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Interfacial Adsorption of Dibutyl Ester of Sodium Sulphosuccinic Acid at the Liquid Hydrocarbon Mixture – 0.1 M KCl Interfaces

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Interfacial tension (γ) measurements were determined by using a modified drop volume technique at mixture of benzene and toluene – 0.1 M KCl interfaces with varying concentration of dibutyl ester of sodium sulphosuccinic acid (BSS) using AGLA micrometer syringe. The value of interfacial tension regularly decreases with increase in concentration of BSS. The values of surface excess (Γs) at different concentrations of BSS have been calculated from the gradients of γ - log C curves and appropriate form of Gibb's adsorption equation. From these data, number of surfactant ions adsorbed per cm^2 of interface area occupied per surfactant ion have also been calculated. From π - A curves, it is clear that at low surfactant concentration, slight increase in surface pressure (π) reduces the area to a greater extent but at higher concentrations a large increase in surface pressure produces little decrease in surface area. At low surface pressure the film of surfactant ions is fully expanded and ions are stretched out in disorder manner. The surface area occupied per surfactant ion does not appreciably decrease when surfactant ions are tightly packed together which is seen from the vertical portion of π - A curves. It has been observed that as the mole fraction of benzene in hydrocarbon mixture increases, the area occupied per surfactant ion corresponding to closest packing of mono-molecular film increases.

Key Words: Interfacial adsorption, Interfacial tension, Dibutyl ester, Sodium sulphosuccinic acid, Surface excess.

INTRODUCTION

Surfactants adsorbed at the surface or interface of the system forming film and reduce the interfacial free energy. Surfactant adsorption is widely used to achieve changes in wetting, colloidal properties and lubrication. The adsorption of cationic surfactants to solid-aqueous interfaces has recently been reviewed[1]. The adsorption of surfactants from aqueous solution is a phenomenon of major importance in ore flotation, paint technology and enhanced oil recovery[2,3]. Becher[4] has reviewed the surfactant adsorption at oil-water interface and has correlated the adsorption data with surface charge density and surface potential of the dispersion system. The role of surface charge density[5-7] on surfactant adsorption at solid-aqueous and air-water interfaces have been discussed. Shukla and Tyagi[8] studied the effects of various cationic surfactants on adsorption of ionic surfactants at air-water interface. Adsorption of benzotriazol on steel surface from hydrochloric acid solutions was studied[9] indicating decrease of corrosion inhibition effectiveness. From the survey of literature, it appears that studies on adsorption of dibutyl ester of sodium sulphosuccinic acid (BSS) at aromatic hydrocarbon mixture - 0.1 M KCl interfaces is still lacking. The present work has been undertaken to deal with the adsorption of BSS at aromatic hydrocarbon mixture - 0.1 M KCl interface and its role in the formation of molecular film at the interface. Efforts have also been made to calculate different adsorption parameters such as surface excess (Γs), number of molecules adsorbed per cm^2 (n) and area occupied per surfactant ion (A) at the interface.

EXPERIMENTAL

Dibutyl ester of sodium sulphosuccinic acid (BSS) was obtained from BDH England. Benzene and toluene were ExcelaR grade obtained from Qualigens. Potassium chloride used was AnalaR grade chemical obtained from E. Merck. Double distilled water was used throughout the experiment.

AGLA micrometer syringe was used to measure interfacial tension by drop volume technique[10], using relation

$$\gamma_{\text{oil}-\text{water}} = \frac{v(\rho_{H_2O} - \rho_{\text{oil}})}{r} f.g.$$

where v = volume of the drop from the edge of the capillary of radius 'r';

$\rho_{H_2O} - \rho_{\text{oil}}$ = difference in the densities of aqueous surfactant solution and oil phase (mixture of benzene and toluene); f = Correction factor which depends on the value of v/r^3, taken from International Critical Table[11].

Four sets of solutions containing benzene and toluene with entire mole fraction range of benzene were prepared by mixing their calculated volume.

(i) Mole fraction of benzene = 0.231
20 mL benzene + 80 mL toluene.
(ii) Mole fraction of benzene = 0.445
40 mL benzene + 60 mL toluene.
(iii) Mole fraction of benzene = 0.643
60 mL benzene + 40 mL toluene.
(iv) Mole fraction of benzene = 0.828
80 mL benzene + 20 mL toluene

The density measurements were made by using stoppered pyrex pyknometer. The drop of the aqueous solution of BSS in presence of 0.1 M KCl was slowly developed at a constant temperature of 27 ºC.

RESULTS AND DISCUSSION

From γ-log C curves (Fig. 1) of BSS at hydrocarbon mixture - 0.1 M KCl interfaces, it is observed that with increase in concentration of surfactant, interfacial tension values lowers. With increasing value of mole fraction of benzene in

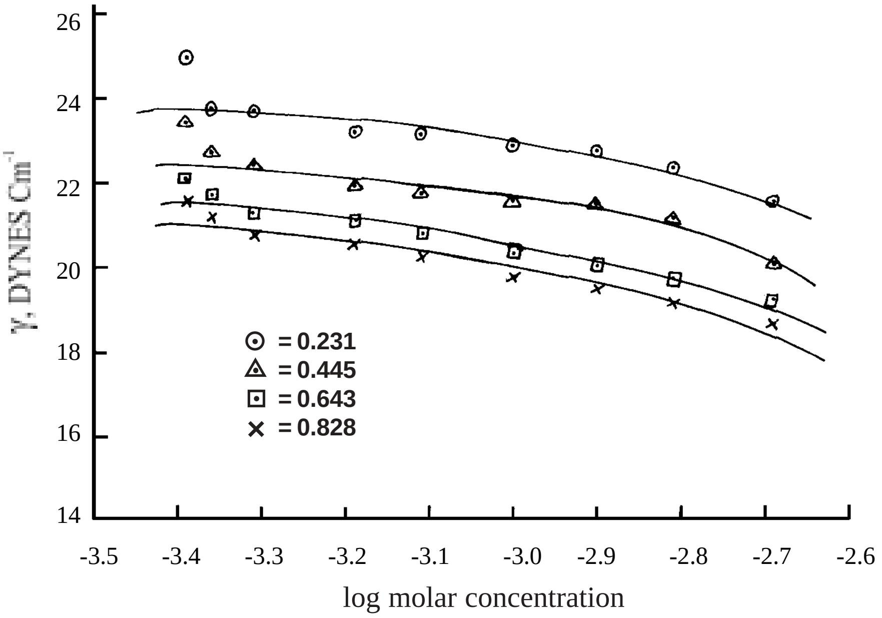

Fig. 1. Plot of interfacial tension *vs.* log molar concentration of BSS at various mole fraction range of benzene in benzene and toluene mixture - 0.1 M KCl interfaces

mixture of benzene and toluene, the interfacial tension values decreases owing to the decrease in the difference of densities between 0.1M KCl and hydrocarbon mixture. Table-1 shows the observed values of interfacial tension and calculated values of surface excess (Γs), area per molecule and number of BSS molecules adsorbed per cm^2 of interface at various concentration of BSS. Appropriate form of Gibb's adsorption equation was employed to calculate the values of surface excess (Γs) from the gradients of γ-log C curves. BSS molecule were found to be strongly adsorbed at the interface in presence of 0.1 M KCl than in its absence. This was due to the neutralization of repulsive anionic head group charges of surfactant ions. From π-A curves (Fig. 2), it is clear that at low surfactant concentration, slight increase in surface pressure (π) reduces the area to a greater extent because the film of surfactant ions is fully expanded and the ions are stretched out in disorder manner in such a way that each polar head group is toward the aqueous phase while non-polar hydrocarbon chain of surfactant ions remains towards the oil phase. At higher surfactant concentrations a large increase in surface pressure produces a little decrease in surface area, as the surfactant ions in the film are compressed and the area occupied per surfactant ion decreases. This area does not appreciably decrease when surfactant ions in the film are tightly packed together as shown from the vertical portion of π-A curves. The area corresponding to the closest packing of the interfacial film, which is by nature mono-molecular, is determined from extrapolation of π-A curves back to zero surface pressure and are found to be 320, 390, 410 and 550 Å^2 for 0.231,

TABLE-1
INTERFACIAL TENSION (γ), SURFACE PRESSURE (π), SURFACE EXCESS (Γs), NUMBER OF MOLECULES (n) ADSORBED PER cm^2 AND AREA (A) OCCUPIED PER MOLECULE OF BSS AT HYDROCARBON MIXTURE – 0.1 M KCl INTERFACE

Concentration ($C \times 10^4$)	Γ ($dynes\ cm^{-1}$)	π (γ_0-γ) ($dynes\ cm^{-1}$)	Γs ($g\ cm^{-2}$)	$n \times 10^{-11}$	A ($Å^2$)
Mole fraction of benzene = 0.231, γ_0 = 27.64					
4.00	24.94	2.70	21.77×10^{-12}	131.12	767
4.30	23.74	3.90	30.65×10^{-12}	184.60	541
4.87	23.68	3.96	34.83×10^{-12}	209.78	476
6.45	23.23	4.41	40.06×10^{-12}	241.28	414
7.60	23.12	4.52	40.93×10^{-12}	246.52	405
10.00	22.82	4.82	69.67×10^{-12}	419.62	238
12.50	22.68	4.96	87.09×10^{-12}	524.54	190
15.38	22.34	5.30	94.93×10^{-12}	571.76	174
20.00	21.53	6.11	111.82×10^{-12}	673.49	148
Mole fraction of benzene = 0.445, γ_0 = 26.84					
4.00	23.36	3.48	19.16×10^{-12}	115.40	866
4.30	22.67	4.17	28.91×10^{-12}	174.12	574
4.87	22.40	4.44	40.06×10^{-12}	241.28	414
6.45	21.94	4.90	43.54×10^{-12}	262.24	381
7.60	21.66	5.18	51.21×10^{-12}	308.43	324
10.00	21.54	5.30	57.48×10^{-12}	346.20	288
12.50	21.39	5.45	63.22×10^{-12}	380.77	262
15.38	21.12	5.72	99.46×10^{-12}	599.04	166
20.00	20.01	6.83	156.76×10^{-12}	944.16	105
Mole fraction of benzene = 0.643, γ_0 = 25.87					
4.00	22.10	3.77	17.41×10^{-12}	104.86	953
4.30	21.73	4.14	28.91×10^{-12}	174.12	574
4.87	21.28	4.59	38.66×10^{-12}	232.84	429
6.45	21.08	4.79	54.34×10^{-12}	327.28	305
7.60	20.75	5.12	64.10×10^{-12}	386.07	259
10.00	20.31	5.56	66.88×10^{-12}	402.81	248
12.50	19.92	5.95	72.46×10^{-12}	436.42	229
15.38	19.68	6.19	87.09×10^{-12}	524.54	190
20.00	19.21	6.66	118.62×10^{-12}	714.44	139
Mole fraction of benzene = 0.828, γ_0 = 25.34					
4.00	21.47	3.87	17.41×10^{-12}	104.86	953
4.30	21.11	4.23	20.37×10^{-12}	122.68	815
4.87	20.67	4.67	34.83×10^{-12}	209.78	476
6.45	20.52	4.82	51.21×10^{-12}	308.43	324
7.60	20.15	5.19	53.47×10^{-12}	322.04	310
10.00	19.72	5.62	72.46×10^{-12}	436.42	229
12.50	19.38	5.96	87.09×10^{-12}	524.54	190
15.38	19.09	6.25	95.80×10^{-12}	577.00	173
20.00	18.64	6.70	124.36×10^{-12}	749.02	133

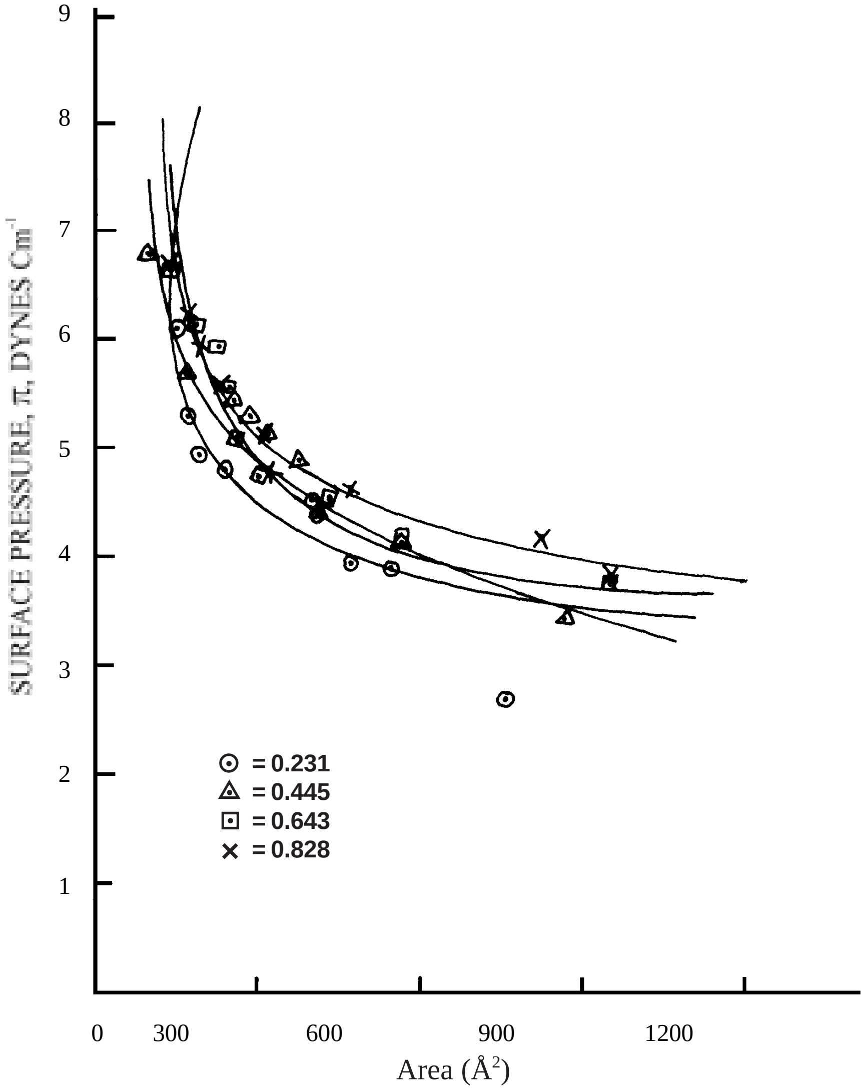

Fig. 2. Surface pressure - area isotherms for BSS at various mole fraction range of benzene in benzene and toluene mixture - 0.1 M KCl interfaces

0.445, 0.643 and 0.828 mole fraction of benzene in mixture of benzene and toluene, respectively. It has been observed that as the mole fraction of benzene in hydrocarbon mixture increases, the value of interfacial tension decreases and the area corresponding to closest packing of mono-ionic film of BSS increases because interfacial tension decreases if surfactant adsorption increases, so there are more surfactants at the interface with increased proportion of benzene in the mixture. Toluene is more polar than benzene and thus with increasing benzene the interface becomes more non-polar thus to accommodate more amphiphile and hence the tension decreases.

This area was always found to be greater than the area of close packed monolayer of long chain paraffin compound (20-25 Å^2 per molecule[12]) which might be due to entry of hydrocarbon mixture in between polar head groups and the long carbon chains of surfactant ions.

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