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A STUDY OF SUPERHEAT PROPERTY OF LIQUIDS

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(Received February 27, 1968)

ABSTRACT. This paper presents the results of the study of maximum attainable superheat temperature of eleven low-boiling organic liquids by the film superheating method. The experimental values have been compared with the theoretical values as obtainable from the Kinetic theory and also from the Statistical Mechanical theory. The difference between the theoretical and the experimental superheat values is seen to increase with the increasing molecular weight of the liquid. The Radiation length of the liquids under test have also been calculated at the theoretical maximum superheat temperature of the liquids.

INTRODUCTION

The study of superheat property of the liquid is important from the standpoint of nucleation theory and the bubble chamber.

Till now different workers have used different methods for investigating the maximum superheat temperature attainable in a liquid at atmospheric, subatmospheric and superatmospheric pressures. Amongst them the works of Wismer et al. (1922), Harvey et al. (1947), Glaser (1952), Briggs (1955) and Wakeshima and Takata (1958) are more important. The common purpose of all these methods was to reach the theoretical maximum superheat temperature.

These methods are hardly applicable to practical heat transfer systems in which a thin layer of the liquid in contact with the heater surface becomes strongly heated and the bulk of the liquid remains near the boiling temperature.

The method suggested by Sinha and Jalaluddin (1961) is however more practical in this context. The maximum superheat values obtained by this method are lower than that obtained by other methods. But in this method the liquid film remains in the superheated state for pretty long time, offering the scope for studying the liquid properties in the superheated state.

In the present work the method of Sinha and Jalaluddin (1961) has been followed.

THEORETICAL VALUES OF MAXIMUM SUPERHEAT TEMPERATURE

From equation of State (Kinetic Theory)

Temperley (1947) calculated the value of maximum superheat temperature of a liquid from the Van der Waals' equation of state. This equation is ordinarily...
regarded as capable of offering qualitatively adequate account of the vapour-liquid equilibrium. The superheated state of a liquid is a metastable state, and the end of this metastable state is represented on the P-V diagram by the Spinodal Lines. The equation of the Spinodal Line is

\[ \left( \frac{dP}{dV} \right)_T = 0 \]  

(1)

The Van der Waals’ equation is

\[ \left( P + \frac{a}{V^2} \right)(V-b) = RT \]  

(2)

\[ \left( \frac{dP}{dV} \right)_T = P - \frac{a}{V^2} + \frac{2ab}{V^3} \]

Therefore for the Spinodal Line,

\[ P - \frac{a}{V^2} + \frac{2ab}{V^3} = 0 \]  

(3)

Now if the liquid is just capable of existing in the metastable state at zero pressure i.e. \( P = 0 \), equation (3) becomes

\[ V = 2b \]  

(4)

Substituting this value of \( V \) in equation (2), we get

\[ \frac{RT_m}{4b} = \frac{a}{4b} \]  

(5)

But we have

\[ RT_c = \frac{8a}{27b} \]  

(6)

where \( T_c \) = Critical temperature, and \( a, b \) = Vander Waals’ constants.

\[ t_m = \frac{27T_c}{32} \]  

(7)

By equation (7) the value of maximum superheat temperature for a liquid can be calculated from the knowledge of the critical temperature of the liquid at zero pressure. At \( P = 1 \) i.e., the atmospheric pressure, \( t_m \) will be slightly greater than the corresponding value at \( P = 0 \). So for mathematical simplicity \( t_m \) is calculated taking \( P = 0 \).
A more appropriate value of $t_m$ can be obtained from the Rate Theory of Nucleation in a superheated liquid. This theory is based on statistical mechanical considerations. The formulation of this theory was due to Volmer. It was improved upon by Becker and Doring where from we have got the present form.

The Volmer-Doring formula for calculating the limit of superheat theoretically is

$$J = z_1 \sqrt{\frac{6\sigma}{nm(3-b)}} \exp \left[ -\frac{\lambda}{Kt} - \frac{16\pi\sigma^3}{3K(t^2 - p_L)} \right]$$

Where

- $J =$ The time rate of homogeneous nucleation.
- $b = \frac{p_L - p_v}{p_v}$, where $R_0 =$ critical radius.
- $z_1 =$ Number of molecules in the superheated state.
- $\lambda =$ Latent heat of vaporization per mol. in ergs.
- $\sigma =$ Surface tension of the liquid at the operating temperature.
- $p_v =$ Saturated vapour pressure inside the bubble at the operating temperature.
- $p_L =$ Pressure on the liquid = 1 atmosphere $\approx 10^6$ dynes/cm$^2$
- $K =$ Boltzmann's constant.
- $m =$ Molecular mass
- $t =$ Temperature of the superheated liquid.

The limit of superheat is supposed to be the temperature at which $J = 1$. This is rather an arbitrarily selected value of the time rate of homogeneous nucleation, but this value is now well accepted.

**EXPERIMENTAL SETUP AND RESULTS**

The same set-up as reported by Sinha and Jalaluddin (1951) has been used. The liquids investigated are carbon tetrachloride (E. Merck), chloroform (E. Merck), $n$-hexane (E. Merck), $n$-heptane (E. Merck), iso-butanol (E. Merck), methylene chloride (E. Merck), ethylene chloride (Riedel), diethylamine (E. Merck), methyl acetate (E. Merck), methyl formate (Riedel) and ethyl formate (Bush).
## Superheat Property of Liquids

### Table 1
Maximum superheat values $t_{\text{m}}$, experimental

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Boiling point $t_b \degree C$</th>
<th>Max steady mercury temp. $t_m \degree C$</th>
<th>Temp. drop across the meniscus of the bulb $t_m \degree C$</th>
<th>Max. superheat temp. $T_m \degree C$</th>
<th>Degree of superheat $\Delta T = T_m - t_m \degree C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Carbon tetrachloride</td>
<td>76.7</td>
<td>156.9</td>
<td>12.8</td>
<td>144.1</td>
<td>73.4</td>
</tr>
<tr>
<td>2. Chloroform</td>
<td>61.1</td>
<td>161.7</td>
<td>14.7</td>
<td>146.9</td>
<td>85.8</td>
</tr>
<tr>
<td>3. n-Hexane</td>
<td>68.6</td>
<td>153.8</td>
<td>16.75</td>
<td>137.05</td>
<td>66.45</td>
</tr>
<tr>
<td>4. n-Heptane</td>
<td>98.3</td>
<td>165.1</td>
<td>8.13</td>
<td>156.87</td>
<td>58.7</td>
</tr>
<tr>
<td>5. Iso-butanol</td>
<td>107.8</td>
<td>177.1</td>
<td>13.1</td>
<td>164.0</td>
<td>58.2</td>
</tr>
<tr>
<td>6. Methylene chloride</td>
<td>40.7</td>
<td>137.7</td>
<td>16.1</td>
<td>121.6</td>
<td>80.9</td>
</tr>
<tr>
<td>7. Ethylene chloride</td>
<td>83.7</td>
<td>185.4</td>
<td>18.5</td>
<td>166.9</td>
<td>83.2</td>
</tr>
<tr>
<td>8. Diethylamine</td>
<td>55.9</td>
<td>146.6</td>
<td>11.3</td>
<td>125.3</td>
<td>70.4</td>
</tr>
<tr>
<td>9. Methyl acetate</td>
<td>50.0</td>
<td>157.1</td>
<td>13.7</td>
<td>143.4</td>
<td>86.5</td>
</tr>
<tr>
<td>10. Methyl formate</td>
<td>31.9</td>
<td>168.7</td>
<td>13.7</td>
<td>150.0</td>
<td>118.1</td>
</tr>
<tr>
<td>11. Ethyl formate</td>
<td>63.9</td>
<td>171.6</td>
<td>16.35</td>
<td>155.25</td>
<td>101.35</td>
</tr>
</tbody>
</table>

### Table 2
Comparison of experimental values $t_{\text{m}}$ with theoretical

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Molecular weight</th>
<th>Theoretical values $T_{\text{theo}} \degree C$</th>
<th>Rate of change $\Delta T \degree C$</th>
<th>Experimental value $T_{\text{exp}} \degree C$</th>
<th>Difference between theoretical and experimental value $\Delta T = T_{\text{theo}} - T_{\text{exp}} \degree C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Carbon tetrachloride</td>
<td>154</td>
<td>196.0</td>
<td>223.0</td>
<td>144.1</td>
<td>57.9</td>
</tr>
<tr>
<td>2. Chloroform</td>
<td>119.5</td>
<td>180.0</td>
<td>199.0</td>
<td>146.9</td>
<td>33.1</td>
</tr>
<tr>
<td>3. n-Hexane</td>
<td>86</td>
<td>155.0</td>
<td>181.0</td>
<td>137.05</td>
<td>17.95</td>
</tr>
<tr>
<td>4. n-Heptane</td>
<td>100</td>
<td>182.0</td>
<td>210.0</td>
<td>156.87</td>
<td>25.13</td>
</tr>
<tr>
<td>5. Iso-butanol</td>
<td>74</td>
<td>181.0</td>
<td>207.0</td>
<td>164.0</td>
<td>17.0</td>
</tr>
<tr>
<td>6. Methylene chloride</td>
<td>85</td>
<td>129.0</td>
<td>152.0</td>
<td>121.0</td>
<td>8.0</td>
</tr>
<tr>
<td>7. Ethylene chloride</td>
<td>99</td>
<td>190.0</td>
<td>216.0</td>
<td>166.9</td>
<td>23.1</td>
</tr>
<tr>
<td>8. Diethylamine</td>
<td>73</td>
<td>145.0</td>
<td>172.0</td>
<td>136.3</td>
<td>9.7</td>
</tr>
<tr>
<td>9. Methyl acetate</td>
<td>74</td>
<td>154.0</td>
<td>179.0</td>
<td>143.4</td>
<td>10.6</td>
</tr>
<tr>
<td>10. Methyl formate</td>
<td>80</td>
<td>138.0</td>
<td>164.0</td>
<td>150.0</td>
<td>-12.0</td>
</tr>
<tr>
<td>11. Ethyl formate</td>
<td>74</td>
<td>155.0</td>
<td>181.0</td>
<td>155.25</td>
<td>-9.25</td>
</tr>
</tbody>
</table>

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**Note:** The values in Table 1 and Table 2 are presented as they appear in the document, including any apparent errors or inconsistencies.
From figure 1 it is seen that the difference between the theoretical and the experimental values of $t_m$ increase with the increasing molecular weight of the liquid.

![Comparison of experimental and theoretical values, plotted as their differences against molecular weights.](image)

**Radiation Length**

The importance of the study of superheat property of liquids has increased to a considerable amount after the development of the bubble chamber. A large number of chambers has been constructed with different liquids to study different nuclear phenomena. It is the property of a particular liquid that is most important for the study of a particular phenomenon. Radiation length is one of the most important properties of a bubble chamber liquid. It is a measure of accuracy that can be obtained in momentum determinations. On the other hand, it is also a measure of the efficiency that can be expected in pair production by gamma rays.

We shall use Bugg's (1958) modified expression for calculating radiation length ($X_0$). According to him,

$$\frac{1}{X_0} = \frac{4}{137} \cdot \frac{N}{\bar{M}} \sum \frac{\rho_i z_i}{z_i^2} \ln \frac{183}{z_i^{1/3}}$$  \hspace{1cm} (9)
Superheat Property of Liquids

where \( N \) = Avogadro's number = \( 6.023 \times 10^{23} \)

\( r_e \) = Classical radius of an electron

\[
\frac{e^2}{m_e c^2} = 2.818 \times 10^{-3} \text{ cm}
\]

\( M \) = Molecular weight.

\( P \) = Density of the compound at the operating point.

\( Z \) = Atomic number.

The sum is taken over all atoms in the molecule.

Equation (9) can be further simplified, as we know that \( N \) and \( r_e \) are constants.

\[
\frac{1}{X_0} = \frac{4N r_e^2}{137} \cdot \frac{\rho}{M} \sum_i \frac{Z_i (z_i + 1) \ln \left( \frac{183}{z_i^{3/2}} \right)}{z_i^{3/2}}
\]

\[
= 1.39 \times 10^{-3} \cdot \frac{\rho}{M} \sum_i \frac{Z_i (z_i + 1) \ln \left( \frac{183}{z_i^{3/2}} \right)}{z_i^{3/2}}
\]

(10)

The value of radiation length is calculated from equation (10). Density of the liquid, \( \rho_0 \), at the operating point is calculated from the equation

\[
\rho_t = \rho_0 + 10^{-3} \alpha (t - t_0) + 10^{-6} \beta (t - t_0)^2
\]

(11)

The value of \( \rho_0 \), \( \alpha \) and \( \beta \) are taken from the table of critical constants.

### Table 3

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Formula</th>
<th>Theoretical max. superheat temp. (^\circ\text{ C})</th>
<th>Density at the theoretical max. superheat temp. (\rho_t)</th>
<th>Radiation length at (t_0) (^\circ\text{ C}) in cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Carbon tetrachloride</td>
<td>CCl(_4)</td>
<td>222.0</td>
<td>1.1723</td>
<td>17.5</td>
</tr>
<tr>
<td>2. Chloroform</td>
<td>CHCl(_3)</td>
<td>195.0</td>
<td>1.13642</td>
<td>18.4</td>
</tr>
<tr>
<td>3. n-Hexane</td>
<td>C(<em>6)H(</em>{14})</td>
<td>181.0</td>
<td>0.4880</td>
<td>96.5</td>
</tr>
<tr>
<td>4. n-Heptane</td>
<td>C(<em>7)H(</em>{16})</td>
<td>216.0</td>
<td>0.53076</td>
<td>89.3</td>
</tr>
<tr>
<td>5. Iso-butanol</td>
<td>(CH(_3))(_2)CH(_2)OH</td>
<td>207.0</td>
<td>0.6494</td>
<td>68.0</td>
</tr>
<tr>
<td>6. Ethylene chloride</td>
<td>C(_2)H(_4)Cl</td>
<td>216.0</td>
<td>0.93198</td>
<td>25.4</td>
</tr>
<tr>
<td>7. Methyl acetate</td>
<td>CH(_3)CO(_2)H</td>
<td>181.0</td>
<td>0.72532</td>
<td>49.0</td>
</tr>
<tr>
<td>8. Methyl formate</td>
<td>HCO(_3)CH(_4)</td>
<td>164.0</td>
<td>0.75129</td>
<td>53.0</td>
</tr>
<tr>
<td>9. Ethyl formate</td>
<td>HCO(_3)C(_2)H(_5)</td>
<td>181.0</td>
<td>0.88622</td>
<td>60.0</td>
</tr>
</tbody>
</table>

The density-temperature data for methylene chloride and diethylamine was not available.
ACKNOWLEDGMENT

One of the authors (D.K.B) is grateful to the University Grants' Commission, Government of India for financial help.

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Study of Superheat Property of Liquid-Liquid Binary Systems

D. K. Basu and D. B. Sinha *

ABSTRACT: The paper presents the results of the study of the superheat property of Acetone-Carbon Tetrachloride and Chloroform-Carbon Tetrachloride binary systems. For experimental study the steady state method (Sinha and Jalaluddin, 1961) of superheat temperature measurement has been used. The maximum superheat temperature obtainable by the mixture of different mole % of the components has been determined experimentally. The change of maximum superheat temperature, $t_m$, with concentration ($) in mole % has been shown.

Experimental Set up:

In their methods of determination of the superheat of a liquid Wismer et al (1922) used a solid-liquid interface in a capillary tube and Wakeshima and Takata (1958) used a liquid-liquid interface. To avoid heterogeneity Sinha and Jalaluddin (1961) used a glass-liquid interface in which the contact angle is near zero, and therefore the heterogeneity has only little effect on the results.

A spherical bulb of about 2 to 3 cm. dia. and fairly uniform wall thickness was blown at the end of a pyrex glass tube of approximately 0.80 cm. bore and 30 cm. length. The bulb was filled with mercury and a glass insulated nichrome wire (33 S. W. G.) heater coil was immersed in it. A previously calibrated copper-constantan thermocouple enclosed in a thin glass sheath was introduced to measure the temperature of the mercury. The heater current was supplied from 220 volts D.C. mains and the current was closely controlled by a bank of rheostats. At each step the mercury temperature was measured by the thermocouple. For the measurement of the thermocouple voltage a Diesselhorst potentiometer (thermo-electric free) with a Tinsley galvanometer was used.

The most important part of the superheat experiment is to make the bulb clean and free from absorbed gas. So it was very carefully cleansed by washing with a solution of sulphuric acid saturated with potassium dichromate, distilled water, acetone etc. successively. Then it was degassed at about 100 micron pressure with simultaneous heating for about one hour.

*Department of Applied Physics, Calcutta University. Received on 2. 8. 67.
The present systems, mixtures of two miscible liquids are single phase two component bodies having three degrees of freedom e.g., temperature, pressure and composition. The pressure above the liquid being atmospheric was a constant. So it was important to keep the composition constant while studying temperature variation.

To do this the experimental liquid was taken in a container having three openings, one for the heater tube the second for the condenser and the third for measuring the bulk liquid temperature with a thermometer. The container was surrounded with a liquid jacket. The temperature of the jacketing bath was controlled with the help of an auxiliary heating and cooling coils. By suitable adjustment of the heater and the cooling coil the experimental liquid was kept near the boiling point. Cold water was circulated through the outer jacket of the condenser for condensing the out going vapour and the condensate introduced to the mixture for keeping the composition of the mixture constant.

After a few heat runs the liquid mix. shows a colour change prohibiting its use again. So for each composition a new sample was used. To introduce a new mix. the bulb was shifted very quickly and carefully to another vessel containing a mixture of similar strength. The experimental container was then washed and filled up with new mixture and the bulb was quickly replaced in it.

For determining the boiling point of a mix. about 15 c.c. of the mixture was taken in a test tube and a few pieces of stone beads were dropped into the mix to avoid superheating and mercury-in-glass thermometer (reading up to 1/10 of a degree) was introduced into the liquid. The test tube was heated in an electrically heated water bath. The temperature of the bath was raised slowly. The temperature at which the liquid just began to boil was noted. Now the bath water was allowed to cool slowly. The temperature at which bubbling ceased was then noted. The mean of these two temperatures was taken as the boiling point of the mixture at the existing superincumbent pressure. If the mixture was allowed to boil vigorously the boiling point of the mix. was found to rise slowly but steadily. This is, as expected due to the change of the composition of the mix. with continued boiling. The less volatile component becoming richer in the mix. So for accurate results the mixture was not allowed to boil vigorously for long.

Experimental Results:

The maximum superheat temperature, $t_m$, of the mixture was measured at different concentrations ($x\%$) of the components. The maximum superheat temperature of the pure liquids i.e. 100% $CCl_4$, 100% $C_2H_5OH$ and 100% $CHCl_3$ were also measured experimentally and the values obtained are found comparable to those of the previous workers. The boiling points, $t_b$, of the mixtures were also found for each concentration. The degree of superheat $\Delta t$ was taken as,

$$\Delta t = t_m - t_b.$$

$A=CCl_4=Carbon Tetra chloride$  \hspace{1cm} E. Merck. E. P. Variety.

$B=C_2H_5OH=Acetone$  \hspace{1cm} B. D. H. A. R. Variety.

$C=CHCl_3=Chloroform$  \hspace{1cm} E. Merck E. P. Variety.

<table>
<thead>
<tr>
<th>Composition in Mole %</th>
<th>Boiling point of the mixture $t_b$°C</th>
<th>Maximum mercury temp. °C</th>
<th>Temp. drop across the glass wall of the heater °C</th>
<th>Maximum superheat temp. $t_m$°C</th>
<th>Degree of superheat $\Delta t=t_m-t_b$°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A=Carbon Tetrachloride</td>
<td>$t_b°$C</td>
<td>$1493^\circ$</td>
<td>$12.5^\circ$</td>
<td>$1368^\circ$</td>
<td>$60.2^\circ$</td>
</tr>
<tr>
<td>B=Acetone</td>
<td>$t_b°$C</td>
<td>$1493^\circ$</td>
<td>$12.5^\circ$</td>
<td>$1368^\circ$</td>
<td>$60.2^\circ$</td>
</tr>
<tr>
<td>C=Chloroform</td>
<td>$t_b°$C</td>
<td>$1493^\circ$</td>
<td>$12.5^\circ$</td>
<td>$1368^\circ$</td>
<td>$60.2^\circ$</td>
</tr>
</tbody>
</table>
D. K. Basu and D. B. Sinha

Carbon Tetrachloride—Chloroform

A = Carbon Tetrachloride \( \ldots \) \( \text{CCl}_4 \)

C = Chloroform \( \ldots \) \( \text{CHCl}_3 \)

Heater No. II \( \rightarrow \) Thickness \( \frac{\text{Area}}{} = 5.52 \times 10^{-3} \text{cm} \)

<table>
<thead>
<tr>
<th>position in Mole %</th>
<th>Boiling point of the mixture ( t_b ) °C</th>
<th>Maximum steady mercury temp. ( \Delta t ) °C</th>
<th>Temp. drop across the glass wall of the heater ( \Delta t ) °C</th>
<th>Maximum superheat temp. ( t_m ) °C</th>
<th>Degree of superheat ( \Delta t = t_m - t_b ) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>00</td>
<td>0</td>
<td>76.5</td>
<td>15.7</td>
<td>19.20</td>
<td>144.80</td>
</tr>
<tr>
<td>8%</td>
<td>13%</td>
<td>73.3</td>
<td>15.7</td>
<td>19.20</td>
<td>144.10</td>
</tr>
<tr>
<td>5%</td>
<td>24.3</td>
<td>71.1</td>
<td>14.9</td>
<td>12.45</td>
<td>136.35</td>
</tr>
<tr>
<td>7%</td>
<td>32%</td>
<td>69.8</td>
<td>14.6</td>
<td>11.30</td>
<td>134.20</td>
</tr>
<tr>
<td>0%</td>
<td>39%</td>
<td>68.5</td>
<td>14.3</td>
<td>11.30</td>
<td>132.40</td>
</tr>
<tr>
<td>9%</td>
<td>50.3</td>
<td>67.0</td>
<td>14.2</td>
<td>12.04</td>
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</tr>
<tr>
<td>6%</td>
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<td>65.6</td>
<td>14.1</td>
<td>11.90</td>
<td>134.20</td>
</tr>
<tr>
<td>5%</td>
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<td>64.5</td>
<td>14.0</td>
<td>11.90</td>
<td>136.30</td>
</tr>
<tr>
<td>5%</td>
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<td>63.0</td>
<td>14.0</td>
<td>11.78</td>
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<td>6%</td>
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<tr>
<td>7%</td>
<td>92.5</td>
<td>61.5</td>
<td>15.9</td>
<td>13.29</td>
<td>146.11</td>
</tr>
<tr>
<td>0%</td>
<td>100</td>
<td>61.3</td>
<td>15.8</td>
<td>13.90</td>
<td>147.70</td>
</tr>
</tbody>
</table>

The value of maximum superheat temperature for a pure liquid can be estimated theoretically both from Rate Theory and Van der Waal’s Equation of State. The Volmer-Doring formula for the rate of formation of vapour nuclei in a superheated liquid under positive pressure can be modified in the case of binary liquid mixtures as,

\[ J = \rho_0 \left( \frac{6 \sigma_{\text{mix}}}{\pi n_{\text{mix}} (3-b)} \right)^{1/2} \exp \left( -\frac{H_{\text{mix}} + W_{\text{mix}}}{kT} \right) \] ...

\( W_{\text{mix}} = \frac{16 \pi \sigma_{\text{mix}}^3}{3 (\rho_{\text{mix}} - p)^2} \), \( b = \frac{\rho_{\text{mix}} - p}{\rho_{\text{mix}}} \)

where,

\( J = \text{Rate of formation of bubble of critical size per unit volume.} \)

\( W_{\text{mix}} = \text{Work of formation of bubble of critical size in the mixtures.} \)

\( \sigma_{\text{mix}} = \text{Surface tension of the mixture.} \)

\( \rho_{\text{mix}} = \text{Pressure inside the critical bubble.} \)

\( p = \text{Hydrostatic pressure.} \)
A study of Superheat Property of Liquid-Liquid Binary Systems

- Latent heat of vaporization per molecule.
- Number of molecule per c. c.
- Boltzmann's constant.
- Temperature of the mixture at the onset of nucleation in °A.

The estimation of the values of $t_m$ for binary liquid mixtures made from equation (1) can at best be approximate only. Such calculations have some limitations due to the departure of complex solutions from ideal behaviour. Direct experimental determination of the parameters, like surface tension, latent heat of vaporization, vapour pressure, etc. for mixtures in the highly superheated state is not a simple task. Some empirical relations are however available with the help of which the above quantities for mixtures can be evaluated from the parameters of the components. Such values if used in equation (1) may lead to values of $t_m$ which are expected to compare well with the directly determined values, though only in the case of simple mixtures.

The value of maximum superheat temperature, $t_m$, of a single component system can be calculated from the Vander Waal's equation of state. We know that the equation of the spinodal (i.e., the theoretical boundary of metastable state) for a single component system can be written as

$$
\left( \frac{\partial^2 p}{\partial V^2} \right)_T = 0 \quad \text{(2)}
$$

where $p = f(T, V)$

But in the case of two component systems equation (2) is not valid. Prigogine developed the phase diagram of binary liquid mixtures and introduced the following condition as the equation of spinodal in that case,

$$
\left( \frac{\partial^2 g}{\partial x^2} \right)_{T, p} = 0 \quad \text{(3)}
$$

and $g = F(T, p, x_\beta)$

where $g$ is the Molar Gibbs’ free energy and $x_\beta$ is the mole fraction of the component B.

The theoretical estimation of the values of $t_m$ for complex liquid mixtures either from equation (1) or from equation (3) has not yet been possible for the unavailability of experimental values of different physical quantities involved in these equations.

Acknowledgment:

One of the authors (D. K. B) is grateful to the University Grants’ Commission, Govt. of India, for financial grants.

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study of Heat-transfer in Carbontetrachloride-Acetone Binary Mixture

D. K. Basu and S. P. Basu

Abstract: In this work attempts have been made to study experimentally the heat-transfer property of the Carbontetrachloride-Acetone binary system boiling on a horizontal Platinum-Iridium Wire. The effect of addition of Acetone to Carbontetrachloride on the heat transfer property of the later was been shown both in the nucleate boiling and in the film boiling ranges.

Effect of trace additives on the boiling characteristics of liquids has been investigated by a number of authors. Bonilla and Perry (1941) worked with toluol, water-acetone and water-butanol binary mixtures in the nucleate boiling range and during nucleate boiling the heat flux difference characteristics of the mixture diate between those for the pure components. Pettit et al (1958) used methanol and ethyl additives to water and reported that addition of methanol increased the heat flux at a rate on the other hand small quantities of added both decrease (for 0.5% propanol in water) and increase (for 1.5% propanol in water). Bonilla and Perry (1941) pointed out like other observers that some boiling mixtures do not show a one way trend when the composition is varied.

Kautzky and Westwater (1967) is possibly the first of its kind. These workers studied binary mixtures of Carbontetrachloride (CCl₄) and Freon 113 (C₂Cl₈F₃). Their boiling (film) curves show that pure CCl₄ gives lower heat fluxes than pure Freon 113 at all values of Δt. But the various mixtures generally do not give intermediate values. These authors also concluded that the use of weighted physical property to predict theoretically the film boiling heat transfer characteristics of the mixture by the help of the equations meant for pure liquids is not valid, and hence no such attempt is made in this study.

EXPERIMENTAL SET-UP

The experimental arrangement for this investigation was the same, with minor modifications, as used by Basu and Sinha (1967). The experimental liquid was taken in a dewar of 3 litres capacity, fitted with a spiral condenser to recondense the issuing vapour and thereby to keep the composition of the mixture unaltered during a heat run. The liquid was kept near to its boiling point by an auxiliary heater to avoid subcooled boiling. The bulk temperature of the liquid was measured by two thermocouples dipped at different positions and depths. The main heater wire was itself used as the resistance thermometer to measure the heater temperature. Diesselhorst type (thermoelectric free) potentiometer was used to measure all the potentials. Figure (1) shows the electrical circuit diagram.
A study of heat-transfer in carbontetrachloride-acetone binary mixture

RESULTS

Liquids used:
(1) Carbontetrachloride (CCl₄)—E. Merck, Germany-Extra pure Quality, Density = 1.59 gm/cc.
(2) Acetone (C₃H₆O)—B.D.H. India, Analytical Reagent Quality, Density = 0.79 gm/cc.

Figure 1—Electrical connection diagram.

Figure 2—Heat flux—temperature difference characteristics for CCl₄–C₃H₆O binary system in the nucleate boiling range.

Figure 3—Heat flux-temperature difference characteristics for CCl₄–C₃H₆O binary system in the Film boiling range.
DISCUSSION

In these sets of experiments the auxiliary heater was used to keep the temperature of the liquid mixture at the boiling point and this could be attained by introducing any eddy in the pool by suitable variation of the current in the auxiliary heater circuit. The temperature of the experimental heater increases with the length of the wire and correspondingly the heater surface also increases. So for a given value of heat input, the quantity $Q/A$ changes with change of temperature. Taking the value of the coefficient of linear expansion ($\alpha$) of platinum to be $8.7 \times 10^{-6}/^\circ\text{C}$ the decrease in the $1/A$ at a temperature as high as $1000^\circ\text{C}$ is negligible. This is well within the limit of experimental error and hence may be considered as negligible without affecting the result.

Figure (2) shows the nucleate boiling characteristics of a mixture starting from the heat flux value below the transition from film to nucleate boiling. It was observed that the heat flux for a particular $\Delta t$ did not change monotonically with the change of the concentration of Acetone in Carbontetrachloride. The curves for the mixtures necessarily lie intermediate between the curves for the pure components. On the contrary from Figure (3) it is clear that the heat flux just after the temperature jump from film boiling to nucleate boiling in a regular fashion with the addition of Carbontetrachloride. This is shown in Figure 3.

Figure (3) shows the film boiling characteristics of Acetone- Carbontetrachloride binary system. In the film boiling region the addition of Acetone to carbontetrachloride makes the $Q/A - \Delta t$ curves steeper. For a particular temperature difference the value of $Q/A$ was found to increase with the increase of Mol% of Acetone in Carbontetrachloride.

![Figure 3](image)

**Figure 3**
Heat flux vs Mol% of Acetone.

Figure (5) shows the curve of $Q/A$ vs Mol% of Acetone for temperature differences 400, 500 and 600°F of Acetone-Carbontetrachloride system in the film boiling range.

Acknowledgment:

The authors are highly indebted to Late Dr. D. B. Sinha for suggesting the problem and for his keen interest in the work. The authors are also grateful to Prof. A. K. Sen Gupta, Head of the Department of Applied Physics, Calcutta University for his valuable suggestions during the progress of the work.

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