



Adsorption of cetyl trimethyl ammonium bromide (CTABr) at various interfacial in presence and absence of potassium chloride (KCl)

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Abstract

Interfacial tension γ measurements were made using AGLA micrometer syringe (Burroughs Welcome) at benzene water, toluene water and air water interfaces with varying concentration of cetyl trimethyl ammonium bromide in presence and absence of potassium chloride. There was regular decrease in γ values with increase in concentration of CTABr. The γ values in presences of KCl were less than in its absence because surfactant ions were strongly adsorbed at interface owing to the neutralization of repulsive ionic head group charge of surfactant ions. From these data, surface pressure (π), surface excess (Γ_s) and area occupied per surfactant ion at various concentration have been calculated. The values of Γ_s have been determined from gradients of γ -log C curves using appropriate form the Gibb's adsorption equation. The adsorption data have been analysed by plotting the π -A curves. Initially at low CTABr concentration only slight increase in surface pressure were capable of reducing the area to a greater extent but at higher concentration a large increase in π produces very little decrease in area. At low surface pressure, surfactant ions are stretched out helter-skelter to the interface. At higher values these surfactant ions are compressed and value of area occupied per surfactant ion decreases, when surfactant ions are highly packed together then the area per surfactant ions does not appreciably decrease which is seen by vertical portion of π -A curves,

Keywords: Adsorption, surfactant, CTABr, Interfacial tension, KCl

Introduction

The adsorption of surfactants from aqueous solutions is the phenomenon of major importance ranging from ore flotation, paint technology and enhance oil recovery [1, 2], Becher [3] has reviewed good account of work on surfactant adsorption at oil water interface and has co-related the adsorption data with surface charge and surface potential of dispersion system. Thermodynamic adsorption of cationic surfactants on solid-liquid [4, 5] surface has shown that the orientation of surfactant molecule may change depending upon the polarity of solid surfaces. The kinetics of the adsorption of surfactant at interface have also been studied by some workers [6, 7, 8], William [9], have studied the role of surface charge density on surfactant adsorption at solid-aqueous and air-water interfaces. The above survey of literature reveals that detailed and systematic studies on the adsorption of surfactants in presence and absence of various additives at the aromatic hydrocarbon-water interfaces. It appears that not much work has been done to investigate the structural aspect. of ionic surfactants at hydrocarbon-water interfaces. With this object in view, attempts for quantitative study on the interfacial adsorption of ionic surfactant at toluene-water, benzene-water and in air-water in presence and absence of potassium chloride have been taken up to know the manner of packing of surfactant ions at the interfaces.

Materials and Methods

Cetyl trimethyl ammonium bromide IC 16 H ait [C₁₆H₃₃(CH₃)₃NBr] was used as cationic from BDH England. Benzene, toluene and potassium chloride used were all BDH Analar grade chemicals. The water used was always doubly distilled with specific conductivity $2 \times 10^{-6} \text{ohm}^{-1} \text{Cm}^{-1}$ All

the experiments were carried out at temperature 30°C using pyrex glass apparatus. Measurements of interfacial tension were made by drop volume technique [10, 11] using "AGLA" micrometer syringe which can deliver liquids accurate upto 0.002 ml in volume and having a finite capillary bore with its radius 0.2 cm. Estimations were made with benzene as well as toluene and aqueous phase containing varying concentration of CTABr.

The drops of aqueous phase were developed in benzene as well as in toluene at a very slow speed. The average volume of not less than five drops was used. The value of interfacial

tension of the clean interface γ_0 has been calculated in dynes per cm using equation:

$$\gamma_{\text{oil.water}} = \frac{V(\rho_{\text{water}} - \rho_{\text{oil}})F.g.}{r} \quad (1)$$

Where $\gamma_{\text{oil.water}}$ is the interfacial tension at oil-water V is the volume of drop developed from the edge of the capillary of radius (r).

$(\rho_{\text{water}} - \rho_{\text{oil}})$ is the difference in densities of water and oil, g is the gravitational force and F is the correction factor that depends on the values of V/r^3 the values of F have been obtain from international critical table,

γ_0 is the interfacial tension of the clean interface γ is the interfacial tension in presence of surfactant ion at the same interface? The surface pressure π or the expanding pressure exerted by film of surfactant ions is given by the relation.

$$\pi = \gamma_0 - \gamma \quad (2)$$

To make a determination of the interfacial tension, the jet of the syringe was immersed in the less dense of the two liquid i.e. benzene/toluene in a 50ml pyrex beaker and aqueous solution of surfactant was in the syringe. The drops of the heavier liquid (aqueous surfactant solution) were slowly developed at a constant temperature of 30°C. The densities (ρ) of two liquids were determined with the help of pyrex stoppered pycnometer. The interfacial tension measurements were made in presence and absence of KCl.

Results and Discussion

The variation of interfacial tension (γ) against log molar

concentration of CTABr at benzene water, toluene-water and air-water interface respectively in presence and absence of KCl. The interfacial tension at clean benzene water, toluene-water and air-water interface was found to be 34.0 and 35.1 and 71.0 dynes/cm respectively. It has been observed from the curves that each addition of surfactant lowers the interfacial tension (γ) values in presence as well as in absence of KCl. These γ values in presence of KCl were less than in absence of KCl because surfactant molecules are strongly adsorbed at the interface presumably owing to the neutralization of repulsive ionic head group charges of surfactant ions,

Table 1: Interfacial tension (γ), surface pressure (π), surface excess (Γ_s), number of molecules (n) adsorbed/cm² and area (A) occupied per molecule of CTABr at benzene - water interface. γ_0 (benzene-water) = 34.0 dynes/cm, Temperature = 30°C

Molarity (C)	Interfacial Tension (dynes cm ⁻¹)	Surface Pressure (dynes cm ⁻¹)	Surface Excess (g.m./cm ²)	n x 10 ⁻¹²	Area occupied molecule \AA^2
0.5 x 10 ⁻⁵	25.1	8.8	1.73 x 10 ⁻¹¹	10.4	961.0
1.0 x 10 ⁻⁵	24.7	9.2	4.15 x 10 ⁻¹¹	24.9	401.6
1.5 x 10 ⁻⁵	22.8	11.2	5.22 x 10 ⁻¹¹	31.4	318.4
2.0 x 10 ⁻⁵	21.8	12.1	6.9 x 10 ⁻¹¹	41.5	340.0
0.5 x 10 ⁻⁴	19.8	14.1	8.65 x 10 ⁻¹¹	52.0	192.0
1.0 x 10 ⁻⁴	15.6	18.3	9.84 x 10 ⁻¹¹	59.2	168.0
2.0 x 10 ⁻⁴	11.1	22.8	12.3 x 10 ⁻¹¹	74.0	135.0
3.0 x 10 ⁻⁴	8.6	25.4	13.8 x 10 ⁻¹¹	83.3	120.0

Table 2: Interfacial tension (γ), surface pressure (π), surface excess (Γ_s), number of molecules (n) adsorbed/cm² and area (A) occupied per molecule of CTABr at benzene - 0.1 M KCl interface. γ_0 (benzene-water) = 34.0 dynes/cm, Temperature = 30°C

Molarity (C)	Interfacial Tension (dynes cm ⁻¹)	Surface Pressure (dynes cm ⁻¹)	Surface Excess (g.m./cm ²)	n x 10 ⁻¹²	Area occupied molecule \AA^2
0.5 x 10 ⁻⁵	19.7	14.2	3.84 x 10 ⁻¹¹	23.1	432.0
1.0 x 10 ⁻⁵	18.8	15.1	9.88 x 10 ⁻¹¹	59.5	168.0
1.5 x 10 ⁻⁵	17.1	16.8	15.57 x 10 ⁻¹¹	92.7	106.0
2.0 x 10 ⁻⁵	15.6	18.3	16.14 x 10 ⁻¹¹	97.2	102.0
0.5 x 10 ⁻⁴	12.7	21.3	20.2 x 10 ⁻¹¹	121.8	82.6
1.0 x 10 ⁻⁴	9.0	24.9	21.2 x 10 ⁻¹¹	128.2	78.0
2.0 x 10 ⁻⁴	4.4	29.5	14.9 x 10 ⁻¹¹	90.0	110.0
3.0 x 10 ⁻⁴	3.6	30.4	16.6 x 10 ⁻¹¹	100.0	100.0

Table 3: Interfacial tension (γ), surface pressure (π), surface excess (Γ_s), number of molecules (n) adsorbed/cm² and area (A) occupied per molecule of CTABr at toluene - water interface. γ_0 (toluene-water) = 35.1 dynes/cm, Temperature = 30°C

Molarity (C)	Interfacial Tension (dynes cm ⁻¹)	Surface Pressure (dynes cm ⁻¹)	Surface Excess (g.m./cm ²)	n x 10 ⁻¹²	Area occupied molecule \AA^2
0.5 x 10 ⁻⁵	27.2	7.9	3.46 x 10 ⁻¹¹	20.8	480.7
1.0 x 10 ⁻⁵	25.7	9.4	5.19 x 10 ⁻¹¹	31.2	320.5
1.5 x 10 ⁻⁵	23.9	11.2	6.10 x 10 ⁻¹¹	36.2	276.2
2.0 x 10 ⁻⁵	23.2	11.9	7.31 x 10 ⁻¹¹	44.5	222.2
0.5 x 10 ⁻⁴	19.4	15.7	8.20 x 10 ⁻¹¹	49.3	202.8
1.0 x 10 ⁻⁴	16.9	18.2	10.0 x 10 ⁻¹¹	60.4	165.5
2.0 x 10 ⁻⁴	11.5	23.6	11.4 x 10 ⁻¹¹	68.7	145.5
3.0 x 10 ⁻⁴	10.7	24.4	11.9 x 10 ⁻¹¹	71.6	139.6

Table 4: Interfacial tension (γ), surface pressure (π), surface excess (Γ_s), number of molecules (n) adsorbed/cm² and area (A) occupied per molecule of CTABr at toluene - 0.1 M KCl interface. γ_0 (toluene-0.1 M KCl) = 35.1 dynes/cm, Temperature = 30°C

Molarity (C)	Interfacial Tension (dynes cm ⁻¹)	Surface Pressure (dynes cm ⁻¹)	Surface Excess (g.m./cm ²)	n x 10 ⁻¹²	Area occupied molecule \AA^2
0.5 x 10 ⁻⁵	23.2	11.9	2.30 x 10 ⁻¹¹	13.8	724.0
1.0 x 10 ⁻⁵	22.9	12.2	7.6 x 10 ⁻¹¹	45.8	218.0
1.5 x 10 ⁻⁵	21.6	12.6	12.4 x 10 ⁻¹¹	74.9	133.0
2.0 x 10 ⁻⁵	20.8	13.2	16.2 x 10 ⁻¹¹	98.1	101.0
0.5 x 10 ⁻⁴	16.1	19.0	21.8 x 10 ⁻¹¹	131.5	76.0
1.0 x 10 ⁻⁴	11.24	23.8	24.7 x 10 ⁻¹¹	148.7	67.2
2.0 x 10 ⁻⁴	5.93	29.1	31.8 x 10 ⁻¹¹	191.7	52.1
3.0 x 10 ⁻⁴	4.47	30.6	32.9 x 10 ⁻¹¹	198.3	50.4

Table 5: Surface tension (γ), surface pressure (π), surface excess (Γ_s) number of molecules (n) adsorbed / cm² and area (A) occupied per molecule of CTABr at Air-water interface. γ_0 (air-water) = 71.0 dynes/cm, Temperature = 30°C

Molarity (C)	Interfacial Tension (dynes cm ⁻¹)	Surface Pressure (dynes cm ⁻¹)	Surface Excess (g.m./cm ²)	n x 10 ⁻¹²	Area occupied molecule Å ²
0.5 x 10 ⁻⁵	69.2	1.8	3.32 x 10 ⁻¹¹	20.0	500.0
1.0 x 10 ⁻⁵	68.2	2.8	7.6 x 10 ⁻¹¹	45.8	218.3
1.5 x 10 ⁻⁵	67.4	3.6	10.51 x 10 ⁻¹¹	63.3	157.8
2.0 x 10 ⁻⁵	66.2	4.8	16.3 x 10 ⁻¹¹	98.3	101.6
0.5 x 10 ⁻⁴	61.1	9.9	22.7 x 10 ⁻¹¹	136.9	73.5
1.0 x 10 ⁻⁴	57.7	13.3	26.0 x 10 ⁻¹¹	157.1	63.6
2.0 x 10 ⁻⁴	51.3	19.9	32.9 x 10 ⁻¹¹	198.3	50.4
3.0 x 10 ⁻⁴	50.1	20.9	26.2 x 10 ⁻¹¹	158.3	63.2

Table 6: Surface tension (γ), surface pressure (π), surface excess (Γ_s) number of molecules (n) adsorbed / cm² and area (A) occupied per molecule of CTABr at Air – 0.1 M KCl interface. γ_0 (air-water) = 71.0 dynes/cm, Temperature = 30°C

Molarity (C)	Interfacial Tension (dynes cm ⁻¹)	Surface Pressure (dynes cm ⁻¹)	Surface Excess (g.m./cm ²)	n x 10 ⁻¹²	Area occupied molecule Å ²
0.5 x 10 ⁻⁵	65.3	5.7	3.46 x 10 ⁻¹¹	20.8	480
1.0 x 10 ⁻⁵	64.7	6.3	8.35 x 10 ⁻¹¹	50.3	198.3
1.5 x 10 ⁻⁵	63.3	7.7	14.9 x 10 ⁻¹¹	90.0	111.0
2.0 x 10 ⁻⁵	61.6	9.4	22.1 x 10 ⁻¹¹	133.3	75.1
0.5 x 10 ⁻⁴	56.2	14.8	28.7 x 10 ⁻¹¹	173.1	57.7
1.0 x 10 ⁻⁴	51.3	19.7	-	-	-
2.0 x 10 ⁻⁴	46.6	24.4	-	-	-
3.0 x 10 ⁻⁴	45.2	25.8	-	-	-

The observed values of the interfacial tension (γ) and calculated values of surface excess (Γ_s), area per molecule (A) and number of molecules adsorbed per cm³ at various molar concentration of CTABr are reported in Table- 1-6. The values of surface excess (Γ_s), area per molecule (A) and number of molecules/cm² have been calculated from the gradients of γ -log C curves and appropriate form of Gibbs adsorption equation.

$$\Gamma_s = -\frac{1}{2.303KT} \left(\frac{d\gamma}{d \log C} \right) \quad (3)$$

It is evident that initially at low concentrations, only slight increase in surface pressure is capable of reducing the area to a greater extent but at higher concentrations a large increase in surface pressure produces very little decrease in area.

Initially at low surface pressure the area per molecule is large which may be explained on the grounds that, at low surface pressure the film of surfactant ions is fully expanded and ions are stretched out helter-skelter to the interface, i.e. most of the surfactant ions lie in such a manner that each polar head group is towards aqueous phase while non-polar hydrocarbon chain of surfactant ion remains towards oil phase. At higher surface pressure values, the surfactant ions are compressed and the value of area per molecule decreases. When molecules are tightly packed together then the area occupied per surfactant ion does not appreciably decrease which can be easily seen by the vertical portion of π - A curves.

It is seen that the area at highest surface pressure value was always found to be greater than that of a close packed monolayer of a long chain paraffin compound (20-25Å⁰² per molecule). The higher values of area might be due to the penetration of oil phase between the hydrocarbon chains of surfactant ions present in the monomolecular film. This suggest that structure of monomolecular film formed at the

interface where some surfactant ions in the film are not vertically oriented but are tilted at the interface.

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