Title
Specific volume and viscosity of methanol-water mixtures under high pressure

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SPECIFIC VOLUME AND VISCOSITY OF METHANOL-WATER MIXTURES UNDER HIGH PRESSURE

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TAKEI HAMAMOTO, YOSHIYUKI TANAKA AND TADASHI MAKITA

New experimental data on the specific volume and the viscosity of methanol-water mixtures are presented as functions of temperature, pressure and composition.

The specific volume has been measured by means of an improved "high pressure burette" apparatus within an error of 0.05 percent, covering temperatures from 10 to 75°C and pressures up to 1000 bar. The viscosity has been obtained by a falling-cylinder viscometer with the uncertainty of less than two percent, covering the same temperature range and pressures up to 700 bar.

The specific volume of this system is found to decrease monotonously with increasing pressure. The experimental results agree well with several literature values. The numerical data at each temperature and composition are correlated satisfactorily as a function of pressure by the Tait equation. The isothermal compressibilities and the excess volumes are also determined from the experimental data. It is found that a definite minimum appears on the isothermal compressibility versus composition isobars at temperatures lower than 25°C. The excess volumes are always negative and increase with increasing pressure or lowering temperature.

The viscosity of pure methanol and its water mixtures is found to increase almost linearly with increasing pressure, whereas that of water decreases with pressure at 10°C and 25°C within the present experimental conditions. The viscosity isotherms can be represented by a quadratic equation of pressure within the experimental errors. As for the composition dependence of the viscosity, a distinct maximum appears near 0.3 mole fraction of methanol on all isobars at each temperature. The maximum shifts slightly to higher methanol fraction with increasing temperature or pressure.

Introduction

It is well known that alcohol molecules in aqueous solutions give strong influence on the water structure 1,2) and that alcohol-water systems show consequently some anomalies in various physical properties.

Recently, the reliable experimental data of these systems on various physical properties are required for both theoretical works and engineering calculations. Although a number of measurements at atmospheric pressure have been reported, a few are available under high pressure.

This paper provides extensive and accurate data on PVT relations and viscosity for methanol-water binary mixtures as functions of temperature, pressure and composition. Numerical data have

(Received November 13, 1979)

1) F. Franks and D. J. G. Ives, Quart. Rev., 20, 1 (1966)
been determined at temperatures ranging from 10°C to 75°C, and pressures up to 2000 bar for the specific volume, and to 700 bar for the viscosity, employing a modified piezometer and a falling-cylinder viscometer. Empirical correlation formulas have also been presented for both properties using the present results.

**Experimentals**

**PVT measurements**

The schematic diagram of the experimental apparatus is shown in Fig. 1. The sample liquid of known weight is introduced into a high pressure vessel D and upper part of burette G. The pressure is transmitted through mercury filled in C and G from an oil pump A. The volume change of the test liquid is detected from the displacement of a small iron float on the surface of the mercury column by means of a differential transformer. The high pressure vessel D consists of coaxial double cylinders as shown in Fig. 2. The inner cylinder is a thin-walled sample cell, to the outer wall of which somewhat lower pressure is applied separately from the oil pump in order to minimize the deformation of the cell.3)

The vessel D and burette G are immersed in a liquid thermostat controlled within ±0.01°C.

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Specific Volume and Viscosity of Methanol-Water Mixtures

The pressure is measured by Bourdon gauges calibrated against a pressure balance. The uncertainty in pressure measurements is estimated to be less than 0.1 percent.

Using the displacement of the iron float, the specific volume of the sample liquid is calculated by the following equation:

\[ v = v_0 - \frac{1}{W} \left( dV_{\text{app}} - (dV_{\text{tub}} + dV_{\text{bar}} + dV_{\text{cell}}) \right) \]  

(1)

where

- \( v_0 \): specific volume in cm\(^3\)g\(^{-3}\) of the sample at pressure \( P_0 \) bar,
- \( dV_{\text{app}} \): apparent volume change in cm\(^3\) of the sample at \( P \) bar,
- \( dV_{\text{tub}} \): volume change in cm\(^3\) of the connecting tube at \( P \) bar,
- \( dV_{\text{bar}} \): volume change in cm\(^3\) of the high pressure burette at \( P \) bar,
- \( dV_{\text{cell}} \): volume change in cm\(^3\) of the thin-walled sample cell at \( P \) bar,
- \( W \): total weight in g of the sample.

\( dV_{\text{tub}}, dV_{\text{bar}}, \) and \( dV_{\text{cell}} \) were calculated employing the elasticity theory. The uncertainty of the present specific volume values is estimated to be less than 0.05 percent.

Viscosity measurements

The viscosity is measured by a falling-cylinder viscometer. The details of the viscometer were described elsewhere\(^4\).

The apparatus consists of a precisely bored Pyrex glass tube equipped coaxially in a high pressure vessel and a glass cylindrical plummet with hemispherical ends. The plummet is provided with four small projecting lugs at each end of the cylindrical part, which acts as a guide to keep plummet concentric when it falls. The falling time of the plummet is determined within ±0.1 ms by an electronic time-interval counter using a He-Ne gas laser beam passed through a pair of optical windows and a phototransistor. The temperature of the sample is maintained constant within ±0.05°C by circulating a thermostatic fluid through the jacket around the pressure vessel. The pressure is measured by a Bourdon gauge with the same accuracy as in the case of PVT measurements.

The instrument constant and its change with both temperature and pressure are calibrated with the aid of the experimental viscosity values under atmospheric pressure obtained by an Ostwald viscometer and of the reference viscosity of water correlated by the International Association for the Properties of Steam (1974). The uncertainty of the present viscosity values is estimated to be less than 2.0 percent.

Materials

Methanol used was obtained from Wako Pure Chemical Industries Ltd. The reported purity is more than 99.5% in volume. Methanol and water were purified several times by the fractional distillation.

The mixtures of methanol and water were prepared by weighing, using an analytical balance.

with a sensitivity of ±0.1 mg. Therefore their composition, mole fraction of methanol, should be substantially accurate within 0.01%.

Table 1 The Specific Volume of Methanol-Water Mixtures in cm³/g

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>X = 0.00</th>
<th>X = 0.25</th>
<th>X = 0.50</th>
<th>X = 0.75</th>
<th>X = 1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0005</td>
<td>1.0</td>
<td>1.0594</td>
<td>1.0</td>
<td>1.1214</td>
</tr>
<tr>
<td>178.9</td>
<td>0.9818</td>
<td>0.9773</td>
<td>0.9727</td>
<td>0.9690</td>
<td>0.9653</td>
</tr>
<tr>
<td>343.7</td>
<td>0.9845</td>
<td>0.9837</td>
<td>0.9831</td>
<td>0.9824</td>
<td>0.9817</td>
</tr>
<tr>
<td>578.7</td>
<td>0.9774</td>
<td>0.9763</td>
<td>0.9756</td>
<td>0.9750</td>
<td>0.9744</td>
</tr>
<tr>
<td>808.5</td>
<td>0.9706</td>
<td>0.9694</td>
<td>0.9686</td>
<td>0.9680</td>
<td>0.9674</td>
</tr>
<tr>
<td>893.6</td>
<td>0.9843</td>
<td>0.9837</td>
<td>0.9832</td>
<td>0.9827</td>
<td>0.9822</td>
</tr>
</tbody>
</table>

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Results and Discussion

Specific Volume

A part of experimental results is given in Table 1, where \( P, v \) and \( X \) denote pressure in bar, specific volume in \( \text{cm}^3/\text{g} \) and mole fraction of methanol in the mixtures, respectively. Specific volume values at 10°C and 75°C are also plotted in Figs. 3 and 4, together with the literature values for pure water. The specific volume decreases monotonously with increasing pressure throughout the experimental conditions at each composition. At the experimental temperatures except 75°C, the present results of pure water is found to agree quite well with the values given by Chen et al., Kell et al. and Grindley et al. The discrepancy between the present results and literature values at 75°C is within 0.09%. For the mixtures, there exist reliable data only at 25°C and 1000 bar by Gibson and 25°C and 1013 bar by Moriyoshi et al. As for the compression, literature values differ from the present results by less than 1.46% and 0.91%, respectively.

For each temperature and composition, the specific volume data are correlated as a function of pressure by the Tait equation:

\[
\frac{v_0 - v}{v_0} = C \log \left( \frac{B + P}{B + P_0} \right)
\]

![Fig. 3](image)

Fig. 3 Pressure dependence of the specific volume of Methanol-Water mixtures at 10°C

![Fig. 4](image)

Fig. 4 Pressure dependence of the specific volume of Methanol-Water mixtures at 75°C

* Data of \( X = 0.15, 0.30, 0.35 \) at 10°C and 75°C, and of \( X = 0.10, 0.15, 0.35 \) at 25°C and 50°C are available on request.
Table 2 Coefficients of the Tait Equation

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Comp. X bar</th>
<th>Temp. °C</th>
<th>Comp. X bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2366 0.2691</td>
<td>0.00</td>
<td>3388 0.3466</td>
</tr>
<tr>
<td>0.15</td>
<td>3172 0.2111</td>
<td>0.15</td>
<td>2480 0.2855</td>
</tr>
<tr>
<td>0.25</td>
<td>2788 0.2596</td>
<td>0.25</td>
<td>2541 0.2903</td>
</tr>
<tr>
<td>0.30</td>
<td>2471 0.2697</td>
<td>0.30</td>
<td>2458 0.2888</td>
</tr>
<tr>
<td>0.35</td>
<td>2347 0.2747</td>
<td>0.35</td>
<td>2311 0.2503</td>
</tr>
<tr>
<td>0.50</td>
<td>1564 0.2285</td>
<td>0.50</td>
<td>2098 0.2398</td>
</tr>
<tr>
<td>0.75</td>
<td>1164 0.2385</td>
<td>0.75</td>
<td>2311 0.2398</td>
</tr>
<tr>
<td>1.00</td>
<td>668 0.2235</td>
<td>1.00</td>
<td>1568 0.2214</td>
</tr>
<tr>
<td>2.00</td>
<td>2908 0.3069</td>
<td>2.00</td>
<td>1000 0.2639</td>
</tr>
<tr>
<td>3.00</td>
<td>3124 0.3223</td>
<td>3.00</td>
<td>1568 0.2450</td>
</tr>
<tr>
<td>5.00</td>
<td>3168 0.3196</td>
<td>5.00</td>
<td>1568 0.2419</td>
</tr>
</tbody>
</table>

where \( v_0 \) is the specific volume at a pressure \( P_0 \), and \( B \) and \( C \) are constants. The obtained Tait equations could reproduce experimental data with an average deviation of 0.03%. The coefficients for the Tait equation are listed in Table 2.

The isothermal compressibilities:

\[
\beta_T = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T
\]

(3)

calculated using the Tait equation, at 10°C and 75°C, are plotted against the mole fraction of methanol in Figs. 5 and 6, respectively. It is found that a definite minimum exists near \( X=0.15 \) at 10°C and 25°C, but these minima fade out gradually as the temperature increases. At 75°C these minima
Specific Volume and Viscosity of Methanol-Water Mixtures

disappear completely. This anomaly was also found in the ethanol-water system as reported in previous paper\(^9\).

Excess volumes are also calculated at each experimental temperature by the following equation:

\[
V^e = V_{\text{mix}} - \left( V_{\text{MeOH}}X + V_{\text{water}}(1-X) \right)
\]

The results of 25°C and 75°C are given in Figs. 7 and 8, respectively. At all the experimental conditions, excess volumes obtained are always negative, and it seems that pressure makes the excess volumes less negative and, in a sense, the mixture approaches the ideal solution with increasing pressure. At 25°C, the present results agree well with the literature values\(^{10}\).

Viscosity

The experimental results are tabulated in Table 3. The data obtained at atmospheric pressure are plotted as a function of composition in Fig. 9, where other experimental data\(^{11-13}\) are also plotted for comparison. Each viscosity isotherm has a maximum at a composition near \(X=0.30\sim0.35\). Agreement with the available data is satisfactory at 10°C and 25°C. However, the discrepancy among them is somewhat notable at 50°C, where the largest deviation between the data of Sabnis et al.\(^{13}\) and those of Traube\(^{14}\) is about 11% near the maximum. The present data agree quite well

\(^{13}\) S. W. Sabnis, W. V. Bhagwat and R. B. Kanugo, J. Indian Chem. Soc., 25, 575 (1948)
\(^{14}\) J. Traube, Ber., 19, 871 (1886)
H. Kubota, S. Tsuda, M. Murata, T. Yamamoto, Y. Tanaka and T. Makita

Table 3 The Viscosity of Methanol-Water Mixtures in 10^{-3} Pa·s

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( \rho ) bar</th>
<th>( X = 0.0 )</th>
<th>( X = 0.15 )</th>
<th>( X = 0.25 )</th>
<th>( X = 0.35 )</th>
<th>( X = 0.50 )</th>
<th>( X = 0.75 )</th>
<th>( X = 1.0 )</th>
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</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0</td>
<td>1.311</td>
<td>2.360</td>
<td>2.551</td>
<td>2.560</td>
<td>2.419</td>
<td>1.971</td>
<td>1.272</td>
</tr>
<tr>
<td></td>
<td>0.991</td>
<td>1.301</td>
<td>2.364</td>
<td>2.564</td>
<td>2.563</td>
<td>2.407</td>
<td>1.957</td>
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<td></td>
<td>1.972</td>
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<td>2.361</td>
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<td>2.562</td>
<td>2.373</td>
<td>1.922</td>
<td>1.172</td>
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<tr>
<td></td>
<td>3.933</td>
<td>1.778</td>
<td>2.395</td>
<td>2.708</td>
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<td>2.694</td>
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<tr>
<td></td>
<td>4.914</td>
<td>1.270</td>
<td>2.468</td>
<td>2.733</td>
<td>2.783</td>
<td>2.757</td>
<td>2.275</td>
<td>1.528</td>
</tr>
<tr>
<td></td>
<td>5.894</td>
<td>1.269</td>
<td>2.438</td>
<td>2.706</td>
<td>2.848</td>
<td>2.835</td>
<td>2.346</td>
<td>1.681</td>
</tr>
<tr>
<td></td>
<td>6.875</td>
<td>1.264</td>
<td>2.448</td>
<td>2.729</td>
<td>2.882</td>
<td>2.896</td>
<td>2.384</td>
<td>1.824</td>
</tr>
</tbody>
</table>

* IAPS (1974)

![Fig. 9 Composition dependence of the viscosity of Methanol-Water mixtures at 1.0 bar](image)

Specific Volume and Viscosity of Methanol-Water Mixtures

with the results of Yergovich et al.\textsuperscript{19} at 10°C and those of Mikhail et al.\textsuperscript{11} at 25°C and 50°C obtained by the modified Ostwald viscometer.

The pressure dependences of the viscosity of this mixture at 10°C and 75°C are shown in Fig. 10. So far as we know, there exist no experimental viscosity data for this binary system under high pressure. On the other hand, three sets of experimental data are found in literature\textsuperscript{20–22} for pure methanol under pressures as shown in Fig. 11. Although the overlap of experimental conditions is limited, the consistence between our data and others is reasonable in view of the distances between the viscosity isotherms and their gradients.

The viscosity isotherms both in Fig. 10 and Table 3 show the following features:

1) The viscosity of mixtures always increases with pressure almost linearly, whereas the pressure coefficient of viscosity, \(\frac{\partial \eta}{\partial P}\), for pure water is slightly negative at 10°C and 25°C within the present pressure range.

2) \(\frac{\partial \eta}{\partial P}\) increases with the mole fraction of methanol at each temperature.

3) \(\frac{\partial \eta}{\partial P}\) decreases with rising temperature for the mixture of a constant composition.

---

Fig. 10 Pressure dependence of the viscosity of Methanol-Water mixtures at 10°C and 75°C. ○: 10°C, ■: 75°C

Fig. 11 Pressure dependence of the viscosity of Methanol. ○: This work, Δ: 21), ■: 22) 20, 21)

---

Table 4

<table>
<thead>
<tr>
<th>Temp</th>
<th>x</th>
<th>$B_1$</th>
<th>$B_2 \times 10^4$</th>
<th>$B_3 \times 10^8$</th>
<th>Ave. Dev. %</th>
<th>Max. Dev. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.15</td>
<td>2.35982</td>
<td>0.4909</td>
<td>11.222</td>
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<td>0.2</td>
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<tr>
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<td>2.34964</td>
<td>4.4094</td>
<td>-14.446</td>
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<td>0.3</td>
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<td>30</td>
<td>0.30</td>
<td>2.50401</td>
<td>6.6200</td>
<td>2.381</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>40</td>
<td>0.35</td>
<td>2.41965</td>
<td>6.07570</td>
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<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>50</td>
<td>0.50</td>
<td>1.91211</td>
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<td>0.5</td>
</tr>
<tr>
<td>75</td>
<td>0.75</td>
<td>1.27107</td>
<td>3.1918</td>
<td>-0.765</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>1.00</td>
<td>0.89599</td>
<td>4.37600</td>
<td>-13.2657</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
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<td>7.888</td>
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<td>20</td>
<td>0.23</td>
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<td>0.4</td>
</tr>
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<td>0.30</td>
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<td>3.2794</td>
<td>-8.529</td>
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<td>0.8</td>
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<tr>
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</tr>
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<tr>
<td>75</td>
<td>0.75</td>
<td>0.91291</td>
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<td>1.6</td>
</tr>
<tr>
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<td>1.00</td>
<td>0.58255</td>
<td>3.4827</td>
<td>-7.8468</td>
<td>0.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* For 75°C isotherms, Eq. (5) is valid from 99 to 688 bar.

The viscosity isotherms can be represented by a quadratic equation of pressure:

$$n = B_1 + B_2 P + B_3 P^2$$

where $n$ is the viscosity in $10^{-3}$ Pa•s ($\equiv cP$) and $P$ the pressure in bar. The empirical coefficients for each mixture are listed in Table 4, with the average and the maximum deviations of the experimental data from the equation.

The composition dependence of the viscosity under high pressure is shown in Fig. 12. The viscosity isobars have the following features:

1) The composition dependence of the viscosity is evident at low temperatures, but it diminishes gradually with rising temperature.
2) Each isobar has a maximum near the composition of $X = 0.30 - 0.35$. The maximum shifts slightly to higher methanol fraction with rising temperature or increasing pressure. The shift is more explicit at low temperatures.

These characteristic behaviors of viscosity for methanol-water mixtures under pressures are quite similar to those of ethanol-water system as reported in our previous paper. The large positive departure in the viscosity-composition isobars from those of regular solutions, in which the additive law is held approximately, shows that the interaction between unlike molecules is seriously strong, as well as the behavior of the excess volume in Figs. 7 and 8. Water and alcohol molecules form various complex “clusters” according to the composition of mixtures, in addition to the “ice-
 Specific Volume and Viscosity of Methanol-Water Mixtures

bergs" of water molecules themselves and the association of alcohols. It is quite interesting that the maximum of viscosity and the minimum of excess volume occur at different compositions of mixtures.

The authors wish to thank Mr. Yasuhare Kimura, Kobe Agricultural and Forestry Products Inspection Institute, for his careful experimental efforts in this work.

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