Densities and Viscosities of Binary Solutions Containing Butylamine, Benzylamine, and Water

Ming-Jer Lee,* Shou-Ming Hwang, and Yung-Chieh Kuo

Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei 106, Taiwan

Densities and viscosities of the binary mixtures composed of butylamine, benzylamine, and water are measured at 303.15, 313.15, and 323.15 K over the entire molar fraction range. The excess volume and viscosity deviation are calculated from the experimental data and correlated by a Redlich–Kister-type equation in terms of molar fraction. McAllister's models are also used to correlate the kinematic viscosities.

Introduction

Density and viscosity data are of importance in engineering applications. However, few existing models can predict satisfactorily the viscosity of polar liquid mixtures, especially aqueous solutions (*1*, *2*). To provide useful data for model development, we have measured the density and viscosity for polar mixtures (*3*) with the emphasis on aqueous solutions. In this work, three binary systems containing butylamine, benzylamine, and water were investigated at atmospheric pressure (nominal value 0.1 MPa) and 303.15, 313.15, and 323.15 K over the molar fraction range.

Experimental Section

Butylamine (99 mass %) and benzylamine (98 mass %) were purchased from Ferak, Germany. The presence of water in the amines is less than 0.5 mass %. Deionized distilled water, conductivity better than $2 \times 10^{-6}\ \Omega^{-1}\cdot cm^{-1}$, was prepared in our laboratory. All the substances were used without further purification.

Three pycnometers (nominal internal volume 25 cm^3) and a HAAKE falling-ball viscometer were employed to measure the density and viscosity, respectively. To prevent the viscometer from corroding by amines, the metal surfaces where in contact with the sample were gold plated. The detailed experimental procedure has been described elsewhere (*3*). In general, the accuracy of measurements is better than ±0.1% for density, ±1% for viscosity, ±0.1 K for temperature, and ±0.5 mg for mixture preparation. The falling time (t) can be converted into dynamic viscosity (η) by

$$\eta = K(\rho_b - \rho)t \qquad (1)$$

where ρ_b is the density of the ball, ρ is the density of the liquid determined at the measuring temperature, and K is the ball constant that was calibrated with literature viscosity values and expressed as a function of liquid density.

Results and Discussion

Oswal et al. (*4*) discussed the inconsistency in the published results for the viscosity of butylamine. Table I compares the values from different sources. Our results are close to those of Kohler et al. (*5*) and of Oswal and Patel (*6*). However, the viscosities reported by Sreenivasulu and Naidu (*7*), Friend and Hargreaves (*8*), and van Velzen et al. (*9*) are higher than ours.

* To whom correspondence should be addressed.

Table I. Viscosity (η) of Butylamine

T/K	lit.	this work
293.15	0.523 (*5*)	0.530
298.15	0.680 (*9*), 0.578 (*8*)	0.495
303.15	0.501 (*7*), 0.443 (*6*)	0.458
308.15		0.425
313.15	0.401 (*5*)	0.398
318.15		0.375
323.15		0.353

Table II. Density (ρ) and Viscosity (η) for Butylamine (1) + Benzylamine (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	0.9737	1.497	0.9656	1.262	0.9570	1.071
0.1	0.9537	1.324	0.9453	1.125	0.9360	0.965
0.2	0.9327	1.204	0.9241	1.021	0.9150	0.878
0.3	0.9107	1.068	0.9010	0.929	0.8925	0.791
0.4	0.8872	0.964	0.8790	0.835	0.8696	0.718
0.5	0.8634	0.847	0.8548	0.737	0.8456	0.639
0.6	0.8392	0.748	0.8305	0.642	0.8209	0.567
0.7	0.8135	0.654	0.8049	0.567	0.7953	0.500
0.8	0.7863	0.578	0.7788	0.506	0.7691	0.446
0.9	0.7605	0.513	0.7516	0.450	0.7416	0.396
1.0	0.7325	0.458	0.7232	0.398	0.7132	0.353

Table III. Density (ρ) and Viscosity (η) for Butylamine (1) + Water (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	0.9957	0.860	0.9923	0.657	0.9881	0.539
0.1	0.9213	1.869	0.9122	1.430	0.9053	1.133
0.2	0.8710	2.115	0.8637	1.604	0.8552	1.250
0.3	0.8394	1.933	0.8310	1.462	0.8222	1.143
0.4	0.8158	1.597	0.8073	1.234	0.7980	0.979
0.5	0.7963	1.273	0.7874	0.996	0.7779	0.808
0.6	0.7800	0.993	0.7710	0.796	0.7611	0.654
0.7	0.7658	0.786	0.7565	0.649	0.7471	0.547
0.8	0.7537	0.626	0.7442	0.533	0.7346	0.453
0.9	0.7431	0.541	0.7340	0.454	0.7241	0.393
1.0	0.7325	0.458	0.7232	0.398	0.7132	0.353

The results of density and viscosity measurements for the binary solutions of butylamine + benzylamine, butylamine + water, and benzylamine + water are listed in Tables II–IV, respectively. Figure 1 shows the variation of the viscosity of those three systems with mole fraction at 313.15 K. For the aqueous systems, each isotherm increases markedly as a small amount of amine is added to water, reaches a maximum at a certain composition, and then decreases to the value of pure amine. It also shows that a certain amount of water in amines could result in significantly increasing the viscosity. As the comparison made in Table I, the impurity of water could be the reason that the viscosity measurements from

0021-9568/93/1738-0577$04.00/0

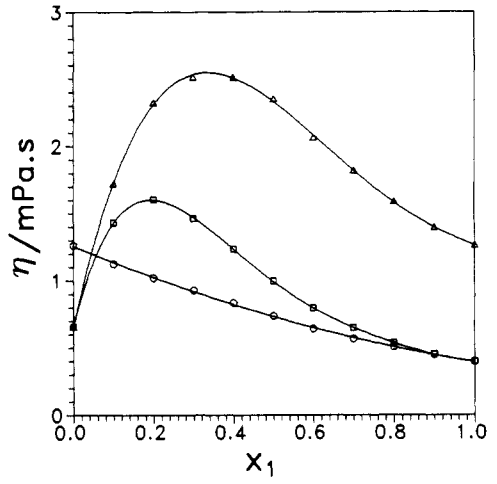

Figure 1. Viscosity at 313.15 K: (○) butylamine (1) + benzylamine (2); (□) butylamine (1) + water (2); (△) benzylamine (1) + water (2).

Table IV. Density (ρ) and Viscosity (η) for Benzylamine (1) + Water (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	0.9957	0.856	0.9927	0.658	0.9881	0.539
0.1	0.9991	2.231	0.9930	1.725	0.9869	1.385
0.2	0.9998	3.098	0.9924	2.324	0.9848	1.793
0.3	0.9988	3.387	0.9911	2.512	0.9827	1.956
0.4	0.9983	3.323	0.9891	2.510	0.9806	1.930
0.5	0.9943	3.100	0.9862	2.353	0.9770	1.831
0.6	0.9907	2.669	0.9822	2.064	0.9734	1.648
0.7	0.9870	2.308	0.9782	1.823	0.9694	1.469
0.8	0.9827	1.957	0.9741	1.591	0.9656	1.309
0.9	0.9783	1.681	0.9700	1.396	0.9613	1.182
1.0	0.9737	1.497	0.9656	1.262	0.9570	1.071

Table V. Coefficients of Equation 5 for Excess Volume

mixture	T/K	A_0	A_1	A_2	A_3	AAD[a]/%
butylamine +	303.15	−2.1801	0.8819	−0.3696	−0.9977	0.03
benzylamine	313.15	−2.3811	−0.4515	−0.6977	0.2287	0.02
	323.15	−2.6623	−0.1853	0.0208	−0.7981	0.01
butylamine +	303.15	−6.7355	0.0712	−1.2641	0.5175	0.08
water	313.15	−6.8838	0.6495	−0.7649	−1.3934	0.06
	323.15	−7.0535	0.3882	−0.8703	−1.1299	0.05
benzylamine +	303.15	−4.5316	−0.5131	0.5326	−0.3873	0.02
water	313.15	−4.3075	−0.4090	0.5281	−0.4441	0.01
	323.15	−4.1643	−0.5635	0.2897	−0.0372	0.02

[a] AAD = $[\sum_{i=1}^{n}(|V^{cal} - V^{exp}|/V^{exp})_i \times 100]/n$.

Table VI. Coefficients of Equation 6 for Viscosity Deviation $\delta\eta$

mixture	T/K	B_0	B_1	B_2	B_3	AAD[a]/%
butylamine +	303.15	−0.5048	−0.1012	−0.2180	0.3563	0.37
benzylamine	313.15	−0.3703	−0.1598	−0.1609	0.4363	0.25
	323.15	−0.2920	−0.0555	−0.0932	0.1462	0.20
butylamine +	303.15	2.4301	−5.5834	5.6592	−2.2474	0.72
water	313.15	1.8497	−3.9230	4.2849	−2.2314	0.39
	323.15	1.3997	−2.8339	3.2756	−1.9913	0.73
benzylamine +	303.15	7.6456	−8.3156	1.7279	1.4079	0.72
water	313.15	5.4917	−5.6764	1.8814	0.0397	0.46
	323.15	4.0226	−4.0394	1.9632	−0.4999	0.40

[a] AAD = $[\sum_{i=1}^{n}(|\eta^{cal} - \eta^{exp}|/\eta^{exp})_i \times 100]/n$.

some previous researchers are higher. Unlike the aqueous systems, the viscosity of butylamine + benzylamine decreases monotonically with the molar fraction of butylamine.

Furthermore, Kohler et al. (5) stated that the existence of a maximum viscosity on an isotherm is evidence of complex formation in the mixture and the molecular ratio of the complex can be deduced from the composition where the maximum occurs. According to our measurements, a 1:4 aggregate may form in the butylamine + water system and a 1:2 aggregate may form in the benzylamine + water system. This deduction can be checked with the congruent composition of the mixtures, if those solid–liquid equilibrium data are available.

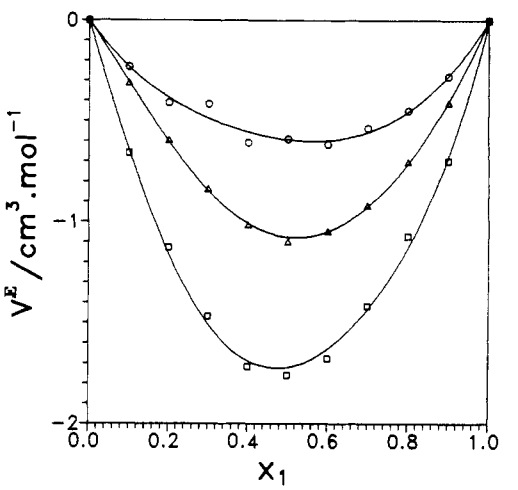

Figure 2. Excess volume at 313.15 K: (○) butylamine (1) + benzylamine (2); (□) butylamine (1) + water (2); (△) benzylamine (1) + water (2); (—) calculated.

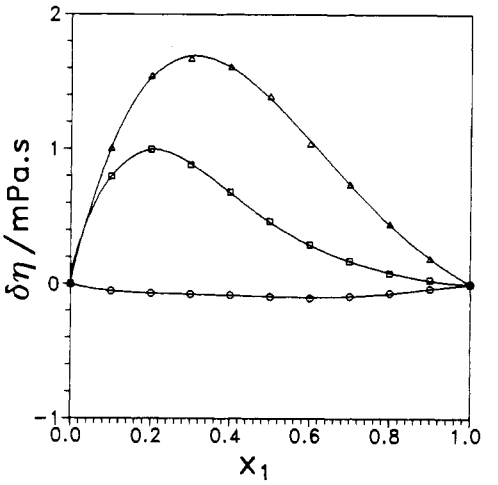

Figure 3. Viscosity deviation at 313.15 K: (○) butylamine (1) + benzylamine (2); (□) butylamine (1) + water (2); (△) benzylamine (1) + water (2); (—) calculated.

The excess volume (V^E) was calculated from the observed data with the following equation:

$$V^E = V - (x_1V_1 + x_2V_2) \quad (2)$$

The viscosity deviation from a mole fraction average ($\delta\eta$) is given by

$$\delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where V, x, and η are the molar volume, molar fraction, and dynamic viscosity. The subscripts 1 and 2 refer to the corresponding properties of pure components. The molar volume of the mixture was computed from the measured density (ρ) via

$$V = (x_1M_1 + x_2M_2)/\rho \quad (4)$$

where M is the molecular weight.

Figure 2 presents the excess volumes at 313.15 K, indicating negative volume changes of mixing for those three systems. The contraction for butylamine + water is much greater than that for benzylamine + water, and the excess volumes of

Table VII. Coefficients for Kinematic Viscosity with McAllister's Models

mixture	T/K	three-body model			four-body model			
		ν_{12}	ν_{21}	AAD[a]/%	ν_{1112}	ν_{1122}	ν_{2221}	AAD[a]/%
butylamine + benzylamine	303.15	0.8077	1.1760	0.69	0.7336	1.0579	1.1936	0.39
	313.15	0.7164	1.0506	0.85	0.6545	0.9281	1.0427	0.73
	323.15	0.6421	0.8872	0.49	0.5897	0.7928	0.9181	0.27
butylamine + water	303.15	0.6673	8.7619	9.20	0.9980	0.8074	12.9857	3.13
	315.15	0.5722	6.3657	9.35	0.8844	0.5987	9.9159	3.51
	325.15	0.4810	5.1583	8.94	0.7330	0.5261	7.1183	3.63
benzylamine + water	303.15	1.7151	16.0918	8.35	2.4035	1.9568	18.3068	3.56
	313.15	1.3717	11.3535	8.67	2.0135	1.4042	13.7016	3.73
	323.15	1.0388	9.9139	8.98	1.6097	1.2406	8.5776	3.76

[a] AAD = $[\sum_{i=1}^{n}(|\nu_m^{cal} - \nu_m^{exp}|/\nu_m^{exp})_i \times 100]/n$.

butylamine + benzylamine are less negative than those of the two aqueous systems. We also found that the viscosity deviations are positive for the aqueous mixtures as shown in Figure 3.

The properties of each isotherm were correlated by a Redlich–Kister-type equation:

$$V^E/(\mathrm{cm^3 \cdot mol^{-1}}) = x_1 x_2 \sum_{i=0}^{3} A_i (x_1 - x_2)^i \quad (5)$$

$$\delta\eta/(\mathrm{mPa \cdot s}) = x_1 x_2 \sum_{i=0}^{3} B_i (x_1 - x_2)^i \quad (6)$$

The coefficients A_i and B_i were obtained by fitting the equations to the experimental data. Tables V and VI list the coefficients together with the average absolute deviations (AAD). Those calculated values were illustrated by the smooth curves in Figures 2 and 3.

McAllister's multibody interaction model (*10*) is widely used for correlating the kinematic viscosity (ν_m) of liquid mixtures. The three-body model (*10*) is defined as

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

and the four-body model (*10*) is given by

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

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are the model parameters. Table VII reports the calculated results. It shows that the three-body model is adequate for the butylamine + benzylamine mixtures, whereas the four-body model is required for the aqueous mixtures.

Literature Cited

(1) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
(2) Lee, M. J.; Wei, M. C. *J. Chem. Eng. Jpn.* **1993**, *26*, 158.
(3) Lee, M. J.; Wei, M. C. *J. Chem. Eng. Data* **1992**, *37*, 209.
(4) Oswal, S. L.; Sindhe, R. G.; Patel, A. T.; Dave, J. P.; Patel, S. G.; Patel, B. M. *Int. J. Thermophys.* **1992**, *13*, 617.
(5) Kohler, F.; Atrops, H.; Kalali, H.; Liebermann, E.; Wilhelm, E.; Ratkovics, F.; Salamon, T. *J. Phys. Chem.* **1981**, *85*, 2520.
(6) Oswal, S. L.; Patel, A. T. *Int. J. Thermophys.* **1991**, *12*, 821.
(7) Sreenivasulu, M.; Naidu, P. R. *Indian J. Chem., Sect. A* **1980**, *19*, 470.
(8) Friend, J. N.; Hargreaves, W. D. *Philos. Mag.* **1944**, *35*, 619.
(9) van Velzen, D.; Cardozo, R. L.; Langenkamp, H. *Liquid Viscosity and Chemistry Constitution of Organic Compounds: A New Correlation and a Compilation of Literature Data*; Joint Nuclear Research Centre: Ispra Establishment, Italy, 1972; Euratom, 4735e.
(10) McAllister, R. A. *AIChE, J.* **1960**, *6*, 427.

Received February 5, 1993. Revised June 2, 1993. Accepted June 28, 1993.• Financial support from the National Science Council, ROC, through Grant No. NSC82-0402-E011-065 is gratefully acknowledged.

• Abstract published in *Advance ACS Abstracts*, September 15, 1993.