Significant Structure of Liquid Ethylene Chloride

by

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Abstract

Upon melting, a part of ethylene-chloride molecules in trans-form in the solid state changes into gauche-form. The partition function for the material was developed according to the significant structure theory of liquid proposed by H. Eyring and his co-workers, and the parameters $E_n$, $\theta$, $V_s$ and $a$, therein, are determined by the manner developed by Chang, et al.

The molal volume, vapor pressure, vaporization entropy, critical point properties and surface tension of the liquid were calculated. The results are in good agreement with experimental values.

Introduction

Henry Eyring and his co-workers $^{1-3}$ assumed, in their significant structure theory of liquid, a liquid molecule to possess both the solid-like and the gas-like degrees of freedom. A molecule around the vacant hole in the liquid assumes the gas-like degree of freedom when it jumps into the hole. They liquid as a product of two partition functions for the liquid as a product of two partition functions, one for the portion having the solid-like degree of freedom and the other having the gas-like degree of freedom:

where $N$ is the Avogadro number and $1/\alpha$, which

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partition function

From consistency of the two isomeric forms in the liquid state, we assume the gas-like molecules in the liquid alone are under the thermal equilibrium between the two forms. The partition function for the ethylene chloride, therefore, may be written as

\[
 f = f_s N^2 \frac{N_{C_2}}{N_{C_1} + N_{C_2}} \left( f_{C_1} - f_{C_2} \right),
\]

where \( \frac{N_{C_2}}{N_{C_1} + N_{C_2}} \) and \( \frac{N_{C_2}}{N_{C_1} + N_{C_2}} \) represent the fraction of the trans form and the gauche form, respectively. It can be determined at various temperatures by the following equations 5:

\[
 \begin{align*}
 f_{C_1} = & \left( \frac{J_{C_1} J_{C_1} I_{C_1}}{J_{C_1} J_{C_1} I_{C_1}} \right)^{3/2} \frac{1}{T_{C_1}} \frac{T_{C_2}}{T_{C_2}} \frac{T_{C_1}}{T_{C_2}} \\
 f_{C_2} = & \left( \frac{J_{C_2} J_{C_2} I_{C_2}}{J_{C_2} J_{C_2} I_{C_2}} \right)^{3/2} \frac{1}{T_{C_1}} \frac{T_{C_2}}{T_{C_2}} \frac{T_{C_1}}{T_{C_2}} \\
 T_{C_1} = & \frac{I_{C_1}}{(1 - e^{-\hbar \nu_1/vT})} \\
 T_{C_2} = & \frac{I_{C_2}}{(1 - e^{-\hbar \nu_2/vT})}
\end{align*}
\]

where the 2 in the first equation comes from the two symmetric gauche forms, the transition energy between the trans form and gauche form at the ground state, \( \Delta E^g \), is known to be 1100 cals, through the spectroscopic study 5. The principal moment of inertia is calculated from the molecular configuration 8, 9.

\[
 \Pi I_{C_1} = (J_{C_1} J_{C_1} I_{C_1})^{1/2} = 335.726 \times 920 \times 591 \times 588 \times 114 \times 10^{-12}
\]

\[
 \Pi I_{C_2} = (J_{C_2} J_{C_2} I_{C_2})^{1/2} = 1.356
\]

where the vibrational frequencies, \( \nu_1 \) and \( \nu_2 \), are available from the literature 7.

We have assumed the free molecular rotation in the gaseous phase alone and wrote the partition function in detail as follows:

\[
 \begin{align*}
 f_{C_1} = & \frac{e^{J_{C_1}/kT} \epsilon^\hbar \nu_1}{(1 + e^\hbar \nu_1/vT)} \left( \frac{1}{N_{C_1}} \right)^{1/2} \frac{1}{T_{C_1}} \\
 f_{C_2} = & \frac{e^{J_{C_2}/kT} \epsilon^\hbar \nu_2}{(1 + e^\hbar \nu_2/vT)} \left( \frac{1}{N_{C_2}} \right)^{1/2} \frac{1}{T_{C_2}}
\end{align*}
\]

where \( E \) and \( \theta \) are parameters corresponding to the heat of sublimation and the Einstein characteristic temperature of the solid-like molecules, respectively. Values of \( E \) and \( \theta \) do not coincide with those of the solid due to the different environment in the solid and liquid states. And \( \theta \) is also a parameter involved in the strain energy term \( -aE \frac{V_m}{n(V-V_m)} \) for a molecule shifting to one of the available neighboring sites.

The \( n \) is a number of the nearest neighboring sites around a molecule. It is given by the relation \( n = Z \frac{V_m}{V_m} \), where \( V_m \) is the molar volume of the liquid at the melting point and \( Z \) is the number of all the accessible neighboring sites nearest to a molecule. \( Z \) is taken 15, assuming a closed-packed model. The parameters \( E \), \( V_m \), and \( \theta \) are determined at the melting point in a similar way as developed by Chang, et al. 10

**Results**

Owing to the low vapor pressure and low melting point, the vapor pressure and molar volume are extrapolated 10 11. The heat of vaporization was taken as 8665 cals/mole. The melting point data and the parameters determined are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1, Melting Point Data and Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V = 74.20 \text{ cc} )</td>
</tr>
<tr>
<td>( F = 2.5 \text{ atm Hg} )</td>
</tr>
<tr>
<td>( T = 221.85 \text{K} )</td>
</tr>
<tr>
<td>( \Delta H_{vap} = 8665 \text{ cals/mole} )</td>
</tr>
</tbody>
</table>

Calculations are made from this partition function for molar volumes and vapor pressures at the various temperatures between the melting and the boiling point. The results are shown in Table 2 with an observed value. Relative error of 15% for the vapor pressure near the melting point is not so serious, since the observed value may also have 2 or 3 mm Hg error which may amount up to 20% relative error.

<table>
<thead>
<tr>
<th>Table 2, Molar Volume and Vapor Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°K)</td>
</tr>
<tr>
<td>( V_{calc./Vobs.} \text{ error} )</td>
</tr>
<tr>
<td>( V_{calc./Vobs.} \text{ error} )</td>
</tr>
<tr>
<td>237.85</td>
</tr>
<tr>
<td>262.75</td>
</tr>
<tr>
<td>302.55</td>
</tr>
<tr>
<td>323.14</td>
</tr>
<tr>
<td>337.15</td>
</tr>
<tr>
<td>587.15</td>
</tr>
</tbody>
</table>
The vaporization entropy at the boiling point and critical point properties are calculated. Except the critical pressure, the results are in good agreement with observed values as shown in Table 3.

Table 3. Critical Point Properties and Entropy of Vaporization.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Calculated</th>
<th>Observed</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc (K)</td>
<td>645.94</td>
<td>641.63</td>
<td>1.97</td>
</tr>
<tr>
<td>Pc (atm)</td>
<td>79.17</td>
<td>79.19</td>
<td>0.03</td>
</tr>
<tr>
<td>Vc (cc)</td>
<td>241.88</td>
<td>241.92</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Surface tensions are calculated in a similar way as proposed by Chang, et al. The calculated values exceed those of experimental values by more than 40 per cent. The deviation may be attributed to the assumption that the ethylene-chloride molecule is an ideal one, with non-polar and spherical structure. However, the tendency of variation with the temperature is close to the experiments.

Table 4. Surface Tension.

<table>
<thead>
<tr>
<th>Temp (°K)</th>
<th>% contribution of layers</th>
<th>Tcalc. (dyn/cm)</th>
<th>Ttab. (dyn/cm)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>237.85</td>
<td>92.62 1st, 8.88 2nd, 0.39 3rd</td>
<td>63.04</td>
<td>63.86</td>
<td>4.6</td>
</tr>
<tr>
<td>270.75</td>
<td>93.81 1st, 9.24 2nd, 0.96 3rd</td>
<td>48.54</td>
<td>48.55</td>
<td>0.5</td>
</tr>
<tr>
<td>302.55</td>
<td>88.94 1st, 11.25 2nd, 0.81 3rd</td>
<td>43.33</td>
<td>43.32</td>
<td>0.3</td>
</tr>
<tr>
<td>337.15</td>
<td>84.34 1st, 14.21 2nd, 1.45 3rd</td>
<td>37.34</td>
<td>37.40</td>
<td>1.4</td>
</tr>
</tbody>
</table>

References

9) G. Herzberg, Infra-red and Raman-spectra of Polyatomic Molecule, p. 509.
12) International Critical Tables.
14) Hyungsuk Pak and Seihun Chang, This Journal 7, 174-8, (1963).