Measurement and Correlation of the Densities and Viscosities of 2-Bromopropane + Ethanol Binary Mixtures at Temperatures from (298.15 to 318.15) K

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The densities and viscosities of 2-bromopropane + ethanol binary mixtures had been determined using an digital vibrating U-tube densimeter and Ubbelohde capillary viscometer respectively from (298.15 to 318.15) K. The dependence of densities and viscosities on temperature and concentration had been correlated. The excess molar volume of the binary system was calculated from the experimental density data. The excess molar volumes were related to compositions by polynomial regression and regression parameters, and total rmsd deviations were obtained. The results showed that the model agreed very well with the experimental data.

Introduction

Isopropyl mercaptan is an important pharmaceutical intermediate and chemical material with wide use and optimum application prospects.[1,2] Li et al.[3] have developed a new technique for the synthesis of isopropyl mercaptan by using ethanol as the solvent and NaHS and 2-bromopropane as the raw material.[3,4] This new technique is characterized by mild reaction conditions, high product purity, and a simple process. In the synthesis and purification process of isopropyl mercaptan, it is useful to know the basic data of densities and viscosities and so on of 2-bromopropane in ethanol. The densities and viscosities are basic data used in the chemical engineering designs, process optimization, and molecular thermodynamics study of solution. Therefore, in this study, densities and viscosities of 2-bromopropane in ethanol have been measured at temperatures from (298.15 to 318.15) K. From measurements of densities and viscosities, the excess molar volumes of 2-bromopropane in ethanol were calculated. Results were fit to obtain the adjustable parameters and the deviations between the measured and the fitted values. These quantities can be used to study the molecular interactions among the components of the mixture.

Experimental Section

Materials. 2-Bromopropane and ethanol were of AR grade, and they were obtained from Shanghai Chemical Reagent Co. and had mass fraction purities of 0.995. The water used in the experiments was deionized. The conductivity was less than $1 \cdot 10^{-4}$ S·m^{-1}.

Measurements of Densities. The density of the mixtures and the corresponding pure substances was measured with an Anton Paar model DMA 5000 digital vibrating U-tube densimeter, provided with automatic viscosity correction, having a stated accuracy of $\pm 5 \cdot 10^{-6}$ g·cm^{-3}. The temperature in the cell was regulated to ± 0.001 K with a built-in solid-state thermostat. The temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers, and the stability was better then ± 0.002 K. Before each series of measurements, the apparatus was calibrated with double-distilled and degassed water. To minimize the errors in composition, all mixtures were prepared by mass using the cell and the procedure described previously[5] and a Mettler AG 204 balance with a precision of $1 \cdot 10^{-4}$ g. The uncertainty of the mole fraction calculation was less than $\pm 1 \cdot 10^{-4}$. All molar quantities were based on the IUPAC relative atomic mass table. The experimental uncertainty in density is about $\pm 1 \cdot 10^{-4}$ g·cm^{-3}.

Measurements of Viscosities. The viscosity was measured using a commercial Ubbelohde capillary viscometer (type 1836-A, Shanghai Glass Instruments Factory, China) of 0.55 mm diameter, calibrated with double-distilled water at (298.15 and 313.15) K. A thoroughly cleaned and dried viscometer, filled with experimental solutions, was placed vertically in an insulated jacket, wherein constant temperature (± 0.02 K) was maintained by circulating water from a thermoelectric controller (type 501, Shanghai Laboratory Instrument Works Co., Ltd.) at the required temperature. After thermal stability was attained, the flow times of the solutions were recorded with an electronic digital stopwatch correct to ± 0.01 s. At least five repetitions of each datum point obtained were reproducible to ± 0.06 s, and the results were averaged. Because all flow times were greater than 200 s and the capillary diameter (0.55 mm) was far less than its length (100 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity was then calculated from the relationship[6]

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \tag{1}$$

where η, ρ, and t and η_w, ρ_w, and t_w are the viscosity, density, and flow time of the mixture and water, respectively, from the literature.[7] The uncertainty in the viscosity measurement is estimated to be ± 0.006 mPa·s.

Experimental Reliability Proof. The measured densities and viscosities of 2-bromopropane and ethanol at 313.15 K have been compared with literature values. The results are listed in

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Table 1. Densities and Viscosities of 2-Bromopropane and Ethanol at 313.15 K

substance	ρ / g·cm^{-3}	ρ(lit)[7] / g·cm^{-3}	100 RD	η / mPa·s	η(lit)[8] / mPa·s	100 RD
ethanol	0.7799	0.7879	−1.03	0.8172	0.8140	0.39
2-bromopropane	1.2854	1.2843	0.09	0.4389	0.4330	1.34

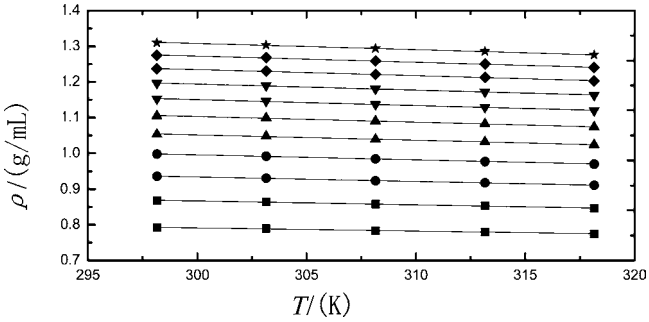

Figure 1. Relative changes in density of 2-bromopropane in ethanol on temperature at different mole fractions: ■, 0.0; □, 0.1; ●, 0.2; ○, 0.3; ▲, 0.4; △, 0.5; ▼, 0.6; ▽, 0.7; ◆, 0.8; ◇, 0.9; ★, 1.0.

Table 1. It could be seen that our experimental values of densities and viscosities were in good agreement with those reported in the literature.[8]

Results and Discussion

The experimental densities at various temperatures as a function of mole fraction for 2-bromopropane in ethanol are presented in Table 2 and Figure 1. It could be found from Table 2 that densities decreased with increasing temperature under the same concentration of 2-bromopropane in ethanol and increased with increasing concentration of 2-bromopropane in ethanol at constant temperature. From Figure 1, it can be found that densities and temperature give the straight linear relationship.

The experimental viscosities at various temperatures as a function of mole fraction for 2-bromopropane in ethanol are presented in Table 3 and Figures 2 and 3. It could be found from Table 3 and Figure 2 that viscosities decreased with increasing temperature under the same concentration of 2-bromopropane in ethanol and decreased with increasing concentration of 2-bromopropane in ethanol at a constant temperature but when the concentration reached a minimum value at about $x = \sim 0.6$ then increased. The temperature influenced strongly the viscosity, but the compositions for the minimum in viscosity were found to be almost constant and independent of temperature. From Figure 3, it could be found that viscosities and temperature gave the straight linear relationship.

Correlation of Density. The dependence of density on temperature and concentration was calculated from eq 2.[9]

Table 3. Experimental Viscosities η of 2-Bromopropane (1) in Ethanol (2) as a Function of Mole Fraction from T = (298.15 to 313.15) K as a Function of Mole Fraction x

	η/mPa·s				
x	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0	1.096	1.010	0.917	0.898	0.817
0.1	0.958	0.886	0.808	0.791	0.721
0.2	0.839	0.778	0.711	0.701	0.644
0.3	0.742	0.690	0.641	0.633	0.580
0.4	0.668	0.623	0.577	0.567	0.526
0.5	0.601	0.562	0.525	0.516	0.483
0.6	0.546	0.517	0.488	0.474	0.450
0.7	0.505	0.482	0.462	0.449	0.427
0.8	0.481	0.465	0.447	0.435	0.415
0.9	0.478	0.465	0.451	0.429	0.414
1.0	0.498	0.484	0.471	0.439	0.419

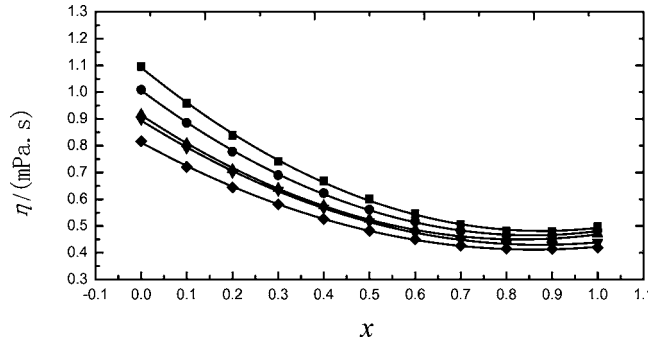

Figure 2. Viscosity of 2-bromopropane in ethanol at various temperatures: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; □, 318.15 K; —, calculated.

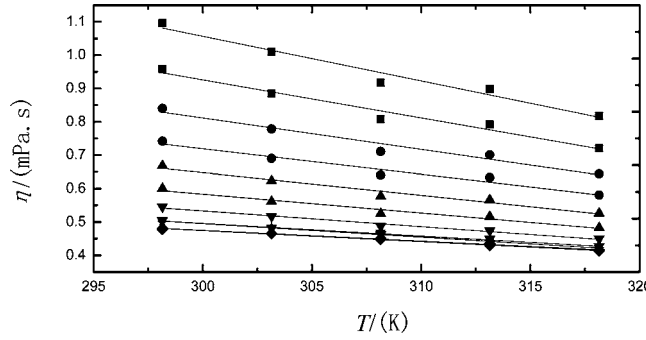

Figure 3. Relative changes in the viscosity of 2-bromopropane in ethanol on temperature at different mole fractions: ■, 0.0; □, 0.1; ●, 0.2; ○, 0.3; ▲, 0.4; △, 0.5; ▼, 0.6; ▽, 0.7; ◆, 0.8; ◇, 0.9; ★, 1.0.

$$\rho = A_0 + A_1 x + A_2 x^2 \qquad (2)$$

in which $A_0 = a_0 + a_1 T$, $A_1 = a_2 + a_3 T$, and $A_2 = a_4 + a_5 T$, where x represents the mole fraction of 2-bromopropane, ρ

Table 2. Experimental Densities ρ[3] of 2-Bromopropane (1) in Ethanol (2) as a Function of Mole Fraction from T = (298.15 to 313.15) K as a Function of Mole Fraction x

	ρ/g·cm^{-3}				
x	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0	0.7924	0.7893	0.7836	0.7799	0.7750
0.1	0.8686	0.8642	0.8577	0.8530	0.8466
0.2	0.9363	0.9312	0.9236	0.9178	0.9111
0.3	0.9973	0.9919	0.9839	0.9772	0.9697
0.4	1.0531	1.0476	1.0390	1.0318	1.0236
0.5	1.1048	1.0988	1.0899	1.0823	1.0735
0.6	1.1523	1.1459	1.1369	1.1288	1.1197
0.7	1.1961	1.1896	1.1803	1.1719	1.1627
0.8	1.2369	1.2304	1.2209	1.2128	1.2028
0.9	1.2746	1.2682	1.2586	1.2501	1.2402
1.0	1.3099	1.3036	1.2939	1.2854	1.2754

Table 4. Regression Coefficient and Deviation of Densities and Viscosities for the 2-Bromopropane (1) + Ethanol (2) Binary System

T/K	A_0	A_1	A_2	10^3 RAD	10^3 rmsd	B_0	B_1	B_2	10^3 RAD	10^3 rmsd
295.15	0.7971	0.724	−0.214	2.09	2.55	1.09	−1.39	0.792	6.88	4.73
300.15	0.793	0.716	−0.209	2.03	2.46	1.01	−1.26	0.739	4.88	3.27
305.15	0.788	0.708	−0.204	1.94	2.33	0.914	−1.12	0.672	3.89	2.87
310.15	0.784	0.696	−0.198	1.90	2.25	0.894	−1.06	0.608	3.36	2.57
315.15	0.779	0.687	−0.193	1.86	2.20	0.812	−0.930	0.541	3.67	2.67

Table 5. Regression Coefficients of Densities and Viscosities for the 2-Bromopropane (1) + Ethanol (2) Binary System

a_0	a_1	a_2	a_3	a_4	a_5	b_0	b_1	b_2	b_3	b_4	b_5
1.07	−0.000915	1.28	−0.00188	−0.531	0.00107	5.05	−0.0135	−8.00	0.0224	4.54	−0.0127

Table 6. Excess Molar Volumes V_m^E of 2-Bromopropane (1) + Ethanol (2) as a Function of Temperature T and Mole Fraction x

	V_m^E/cm^3·mol^{-1}				
x	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.1828	0.2441	0.2647	0.2942	0.3570
0.2	0.3456	0.4290	0.4930	0.5660	0.6099
0.3	0.4675	0.5464	0.6051	0.7034	0.7647
0.4	0.5196	0.5854	0.6565	0.7547	0.8263
0.5	0.4961	0.5732	0.6313	0.7280	0.8050
0.6	0.4415	0.5233	0.5678	0.6628	0.7256
0.7	0.3673	0.4368	0.4765	0.5573	0.5982
0.8	0.2533	0.3069	0.3351	0.3632	0.4259
0.9	0.1408	0.1663	0.1824	0.2098	0.2335
1.0	0.0000	0.0000	0.0000	0.0000	0.0000

Table 7. Regression Coefficients and Deviation of the Excess Volume for the 2-Bromopropane (1) + Ethanol (2) Binary System

T/K	A'_0	A'_1	A'_2	A'_3	correlation coefficient	100 RAD	100 rmsd
298.15	−0.0167	2.58	−3.67	1.1	0.9929	2.97	1.34
303.15	−0.00330	2.96	−4.22	1.27	0.9994	0.860	0.443
308.15	−0.00600	3.36	−4.94	1.59	0.9982	1.61	0.858
313.15	−0.0128	3.92	−5.78	1.87	0.9963	2.57	1.44
318.15	−0.000890	4.21	−6.15	1.95	0.9997	0.650	0.429

is the density of the mixtures, T is the absolute temperature, and a_0 to a_5 are regression coefficients. The calculated values and deviations are listed in Table 4. Densities were calculated according to eq 2 using values for parameters a_0 to a_5 that were listed in Table 5.

The root-mean-square deviation (rmsd) is defined by[10]

$$\text{rmsd} = \left[\frac{1}{N-1}\sum_{i=1}^{N}(\rho_{ci} - \rho_i)^2\right]^{1/2} \tag{3}$$

where N is the number of experimental points, ρ_{ci} represents the densities calculated from equations, and ρ_i represents the experimental density values.

The relative average deviation (RAD) is defined as,[10]

$$\text{RAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\rho_i - \rho_{ci}}{\rho_i}\right| \tag{4}$$

From a comparison of the calculated and experimental values, the total rmsd and RAD of 55 data points were less than 0.26 % and 0.21 %, respectively. It was clear that eq 2 could be successfully used to correlate densities of the ethanol + 2-bromopropane binary mixtures.

Correlation of Viscosity. The dependence of viscosity on temperature and concentration was calculated from the eq 5.[9]

$$\eta = B_0 + B_1x + B_2x$$
$$B_0 = b_0 + b_1T \qquad B_1 + b_2 + b_3T \qquad B_2 = b_4 + b_5T \tag{5}$$

where x represents the mole fraction of 2-bromopropane, η is the viscosity of the mixtures, T is the absolute temperature, and b_0 to b_5 are regression coefficients. The calculated values and deviations are listed in Table 4. Viscosities of ethanol + 2-bromopropane binary mixtures were calculated according to eq 5 using values for parameters b_0 to b_5 that were listed in Table 5. Some results could be seen in Figure 2. From a comparison of the calculated and experimental values, the total rmsd and RAD of 55 data points were less than 0.5 % and 0.7 %, respectively. It was clear that eq 5 could be successfully used to correlate viscosities of the ethanol + 2-bromopropane binary mixtures.

Excess Molar Volumes. The excess molar volumes V^E were calculated from the eqs 6 and 7, respectively.[9]

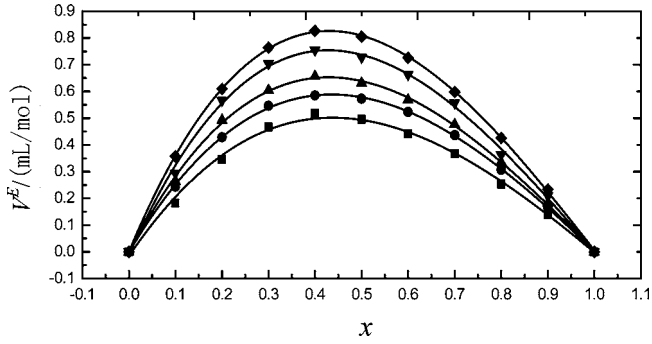

Figure 4. Excess molar volume for 2-bromopropane and ethanol for the whole range of mole fraction at different temperatures: ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; □, 318.15 K; —, calculated.

$$V^{E} = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \quad (6)$$

where x_1 and x_2 represent mole fractions of 2-bromopropane and ethanol, respectively, M_1 and M_2 represent the molar masses of 2-bromopropane and ethanol, respectively, and ρ_{12}, ρ_1, and ρ_2 are the densities of the mixtures, 2-bromopropane, and ethanol, respectively.

The excess molar volume (V^E) calculated from the density data was listed in Table 6. The excess molar volumes over the entire range of mole fraction x and temperature range between (298.15 and 318.15) K are plotted in Figure 4. It could be seen that the values of the excess molar volume (V^E) were found to be positive and a great temperature effect for the whole concentration was found. The excess molar volume maximum was found to be almost temperature-independent at $x = \sim 0.4$. The excess molar volume represents the difference in a molar specific value for 2-bromopropane and ethanol, if the value was large; it indicated that there was a volume contraction in the system.

The excess molar volume (V^E) was correlated by the eq 8,[9]

$$V^{E} = A'_0 + A'_1 x + A'_2 x^2 + A'_3 x^3 \quad (7)$$

where A'_0, A'_1, A'_2, and A'_3 are equation parameters; x is the mole fraction of 2-bromopropane.

The optimum values for polynomial regression coefficients (A'_i) were obtained respectively by fitting experimental data at various temperatures and concentrations, and the regression coefficients of the excess volume along with their deviations are listed in Table 7. Some results can be seen in Figure 4. From a comparison of the calculated and experimental values of the excess volume, the total rmsd of 55 data points was less than 1.5 %, and the RAD was less than 2.97 %. On the basis of the obtained RAD and rmsd values, we could conclude that eq 7 could be successfully used for the correlation of the excess volume.

Conclusion

Densities and viscosities of 2-bromopropane and ethanol binary mixtures were measured for the entire range of molar fractions and for the temperature range between (298.15 and 318.15) K, and the densities and viscosities on temperature and concentration were calculated by the regression. Regression coefficients and deviation were obtained.

The excess molar volumes were determined from the experimental density and viscosity data. The excess molar volumes were related to compositions by polynomial regression, and regression parameters and total rmsd values were obtained. The total rmsd values of the two equations are less than 1.5 %. The results showed that the model agrees very well with the experimental data.

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