Surface tension studies of ternary system: Copper soap plus benzene plus methanol at 313 K

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Colloidal behaviour of copper soap solution in benzene plus methanol mixture from the surface tension studies confirms that cmc values depend upon the composition of the solvent mixture and are found to decrease with increase in chain length of the soap anion. The results of the surface tensions have been explained on the basis of Szyszkowski's empirical equation and it is observed that the values X, Y, and (-X In Y) lead to the confirmation of the fact that the change in the behaviour of the soap takes place at 50% methanol concentration. The plots of the parachor against the mole fraction of the soap are characterised by an intersection of two straightlines at the cmc of the soap. Hammic and Andrew's equation has been successfully applied to explain the behaviour of soap in benzene-methanol mixture.

In our previous communications, the critical micelle concentration (cmc), solvent-solute and solute-solute interactions at various temperatures were determined and analysed from various physical properties like viscosity, apparent molar volume, ultrasonic velocity and dielectric constant. In the present work, the surface tension and parachor behaviour of copper soaps in binary mixtures of benzene and methanol of varying compositions at 313 K have been investigated as surfactants possess valuable characteristics such as wetting, emulsification, lubrication etc. and play a significant role in various fields like rubber industries, paints, water proofing, preservation of wood etc.

Results and discussion

The surface tension γ of the solutions of copper caprylate and caprate in mixtures of varying compositions of benzene and methanol decreases with increase in soap concentration. This may be due to increasing tendency of soap molecules to form aggregates in the surface of the solvent. The plots of surface tension against soap concentration are characterised by two straightlines corresponding to cmc of soap (Table 1). The values of cmc in the solution containing methanol up to 50% are lower as compared with the cmc values of solution containing higher volume per cent of methanol. This may be ascribed to the predominance of non-hydrogen bonded solvent (benzene) below 50% methanol. It is suggested that methanol takes quite different position in the palisade layers and soap exhibits different degree of aggregation in mixed solvents of varying compositions. The value of cmc of soap agrees with that determined by us using other physical properties like density, viscosity, ultrasonic velocity etc.

The plot of γ vs log C (Fig. 1) are characterized by an intersection of two straightlines for all the compositions of the solvent mixture.

The linear variation of γ against log C is in agreement with Szyszkowski's empirical equation for solution of fatty acids.

\[
\frac{\gamma}{\gamma_0} = 1 - X \ln \frac{C}{Y} \quad \ldots (1)
\]

where γ and γ₀ are surface tensions of the solution of concentration C (M) and that of the pure solvent respectively; X and Y are constants.

Equation (1) can also be written as:

\[
\gamma = \gamma_0 (1 + X \ln Y) - \gamma_0 \frac{X}{Y} \ln C \quad \ldots (2)
\]

Hence,

\[
\frac{d\gamma}{d \ln C} = -X \gamma_0 \quad \ldots (3)
\]

and by substitution in Gibb's adsorption equation, the adsorption excess, τ, (i.e. the excess concentration of the solute per unit area of the surface) is found to be:
\[ \tau = -1/RT \frac{d\gamma}{d \ln C} = Xy_0 / RT \] ... (4)

Hence, the surface area, \( A \), covered by the soap micelles formed by 1 g mol of the soap is:

\[ A = RT / Xy_0 \] ... (5)

The values of \( X \) evaluated from the slopes \((-2.303 y_0 X)\) and values of \( Y \) and \((-X \ln Y)\) calculated from the intercept \(\{y_0 (1 + X \ln Y)\}\) of the plots of \( \gamma \) vs \( \log C \) are summarized in Table 2. Plots of \( \gamma \) against \( \log C \) are characterized by an intersection of two straightlines at \( \text{cmc} \), hence these equations have different values of slopes and intercepts [i.e. \( X_1 \), \( X_2 \), \( Y_1 \), \( Y_2 \), \( -X \ln Y_1 \), \( -X \ln Y_2 \), \( A_1 \) and \( A_2 \)] below and above \( \text{cmc} \) respectively.

A perusal of (Table 2) shows that the parameters \( X \), \( Y \), and \(-X \ln Y\) are not independent of the composition of the solvent mixture.

It is interesting to note that: i) \( X \) increases up to 50% methanol and drops suddenly and then again increases; ii) two values of \( Y \) have been enumerated.

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**Fig. 1**—Surface tension of the system copper caprylate, benzene+methanol against \( \log C \) at 313 K

<table>
<thead>
<tr>
<th>Name of soap</th>
<th>Parameter</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprylate</td>
<td>Surface tension</td>
<td>.066</td>
<td>.067</td>
<td>.068</td>
<td>.070</td>
<td>.071</td>
<td>.070</td>
</tr>
<tr>
<td></td>
<td>Parachor</td>
<td>.066</td>
<td>.066</td>
<td>.067</td>
<td>.069</td>
<td>.070</td>
<td>.070</td>
</tr>
<tr>
<td>Caprate</td>
<td>Surface tension</td>
<td>.053</td>
<td>.054</td>
<td>.055</td>
<td>.056</td>
<td>.058</td>
<td>.060</td>
</tr>
<tr>
<td></td>
<td>Parachor</td>
<td>.054</td>
<td>.054</td>
<td>.054</td>
<td>.055</td>
<td>.056</td>
<td>.058</td>
</tr>
</tbody>
</table>

**Table 1**—Values of \( \text{cmc} \) (M) for copper soaps in benzene plus methanol mixtures at 313K
below and above cmc and at the periphery of 50% methanol concentration, there is change in the observed trend; and iii) \(-X \ln Y\) too, have been stipulated from the referred equation and two such values corresponding to below and above cmc are recorded in Table 2.

Obviously, these observations reinforce the argument that the change in behaviour of soap takes place in the proximity of 50% methanol concentration.

However, this condition reveals that process of agglomeration of soap molecules into micelles above and below 50% methanol is quite different. Furthermore it is argued that the ordering of micellar structure is less pronounced above 50% methanol because methanol being a polar solvent having resultant dipole moment, exhibits a perturbing effect on the micelles formed in such a system.

Table 2—Values of slopes \(X_1, X_2\), intercept \(Y_1, Y_2\), and range of area covered by the soap micelles formed from 1 \(M\) of the copper caprylate (caprate) below and above the cmc in ternary system at 313K

<table>
<thead>
<tr>
<th>Volume % of methanol in the solvent mixture</th>
<th>(X_1 \times 10^2)</th>
<th>(X_2 \times 10^2)</th>
<th>(Y_1 \times 10^3)</th>
<th>(Y_2 \times 10^3)</th>
<th>(-X \ln Y_1)</th>
<th>(-X \ln Y_2)</th>
<th>(A_1 \times 10^3)</th>
<th>(A_2 \times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.82</td>
<td>0.74</td>
<td>4.89</td>
<td>53.57</td>
<td>15.42</td>
<td>8.07</td>
<td>5.02</td>
<td>12.23</td>
</tr>
<tr>
<td></td>
<td>(3.96)</td>
<td>(1.57)</td>
<td>(2.42)</td>
<td>(1.13)</td>
<td>(3.50)</td>
<td>(0.19)</td>
<td>(2.30)</td>
<td>(5.79)</td>
</tr>
<tr>
<td>40</td>
<td>1.96</td>
<td>0.92</td>
<td>3.87</td>
<td>19.15</td>
<td>16.16</td>
<td>9.08</td>
<td>4.68</td>
<td>9.68</td>
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<tr>
<td></td>
<td>(3.98)</td>
<td>(1.82)</td>
<td>(2.01)</td>
<td>(1.14)</td>
<td>(2.78)</td>
<td>(0.25)</td>
<td>(2.30)</td>
<td>(5.02)</td>
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<td>50</td>
<td>1.89</td>
<td>0.88</td>
<td>4.68</td>
<td>23.26</td>
<td>16.00</td>
<td>8.90</td>
<td>4.85</td>
<td>10.38</td>
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<tr>
<td></td>
<td>(3.79)</td>
<td>(1.83)</td>
<td>(2.06)</td>
<td>(1.16)</td>
<td>(2.74)</td>
<td>(0.28)</td>
<td>(2.42)</td>
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<tr>
<td>60</td>
<td>2.12</td>
<td>0.96</td>
<td>2.06</td>
<td>11.54</td>
<td>16.17</td>
<td>9.00</td>
<td>4.35</td>
<td>9.599</td>
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<tr>
<td></td>
<td>(4.47)</td>
<td>(1.77)</td>
<td>(1.95)</td>
<td>(1.35)</td>
<td>(2.99)</td>
<td>(0.53)</td>
<td>(2.06)</td>
<td>(5.21)</td>
</tr>
<tr>
<td>70</td>
<td>2.05</td>
<td>0.86</td>
<td>2.58</td>
<td>36.35</td>
<td>16.69</td>
<td>8.98</td>
<td>4.51</td>
<td>10.81</td>
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<tr>
<td></td>
<td>(4.48)</td>
<td>(1.78)</td>
<td>(1.93)</td>
<td>(1.38)</td>
<td>(2.54)</td>
<td>(0.57)</td>
<td>(2.06)</td>
<td>(5.21)</td>
</tr>
<tr>
<td>80</td>
<td>1.98</td>
<td>0.93</td>
<td>3.22</td>
<td>14.15</td>
<td>16.03</td>
<td>8.89</td>
<td>4.68</td>
<td>9.99</td>
</tr>
<tr>
<td></td>
<td>(4.26)</td>
<td>(1.72)</td>
<td>(1.92)</td>
<td>(1.33)</td>
<td>(2.77)</td>
<td>(0.50)</td>
<td>(2.18)</td>
<td>(5.40)</td>
</tr>
</tbody>
</table>
It is also observed that the plots of parachor against mole fraction of the soap are characterised by an intersection of two straightlines at a point which corresponds to cmc of the soap. The values of cmc (Table 1) are in good agreement with those obtained from the $\gamma$ vs $C$ plots. A change in parachor at cmc may be attributed to the fact that the soap exists in different forms below and above cmc (Fig. 2). The parachor behaviour may be represented by two linear equations having different values of the constants, $K_1$ and $K_2$ below and above cmc respectively. It is observed that the calculated values of $K_1$ using Eq. (10) are in agreement with the values obtained graphically. The values of $K_2$ i.e. the parachor of the solvent obtained graphically are in close agreement with the corresponding experimental values of the parachor of the solvent mixture of benzene and methanol. Hence, there is a justification in applying Hammic and Andrew's equation to the solution of copper caprylate and caprate in mixture of benzene and methanol.

Acknowledgement

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References

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