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Adsorption of Di-butylester of Sodiumsulpho Succinic Acid at the Hydrocarbon Mixture-Water Interfaces

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A modified drop volume technique was used for measuring interfacial tension (γ) at mixture containing entire mole fraction range of benzene in benzene and toluene-water interfaces with varying concentration of di-butylester of sodiumsulpho succinic acid (BSS) at 27°C using AGLA micrometer syringe (Burroughs Wellcome). It has been observed that there was regular decrease in interfacial tension with increase in concentration of BSS. From the data of interfacial tension at various concentration of surfactant, γ-log C curves were plotted. The values of surface excess, Γs, have been calculated from the gradients of γ-log C curves using appropriate form of Gibb's adsorption equation. From these data, number of surfactant ions adsorbed per cm^2 of interface and the area occupied per surfactant ion have been estimated. The area corresponding to closest packing of mono-molecular film was determined by extrapolation of π-A curves back to zero surface pressure. It has been observed that as the mole fraction of benzene in mixture of benzene and toluene increases, the value of interfacial tension decreases and area corresponding to closest packing of mono-molecular film of BSS increases.

Key Words: Adsorption, Di-butylester of sodiumsulpho succinic acid, Hydrocarbon mixture, Interfacial tension, Surface excess.

INTRODUCTION

Surfactant molecule contains long hydrocarbon chain which is hydrophobic in nature terminating to a hydrophilic polar group. These surfactants are adsorbed at interface forming mono-molecular film. The adsorption of some cationic and anionic surfactants at benzene-water interface have been reported by Singh *et al.*[1]. The charge and size of head group affects the amounts of adsorption, the shape of adsorption isotherm[2-4] and organisation of surfactant ions[5] at the interface. The adsorption of surfactants at solid-aqueous interfaces have recently been reviewed[6]. The present work was undertaken to study the adsorption of di-butylester of sodiumsulpho succinic acid (BSS) at hydrocarbon mixture (entire mole fraction range of benzene in mixture of benzene and toluene)-water interfaces. The value of interfacial tension was calculated with drop volume technique[7], using relation

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

where v = volume of the drop form the edge of the capillary of radius r. ρ_{H_2O}–ρ_{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[8].

EXPERIMENTAL

The surfactant BSS used was obtained from BDH and was used as such. Benzene and toluene used were ExcelaR grade from Qualigens. Double distilled water of specific conductivity ≈ 2×10^{-6} ohm^{-1} cm^{-1} was used throughout the experiment. The following 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 densities of the mixture of benzene and toluene and aqueous solution of BSS were determined with the help of pyrex stoppered pyknometer. A modified drop volume technique was used for measuring interfacial tension (γ) values using AGLA Micrometer syringe (Burrough, Wellcome Co. Ltd.) having a finite capillary bore with its radius of 0.2 cm which can deliver the liquid upto 0.0002 mL volume. For determining the volume of the drop, the jet of the syringe was immersed in the less dense mixture of benzene and toluene in a 50 mL pyrex beaker and the aqueous solution of surfactant was in the syringe. The drop of the aqueous solution of BSS was slowly developed at a constant temperature of 27°C. The average volume of not less than five drops was used to calculate the interfacial tension.

RESULTS AND DISCUSSION

Fig. 1 shows the variation of interfacial tension (γ) against log molar concentration of BSS at hydrocarbon mixture-water interfaces. It is observed that each addition of surfactant lowers the interfacial tension (γ)

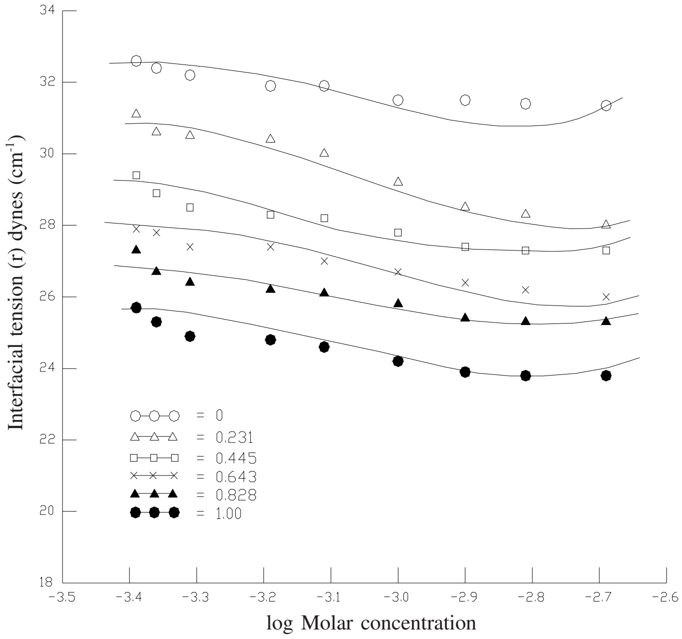

Fig. 1. Plot of interfacial tension *vs.* log molar concentration of BSS at various mole fraction range of benzene in benzene and toluene mixture-water interfaces

values. As the mole fraction of benzene in mixture of benzene and toluene increases, the value of interfacial tension decreases owing to the decrease in the difference of densities between water and hydrocarbon mixture. 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 at various concentrations of BSS are reported in Table-1.

The values of surface excess Γs, have been calculated from the gradients of γ-log C curves and appropriate form of Gibb's adsorption equation. It is clear from π-A curves (Fig. 2) that at low concentration range the area occupied per BSS molecule decreases rapidly with slight increase in the value of surface pressure (π); but at higher concentration range the area decreases slowly with large increase in surface pressure. This may be explained on the basis that at low pressure range surfactant ions are fully expanded at the interface and ions are oriented in such a manner that negatively charged polar head group remains towards aqueous phase of the interface and non-polar hydrocarbon part remains towards the ideal solution of benzene and toluene. At higher π values these surfactant ions are compressed and so the area occupied per surfactant ion decreases. When surfactant ions are closely packed the area occupied per surfactant ion remains approximately same which is shown by vertical portion of π-A curves.

TABLE-1
INTERFACIAL TENSION (γ), SURFACE PRESSURE (π), SURFACE EXCESS (Γs) NUMBER OF MOLECULES (n) ADSORBED/cm^2 AND AREA (A) OCCUPIED PER MOLECULE OF BSS AT DIFFERENT INTERFACES AT TEMPERATURE 27ºC

Concentration ($C \times 10^4$)	γ (dynes cm^{-1})	π (γ_0-γ) (dynes cm^{-1})	Γs (gm/cm^2)	$n \times 10^{-11}$	A (Å^2)
Toluene-Water Interface Mole fraction of benzene = 0, γ_0 = 34.56					
4.00	32.61	1.95	8.710×10^{-12}	52.46	1900.0
4.30	32.39	2.17	9.494×10^{-12}	57.18	1700.0
4.87	32.24	2.32	12.195×10^{-12}	73.45	1300.0
6.45	31.93	2.63	32.055×10^{-12}	193.06	517.9
7.60	31.90	2.66	41.376×10^{-12}	249.20	401.2
10.00	31.53	3.03	47.038×10^{-12}	283.30	352.9
12.50	31.51	3.05	–	–	–
15.38	31.41	3.15	–	–	–
20.00	31.35	3.21	–	–	–
Hydrocarbon Mixture-Water Interface Mole fraction of benzene = 0.231, γ_0 = 34.38,					
4.00	31.11	3.27	8.710×10^{-12}	52.46	1900
4.30	30.64	3.74	11.585×10^{-12}	69.77	1430
4.87	30.47	3.91	25.871×10^{-12}	155.82	642
6.45	30.37	4.01	45.731×10^{-12}	275.43	363
7.60	30.06	4.32	55.139×10^{-12}	332.10	301
10.00	29.21	5.17	58.536×10^{-12}	352.56	283
12.50	28.47	5.91	–	–	–
15.38	28.32	6.06	–	–	–
20.00	28.08	6.30	–	–	–
Hydrocarbon Mixture-Water Interface Mole fraction of benzene = 0.445, γ_0 = 33.68					
4.0	29.39	4.29	29.006×10^{-12}	174.70	572
4.3	28.89	4.79	31.358×10^{-12}	188.86	529
4.87	28.52	5.16	41.376×10^{-12}	249.20	401
6.45	28.34	5.34	43.554×10^{-12}	262.32	381
7.60	28.22	5.46	45.296×10^{-12}	272.81	366
10.00	27.80	5.88	–	–	–
12.5	27.83	6.30	–	–	–
15.38	27.30	6.38	–	–	–
20.00	27.26	6.42	–	–	–

Concentration ($C \times 10^4$)	γ (dynes cm^{-1})	π (γ_0-γ) (dynes cm^{-1})	Γs (gm/cm^2)	$n \times 10^{-11}$	A ($Å^2$)
Hydrocarbon Mixture-Water Interface Mole fraction of benzene = 0.643, $\gamma_0 = 32.70$					
4.00	27.98	4.72	8.710×10^{-12}	52.46	1900.0
4.30	27.82	4.88	13.066×10^{-12}	78.69	1200.0
4.87	27.38	5.32	27.177×10^{-12}	163.68	610.9
6.45	27.35	5.35	27.874×10^{-12}	167.88	595.6
7.60	27.05	5.65	37.456×10^{-12}	225.59	443.2
10.00	26.74	5.96	44.425×10^{-12}	267.57	373.7
12.50	26.38	6.32	48.780×10^{-12}	293.80	340.3
15.38	26.15	6.55	–	–	–
20.00	25.87	6.83	–	–	–
Hydrocarbon Mixture-Water Interface Mole fraction of benzene = 0.828, $\gamma_0 = 32.13$					
4.00	27.29	4.84	21.777×10^{-12}	131.16	762
4.30	26.82	5.31	23.170×10^{-12}	139.55	716
4.87	26.46	5.67	27.874×10^{-12}	167.88	595
6.45	26.30	5.83	31.358×10^{-12}	188.86	529
7.60	26.12	6.01	32.317×10^{-12}	194.64	514
10.00	25.78	6.35	–	–	–
12.50	25.38	6.75	–	–	–
15.38	25.31	6.82	–	–	–
20.00	25.27	6.86	–	–	–
Benzene-Water Interface Mole fraction of benzene = 1.00, $\gamma_0 = 31.05$					
4.00	25.70	5.35	8.710×10^{-12}	52.46	1900
4.30	25.25	5.80	9.930×10^{-12}	59.80	1670
4.87	24.91	6.14	17.421×10^{-12}	104.92	953
6.45	24.75	6.30	38.327×10^{-12}	230.84	433
7.60	24.63	6.42	43.554×10^{-12}	262.32	381
10.00	24.25	6.80	48.780×10^{-12}	293.80	340
12.50	23.87	7.18	–	–	–
15.38	23.81	7.24	–	–	–
20.00	23.77	7.28	–	–	–

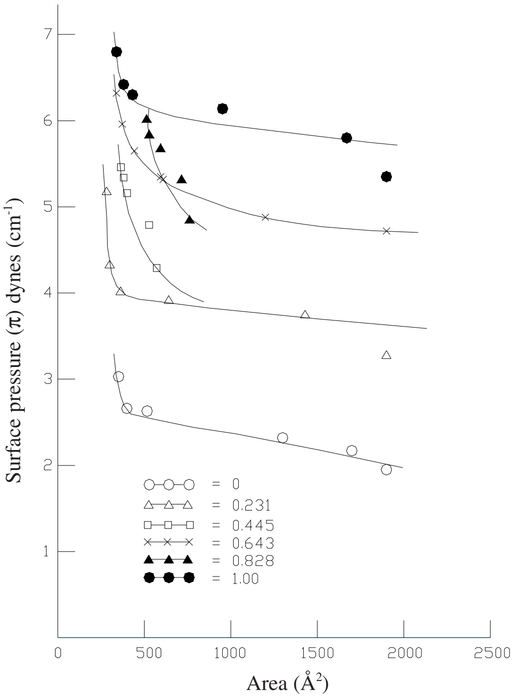

Fig. 2. Surface pressure-area isotherms for BSS at various mole fraction range of benzene in benzene and toluene mixture-water interfaces

The area corresponding to closest packing of monolayer was determined by extrapolation of π-A curves back to zero surface pressure. This area corresponding to 0, 0.231, 0.445, 0.643, 0.828 and 1.00 mol fraction of benzene in mixture of benzene and toluene-water interface was found to be 490, 550, 710, 820, 950 and 980 Å^2, respectively. This area was always found to be greater than the area of close packed monolayer of long chain paraffm compound (20-25Å^2 per molecule[9]) which might be due to the repulsion between polar head groups of surfactant ions and penetration of hydrocarbon mixture in between the long carbon chains of surfactant ions. It concludes that in the ionic film at the interface, surfactant ions are not vertically oriented.

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