INTRODUCTION

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

EXPERIMENTAL SECTION

Materials
2-bromopropane and methanol 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 × 10^{-4} S·m^{-1}.

Measurements of Densities
The densities of the mixtures and the corresponding pure substances were measured with an Anton Paar Model DMA 5000 digital vibrating U-tube densimeter, provided with automatic viscosity correction, having a stated accuracy of ± 5 × 10^{-6}

Densities, Viscosities and Excess Properties of 2-Bromopropane - Methanol Binary Mixtures at Temperature from (298.15 to 318.15) K

Hua Li*, Zhen Zhang, and Lei Zhao
School of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou, Henan, China, 450001
(Received November 11, 2009; Revised December 13, 2009; Accepted December 22, 2009)
Table 1. Densities and Viscosities of 2-bromopropane and Methanol at 313.15 K

<table>
<thead>
<tr>
<th>substance</th>
<th>$\rho$/g·cm$^{-3}$</th>
<th>$\rho$(lit)$^5$/g·cm$^{-3}$</th>
<th>100 RD</th>
<th>$\eta$/mPa·s</th>
<th>$\eta$(lit)$^6$/mPa·s</th>
<th>100 RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0.7829</td>
<td>0.7835</td>
<td>-0.08</td>
<td>0.5045</td>
<td>0.5095</td>
<td>-0.99</td>
</tr>
<tr>
<td>2-bromopropane</td>
<td>1.2854</td>
<td>1.2843</td>
<td>0.09</td>
<td>0.4389</td>
<td>0.4330</td>
<td>1.34</td>
</tr>
</tbody>
</table>

g·cm$^{-3}$. The temperature in the cell was regulated to ± 0.001 K with a built-in solid-state thermo-stat. 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. The reliability of the apparatus was verified daily with dry air and distilled freshly degassed water. To minimize the errors in composition, all mixtures were prepared by mass using the cell and the procedure described previously$^3$ and a Mettler AG 204 balance with a precision of 1 × 10$^{-4}$ g. The uncertainty in the mole fraction calculation was less than ± 1 × 10$^{-4}$. All molar quantities were based on the IUPAC relative atomic mass table. The experimental uncertainty in density was about ± 1 × 10$^{-5}$ g·cm$^{-3}$.

### Measurements of Viscosities

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 perfectly dried viscometer, filled with experimental solutions, was placed exactly vertical 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$^4$

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

where $\eta$, $\rho$, $t$ and $\eta_w$, $\rho_w$, $t_w$ are the viscosity, density, and flow time of the mixture and water respectively come from the literature.$^5$ The uncertainty in the viscosity measurement is estimated to be ± 0.6%.

### Experiment Reliability Proof

The measure densities and viscosities of 2-bromopropane and methanol at 313.15 K had been compared with literature values. The results were listed in Table 1. It could be seen that our experimental values of densities and viscosities were in good agreement with those reported in the literature.$^6$

### RESULTS AND DISCUSSION

The experimental densities at various temperatures as a function of mole fraction for 2-bromopropane in methanol were presented in Table 2, Fig. 1 and Fig. 2. It could be seen from Table 2 and Fig. 1 that densities decreased with increasing temperature at a definite concentration of 2-bromopropane in methanol and increased with increasing concentration of 2-bromopropane in methanol at constant temperature. From Fig. 2, it could be found that densities and temperature gave the straight linear relationship.
The experimental viscosities at various temperatures as a function of mole fraction for 2-bromopropane in methanol were presented in Table 3 and Fig. 3 and Fig. 4. It could be found from Table 3 and Fig. 3 that viscosities decreased with increasing temperature at a definite concentration of 2-bromopropane in methanol, and decreased with increasing concentration of 2-bromopropane in methanol at constant temperature, reached a minimum value at about $x \approx 0.6$ and 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 Fig. 4 it could be found that viscosities and temperature gave the straight linear relationship.

**Correlation of Density**

The dependence of density on temperature and concentration were calculated from the equation 2.7

$$\rho = A_0 + A_1x$$

$$A_0 = a_0 + a_1T$$

$$A_1 = a_2 + a_3T$$

where, $x$ represents mole fraction of 2-bromopropane, $\rho$ is the density of the mixtures, $T$ is the absolute temperature; and $a_0 - a_5$ are regression coefficients. The calculated values and deviations were listed in Table 4. Densities were calculated according to eq 2 using values for parameters $a_0 - a_5$ that were listed in Table 5. Some calculated results could be seen in Fig. 1.

The root-mean-square deviation is defined by.8

$$RMSD = \left(\frac{1}{N-1} \sum_{i=1}^{N} (\rho_{ci} - \rho_i)^2\right)^{1/2}$$

Where $N$ is the number of experimental points, $\rho_{ci}$ represents the densities calculated from equations, and $\rho_i$ represents the experimental density values.

The relative average deviations (RAD) is defined as,8

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

From comparison of the calculated and experimental values, the total RMSD and average relative deviations (RAD) of 55 data points were less than 2% and 0.1%, respectively. It was clear that eq 2 could be successfully used to correlate densities.
**Table 4.** Regression coefficient and deviation of densities and viscosities for the methanol-2-bromopropane binary system

<table>
<thead>
<tr>
<th>T/K</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$10^3$ RAD</th>
<th>$10^3$ RMSD</th>
<th>$B_0$</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$10^3$ RAD</th>
<th>$10^3$ RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>295.15</td>
<td>0.8111</td>
<td>0.516</td>
<td>9.09</td>
<td>1.76</td>
<td>0.553</td>
<td>-0.6164</td>
<td>0.108</td>
<td>1.26</td>
<td>1.23</td>
</tr>
<tr>
<td>300.15</td>
<td>0.806</td>
<td>0.511</td>
<td>7.12</td>
<td>1.41</td>
<td>0.533</td>
<td>-0.175</td>
<td>0.125</td>
<td>1.35</td>
<td>1.23</td>
</tr>
<tr>
<td>305.15</td>
<td>0.799</td>
<td>0.505</td>
<td>5.31</td>
<td>1.07</td>
<td>0.518</td>
<td>-0.193</td>
<td>0.145</td>
<td>1.16</td>
<td>1.09</td>
</tr>
<tr>
<td>310.15</td>
<td>0.790</td>
<td>0.502</td>
<td>3.81</td>
<td>0.759</td>
<td>0.504</td>
<td>-0.226</td>
<td>0.161</td>
<td>1.44</td>
<td>1.15</td>
</tr>
<tr>
<td>315.15</td>
<td>0.781</td>
<td>0.499</td>
<td>2.62</td>
<td>0.491</td>
<td>0.482</td>
<td>-0.240</td>
<td>0.177</td>
<td>1.89</td>
<td>1.62</td>
</tr>
</tbody>
</table>

**Table 5.** Regression coefficients of densities and viscosities for the methanol--2-bromopropane binary system

<table>
<thead>
<tr>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$b_4$</th>
<th>$b_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.27</td>
<td>-0.00154</td>
<td>0.761</td>
<td>-0.000835</td>
<td>1.56</td>
<td>-0.00343</td>
<td>1.04</td>
<td>-0.00406</td>
<td>-0.916</td>
<td>0.00347</td>
</tr>
</tbody>
</table>

**Table 6.** Excess Molar Volumes of 2-Bromopropane-methanol

<table>
<thead>
<tr>
<th>x</th>
<th>298.15 K</th>
<th>303.15 K</th>
<th>308.15 K</th>
<th>313.15 K</th>
<th>318.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1</td>
<td>1.1708</td>
<td>1.2678</td>
<td>1.3383</td>
<td>1.5522</td>
<td>1.8533</td>
</tr>
<tr>
<td>0.2</td>
<td>1.7183</td>
<td>2.1342</td>
<td>2.4878</td>
<td>2.8262</td>
<td>3.1403</td>
</tr>
<tr>
<td>0.3</td>
<td>2.1163</td>
<td>2.5674</td>
<td>3.0109</td>
<td>3.4394</td>
<td>3.7948</td>
</tr>
<tr>
<td>0.4</td>
<td>2.3079</td>
<td>2.6975</td>
<td>3.1146</td>
<td>3.5908</td>
<td>3.9440</td>
</tr>
<tr>
<td>0.5</td>
<td>2.2157</td>
<td>2.5770</td>
<td>2.9711</td>
<td>3.4624</td>
<td>3.8549</td>
</tr>
<tr>
<td>0.6</td>
<td>1.9658</td>
<td>2.3375</td>
<td>2.7594</td>
<td>3.0928</td>
<td>3.5596</td>
</tr>
<tr>
<td>0.7</td>
<td>1.5014</td>
<td>1.9412</td>
<td>2.2566</td>
<td>2.5713</td>
<td>2.9133</td>
</tr>
<tr>
<td>0.8</td>
<td>1.1632</td>
<td>1.3932</td>
<td>1.6675</td>
<td>1.8694</td>
<td>2.1437</td>
</tr>
<tr>
<td>0.9</td>
<td>0.6297</td>
<td>0.7696</td>
<td>0.9412</td>
<td>1.1217</td>
<td>1.2837</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

**Fig. 5.** Excess molar volume for 2-bromopropane and methanol for whole range of mole fractions at different temperatures. ■, 298.15 K; ●, 303.15 K; ▲, 308.15 K; ▼, 313.15 K; ◆, 318.15 K; —, calculated.

**Excess Molar Volumes and Excess Viscosities**

The excess molar volumes ($V^E$) and the excess viscosities were calculated from the equation 6, 7, respectively:

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

(6)

where, $x_1$ and $x_2$ represent mole fraction of 2-bromopropane and methanol, respectively, and $M_1$ and $M_2$ represent molar masses of 2-bromopropane and methanol, respectively; $\rho_{12}, \rho_1$ and $\rho_2$ are the densities of the mixtures, or 2-bromopropane and methanol, respectively.

\[
\Delta \eta = \eta_{12} - (x_1 \eta_1 + x_2 \eta_2)
\]

(7)

where, $\eta_{12}$ is the viscosity of the mixture; $\eta_1$ and $\eta_2$ is the viscosity of 2-bromopropane and methanol, respectively.

The excess molar volume ($V^E$) calculated from the density data was listed in Table 6. The excess molar volume over the entire range of mole fraction $x$ and temperature range between (298.15 and 318.15) K were plotted in Fig. 5. 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 represented the difference in molar specific value for 2-bromopropane and methanol, if the value was large, it indicated that there was a volume contraction in the system and also indicated that 2-bromopropane and methanol were completely miscible system.

The excess viscosities calculated from the viscosity data was listed in Table 7. The excess viscosities over the entire range of mole fraction $x$ and temperature range between (298.15 and 318.15) K were plotted in Fig. 6. It could be seen that the values of the excess viscosities were found to be negative, and the excess viscosities decreased with increasing concentration, reached a minimum value at about $x = \sim 0.5$ and then increased. Increasing temperature decreased the value of the excess viscosities at a definite concentration 2-bromopropane in methanol, but the composition for the minimum value was almost constant.

The excess molar volume ($V^E$) was correlated by the equation 8, 9.
The excess properties indicate the departure from the ideal condition and can be correlated by the Redlich-Kister equation,

\[ \Delta \eta = x_1 x_2 \sum B_i (x_1 - x_2)^i \]  

(9)

where, \( x_1 \) and \( x_2 \) is mole fraction of 2-bromopropane and solvent. \( B_i \) is the optimum values for the Redlich-Kister coefficients.

The optimum values for polynomial regression coefficients (\( A_i \)) and the Redlich-Kister coefficients (\( B_i \)) were obtained respectively by fitting experimental data at various temperature and concentration, the regression coefficients of the excess volume and the excess viscosity along with their deviation were listed in Table 8 and Table 9, respectively. Some results could be seen in Fig. 5 and Fig. 6. From comparison of the calculated and experimental values of the excess volume and the excess viscosity, the total RMSD of 55 data points were less than 9% and 0.1%, respectively, and average relative deviations (RAD) were less than 2.88% and 2.39%, respectively. On the basis of the obtained RAD and RMSD values, we concluded that eq 8 and eq 9 could be successfully used for the correlation of the excess volume and the excess viscosity.

### CONCLUSION

Densities and viscosities of 2-bromopropane and methanol 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 volume and the excess viscosity were determined from the experimental density and viscosity data. The
excess molar volumes were related to compositions by poly-
nomial regression and regression parameters and total RMSD
deviations were obtained; the excess viscosities was related to
compositions by Redlich-Kister equation and regression coeffi-
cients and total RMSD deviation of the excess viscosity for
2-bromopropane and methanol binary system were obtained.
The total RMSD deviations of two equations were less than
8.6% and 0.1%, respectively. The results showed that the model
agreed very well with the experimental data.

REFERENCES
1. Li, H.; Zhang, Z.; Zhao, L.; Guo, F. Chem. Reagents. 2008, 30,
826.
Reagents. 2004, 26, 291.
3. Tasic, A. Z.; Grozdanic, D. K.; Djordjevic, B. D.; Serbanovic, S.
648.
5. Dean, J. A. Lange’s Handbook of Chemistry, 15th ed.; McGraw-
p 19.
7. Song, X. F.; Luo, Y.; Wang, J.; Yu, J. G. J. of East China Univ. of