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# Interfacial Tension of Hydrocarbons (Benzene and Xylene) with Aqueous Cetylpyridinium Chloride at 20° and 25°C

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The interfacial tension (I.F.T.) of hydrocarbons (benzene and xylene) in water + cetyl pyridinium chloride liquid-liquid interface is studied at 20°C and 25°C using molar dynamics computer simulation. The wetting coefficient is calculated using titration technique. Adsorption of interfaces is inversely proportional to temperature.

## INTRODUCTION

Boender *et al.*[1] describe that steady wettings in capillary tube and parallel plate geometries are extended to a spontaneously spreading drop in the presence of a surfactant.

Mixtures of surfactants often exhibit synergisms in their physico-chemical properties thus allowing particular applications. Often mixtures may exhibit superior behaviour as compared to pure surfactant components. Many reports have been published in recent years dealing with the solution properties of mixed surfactants containing ionic, non-ionic or mixed ionic micelles[2]. However, there have been a very few studies analysing the influence of mixed surfactant systems on reaction processes[3]. This prompted us to study the alkaline hydrolysis of hydroxamic acid on mixed surfactant systems. The work reported here is part of a wider programme aimed at the understanding of the reaction mechanism in micellar solution[4]. For the last few years we have been studying the influence of cationic, anionic, zwitter ionic and non-ionic micelles in acidic and alkaline hydrolysis of several hydroxamic acids[5]. Anionic micelles inhibit the reaction and cationic micelles accelerate hydrolysis. The surface-tension variation is governed by the surface transport equation for the surfactant concentration involving a connective term whose magnitude depends on the local meniscus inclination.

When surfactants are present, more than one solution may exist, the one obtained depending on the path followed resulting in hysteresis effect[6]. Surface tension which modifies a motion and the associated pressure field, also modifies the apparent contact angle in presence of surfactant[8]. Wetting includes the motion of surface elements towards the contact line accompanied by a change in their area[9].

## EXPERIMENTAL

In some more recent work by Raney *et al.* (1991), the parameter space was defined where optimal detergency may be observed with non-ionic/anionic-surfactant blends. The more common situation in wetting involves a solid-liquid and a second immiscible wetting of a surfactant surface by water in air, and two fundamental equations result[10].

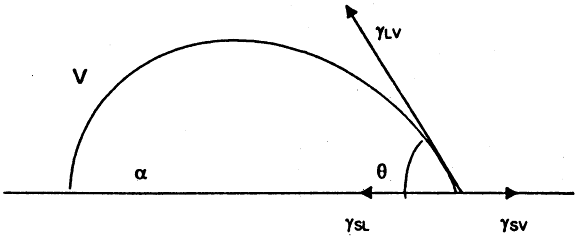
(a) Laplace equation for equilibrium shape of fluid interface

$$\gamma \operatorname{div} n + P_L - P_V = C \tag{1}$$

where C is a constant, n is unit normal to surface directed from L to V, and $P_L$ and $P_V$ are potential energies per unit volume of two fluids at a point of interface. These are due to externally applied fields (gravitational, centrifugal) which are assumed not to alter the values of I.F.T., div n is mean curvature of interface.

(b) Young's equation for the equilibrium contact angle, θ, of fluid interface with solid is defined as the angle between $S_L$ and $L_V$ interfaces[11]:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma} \tag{2}$$



A simple geometry system comprising a solid 'S' with a planar surface wetted by a fluid 'L' surrounded by a second immiscible fluid 'V'. The surface tensions can be regarded as forces acting on the line of contact. The equilibrium constant angle θ of L over S is a property of the three phases".

The benzene-cetyl pyridinium chloride interactions are modelled using a simple 6-12-1 potential between each guest-CPC atom pair.

$$U = \sum_{ij} \left( \frac{A_{ij}}{\gamma_{ij}^{6}} + \frac{B_{ij}}{\gamma_{ij}^{12}} + \frac{q_i q_j}{\gamma_{ij}} \right) \tag{3}$$

i and j referring to guest and CPC atoms, respectively, and using for the culombic parts, the charges defined above. The coefficients $A_{ij}$ and $B_{ij}$ of potential were assigned by comparison of adsorption and diffusion simulations to experimental data for benzene, xylene and CPC. A combination rule based on Slater-Kirkwood's expression of dispersion force was used to relate atomic parameters to the Lennard-Jones coefficients.

Cetyl pyridinium chloride (CPC), benzene and xylene from E. Merck were used as received. Triple distilled, degased and demineralised $H_2O$ was used for solution preparation.

## RESULTS AND DISCUSSION

In the present work, we investigate the effect of changes in geometric structure of surfactant of aromatic hydrocarbons-$H_2O$ interfacial tension. We carried out the experiment for I.F.T. ($\gamma$) as a function for diastereomeric surfactant, concentration (C), at constant salt concentration in xylene-$H_2O$ system and benzene-$H_2O$ system. The plots of the equilibrium I.F.T. *vs.* concentration, *i.e.*, (log C) of aqueous solution of cetylpyridinium-chloride $10^{-4}$ to $10^{-3}$ moles/dm$^3$ in benzene $H_2O$ system at 25°C are shown in Figure 1. The surface activity of the studied the surfactant increases with the alkyl group attached with cyclic ring. Comparison curve of surface tension $\gamma$ for the appropriate surfactant indicates that the studied surfactant shows different efficiency of adsorption at an arene-$H_2O$-CPC interface or arene-aqueous CPC interface.

The benzene-aqueous CPC gives lower I.F.T. than xylene at the same surfactant concentration but the slope (Figure 1) of I.F.T. for xylene-aqueous CPC increases with concentration. The I.F.T. of benzene and xylene with $H_2O$ were reported lower than the literature value ($H_2O = 72.76$ dynes/cm). As the concentration of arenes increases, the surface tension decreases, I.F.T. of xylene increases to a value higher than that of benzene in $H_2O$. The behaviour suggests that as C-atom increases, I.F.T. also increases. On adding the surfactants, arenes containing —$CH_3$ groups have lower efficiency of adsorption than that without —$CH_3$ group, which is a measure of I.F.T. reduction efficiency calculated according to a definition of Rosen[2] as the negative of logarithm of the surfactant aqueous solution concentration necessary to reduce the I.F.T. of alkane-$H_2O$ by $\delta\gamma = 20$ mN/m$^2$.

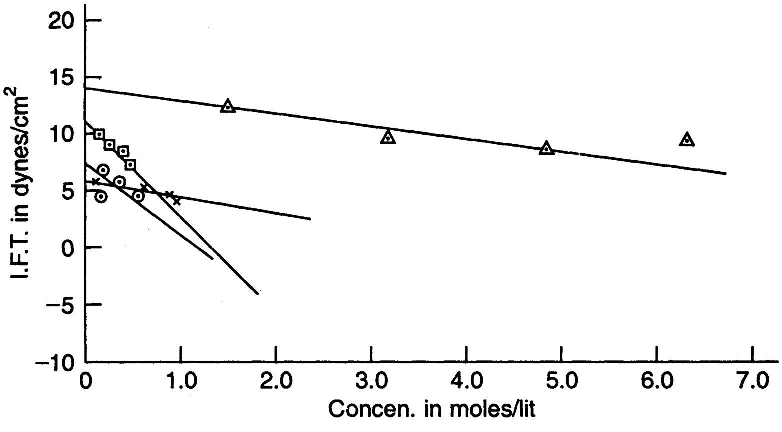


Fig. 1. Comparison of I.F.T. of: △ Xylene + $H_2O$; × Benzene + $H_2O$; ⊡ Benzene + $H_2O$ + CPC; ⊙ Xylene + $H_2O$ + CPC at 25°C.

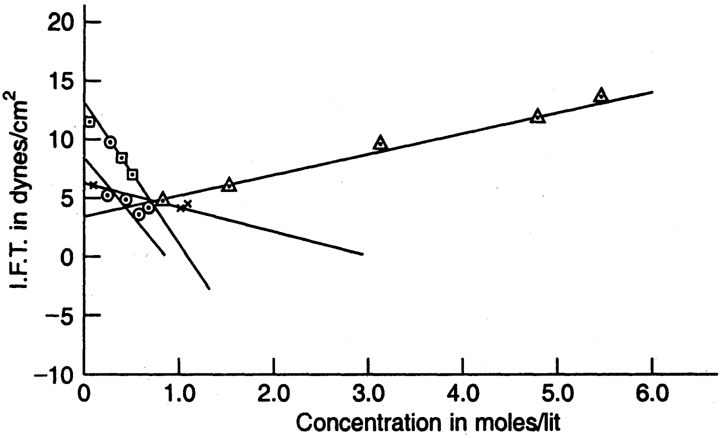


Fig. 2. Comparison of I.F.T. of: ▲ Xylene + $H_2O$; × Benzene + $H_2O$; ⊡ Benzene + $H_2O$ + CPC; ⊙ Xylene + $H_2O$ + CPC at 20°C.

At 20°C, the I.F.T. of xylene is positive while that of benzene negative with $H_2O$. The difference is because —$CH_3$ group of xylene has higher activity coefficient than benzene on increase in concentration. As temperature increases, the I.F.T. of xylene-$H_2O$ decreases; it may be possible that van der Waals force with cyclic C-atom and chain C-atom also decreases. Same case was reported for benzene-$H_2O$ at 20°C and 25°C. The lower values of I.F.T. were also reported for benzene-xylene-aqueous CPC at 20°C. The plot of I.F.T. ($\gamma$) *vs.* log C of aqueous CPC are shown in Fig. 2. It is clear from the plot that xylene has lower efficiency of adsorption than benzene in $H_2O$ with surfactant.

On increasing temperature, I.F.T. decreases. This decrease in I.F.T. for the above plot (Figs. 1 and 2) is due to decrease in van der Waals forces. We investigate the variation of I.F.T. with mole-fraction, the alkyl chain length influences the concentration values. The hydrophobicity decrease of single chain surfactant lowers the formation of films.

## Conclusion

The main conclusions from the study are as follows:

Adsorption of CPC with arenes-$H_2O$ interface is favoured by;

1. Increases in chain length (C-atoms),
2. Decrease in temperature.

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