CHAPTER 6

RESULTS & DISCUSSION
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In our study we have measured the changes in surface tension or more precisely interfacial tension caused due to the presence of surfactants in certain immiscible liquid-liquid systems.

The origin of surface tension in a liquid is the force of attraction between the molecules that make up the liquid in the absence of other forces, this mutual attraction of the molecules caused the liquid to coalesce to form spherical droplets. As a general rule, the greater is the proportion of polar groups (e.g. O-H groups) in a molecule, stronger are the forces of attraction between them. Stronger forces of attraction give rise to a high surface tension and a tendency to form discreet droplets on a surface rather than wet it evenly. The large proportion of O-H groups in water are responsible for it’s high surface tension.

Contact Angle

The definitions of surface tension and surface energy have involved consideration of the behavior of liquids in contact with solids and the formation of droplets or thin films. One convenient way of quantifying this behavior is to measure the angle \( \theta \) formed by the liquid-solid and the liquid-liquid interfaces.

If \( \theta \) is greater than 90\(^0\), the liquid tends to form droplets on the surface. If \( \theta \) is less than 90\(^0\), the liquid tends to spread out over the surface and when the liquid forms a thin film, \( \theta \) tends to zero.
Adsorption of Surfactants

One of the most striking physicochemical characteristics of surfactants is their ability to reduce interfacial tension at low concentration. Surface active agents are defined by this property. Unlike surfactants, inorganic salts increase the interfacial tension. This difference between surfactants and inorganic salts depends on the way the solute is absorbed at an interface, surfactants show positive absorption while inorganic salts show negative adsorption. The extent of positive adsorption of a surfactant depends entirely on its chemical structure and on the solvent.

Bulk phases contact each other at an interface. This region near the interface differs in physicochemical properties from the bulk phase far from the interface. This difference gives rise to interfacial tension.

Solubilization

It has long been known that the aqueous solubility of sparingly soluble or insoluble substances can be increased by adding an appropriate third component. Systematic studies using surfactants led to this phenomenon being called solubilization. Solubilization plays a very important role in industrial and biological processes.

In our study, we have used cationic surfactants, namely Cetyl pyridinium chloride (CPC), Cetyl pyridinium bromide (CPB) and Cetyl pyridinium iodide (CPI) to study the thermodynamic properties occurring at aromatic hydrocarbon H₂O interface. For this purpose, we have measured contact angle (θ) and thereby calculated interfacial tension, for both binary and ternary systems, using Young’s relation.

The contact angle θ for water (single component solvent) system is measured from images of fig.1.1 and from measured value the surface tension (γ ± 0.0042) at 20 to 30⁰C is calculated from eqn. 1 with θ ± 0.0041 standard deviation. The IFT, wetting energy and wetting coefficient for water + (benzene, toluene, xylene), and
1x10^{-4} to 1x10^{-3} moles L^{-1} of CPC, CPB and CPI in water with same hydrocarbons are calculated from $\theta$ images of wet liquid ($\beta$ phase) with $\pm$0.02, $\pm$0.04 and $\pm$0.03 precision by eqn. 1,2 and 3. The trend is shown in figs. 1,2 and 3 and the values are given in tables 1-12 water + benzene systems are repeated several times at $20^0$ for C high precision and was measured with $\pm$0.0041 standard deviation.

In general, $\theta$ for individual solvent water, benzene, toluene and xylene increases with chosen temperatures, and the trend of numerical value of $\theta$ is as xylene > benzene > toluene > water, is fig. 1A. while with water $\theta$ is as xylene > toluene > benzene, the $\theta$ values for them are given in table 1-12 and trend is shown in figs. 1(a, b, c) to 10(a, b, c). For each aromatic hydrocarbon with water + CPC solution, the $\theta$ follows the trend as benzene > toluene > xylene at studied temperatures, the values and graphs are in table 1-12 and fig 1(a, b, c) to 10(a, b, c).

For benzene with CPC + water, the values of $\theta$ and IFT increases on increasing the concentration of CPC (figs. 1a, 8a, table 1 and 2). Perhaps surfactant molecules reduce or weaken the intramolecular forces of each benzene and water, this could be rationalized to the conjugation of benzene and dipoles of water that leads to increase their mutual solubility as is seen from the observed $\theta$ values (fig 5a). The wetting energy that decreases for this explains the increase in wetting on addition of surfactant. The wetting coefficient is also observed to decrease with surfactant (fig. 8a).

The $\theta$ and IFT values for toluene are slightly lower compared to benzene. Probably CH$_3$ group could cause the perturbation in conjugate $\pi$-system, as CH$_3$ group is electron donating group. This concept is supported by $\theta$ and IFT of xylene (fig.3a), as xylene contains two-CH$_3$ groups in the ring and due to this increase in alkyl
chain length, the conjugate $\pi$-system seems to be perturbed i.e. $3\sigma$ bond CH$_3$
structure is attached with carbon at $\text{ortho}$ and $\text{para}$ positions of benzene molecule
that causes the increase in free energy or resonance energy of conjugate $\pi$-system.

The same trend for $\theta$ and IFT values of ternary systems is observed with upside
down as benzene $>$ toluene $>$ xylene (fig. 5b to 8b, table 4 and 6). This could be
explained as the CH$_3$ in the ring counter balances the solublizing effect of CPC
induced by the Cl-ion. That's why the effect CPC on solubility of toluene and
xylene with water is not that much strong as in case of benzene. Therefore, arenes
with CH$_3$ groups are observed to have lower efficiency of wetting with surfactant
than that of without $-\text{CH}_3$ group, which matches the observations of Rosen$^{88}$.

In case of CPB and CPI [Fig. 9(a,b,c) to 10(a,b,c)]. Tables (7-12), although the
same trend is observed but variation in contact angle $\theta$ is lesser in comparison to
CPC. It may be due to bigger size of anion, hence, the trend of wettability among
surfactants taken as CPC $>$ CPB $>$ CPI.

On raising the temperature, $\theta$ and IFT values are seen to decrease in each case, that
leads to the decrease in wettability of arenes.$^{89}$

For thermodynamic properties, we have studied heat-holding capacity of some
electrolytes in water as well as in presence of surfactant.
It was observed that the CP values for NaCl, NaH$_2$PO$_4$, Na$_2$HPO$_4$ and CaCl$_2$ in
water decrease with increase in molality of the system. At lower molality of the
solution, the heat capacity values were the largest for Na$_2$HPO$_4$ followed by NaCl
in water. Whereas NaH$_2$PO$_4$ and CaCl$_2$ in water systems have reduced but almost
similar heat capacities at lower molalities. While Cp. $-$ values for NaCl, NaH$_2$PO$_4$,
Na$_2$HPO$_4$ and CaCl$_2$ in water decrease with increase in molality of the system (table 14 and figs. 11 to 19). The largest heat capacity value observed for Na$_2$HPO$_4$ was probably due to the formation of two Na$^+$ ions per molecule of Na$_2$HPO$_4$ in water. These ions make strong ion-dipole bonds with water molecules. Intermolecular hydrogen bonding also seems to the heat capacity value of Na$_2$HPO$_4$.

The large heat capacity for NaCl in water was due to the very large heat of hydration associated with smaller positively charged Na$^+$ ions$^{90}$. These ions make stronger ion-dipoles bonds with water. This in turn would require more thermal energy, which was also, the heat holding capacity, to break H$_2$O- dipole bonds.

The reduced head capacity for CaCl$_2$ was low, despite large hydration energy of dipositive Ca$^{++}$ ions but this was more than balanced by its partial covalent character$^{99,100}$. The lower (but almost similar) heat capacity of CaCl$_2$ as compared to NaH$_2$PO$_4$ was due to the formation of two intermolecular H-H bonds per anion in NaH$_2$PO$_4$ compensating for the larger size of Na$^+$ ions as compared to Ca$^{++}$ ion towards the heat capacity value.

Table 15 shows that the heat capacity values for CTAB in H$_2$O follow the general trend of decreasing values. Initially, the heat capacity value was very large. This large value was explained by the large quantity of energy required to break the ion – dipole bonds formed between CTAB ions and H$_2$O dipoles. However, for the different molalities of electrolytes in water, the heat capacities as a function of CTAB molalities show a decreasing trend in values for NaCl and NaH$_2$PO$_4$ whereas an upward trend was observed for CaCl$_2$ and NaHPO$_4$ (fig.11to19). The decreasing trend for NaCl and Na$_2$HPO$_4$ in H$_2$O with increasing CTAB molalities suggests that most of the thermal energy was unutilized or most of the thermal
energy was unable to break the cation H₂O- dipolar bonds (fig c). In case of CaCl₂ the large hydration energy of the smaller divalent Ca⁺² ion was responsible for the strong ion – dipolar bonds as compared to the ion – dipolar bonds of CTAB and H₂O molecules. While in Na₂HPO₄, the hydration energy due to the two Na+ ions produced per molecule of the electrolyte seems to be responsible for stronger ion-dipole bonds as compared to the ion-dipole bonds of CTAB-H₂O molecule (fig d).

The observed behavior was fitted to a power equation. Table 16 shows the regression constants for the power equation. The values of regression constants ‘a’, ‘n’ and ‘r²’ remain almost constants with increasing quantity of CTAB addition to electrolyte H₂O system. The near constancy of the regression values with change in CTAB concentration showing a minor effect on the electrolytic behavior suggests that this equation was best suited to explain their behavior.

A fundamental experiment was conducted to eliminate the van der waals forces from water and water + electrolytes raising their thermal energy and noting down the time taken to evaporate the 10g of water and water + electrolytes. The observations as in table 17 depict the status of stronger hydration as Na₂HPO₄ > NaH₂PO₄ > CaCl₂ > NaCl > CTAB. While their Cp status was found as Na₂HPO₄ > NaCl > NaH₂PO₄ > CaCl₂. This experiment was in agreement with Cp values.
Fig c: On boiling CTAB + water solutions whole micelle comes out of boiling cell, this action of micelle continued for NaCl and NaH₂PO₄ solutions in CTAB + water.

Fig d: On boiling CTAB + water solutions whole micelle comes out of boiling cell, this action of micelle continued for NaCl and NaH₂PO₄ solutions in CTAB + water.