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Densities and Viscosities for Binary Mixtures of Butylamine with Aliphatic Alcohols

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Densities and viscosities were measured for the binary mixtures of butylamine with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol at 303.15 K, 313.15 K, and 323.15 K over the entire composition range. Excess molar 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 applied to fit the isothermal excess 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 the mixtures containing highly polar compounds.[1−4] Anisole, butylamine, and benzylamine organic compounds with 1-alkanols or alcohol isomers binary mixture density and viscosity measurements are of major interest for our laboratory. As a part of this continuing work, the experimental results are reported in this paper for the binary systems of butylamine with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol at temperatures from 303.15 K to 323.15 K. These results reveal the molecular interactions of the cross-association between alkanol and amine molecules. Under the comparable conditions of this study, density and viscosity data are available in the literature[5−8] for the constituent compounds. The data from different sources will be compared with our results.

Experimental Section

Butylamine (99 mass %), 1-hexanol (99 mass %), and 1-octanol (99 mass %) were supplied by Fluka Chemie AG (packed in Buchs, Switzerland). 1-Butanol (99 mass %), 1-pentanol (99 mass %), and 1-heptanol (99.5 mass %) were purchased from R.D.H. products (Hannover, Germany). Their purities were verified by gas chromatography (all chemical impurities were less than 1.0%). All reagents were used without further purification.

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

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

Here A and B are apparatus constants determined with the literature density data of pure water and dry air at each temperature of interest and are taken from Harr et al.[9] and Vargaftik,[10] respectively. The uncertainty of density measurement is estimated to be less than $\pm 1 \times 10^{-4}$ g·cm^{-3}. The composition of sample was checked frequently by gas chromatography after the measurement. The changes of composition were found to be minimal.

The kinematic viscosities (ν) were determined experimentally by using a Cannon-Fenske routine viscometer (size 75, supplied by Cannon Instrument Co.). The procedure of measurement has been detailed in our previous paper.[1] The kinematic viscosity was obtained from the following equation:

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

Here k is the capillary constant and t (s) is the flowing time of the sample; the absolute viscosity η was calculated from $\eta = \rho\nu$. The reported viscosity is accurate to within ±1.0%.

Results and Discussion

The densities and viscosities of the pure substances are compares from different sources shown in Table 1. Our results of butylamine and 1-alkanols viscosities are close to the data of Lee et al.[5] and TRC c-5030 and c-5031, 1994,[12] respectively. The binary systems of butylamine with 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol experimental results are listed in Tables 2−6, respectively. There are some data (at 303.15 K and 313.15 K) that were compared with the published data of Oswal and Desai,[8] which show density data containing rich butylamine mixtures (i.e., $x_1 > 0.5$) are lower than those of this work. On the other hand, the viscosity data of alcohols containing rich mixtures (i.e., $x_1 < 0.5$) are higher than ours. Figure 1 compares the results of the absolute viscosity with the mole fraction of butylamine (x_1) for our measured data and the published data of Oswal and Desai[8] at 303.15 K.

Excess molar volume V^E and viscosity deviation $\delta\eta$ are calculated, respectively, from the experimental results with the following equations:

$$V^E = V_m - (x_1V_1 + x_1V_1) \tag{3}$$

$$\delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

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Table 1. Comparison of Measured Densities, ρ, and Viscosities, η, for Pure Components with Literature Values

		ρ/g·cm^{-3}		η/mPa·s	
compd	T/K	exptl	lit.	exptl	lit.
butylamine	303.15	0.7321	0.72865[a] 0.7325[b]	0.464	0.4442[a] 0.458[b]
	313.15	0.7229	0.71917[a] 0.7232[b]	0.397	0.3927[a] 0.398[b]
	323.15	0.7127	0.7132[b]	0.355	0.353[b]
1-butanol	303.15	0.8024	0.80194[a] 0.8022[c]	2.261	2.2853[a] 2.263[c]
	313.15	0.7947	0.79405[a] 0.7946[c]	1.765	1.8170[a] 1.7734[c]
	323.15	0.7852	0.7867[c]	1.393	1.4099[c]
1-pentanol	303.15	0.8072	0.80736[a] 0.8079[c] 0.8071[d]	3.056	2.8315[a] 3.054[c]
	313.15	0.7997	0.79987[a] 0.8005[c]	2.361	2.3443[a] 2.341[c]
	323.15	0.7905	0.7930[c]	1.765	1.826[c]
1-hexanol	303.15	0.8115	0.81195[a] 0.8127[c]	3.861	3.7635[a] 3.90[e] 3.84[f]
	313.15	0.8043	0.80414[a] 0.8046[c]	2.936	3.1101[a]
	323.15	0.7953	0.7970[c]	2.248	
1-heptanol	303.15	0.8153	0.81530[a] 0.8148[c]	5.035	4.7853[a] 5.005[c]
	313.15	0.8082	0.80987[a] 0.8070[c]	3.671	3.5786[a]
	323.15	0.7994	0.7992[c]	2.741	
1-octanol	303.15	0.8181	0.81831[a] 0.8184[c]	6.256	6.1023[a] 6.01[e] 6.24[f] 6.298[g]
	313.15	0.8111	0.81188[a] 0.8108[c]	4.584	4.4132[a]
	323.15	0.8023	0.8031[c]	3.361	

[a] Oswal and Desai.[8] [b] Lee et al.[5] [c] TRC c-5030, c-5031, d-5000, 1994.[12] [d] Hales and Ellender.[13] [e] Matsuo and Makita.[14] [f] Lee et al.[15] [g] Singh et al.[16]

Table 2. Densities, ρ, and Viscosities, η, for Butylamine (1) + 1-Butanol (2)

	T = 303.15 K		T = 313.15 K		T = 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
0.0	0.8024	2.261	0.7947	1.765	0.7852	1.393
0.1008	0.7984	1.909	0.7904	1.518	0.7822	1.228
0.2007	0.7937	1.627	0.7854	1.305	0.7771	1.065
0.3004	0.7881	1.395	0.7797	1.120	0.7711	0.920
0.4000	0.7821	1.191	0.7734	0.976	0.7646	0.803
0.5009	0.7750	1.019	0.7662	0.843	0.7572	0.700
0.6001	0.7674	0.869	0.7585	0.730	0.7493	0.615
0.6997	0.7594	0.734	0.7503	0.622	0.7410	0.534
0.7999	0.7508	0.625	0.7415	0.539	0.7321	0.467
0.9001	0.7417	0.536	0.7332	0.470	0.7226	0.407
1.0	0.7321	0.464	0.7229	0.397	0.7127	0.355

Here 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 uncertainty of the excess molar volume as calculated is estimated to be less than ± 0.005 cm^3·mol^{-1}, and that of the viscosity deviation is about ±0.03 mPa·s. The variations of V^E and $\delta\eta$ with composition are expressed by a Redlich−Kister type equation:

$$Y = x_1 x_2 \sum_{i=0}^{3} a_i (x_1 - x_2)^i \tag{5}$$

Table 3. Densities, ρ, and Viscosities, η, for Butylamine (1) + 1-Pentanol (2)

	T = 303.15 K		T = 313.15 K		T = 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
0.0	0.8072	3.056	0.7997	2.361	0.7905	1.765
0.1020	0.8021	2.520	0.7941	1.956	0.7861	1.551
0.2002	0.7969	2.086	0.7887	1.639	0.7804	1.322
0.2994	0.7915	1.720	0.7831	1.381	0.7746	1.122
0.4012	0.7854	1.431	0.7767	1.162	0.7679	0.957
0.5000	0.7785	1.190	0.7696	0.976	0.7607	0.816
0.6008	0.7703	0.996	0.7613	0.829	0.7522	0.697
0.6995	0.7617	0.819	0.7524	0.693	0.7431	0.592
0.8002	0.7520	0.680	0.7425	0.583	0.7329	0.505
0.8997	0.7420	0.574	0.7324	0.498	0.7226	0.435
1.0	0.7321	0.464	0.7229	0.397	0.7127	0.355

Table 4. Densities, ρ, and Viscosities, η, for Butylamine (1) + 1-Hexanol (2)

	T = 303.15 K		T = 313.15 K		T = 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
0.0	0.8115	3.861	0.8043	2.936	0.7953	2.248
0.1002	0.8074	3.164	0.8001	2.411	0.7913	1.888
0.2005	0.8025	2.593	0.7952	2.026	0.7863	1.608
0.3001	0.7970	2.082	0.7895	1.642	0.7804	1.322
0.4004	0.7904	1.701	0.7831	1.356	0.7735	1.113
0.5002	0.7832	1.371	0.7755	1.120	0.7660	0.923
0.6001	0.7750	1.105	0.7668	0.909	0.7572	0.765
0.6999	0.7654	0.906	0.7581	0.759	0.7472	0.648
0.8001	0.7556	0.729	0.7468	0.622	0.7367	0.537
0.8998	0.7443	0.573	0.7353	0.494	0.7248	0.433
1.0	0.7321	0.464	0.7229	0.397	0.7127	0.355

Table 5. Densities, ρ, and Viscosities, η, for Butylamine (1) + 1-Heptanol (2)

	T = 303.15 K		T = 313.15 K		T = 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
0.0	0.8153	5.035	0.8082	3.671	0.7994	2.741
0.0997	0.8113	4.157	0.8041	3.079	0.7952	2.366
0.2010	0.8065	3.328	0.7992	2.535	0.7901	1.993
0.3000	0.8012	2.671	0.7936	2.069	0.7843	1.627
0.4035	0.7947	2.125	0.7869	1.684	0.7774	1.346
0.5000	0.7875	1.669	0.7797	1.336	0.7699	1.094
0.6006	0.7790	1.294	0.7707	1.056	0.7607	0.879
0.7002	0.7691	0.975	0.7606	0.797	0.7504	0.676
0.8001	0.7582	0.770	0.7493	0.655	0.7389	0.563
0.8999	0.7457	0.606	0.7367	0.518	0.7259	0.451
1.0	0.7321	0.464	0.7229	0.397	0.7127	0.355

Table 6. Densities, ρ, and Viscosities, η, for Butylamine (1) + 1-Octanol (2)

	T = 303.15 K		T = 313.15 K		T = 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
0.0	0.8181	6.256	0.8111	4.584	0.8023	3.361
0.1000	0.8137	5.075	0.8066	3.779	0.7979	2.828
0.2011	0.8093	4.061	0.8021	3.065	0.7931	1.358
0.3000	0.8040	3.239	0.7966	2.487	0.7875	1.942
0.4015	0.7976	2.547	0.7900	1.984	0.7807	1.576
0.5003	0.7906	1.995	0.7827	1.590	0.7731	1.289
0.6002	0.7819	1.528	0.7738	1.235	0.7640	1.021
0.7003	0.7718	1.141	0.7634	0.945	0.7533	0.791
0.7998	0.7605	0.847	0.7517	0.716	0.7414	0.614
0.9000	0.7472	0.623	0.7381	0.537	0.7274	0.466
1.0	0.7321	0.464	0.7229	0.397	0.7127	0.355

Here Y refers to V^E and $\delta\eta$. And the variables of x_1 and x_2 are the mole fractions of butylamine and the alcohol component, respectively. The coefficients a_i's were obtained by fitting the experimental values to eq 5 with least-squares methods. The correlated results for the excess volume and viscosity deviation are given in Tables 7 and 8, respectively. The tabulated standard deviation (σ) in Tables 7 and 8 was defined as

Table 7. Correlated Results for Excess Molar Volume, V^E

system	T/K	a_0	a_1	a_2	a_3	$10^3\sigma$ / $cm^3 \cdot mol^{-1}$
butylamine + 1-butanol	303.15	−4.334	0.095	0.643	−1.126	0.89
	313.15	−4.444	−0.039	0.694	−0.890	0.60
	323.15	−3.463	0.228	−0.371	−2.552	0.69
butylamine + 1-pentanol	303.15	−3.803	−0.230	1.683	0.602	0.74
	313.15	−3.727	−0.212	2.112	0.341	0.30
	323.15	−4.409	−0.557	1.372	−0.732	0.93
butylamine + 1-hexanol	303.15	−3.904	0.167	0.102	−0.033	1.15
	313.15	−4.464	−0.209	0.274	0.290	1.70
	323.15	−4.734	0.162	−0.565	−0.367	1.10
butylamine + 1-heptanol	303.15	−4.010	−0.007	0.649	0.315	0.62
	313.15	−4.229	0.125	0.382	−0.123	0.76
	323.15	−4.418	0.031	0.226	0.022	0.64
butylamine + 1-octanol	303.15	−3.676	0.070	1.208	−0.928	0.92
	313.15	−3.916	0.143	0.932	−1.132	0.83
	323.15	−4.160	0.053	0.536	−0.757	0.61

Table 8. Correlated Results for Viscosity Deviation, $\delta\eta$

system	T/K	a_0	a_1	a_2	a_3	10σ / mPa.s
butylamine + 1-butanol	303.15	−2.295	0.790	−0.569	0.012	0.54
	313.15	−1.595	0.508	−0.046	0.086	0.39
	323.15	−1.115	0.319	0.045	0.072	0.35
butylamine + 1-pentanol	303.15	−2.291	0.786	−0.037	0.007	0.54
	313.15	−1.590	0.502	−0.021	0.074	0.42
	323.15	−1.112	0.323	0.064	0.056	0.38
butylamine + 1-hexanol	303.15	−3.146	1.024	−0.138	−0.244	0.53
	313.15	−2.192	0.617	−0.281	0.135	0.94
	323.15	−1.494	0.385	−0.069	−0.012	0.79
butylamine + 1-heptanol	303.15	−4.382	0.893	0.328	−0.186	0.89
	313.15	−2.830	0.228	0.192	0.224	0.84
	323.15	−1.863	0.030	0.438	−0.127	0.94
butylamine + 1-octanol	303.15	−5.491	1.345	−0.326	−0.132	0.27
	313.15	−3.671	0.836	−0.166	−0.227	0.28
	323.15	−2.313	0.321	−0.067	−0.072	0.30

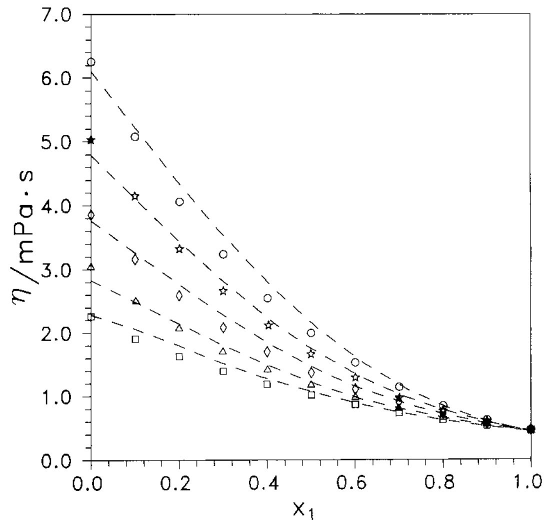

Figure 1. Viscosity, η, at 303.15 K: (□) butylamine (1) + 1-butanol (2); (△) butylamine (1) + 1-pentanol (2); (◇) butylamine (1) + 1-hexanol (2); (☆) butylamine (1) + heptanol (2); (○) butylamine (1) + 1-octanol (2); (- - -) published value of Oswal and Desai.[8]

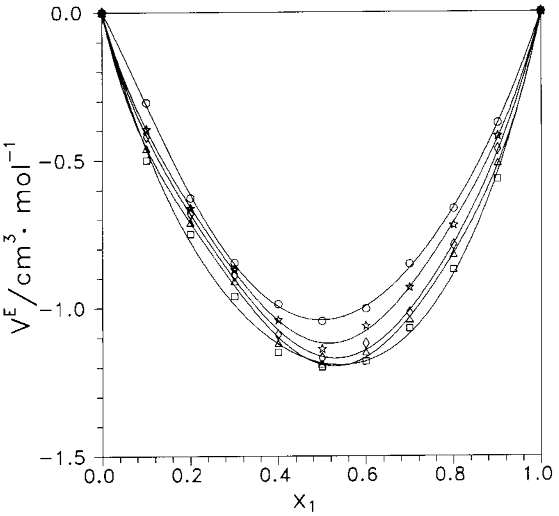

Figure 2. Excess volumes, V^E, at 323.15 K: (□) butylamine (1) + 1-butanol (2); (△) butylamine (1) + 1-pentanol (2); (◇) butylamine (1) + 1-hexanol (2); (☆) butylamine (1) + heptanol (2); (○) butylamine (1) + 1-octanol (2); (—) calculated from eq 5.

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

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

The variations of V^E and $\delta\eta$ with the mole fraction of butylamine at 323.15 K are presented in Figures 2 and 3, respectively. Figure 2 shows that the excess molar volumes are negative for all investigated systems. This may imply that volume contraction takes place upon mixing butylamine with 1-alkanols due to the cross-association between these dissimilar molecules. The magnitude of the volume contraction follows the sequence of 1-butanol > 1-pentanol > 1-hexanol > 1-heptanol > 1-octanol. Moreover, the excess volumes were found to increase with increasing temperature. Figure 3 illustrates that the viscosity deviations are

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]
butylamine + 1-butanol	303.15	0.9869	1.6956	0.50	0.8593	1.3702	1.8616	0.17
	313.15	0.8622	1.3585	0.45	0.7597	1.1332	1.5112	0.34
	323.15	0.7419	1.1395	0.28	0.6749	0.9133	1.2838	0.27
butylamine + 1-pentanol	303.15	1.1561	2.0179	0.49	1.0367	1.4581	2.4124	0.49
	313.15	0.9895	1.6345	0.41	0.8695	1.2335	1.9227	0.39
	323.15	0.8586	1.3528	0.48	0.7694	1.0327	1.5859	0.32
butylamine + 1-hexanol	303.15	1.2448	2.5250	0.64	1.1091	1.6879	2.9764	0.56
	313.15	1.0996	1.9279	0.67	0.9291	1.4566	2.2554	0.67
	323.15	0.9166	1.6174	0.76	0.8382	1.1538	1.8876	0.69
butylamine + 1-heptanol	303.15	1.3966	3.4342	0.80	1.1156	2.2575	3.8906	0.74
	313.15	1.1772	2.6553	0.78	0.9633	1.7923	3.0204	0.75
	323.15	0.9877	2.2209	0.85	0.8513	1.4369	2.4926	0.74
butylamine + 1-octanol	303.15	1.7389	4.0152	0.72	1.2643	2.9272	4.5048	0.31
	313.15	1.4454	3.1127	0.62	1.0709	2.3473	3.4403	0.32
	323.15	1.2185	2.4956	0.49	0.9372	1.8709	2.7623	0.41

[a] AAD % = $(100/n)\sum_{k=1}^{n}|\nu_k^{\mathrm{cal}} - \nu_k^{\mathrm{exp}}|/\nu_k^{\mathrm{exp}}$.

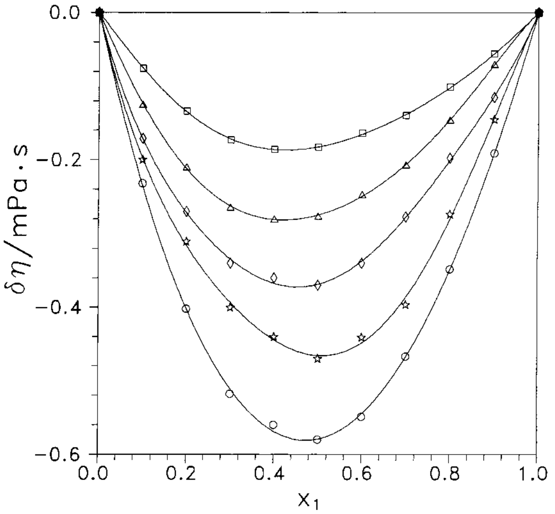

Figure 3. Viscosity deviations, $\delta\eta$, at 323.15 K: (□) butylamine (1) + 1-butanol (2); (△) butylamine (1) + 1-pentanol (2); (◇) butylamine (1) + 1-hexanol (2); (☆) butylamine (1) + heptanol (2); (○) butylamine (1) + 1-octanol (2). (—) calculated from eq 5.

negative for each binary system. As evidenced from the calculations, the viscosity deviations decrease with an increase of temperature.

McAllister's multibody interaction model[11] was widely used to correlate kinematic viscosity (ν) data. The three-body McAllister model was defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2x_2 \ln[(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \tag{7}$$

and the four-body model was given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^22x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln[(M_2/M_1) \tag{8}$$

where ν_{12} ,ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are model parameters and x_i and M_i are the mole fraction and molecule weight of the pure component *i*, respectively. The calculated results are presented in Table 9. The average deviations are about within the experimental uncertainty, regardless of the four-body or the three-body model being used.

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