Title
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VISCOSITY OF LIQUID AMMONIA IN THE TEMPERATURE INTERVAL OF -30°C TO -70°C

Wa S. Wong and Charles W. Tobias

June 1966
Interest in liquid ammonia as an ionizing solvent\textsuperscript{1}, one that also forms metallic solutions with the alkali and alkaline earth metals\textsuperscript{2} has renewed in recent years. Interpretation of conductances in liquid ammonia requires a knowledge of the viscosity of the solvent. Although viscosity data on liquid ammonia have been reported as early as 1912\textsuperscript{6}, no information could be found in the technical literature on the viscosity below -34°C,\textsuperscript{3,4,5,6,7}.

The viscosity of liquid ammonia in the temperature range from -35°C to -70°C was determined in our laboratory using an Ubbelohde viscometer modified for operation under an inert gas blanket (Figure 1). Argon was used to transfer liquid ammonia from flask (A) into bulk (B) after condensation of anhydrous ammonia into (A) from a stainless steel container containing sodium filings. The entire glass apparatus was carefully thermostated in a mechanically refrigerated methanol bath, in which the temperature was controlled to ±0.05°C. The total pressure in the viscometer was always less than one atmosphere. Test runs showed no effect of different argon partial pressures on the viscosity of liquid ammonia. The viscometer was calibrated by measuring the kinematic viscosities of CS\textsubscript{2} and of CCl\textsubscript{4} at 25°C. From these, the constants were evaluated for the equation\textsuperscript{10}

\[
\eta/\rho = A\tau - B/\tau.
\]
where \( \eta \) is the viscosity (centipoise), \( \rho \) is the density \((\text{g/cm}^3)\), \( t \) is the flowing time (sec), \( A \) and \( B \) are constants in the units of centistoke/sec, and centistoke-sec, respectively. The temperature correction of \( A \) and \( B \) calculated from the thermal expansion coefficient of Pyrex glass \((3.6 \times 10^{-6} \text{cm/cm}^\circ\text{C})^9\) are vanishingly small\(^{10}\).

The results for liquid ammonia are tabulated in Table 1 and plotted in Figure 2, along with those reported earlier for higher temperatures.

Table 1. Viscosities and Densities of Liquid Ammonia.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density* (g/cm(^3))</th>
<th>Viscosity (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-35</td>
<td>0.6849</td>
<td>0.2590</td>
</tr>
<tr>
<td>-40</td>
<td>0.6909</td>
<td>0.2742</td>
</tr>
<tr>
<td>-45.5</td>
<td>0.6974</td>
<td>0.3010</td>
</tr>
<tr>
<td>-51</td>
<td>0.7043</td>
<td>0.3286</td>
</tr>
<tr>
<td>-55</td>
<td>0.7102</td>
<td>0.3596</td>
</tr>
<tr>
<td>-60</td>
<td>0.7147</td>
<td>0.3908</td>
</tr>
<tr>
<td>-70</td>
<td>0.7259</td>
<td>0.4843</td>
</tr>
</tbody>
</table>

Three individual runs have been made for each temperature. The reproducibility was within ±0.4%.

It is evident from Figure 2, the viscosities measured in this study fall on a nearly straight line in the log \( \eta \) vs 1/T plane. However, the slope of the line is not identical with the one representing Kikuchi's data for higher temperatures, nor does it coincide with the line connecting Plank and Hunt's three data points at 25°C, 15°C, and 5°C. In fact, for the -35 to -70°C temperature interval, the data points are best represented not by a straight line, but rather by one that curves slightly upward.

The line appears to be more consistent with Plank and Hunt's data points

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* Densities were measured in this laboratory by the pycnometer method. The values agree to within ±0.01% with those reported by Keyes.\(^{11}\)
than with Kikuchi's values. It is interesting to note that these workers also calibrated their apparatus by CS₂ and CCl₄ while Kikuchi used distilled water for the purpose. The single value of 0.2535 cps at -33.5°C determined recently by O'Reilly falls on the line drawn through the data points obtained in the present study.

According to the "hole theory" of liquid, the temperature dependence of viscosity may be represented by

$$\eta = \frac{hN}{V} \exp \left( \frac{\Delta F^+}{RT} \right)$$

where \( \eta \) is the viscosity (centipoise), \( V \) is the molar volume (cm³/mole), \( N \) is Avogadro's number, \( h \) is Plank's constant (erg-sec), and \( \Delta F^+ \) is the free energy of activation for viscous flow (cal/mole). When \( \log \eta \) is plotted against \( 1/T \), a straight line should result if the free energy of activation for viscous flow is constant. The increasing slope of the \( \log \eta \) vs \( 1/T \) curve with decreasing temperature may be due to the fact that liquid ammonia is a polar liquid, and because of increasing hydrogen bonding, its free energy of activation for viscous flow should also increase with decreasing temperature. The viscosity behavior of other polar liquids - among others, water, methanol, and ethanol - shows the same trend. On the basis of the present work, the average free energy of activation for viscous flow of liquid ammonia in the -35°C to -70°C temperature interval is +1.93 Kcal.

The value of the integral temperature coefficient decreases with temperature; using Kikuchi's and Plank and Hunt's data, one obtains a value of -0.9% per degree centigrade for the temperature range of +10°C to +30°C while the present work yields a value of -2.1% per degree centigrade for the temperature range of -50°C to -70°C.
References


Figure 1. Modified Ubbelohde Viscometer
A: 50 cm$^3$ flask for the condensation of NH$_3$
B: 4 cm$^3$ bulb for metering a constant volume of fluid
C: Stopcock, open during a measurement
Figure 2. Viscosity of Liquid Ammonia
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