	0.9187	1.6759	0.60
n-butylamine + 2-methyl-1-pentanol	303.15	1.3039	2.1780	1.66	0.8956	2.1268	2.5025	0.91
	313.15	1.0098	1.9378	0.82	0.8137	1.5803	2.1429	0.38
	323.15	0.7964	1.6907	1.16	0.6743	1.3341	1.7590	0.57
n-butylamine + 2-methyl-2-pentanol	303.15	1.0094	2.6789	0.48	0.8966	1.6422	2.8836	0.48
	313.15	0.9068	1.9932	0.45	0.8160	1.2946	2.1796	0.32
	323.15	0.7679	1.4866	0.56	0.6592	1.1231	1.5312	0.43
n-butylamine + 4-methyl-2-pentanol	303.15	1.0387	1.8572	0.82	0.9763	1.2392	2.4094	0.60
	313.15	0.8916	1.6062	1.07	0.8461	1.0546	1.9786	0.39
	323.15	0.7371	1.3281	0.77	0.6904	0.9058	1.6078	0.46

[a] $\mathrm{AAD\%} = (100/n)\Sigma_{k=1}^{n}|v_k^{\mathrm{calcd}} - v_k^{\mathrm{exptl}}|v_k^{\mathrm{exptl}}$.

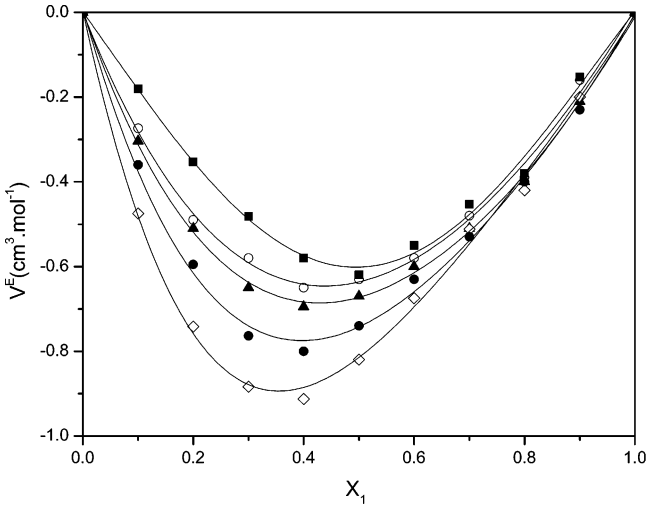

Figure 1. Excess volumes (V^{E}) at 313.15 K: (▲) *n*-butylamine (1) + 2-hexanol (2); (◊) *n*-butylamine (1) + 3-hexanol (2); (■) *n*-butylamine (1) + 2-methyl-1-pentanol (2); (●) *n*-butylamine (1) + 2-methyl-2-pentanol (2); (○) *n*-butylamine (1) + 4-methyl-2-pentanol (2); (−) calculated from eq 5.

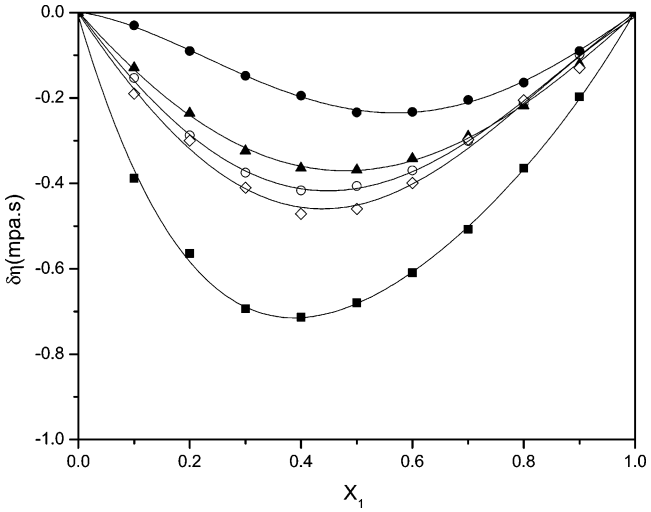

Figure 2. Viscosity deviations ($\delta\eta$) at 313.15 K: (▲) *n*-butylamine (1) + 2-hexanol (2); (◊) *n*-butylamine (1) + 3-hexanol (2); (■) *n*-butylamine (1) + 2-methyl-1-pentanol (2); (●) *n*-butylamine (1) + 2-methyl-2-pentanol (2); (○) *n*-butylamine (1) + 4-methyl-2-pentanol (2); (−) calculated from eq 5.

alcohol component, respectively. The coefficients a_i were obtained by fitting the experimental results to eq 5 with a least-squares method. The correlated results for excess volumes and viscosity deviations are given respectively in Tables 7 and 8, in which the tabulated standard deviation (σ) was defined as

$$\sigma = \left[\frac{\sum (Y_{\mathrm{exptl}} - Y_{\mathrm{calcd}})^2}{n - p}\right]^{1/2} \qquad (6)$$

where n is the number of data points and p is the number of coefficients. The subscript calcd denotes the calculated value.

The variations of V^{E} and $\delta\eta$ with the mole fraction of *n*-butylamine at 313.15 K are presented in Figures 1 and 2, respectively. Figure 1 shows that the excess molar volumes are negative for all of these investigated systems. This may imply that volume contraction takes place upon mixing *n*-butylamine with hexyl alcohol isomers because of the self-association between these dissimilar molecules and the steric hindrance of methyl groups. The magnitude of the volume contraction follows the sequence of 3-hexanol > 2-methyl-2-pentanol > 2-hexanol >4-methyl-2-pentanol >2-methyl-1-pentanol. Moreover, the excess volumes were found to increase with increasing temperature. Figure 2 illustrates that the viscosity deviations are negative for each binary system. As evidenced from the calculations, the viscosity deviations decrease with an increase in temperature.

McAllister's multibody interaction model[14] was widely used to correlate kinematic viscosity (ν) data. The three-body McAllister model was defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \qquad (7)$$

and the four-body model was given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (8)$$

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are model parameters. The calculated results are presented in Table 9. The average deviations are approximately within the experimental uncertainty, regardless of the four-body or the three-body model used.

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