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Enrichment of surfactants in the surface microlayer of the Yamuna river water at Agra U.P. (India)

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Abstract
Sodium dodecylsulfate (SDS), sodium dodecyl benzene sulphonate (SDBS), sodium dodecyl ethoxy sulfate (SDES), dodecyl hexaethoxylate (DHE), isooctylphenoxy-hexaethoxyethanol (trade name Criton X-100 or CTX), n-cetyl trimethyl ammonium bromide (CTAB) and ditallow dimethyl ammonium chloride (DTDMAC) were measured in surface microlayer (SML) and subsurface (30-40 cm deep) water samples collected from 5 glass tanks (1x1x1.5 m²) and 5 dhobi Ghats (within 10 m of the bank) at the Yamuna banks in Agra, U.P.(INDIA) using 1 x 0.5 m² polythene screen. In surface samples, SDBS and CTX were found to be significantly enriched but the enrichments for SDS and CTAB were smaller and in the case of DHE almost negligible. An interesting result was the large decrease of DHE compared with CTX in the surface sample. This is due to the fact that the greatest extent of DHE gets dissolved after being hydrolysed. Both CTAB and DTDMAC were almost equally enriched in the surface films. The high enrichment of SDBS and CTX may be attributed to their greater stability due to the presence of benzene ring in their molecules. The enrichment of SDES was intermediate between SDS and SDBS. SDS is over 10 times more biodegradable than SDBS, so though the lightest SDS was less enriched than SDES. CTAB is more enriched than DTDMAC because CTAB molecules are lighter. Although there was no relationship between the surface excesses of SDS and DHE, there was a strong correlation between SDS and CTAB, SDBS and CTX, SDES and DTDMAC concentrations, and between surface film pressure and SDS concentrations (r =0.84). There is less satisfactory correlation between surface pressure and DTDMAC concentrations (r=0.31). The dominance of SDBS and CTX in the surface film is one of the significant findings of this investigation.

Keywords: Enrichment, surfactant, yamuna river water agra U.P. india

Introduction

Over the past decade there has been increasing concern about the levels of potentially toxic surfactants released into our river systems from domestic, industrial and rural sources. The knowledge of the concentrations and distribution of surfactants at all depths in the water column is important to our understanding of the origin, transport process [1] and fate of surfactants in water system. One important component of the water column in both marine and aquatic environment is the interface between the water body and the surrounding atmosphere known as the surface micro layer (SML) [2, 3, 4, 5]. Enrichment refers to a comparison between the concentrations at the water surface and water subsurface (bulk, 30-40 cm deep). The SML enrichment of species is very significant [6]. Despite the small volume of the SML as compared to the rest of the water body, pollutants are transported mainly by water surface. 1.5 to 50 times enrichment into the top 100-150 µm of water has been found because SML composition is controlled by adsorption, evaporation, atmospheric aerosol deposition and floatation. Its study will provide information about the concentration of surfactants in a water body, their transport modes, cycling and distribution. The knowledge will be of a great help in developing processes for a better management of surfactants, besides enriching our knowledge of surface chemistry. Surface active species accumulate at the boundary forming an immiscible layer capable of trapping particulate matter, binding surfactant and acting both as a sink for particles of tropospheric origin and as a source for the release of species from the water body to the atmosphere, as bubbles or aerosols. This study was undertaken to provide systematic data on surfactant enrichment and their concentrations in the surfactant solutions in glass tanks as well as in the Yamuna river water at Agra, U.P. (INDIA). To the best of our knowledge, no such study has been conducted to ascertain the extent of surface enrichment of surfactants in the Yamuna river water.

Materials and methods

About 100 ml of 1, 10, 40, 80 and 100 mg/l of each of three anionic surfactants namely sodium dodecylsulfate (SDS, an AS), sodium dodecyl benzene sulphonate (SDBS, an LAS), and sodium dodecyl ethoxy sulfate (SDES, an AES); two non-ionic surfactants namely dodecyl hexaethoxylate (DHE, an AE) and isooctylphenoxy-hexaethoxyethanol (trade name Criton X-100 or CTX, an APE); and two cationic surfactants. namely n-cetyl trimethyl ammonium bromide (CTAB) and disallow dimethyl ammonium chloride (DTDMAC) were taken in 5 glass tanks containing 1 m³ water free from surfactants. The contents of each tank was stirred for half an hour with a wooden rod to produce motion to that found in the Yamuna river water at Agra. The surfactants were measured in subsurface and surface film water samples collected from 5 tanks (1.0 x 1.0 x 1.5 m³) and 5 Dhobi Ghats (within 10 m of the bank) at the Yamuna banks in Agra. U.P. (INDIA) using 1.0 x 0.5 m² polythene screen. Glass tanks were used to study the surfactants in desired concentrations that were not found in the Yamuna river water [7]. Physicochemical properties such as surface pressure, dissolved oxygen (DO),

biological oxygen demand (BOD) and chemical oxygen demand (COD) were also measured to establish possible correlations between these parameters and surface enrichment.

Anionic surfactants SDS, SDES and SDBS were analysed by the methylene blue (MB) method using UV-Vis spectrophotometer at 652 nm, non-ionic DHE and Criton X-100 were determined by the cobaltothiocyanate (CT) method at 620 nm and cationics CTAB and DTDMAC were measured by the disulfine blue (DB) method using the spectrophotometer. The DB method becomes more specific in combination with TLC. The results of DB and DB-TLC methods were compared with HPLC method of Wee and Kennedy [8, 9] which is simple, direct, sensitive and specific to give more consistent. Surface tension was determined at 25°C with a precision densitometer (Toshiba). Surface pressure (π) is defined as the lowering of surface tension from that of a clean surface (y-y). The value of y was obtained after sweeping the surface several times with a glass plate until further sweeping produced no increase in the surface tension. The sample was then allowed to stand for 1 h to establish equilibrium, after which the surface tension (1) was measured. In tanks, y indicated the surface tension of water and y was that of surfactant solution.

The fractionation ratio or enrichment factor is simply the ratio of surface to bulk contaminant concentration. Surface enrichment or enrichment ratio E is defined as the fractionation ratio minus one. The surface excess concentration measurement is expressed as a fraction of the bulk or subsurface concentration, i.e.

$$E=\frac{Cs-Css}{Css}$$

Where C_s, and C_{ss} are surface and subsurface concentrations. This parameter should be used when comparing the unique properties of surface films. It is, however, dependent on the depth of surface film sampled, which is a function of the sampling technique. The film is extremely thin and it is, therefore, convenient to use the depth (d) dependent parameter surface excess which expresses this concentration per square meter, d_{cs-Css}.

Results and discussion

The surfactant surface concentrations in the Yamuna river waters at Agra, U.P.(INDIA) were found to be in the ranges SDS 12.5-19.9 mg/l, SDBS 7.1-12.8 mg/l which are within ranges found for many waste water systems throughout the world, but are higher than those concentrations found in other water systems flowing near major cities in developed countries. The surface micro layer enrichment of various surfactants studied are given in Table-1 - 2. At stations S1, S3 and S4 (Hathi Ghats) clothes washing by washermen was being carried out 10 m from the bank while the bridge construction was in process near Water Works. These activities noticeably affected the subsurface contaminant concentration, High surface film concentrations were measured at several occasions which similarly elevated film pressures as evidenced by visible surface slicks.

An interesting result was the large decrease of DHE in the surface sample compared with TX. This is due to the fact that the greater extent of DHE gets dis-solved after being hydrolysed. Both CTAB and DTDMAC were almost equally enriched in the surface films. These results are consistent with the demonstrated complexing ability of the surface film and with the relative stability constants of complexes formed between Cu, Zn and Pb and the postulated organic components of this film. The high enrichment of SDBS and CTX may be attributed to their greater stability due to the presence of benzene ring in their molecules.

The correlation coefficients between the various parametric studies are presented in Table - 3. This includes relationships between surface excess and surface pressure, Although there was no relationship be tween the surface excesses of SDS and DHE, there was a strong correlation between SDS and CTAB, SDBS and CTX, SDES and DTDMAC concentrations, and between surface film pressure and SDS concentrations (r = 0.84) There is less satisfactory correlation between surface pressure and DTDMAC concentrations. It is difficult to explain their origin on the basis of aqueous inputs since, besides requiring high subsurface concentrations of these surfactants, it is necessary to explain why SDS was present in greater concentrations than SDBS in the bulk water should be so poorly too enriched. A likely explanation is that the SDBS and CTX molecules contain benzene ring due to which they are stable and less biodegradable. Also their molecules act as ligands for airborne metal ions in the surface film, in preference to other surfactant molecules. Surface pressures varied from $1.7X10^{-2}$ Nm^{-1} in the quiescent upper reaches of the Yamuna river at stations A. Values of γ_o, the surface tension of water in the absence of surfactant, increased from$7.20X\ 10^{-2}$ N m^{-1} at station B to $7.35X10^{-2}$ N m^{-1} at station end. Surface film pressure measured for subsurface waters were negligible in most instances. Values below 0.1 x $10^{-2}Nm^{-1}$ are indicative of surface molecules being in a two dimensional gaseous states having an approximate unimolecular surface coverage. Higher values indicate the formation of multilayers probably consisting of a strongly adsorbed monolayer surmounted by layers of less strongly adsorbed non-polar compounds, this distribution being induced, e.g., by wind action which compresses the surface film.

A least square analysis of film pressures and DO indicated a linear relationship with a correlation coefficient of 0.86. This was not altogether unexpected, although such a relationship could be upset by variations in the ratios of strongly adsorbing species from station to station. The measurements were conducted mainly on filtered samples, but similar film pressures were obtained for unfiltered samples. In many instances, the surface film pressures were obtained for unfiltered samples and the surface film consisted of a mixture of filtered material and layer particulates including insects, leaves and other debris. Plankton blooms sometimes accumulate in the surface film. During the analysis, we critically questioned the need to filter surface samples. It was finally decided that although filtration might remove some of the soluble surface species by adsorption, it was necessary to use this method to unable valid comparison with dissolved surfactant species in the subsurface samples.

Table 1: Surface microlayer enrichment of SDS, SDES, DHE, CTX and CTAB in the Yamuna river water at Agra,U.P.(India)

Sampling Tanks/ Stations	Concentration/ Description	Surface Concentration C_s	Surface Concentration C_{ss}	E	Surface Pressure $\pi = \gamma_o - \gamma$	DO	BOD	COD
T_1	1 mg/l	1.02	0.53	0.9	0.05	4.0	9.0	17.0
T_2	10 mg/l	10.31	3.22	2.2	2.40	3.2	12.0	25.0
T_3	40 mg/l	40.96	9.99	3.1	3.40	2.4	16.0	33.0
T_4	80 mg/l	81.56	11.82	5.9	6.10	1.8	21.0	54.0
T_5	100 mg/l	102.10	12.92	6.9	7.00	1.4	26.0	70.0
S_1	Dashara Ghat	18.7	5.34	2.5	2.07	0.9	30.0	110.0
S_2	Balkeshwar	12.5	3.78	2.3	1.37	2.8	21.0	46.0
S_3	Belanganj	19.9	5.68	2.5	2.03	1.2	38.0	94.0
S_4	Hathi Ghat	19.1	5.30	2.6	2.06	2.0	29.0	82.0
S_5	Taj Ganj	14.9	4.38	2.4	1.67	1.6	33.0	87.0

Table 2: Surface microlayer enrichment of DTMAC in the Yamuna river water at Agra U.P.(India)

Sampling Tanks/ Stations	Concentration/ Description	Surface Concentration C_s	Surface Concentration C_{ss}	E	Surface Pressure $\pi = \gamma_o - \gamma$	DO	BOD	COD
T_1	1 mg/l	1.05	0.37	1.8	0.07	3.1	19.0	39.0
T_2	10 mg/l	11.01	2.68	3.1	0.46	2.6	26.0	50.0
T_3	40 mg/l	41.65	8.33	4.0	1.01	1.8	31.0	61.0
T_4	80 mg/l	82.51	9.94	7.3	1.51	1.4	39.0	92.0
T_5	100 mg/l	103.42	12.16	8.5	1.62	1.0	48.0	103.0
S_1	Dashara Ghat	6.8	1.78	2.8	2.07	0.9	30.0	110.0
S_2	Balkeshwar	3.2	0.96	2.3	1.37	2.8	21.0	46.0
S_3	Belanganj	6.6	11.73	2.8	2.03	1.2	38.0	94.0
S_4	Hathi Ghat	3.9	1.11	2.5	2.06	2.0	29.0	82.0
S_5	Taj Ganj	3.7	1.02	2.6	1.67	1.6	33.0	87.0

Table 3: Correlation coefficients between different parameters

	π	DO	BOD	COD	SDS	SDES	SDBS	DHE	CTX	CTAB	DTDMAC
π	1	0.86	0.59	0.46	0.84	0.82	0.50	0.12	0.74	0.68	0.31
DO		1	0.52	0.42	0.54	0.50	0.49	0.47	0.43	0.38	0.35
BOD			1	0.86	0.21	0.44	0.56	0.72	0.88	0.69	0.76
COD				1	0.46	0.48	0.59	0.75	0.94	0.72	0.82
SDS					1	0.85	0.72	0.62	0.45	0.96	0.43
SDES						1	0.76	0.68	0.47	0.63	0.86
SDBS							1	0.65	0.45	0.59	0.44
DHE								1	0.94	0.68	0.51
CTX									1	0.74	0.53
CTAB										1	0.81
DTDMAC											1

Conclusion

In surface samples, were collected from Yamuna River water at Agra U.P. (India) for the experimental purposes. The SDBS and CTX were found to be significantly enriched but the enrichments for SDS and CTAB were smaller and in the case of DHE almost negligible. The enrichment of SDES was intermediate between SDS and SDBS. SDS is over 10 times more biodegradable than SDBS, so though the lightest SDS was less enriched than SDES, CTAB is more enriched than DTDMAC because its molecules are lighter. The dominance of sources of surfactants in the surface micro layer, SDBS and CTX in the surface film is one of the significant findings of this investigation.

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