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Mixed Micelle Formation and Solubilization Behavior toward Polycyclic Aromatic Hydrocarbons of Binary and Ternary Cationic–Nonionic Surfactant Mixtures

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Water solubility enhancements of polycyclic aromatic hydrocarbons (PAHs), viz., naphthalene, anthracene and pyrene, by micellar solutions at 25 °C using two series of surfactants, each involving two cationic and one nonionic surfactant in their single as well as equimolar binary and ternary mixed states, were measured and compared. The first series was composed of three surfactants, benzylhexadecyldimethylammonium chloride (C₁₆BzCl), hexadecyltrimethylammonium bromide (C₁₆Br), and polyoxyethylene(20)mono-*n*-hexadecyl ether (Brij-58) with a 16-carbon (C₁₆) hydrophobic chain; the second series consisted of dodecyltrimethylammonium bromide (C₁₂Br), dodecylethyldimethylammonium bromide (C₁₂EBr), and polyoxyethylene(4)mono-*n*-dodecyl ether (Brij-30) with a 12-carbon (C₁₂) chain. Solubilization capacity has been quantified in terms of the molar solubilization ratio, the micelle–water partition coefficient, the first stepwise association constant between solubilize monomer and vacant micelle, and the average number of solubilize molecules per micelle, determined employing spectrophoto-, tensio-, and fluorimetric techniques. Cationic surfactants exhibited lesser solubilization capacity than nonionics in each series of surfactants with higher efficiency in the C₁₆ series compared to the C₁₂ series. Increase in hydrophobicity of head groups of cationics by incorporation of ethyl or benzyl groups enhanced their solubilization capacity. The mixing effect of surfactants on mixed micelle formation and solubilization efficiency has been discussed in light of the regular solution approximation (RSA). Cationic–nonionic binary combinations showed better solubilization capacity than pure cationics, nonionics, or cationic–cationic mixtures, which, in general, showed increase with increased hydrophobicity of PAHs. Equimolar cationic–cationic–nonionic ternary surfactant systems showed lower solubilization efficiency than their binary cationic–nonionic counterparts but higher than cationic–cationic ones. In addition, use of RSA has been extended, with fair success, to predict partition coefficients of ternary surfactant systems using data of binary surfactants systems. Mixed surfactants may improve the performance of surfactant-enhanced remediation of soils and sediments by decreasing the applied surfactant level and thus remediation cost.

Introduction

Mixtures of the surfactants have received wide attention for several decades because of their efficient solubilization, suspension, dispersion, and transportation capabilities.¹ In view of this, numerous bi- and ternary combinations of ionic and nonionic surfactant mixtures have been studied in respect of their mixed micelle formation and adsorption at the air–water interface.^{2–10} Theories of Clint,¹¹ Motomura,¹² Rosen,¹³ Rubingh,¹⁴ Rubingh-Holland,⁶ and Blankschtein¹⁵ have been used to analyze the experimental results to understand synergism in mixed surfactant systems.

Polycyclic aromatic hydrocarbons (PAHs) are formed by natural and anthropogenic pyrolysis of organic matter during forest fires, fossil fuel utilization, and chemical manufacture.^{16,17} The contamination of soils and water by these carcinogenic pollutants is a widespread environmental problem.^{18,19} Numerous attempts, involving physical, chemical, biological, and their combined technologies, have been made to remedy PAH contaminated soils and groundwater. Such remediation of PAHs

in soil–water systems is dependent on the desorption of contaminants from soil or sediments.^{20,21} Owing to the limited success of conventional pump-and-treat processes, considerable effort has been made to develop in situ surfactant-enhanced remediation (SER) processes to remove PAHs existing in the sorbed state in contaminated subsurfaces.^{22–24} In addition, surfactants have also proved to be potential candidates for improving microbial remediation of PAHs in soils by affecting the accessibility of PAHs to microorganisms.^{25–27}

To quantify the efficiency of SER, varied types of studies have been reported. Among them, most extensively studied is the solubilization of PAHs by single surfactant systems.^{25,28–32} However, attempts have been made to improve the performance of SER of contaminated soils by employing mixed surfactant systems.^{33–37} Treiner et al.^{38–41} used the framework of the regular solution approach (RSA) to evaluate partition coefficients of neutral organic solutes between micellar and aqueous phases and have shown that, if the interaction energy between two surfactants forming a mixed micelle is attractive, then solubilization of a solute containing a polar moiety should be less in the mixed system than in either of the pure surfactant systems but greater if the solute is very hydrophobic. From recent studies, Paria et al.³⁶ concluded that solubilization of

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naphthalene by various ionic–nonionic mixed surfactant systems is less than predicted from ideal solubilization though having attractive interaction for mixed micelle formation. However, Zhu et al.^{35,37} have reported a positive deviation of solubilization from the ideal value in the case of a number of mixed SDS–nonionic systems possessing attractive interactions in mixed micelle formation. Therefore, it would be fruitful to investigate this point further to gain insight into the phenomena. Although enough work has been done on solubilization of PAHs in anionic–nonionic mixed surfactant systems,^{33–37} there are scanty reports of the same in cationic–nonionic^{36,37} and cationic–cationic mixed systems. Moreover, to our knowledge, there is no report of solubilization of PAHs in mixed ternary surfactant combinations.

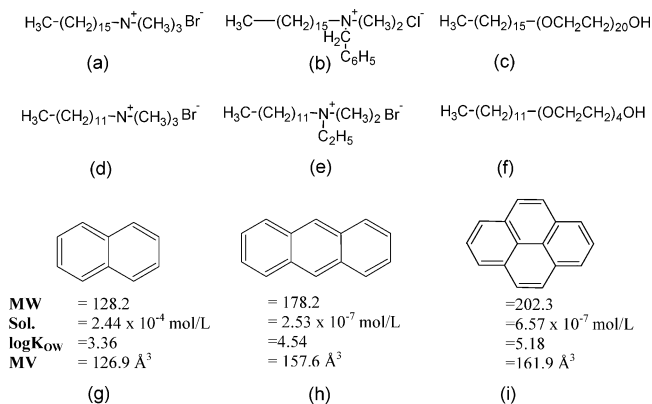
The objective of the present work is to investigate the solubilization aspects of naphthalene, anthracene, and pyrene by single, binary, and ternary surfactant systems. More specifically, the focus has been on (i) the effects of hydrophobic chain length and hydrophilic groups of two series of surfactants with do- (C₁₂) and hexadecyl (C₁₆) chain lengths having cationic and nonionic head groups on the solubilization of PAHs of increasing hydrophobic character; (ii) the evaluation of solubilization capabilities of equimolar cationic–nonionic, cationic–cationic, and cationic–cationic–nonionic mixed systems of the above surfactant series and their intercomparison; and (iii) correlating the interaction parameter for mixed micelle formation with the solubilization interaction parameter, evaluated using RSA, for finding synergism in solubilization capabilities of multicomponent surfactant systems. The experimental results of this study may be useful to understand and predict the solubilization properties of cationic–nonionic, cationic–cationic, and cationic–cationic–nonionic mixed surfactant systems based on those of single surfactant systems and provide valuable information for selection of surfactant mixtures for SER of contaminated soils.

Experimental Section

Materials. The cationic surfactants used were hexadecyltrimethylammonium bromide (C₁₆Br), hexadecylbenzyltrimethylammonium chloride (C₁₆BzCl), dodecyltrimethylammonium bromide (C₁₂Br), and dodecylethyltrimethylammonium bromide (C₁₂EBr). These were obtained from Aldrich Chemical Co. (>98%) and were used after recrystallization three times from acetone–methanol mixtures. The nonionic surfactants Brij58 and Brij30, also Aldrich products, were used as received. The structures of all these surfactants are shown in Scheme 1. The structure and properties of the PAHs, naphthalene (Nap), anthracene (An), and pyrene (Py) (all >98% Aldrich products), used as hydrophobic solutes in the present study and having widespread existence in the environment, are also included in Scheme 1. Surfactant solutions were prepared in triple-distilled water.

Methods. Batch tests for solubilization of various PAHs in surfactant solutions were performed in single and equimolar bi- and ternary combinations of the two surfactant series, viz., the C₁₂ series involving two cationics (C₁₂Br and C₁₂EBr) and one nonionic (Brij30) with 12 carbon hydrophobic groups and a C₁₆ series also containing two cationics (C₁₆Br and C₁₆BzCl) and one nonionic (Brij58) with 16 carbon hydrophobic groups. Single/mixed surfactant solutions in the total surfactant concentration range above cmc were placed in 5–7 borosilicate glass vials of 25 mL capacity, and PAHs were separately added to each tube in amounts slightly more than required to saturate the solution. The vials were sealed with a screw cap fitted with

SCHEME 1: Structure of Surfactant Molecules Used in This Study: (a) Hexadecyltrimethylammonium Bromide (C₁₆Br), (b) Hexadecylbenzyltrimethylammonium Chloride (C₁₆BzCl), (c) Brij58, (d) Dodecyltrimethylammonium Bromide (C₁₂Br), (e) Dodecylethyltrimethylammonium Bromide (C₁₂EBr), and (f) Brij30^a



^a Also included are the structure and physicochemical properties, viz., molecular weight (MW), aqueous solubility (sol),⁴² log K_{ow},⁴² and molecular volume (MV)⁴³ of polyaromatic hydrocarbons used in this study: (g) naphthalene, (h) anthracene, and (i) pyrene.

a Teflon-lined septum to prevent any loss. The samples were then agitated for a period of 48 h in a thermostated shaker bath maintained at the temperature 25 ± 0.5 °C. After this, subsequent centrifugation at 12000g for 15 min was performed to remove the undissolved solid PAH. The concentration of dissolved solute was determined spectrophotometrically with a Shimadzu spectrophotometer (Model UV-1650PC) following appropriate dilution of an aliquot of the supernatant with 1 mL methanol and rest with surfactant–water solution. The surfactant concentration was kept the same in both the reference and the measurement cells to eliminate the effect of surfactant on UV absorbance. Duplicate tests were performed for each surfactant concentration. The solubilities of Nap, An, and Py at each surfactant concentration were determined at 276, 358, and 337 nm, respectively, and then taken as the mean of the duplicate readings.

The cmc values were determined from the surface tension (γ) vs the logarithm of surfactant concentration (log C_i) plots in Figure 1. Surface tension measurements were made with a Krüss 9 tensiometer by the platinum ring detachment method. Surfactant concentration was varied by adding concentrated surfactant solution in small installments using a Hamilton microsyringe, and readings were taken after thorough mixing and temperature equilibration. The temperature was maintained at the desired value (within ± 0.1 °C) by circulating water from a HAAKE GH thermostat. The accuracy of measurements was within ± 0.1 dyn cm⁻¹. Aggregation numbers were determined using steady-state fluorescence experiments as described earlier.⁴⁴

Results and Discussion

cmc and Interaction of Surfactants in Mixed Micelles. The cmc values of single as well as mixed surfactant systems for both the series of surfactants are presented in Table 1. The values for pure surfactants are in good agreement with literature values, given in parenthesis in the table. The cmc values of cationic surfactants with C₁₆ hydrophobic groups, as expected, are almost 2 orders of magnitude lower than with C₁₂ hydrophobic groups. However, the cmc of the nonionic surfactant Brij58 is lower

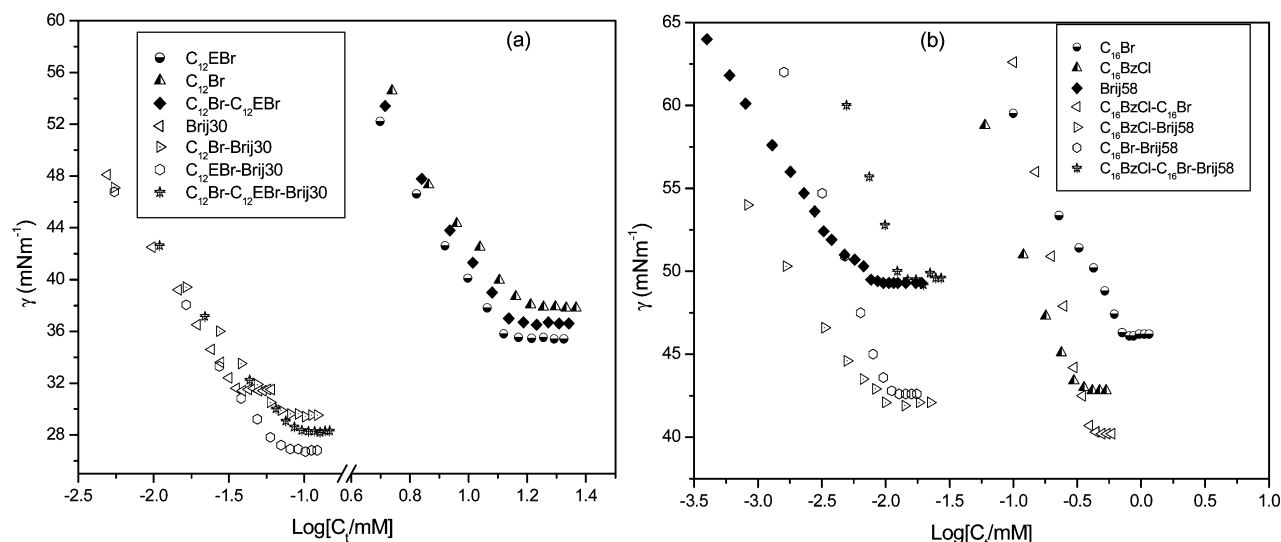


Figure 1. Plots of the surface tension (γ) vs the total surfactant concentration (C_t) of single and equimolar bi- and ternary surfactant combinations for the (a) C_{12} and (b) C_{16} series.

TABLE 1: Critical Micelle Concentration (cmc_{exp}), Micellar Composition (X_i^M), Interaction Parameter (β), and Activity Coefficients (f_i) of Equimolar Binary Surfactant Mixtures Using Rubingh's Method and Equimolar Ternary Surfactant Mixtures Using Rubingh's Pseudobinary and Rubingh–Holland Methods at 25 °C for Both C_{12} and C_{16} Surfactant Series^a

C_{12} series							
single surfactant system	cmc_{exp} (mM)	mixed surfactant system	cmc_{exp} (mM)	$\text{cmc}_{\text{ideal}}$ (mM)	β	$X_1^M/X_2^M/X_3^M$	$f_1/f_2/f_3$
$C_{12}\text{Br}$	14.5 (15.1) ^b	$C_{12}\text{Br}-C_{12}\text{EBr}$	13.4	13.8	-0.14	0.48/0.52/-	0.96/0.97/-
$C_{12}\text{EBr}$	13.2 (14.0) ^b	$C_{12}\text{Br}-\text{Brij30}$	0.0713	0.0762	-3.53	0.06/0.94/-	0.04/0.99/-
Brij30	0.0382 (0.0351) ^c	$C_{12}\text{EBr}-\text{Brij30}$	0.0703	0.0762	-3.66	0.07/0.93/-	0.04/0.98/-
		$C_{12}\text{Br}-(C_{12}\text{EBr}-\text{Brij30})$	0.0995	0.105	-3.38	0.05/0.95/-	0.05/0.99/-
		$C_{12}\text{EBr}-(C_{12}\text{Br}-\text{Brij30})$		0.107	-3.55	0.06/0.94/-	0.04/0.99/-
		$\text{Brij30}-(C_{12}\text{EBr}-C_{12}\text{Br})$		0.114	-3.69	0.90/0.10/-	0.96/0.05/-
		$C_{12}\text{Br}-C_{12}\text{EBr}-\text{Brij30}$		0.114		0.04/0.05/0.91	0.06/0.05/0.97
C_{16} series							
single surfactant system	cmc_{exp} (mM)	mixed surfactant system	cmc_{exp} (mM)	$\text{cmc}_{\text{ideal}}$ (mM)	β	$X_1^M/X_2^M/X_3^M$	$f_1/f_2/f_3$
$C_{16}\text{Br}$	0.764 (0.815) ^d	$C_{16}\text{BzCl}-C_{16}\text{Br}$	0.423	0.469	-0.47	0.66/0.34/-	0.95/0.81/-
$C_{16}\text{BzCl}$	0.338 (0.473) ^e	$C_{16}\text{Br}-\text{Brij58}$	0.0109	0.0121	-3.05	0.09/0.91/-	0.08/0.98/-
Brij58	0.0061 (0.0081) ^f	$C_{16}\text{BzCl}-\text{Brij58}$	0.0100	0.0120	-2.98	0.14/0.86/-	0.11/0.95/-
		$C_{16}\text{BzCl}-(C_{16}\text{Br}-\text{Brij58})$	0.0142	0.0160	-2.49	0.10/0.90/-	0.14/0.97/-
		$C_{16}\text{Br}-(C_{16}\text{BzCl}-\text{Brij58})$		0.0149	-2.20	0.05/0.95/-	0.13/0.99/-
		$\text{Brij58}-(C_{16}\text{BzCl}-C_{16}\text{Br})$		0.0177	-2.84	0.84/0.16/-	0.14/0.93/-
		$C_{16}\text{BzCl}-C_{16}\text{Br}-\text{Brij58}$		0.0178		0.11/0.05/0.84	0.12/0.11/0.92

^a Subscript 1 represents the first surfactant in each combination. The two surfactants in parentheses correspond to the pair taken as a single component in pseudobinary treatment of ternary systems. Error limits of cmc_{exp} , X_i^M , β , and f_i are $\pm 4\%$. cmc_{RH} values for C_{12} and C_{16} ternary surfactant systems were 0.101 and 0.0141 mM, respectively. ^b Reference 45. ^c Reference 46. ^d Reference 47. ^e Reference 48. ^f Reference 35.

by only 1 order of magnitude than that of Brij30 due to a larger number of oxyethylene (OE) units in its hydrophilic head.

For ideal mixing in multicomponent systems, the ideal cmc values, $\text{cmc}_{\text{ideal}}$, calculated using the Clint¹¹ equation are also included in Table 1 for equimolar binary and ternary systems in both the surfactant series. All the observed cmc values were found to be lower than ideal values, indicating negative deviation from ideal behavior for mixed micelle formation. The estimate of negative deviation of experimental cmc values from $\text{cmc}_{\text{ideal}}$ and hence nonideality of mixed binary surfactant systems can be made in light of Rubingh's equation¹⁴

$$\frac{(X_1^M)^2 \ln(\text{cmc}_{12}\alpha_1/\text{cmc}_1X_1^M)}{(1-X_1^M)^2 \ln\{\text{cmc}_{12}(1-\alpha_1)/\text{cmc}_2(1-X_1^M)\}} = 1 \quad (1)$$

on the basis of regular solution theory: cmc_1 , cmc_2 , and cmc_{12} denote the experimental cmc values of the surfactants 1, 2, and their equimolar binary mixture respectively; X_1^M is the micellar mole fraction of surfactant 1 in the mixed micelle. The interaction parameter, β , given by

$$\beta = \frac{\ln(\text{cmc}_{12}\alpha_1/\text{cmc}_1X_1^M)}{(1-X_1^M)^2} = \frac{\ln(\text{cmc}_{12}\alpha_2/\text{cmc}_2X_2^M)}{(1-X_2^M)^2} \quad (2)$$

is an indicator of the degree of interaction between two surfactants in mixed micelles and accounts for deviation from ideality. A negative value implies an attractive interaction. The activity coefficients, f_i , of individual surfactants within the mixed

micelles are related to the interaction parameter through the equations

$$f_1 = \exp\{\beta(1 - X_1^M)^2\} \quad (3a)$$

$$f_2 = \exp\{\beta X_1^{M^2}\} \quad (3b)$$

The values of X_i^M , f_i , and β are presented in Table 1 for the selected equimolar binary systems. A slightly negative value of β and very small deviation of f_i values from unity in the case of cationic–cationic mixed systems for the two series of surfactants indicate their almost ideal behavior for mixed micelle formation. However, more negative deviation of the mixed C_{16} –BzCl– C_{16} Br system over C_{12} EBr– C_{12} Br may be due to the presence of a phenyl ring in the head group of C_{16} BzCl. Although both the surfactants in these binary surfactant systems are positively charged, there is negative deviation from ideal behavior in tune with the results reported in the literature^{10,45,49} for cationic–cationic mixed systems. The values of β are largely negative for cationic–nonionic binary systems, being more negative for the C_{12} surfactant series than for the C_{16} series. It is well-known⁵⁰ that, for cationic–nonionic mixed surfactant systems, significant electrostatic self-repulsion of cationics and weak steric self-repulsion (depending upon the head group size) of nonionics before mixing are weakened by dilution effects after mixing and the electrostatic self-repulsion of the cationic surfactants is replaced by the attractive ion–dipole interaction between hydrophilic groups of cat- and nonionic surfactants. However, less negative values of β in the case of C_{16} BzCl/ C_{16} –Br–Brij58 mixed systems over C_{12} EBr/ C_{12} Br–Brij30 systems may be attributed to the larger head group size of Brij58 (20 OE groups) than Brij30 (4 OE groups), thus making a larger steric self-repulsion contribution toward inter-headgroup interactions. Moreover, these mixed micelles are predominated by nonionic surfactants as indicated by X_i^M values in Table 1, in conformity with the results of other studies on different cationic–nonionic mixed systems.^{44,51}

The above parameters in ternary mixtures, viz., C_{16} BzCl– C_{16} Br–Brij58 and C_{12} EBr– C_{12} Br–Brij30, have been evaluated using pseudobinary Rubingh's treatment. In this case, two surfactants are paired and treated as one component and the third is treated as the second component.^{8,47,52} The cmc of the paired component has been taken as that of an equimolar binary mixture. For our ternary mixtures, six sets of results, three possible pairings for each ternary systems, are presented in Table 1. The subscript 1 stands for the component outside parentheses; 2 stands for the pair in parentheses, being treated as a single component. As evident from the results, X_1^M and β obviously depend, though to a small extent, on the way of selection of components for pairing. The β values obtained are all negative, indicating synergism in the selected ternary systems. As observed in the case of cationic–nonionic binary systems, the average negative value of β is larger for the C_{12} series compared with the C_{16} series, probably due to larger steric self-repulsion contribution toward inter-headgroup interactions by Brij58 in the C_{16} surfactant series. Analysis shows the predominance of the nonionic surfactant in the mixed ternary micelles as well (Table 1).

Holland and Rubingh⁶ have proposed a generalized multi-component nonideal mixed micelle model on the basis of pseudo-phase separation approach. It has been successfully applied in the case of many ternary surfactant systems^{5–7} for evaluation of micellar composition, activity coefficients, and cmc values. It makes an effective use of net interaction

parameters determined experimentally from cmc measurements on binary systems. According to this proposition, the activity coefficients f_i, f_j, \dots of micelle forming surfactant species i, j, \dots in an n -component mixture are represented, on a general basis, by the equation

$$\ln f_i = \sum_{j=1}^n \beta_{ij} X_j^{M^2} + \sum_{j=1}^n \sum_{k=1}^{j-1} (\beta_{ij} + \beta_{ik} - \beta_{jk}) X_j^M X_k^M \quad (4)$$

where β_{ij} represents the net (pairwise) interaction between component i and j and X_j^M is the mole fraction of the j -th component in the micelles. At cmc, the relation

$$X_i^M = \frac{\alpha_i \text{cmc}_j f_j X_j^M}{\alpha_j \text{cmc}_i f_i} \quad (5)$$

holds, where terms cmc_i and cmc_j are cmc values of the i - and j -th components in their pure state, respectively. The interaction parameter, β_{ij} can be obtained independently from binary mixtures using the Rubingh method. The activity coefficients for a three component system, i.e., f_1, f_2 , and f_3 at mixed cmc can be calculated from the above equations by using the method of successive substitutions subject to the constraint that the sum of X_i^M values equals unity. The values of f_i so obtained can then be used to find the mixed micellar cmc, cmc_{RH} , of ternary systems by the equation

$$\frac{1}{\text{cmc}_{\text{RH}}} = \sum_{i=1}^3 \frac{\alpha_i}{f_i \text{cmc}_i} \quad (6)$$

In this study, values of binary interaction parameters β_{12}, β_{13} , and β_{23} following Rubingh's method and cmc values of pure surfactants (Table 1) in the case of both surfactant series were used in eqs 4 and 5 to evaluate $f_1, f_2, f_3, X_1^M, X_2^M$, and X_3^M . The calculations were done using Solver in MS Excel. These values used in eq 6 give the predicted cmc of the ternary system, cmc_{RH} , according to the Rubing–Holland (RH) formulation. The results are presented in Table 1 along with cmc_{RH} values of two equimolar ternary systems as a footnote.

The mole fractions of individual amphiphiles in the mixed micelles are different from stoichiometric composition: X_{cationic} values are much lower than α_{cationic} values, but X_{nonionic} values are fairly higher than α_{nonionic} values in both surfactant series. The activity coefficients of cationics are very low but are close to unity for nonionics. The cmc_{RH} values are found to be in fair agreement with experimental cmc values, but both are lower than the ideal cmc, indicating the synergistic nonideal nature of mixed ternary micellar systems. Fair agreement between cmc_{RH} and cmc_{exp} in both the series indicates fair applicability of the RH method for such systems, although contribution of molecular parameters of component surfactants, counterion binding by mixed micelles, etc. have not been considered.

Molar Solubilization Ratio (MSR) and Micelle-Phase/Aqueous-Phase Partitioning of PAHs. A measure of the effectiveness of a surfactant in solubilizing a given solubilize is the molar solubilization ratio (MSR) equivalent to increase in solubilize concentration per unit increase in micellar surfactant concentration. In the presence of excess of the hydrophobic organic compound MSR, given by the equation^{33–35}

$$\text{MSR} = ([S_t] - [S_{\text{cmc}}]) / (C_t - \text{cmc}) \quad (7)$$

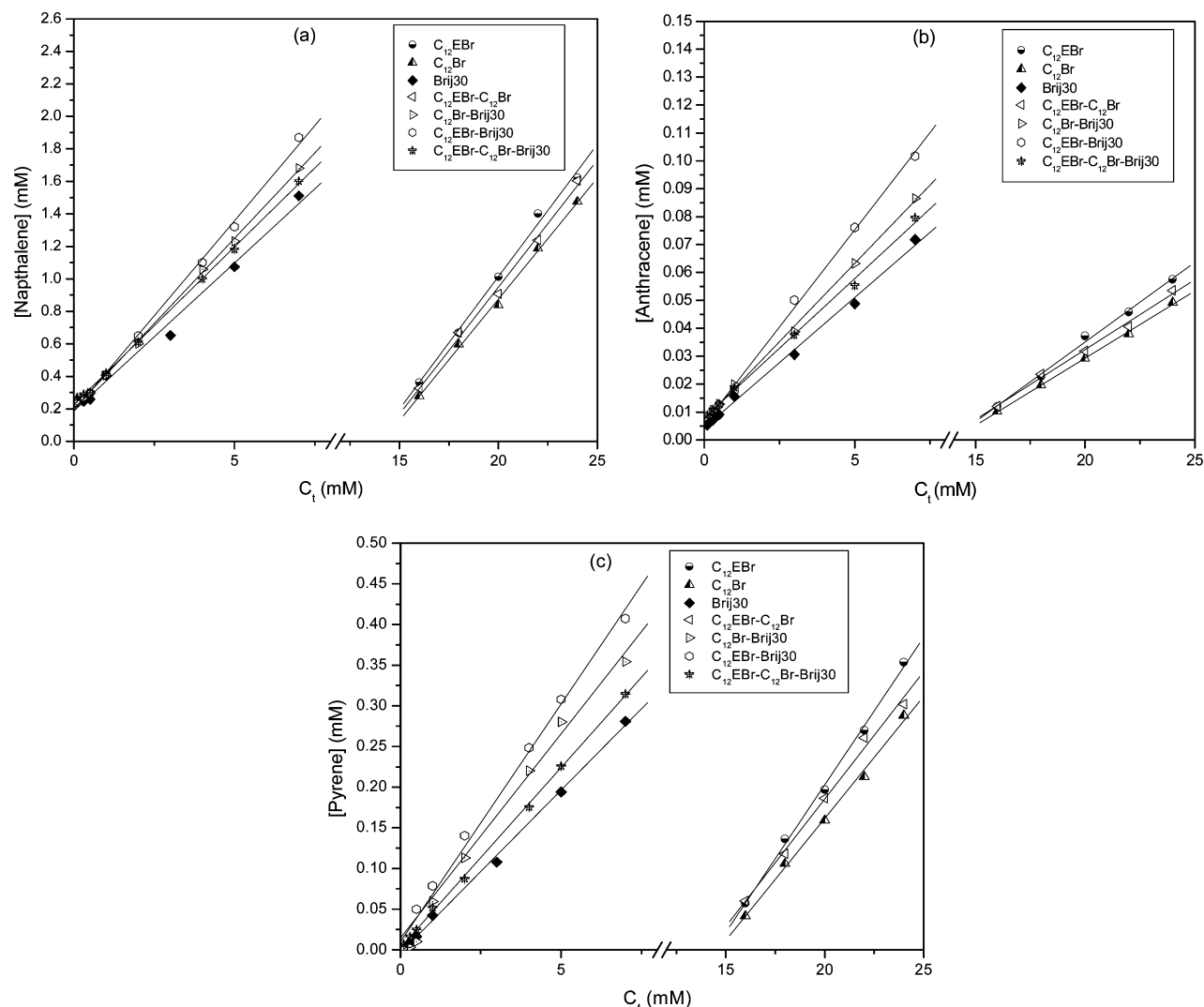


Figure 2. Variation of solubility of (a) naphthalene, (b) anthracene, and (c) pyrene with total surfactant concentration (C_t) of single and equimolar bi- and ternary surfactant combinations for the C_{12} series.

is obtained from the slope of the curve that results when solubilize concentration is plotted against surfactant concentration. $[S_t]$ is the total apparent solubility of PAHs in single/mixed surfactant solutions at a particular total surfactant concentration, C_t , above cmc, and $[S_{cmc}]$ is the apparent solubility of PAHs at cmc, which is taken as their water solubility, $[S]$, because it changes only very slightly up to the cmc of the surfactant. All the concentrations are expressed in mol/L. The variation of solubilities of naphthalene, anthracene, and pyrene in single and equimolar mixed surfactant systems are plotted in Figures 2 and 3 for the C_{12} and C_{16} series, respectively. The aqueous solubilities of PAHs increase linearly over the range of single or mixed surfactant concentrations above cmc indicating their solubility enhancement in water. This phenomena is due to solubilization of organic solutes within single/mixed surfactant micelles. The values of MSR calculated from the above plots using eq 7 for all systems studied herein are given in Table 2 for the C_{12} and C_{16} series of surfactants.

The effectiveness of solubilization can also be expressed in terms of the partition coefficient, K_m , of the organic compound between the micelle and aqueous phases and is defined as $K_m = X_m/X_a$, the ratio of mole fraction of organic compound in the micellar phase, X_m , to that in the aqueous phase, X_a . The value of K_m is a function of temperature and the nature of surfactant and solubilize. The value of X_m in terms of MSR can be written

as $X_m = MSR/(1 + MSR)$; X_a can be expressed as $X_a = [S_{cmc}]V_m$. V_m is the molar volume of water equal to 0.01805 L/mol at 25 °C. With these expressions, K_m becomes

$$K_m = MSR / \{ [S_{cmc}] V_m (1 + MSR) \} \quad (8)$$

The K_m values of various PAHs for single/mixed systems are presented in Table 2 for the C_{12} and C_{16} series of surfactants.

In conformity with early findings,^{53–54} in each surfactant series, MSR and K_m values are found to be higher for nonionic than for cationic surfactants indicating that for the same hydrophobic chain length nonionics have higher solubilizing power for the PAHs. A difference of ethyl group between C_{12} -Br and C_{12} EBr in the C_{12} series produces a significant difference in MSR and K_m values, although both have the same hydrophobic chain length and very close micellar aggregation numbers. Similar is the case with C_{16} BzCl and C_{16} Br in the C_{16} series with the former exhibiting significantly larger values of MSR and K_m compared with latter. Here, the aggregation numbers also differ. In addition to lower counterion (Cl^-) binding, this difference may be attributed to the presence of a phenyl ring in the hydrophilic part of the C_{16} BzCl. The MSR and K_m values are, in general, higher in the C_{16} series than in the C_{12} series of compounds for all PAHs. With the assumption that the inner nonpolar core of the micelle is responsible for

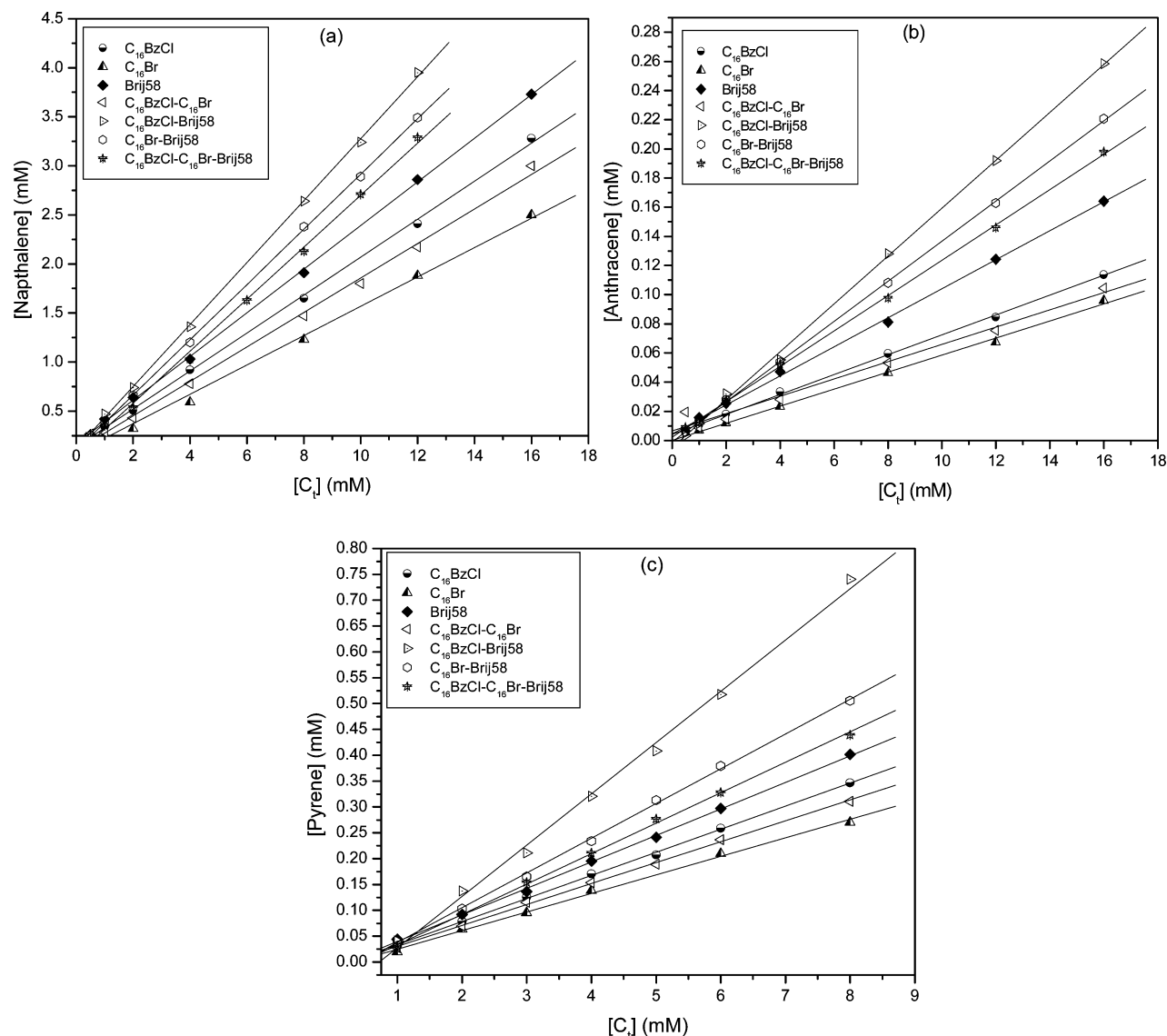


Figure 3. Variation of solubility of (a) naphthalene, (b) anthracene, and (c) pyrene with total surfactant concentration (C_t) of single and equimolar bi- and ternary surfactant combinations for the C_{16} series.

solute solubilization and that the hydration of the outer polar zone of the micelle is localized, K_m should be approximately proportional to the nonpolar content of the surfactant. This has been experimentally observed by Kile et al.⁵³ for solubilization of DDT in nonionic surfactants where the main contributor to solubilization was the nonpolar content of surfactant independent of the oxyethylene chain length. Moreover, their solubilization data for non-, cat-, and anionic surfactants revealed that the values of K_m could be better related with nonpolar content of the surfactant rather than with the micelle size, leading to the conclusion that micellar size may not be a major factor for observed differences in K_m of ionic and nonionic surfactants. This is supported by our data as well, wherein MSR and K_m values for Brij30 are much lower than for Brij58, although the micellar aggregation number of the former is 101 compared with 65 for latter. This might also be due to the larger micelle concentration in Brij58 compared with Brij30 owing to its smaller aggregation number and lower cmc value.

Among the equimolar binary surfactant mixtures, cationic–nonionic mixed systems show greater MSR and K_m values than cationic–cationic mixed systems in each surfactant series. The values are even higher than those of single nonionic surfactants indicating synergism in PAH solubilization enhancement over the

single surfactant systems. The observation is valid in both the surfactant series. The cationic–cationic mixed systems showed intermediate values between those of individual surfactants indicating very little mixing effect. However, MSR and K_m values of cationic–cationic systems are significantly increased on adding nonionic surfactant as observed in the case of ternary systems of both the surfactant series. The possible cause is explained in latter sections.

Estimation of Binding Constants of PAHs with Single and Mixed Micelles. Moroi et al.^{29,55} have demonstrated the evaluation of the first stepwise association constant, K_1 , of a solubilize incorporated into micelles in the case of solubilization to which Poisson distribution can be applied. As per this formulation, K_1 , which serves as interaction parameter between them, is related to the total surfactant concentration, C_t , total micelle concentration $[M]$, cmc, and aggregation number, N , of micelles through the equation

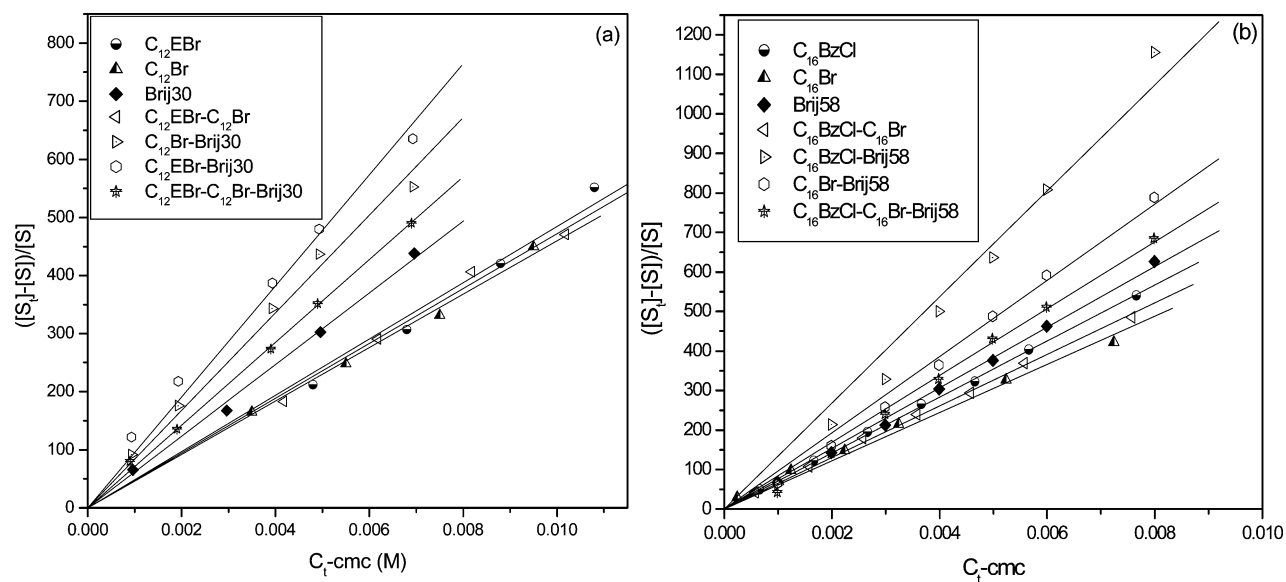
$$([S_t] - [S])/[S] = K_1/N(C_t - \text{cmc}) \quad (9)$$

The value of K_1/N can be evaluated from the slope of $([S_t] - [S])/[S]$ against $C_t - \text{cmc}$. If the aggregation number is known, then the value of K_1 can be evaluated. Further, assuming a

TABLE 2: Aggregation Number (N), Molar Solubilization Ratio (MSR), $\log K_m$, Deviation Ratio (R), and Experimental Interaction Parameter (B) for the C_{12} and C_{16} Series of Surfactants at 25 °C^a

system	N	naphthalene				anthracene				pyrene			
		MSR (MSR _{ideal})	$\log K_m$	R	B	MSR (MSR _{ideal})	$\log K_m$	R	B	MSR (MSR _{ideal})	$\log K_m$	R	B
C ₁₂ series													
C ₁₂ Br	48	0.149	4.46			0.005	5.95			0.030	6.40		
C ₁₂ EBr	53	0.163	4.49			0.006	6.02			0.036	6.48		
Brij30	101	0.187	4.54			0.009	6.23			0.040	6.52		
C ₁₂ EB–C ₁₂ Br	50	0.157 (0.156)	4.48	1.0	0.04	0.005 (0.005)	5.96	0.9	−0.25	0.031 (0.032)	6.42	0.9	−0.20
C ₁₂ Br–Brij30	75	0.212 (0.168)	4.59	1.2	2.34	0.011 (0.007)	6.31	1.6	4.11	0.050 (0.035)	6.62	1.4	4.58
C ₁₂ EBr–Brij30	70	0.234 (0.175)	4.62	1.2	3.15	0.014 (0.007)	6.40	1.8	6.96	0.055 (0.038)	6.66	2.0	5.03
C ₁₂ Br–C ₁₂ EBr–Brij30	67	0.194 (0.166)	4.56 (4.63)	1.1		0.010 (0.007)	6.26 (6.41)	1.5		0.044 (0.034)	6.56 (6.69)	1.2	
C ₁₆ series													
C ₁₆ Br	61	0.157	4.48			0.006	6.03			0.036	6.48		
C ₁₆ BzCl	45	0.194	4.56			0.007	6.09			0.045	6.57		
Brij58	65	0.220	4.60			0.010	6.26			0.051	6.63		
C ₁₆ BzCl–C ₁₆ Br	53	0.179 (0.175)	4.53	1.0	−0.03	0.006 (0.006)	6.07	1.0	0.01	0.040 (0.040)	6.53	1.0	−0.10
C ₁₆ BzCl–Brij58	55	0.314 (0.207)	4.72	1.5	2.46	0.016 (0.008)	6.47	2.0	4.57	0.099 (0.048)	6.89	2.1	5.26
C ₁₆ Br–Brij58	62	0.285 (0.188)	4.69	1.5	2.86	0.014 (0.008)	6.40	1.8	4.56	0.070 (0.044)	6.75	1.6	5.96
C ₁₆ BzCl–C ₁₆ Br–Brij58	60	0.265 (0.190)	4.67 (4.74)	1.4		0.012 (0.007)	6.34 (6.49)	1.6		0.059 (0.044)	6.68 (7.05)	1.3	

^a Error limits in the measurement of N , MSR, and $\log K_m$ are ± 5 , ± 7 , and $\pm 4\%$, respectively.

**Figure 4.** Plots of $([S_i] - [S])/[S]$ of pyrene against surfactant concentration in micellar form (C_s -cmc) of single and equimolar bi- and ternary surfactant combinations for the (a) C_{12} and (b) C_{16} series.

Poisson distribution of solubilize molecules among micelles, the formulation can also be used to evaluate average number of solubilize molecules per micelle, S^M , according to the equation^{29,55}

$$S^M = ([S_i] - [S])/[M_i] = K_1[S] \quad (10)$$

The value of $[S]$ can be taken as water solubility of PAHs, which changes only very slightly up to cmc of the surfactant.²⁸ Figure 4 shows the representative plots of $([S_i] - [S])/[S]$ against C_i -cmc for the C_{12} and C_{16} surfactant series in the case of pyrene, where all the concentrations are expressed in mol/L. The values of the aggregation number of single and mixed surfactant systems (Table 2) determined by steady-state fluorescence

measurement were used with the value of K_1/N to evaluate K_1 and hence S^M . The calculated values of K_1 and S^M are presented in Table 3 for the C_{12} and C_{16} surfactant series.

All the PAHs in each type of micelle satisfy the assumption of Poisson distribution,⁵⁶ because their S^M values are sufficiently low. The S^M values for naphthalene are the largest and those for anthracene the smallest in each of the single or mixed systems. Although S^M values of 5.9–17.3 and 8.5–16.6 for naphthalene in the C_{12} and C_{16} surfactant series, respectively, seem to be quite large, the amount in mole fraction units is less than 0.17 in the case of the former and less than 0.23 in the latter. The volume of the micellar core of the mixed C_{16} BzCl-Brij58 ($N = 55$) according to the Tanford equation⁵⁷ comes out

TABLE 3: Association Constant (K_1) and Average Number of Solubilizate Molecules Per Micelle (S^M) of PAHs in Various Single and Equimolar Mixed Systems for the C₁₂ and C₁₆ Series of Surfactants at 25 °C^a

surfactant system	naphthalene		anthracene		pyrene		
	$K_1/10^4$ (mol ⁻¹ dm ³)	S^M	$K_1/10^5$ (mol ⁻¹ dm ³)	S^M	$K_1/10^6$ (mol ⁻¹ dm ³)	S^M	I_1/I_3
C ₁₂ series							
C ₁₂ Br	2.59	6.5	9.11	0.3	2.44	1.5	1.30
C ₁₂ EBr	2.34	5.9	8.37	0.3	2.33	1.4	1.38
Brij30	6.93	17.3	34.3	1.0	6.23	3.7	1.03
C ₁₂ EB–C ₁₂ Br	2.45	6.1	8.58	0.3	2.36	1.4	1.32
C ₁₂ Br–Brij30	6.10	15.2	31.7	1.0	6.30	3.8	1.15
C ₁₂ EBr–Brij30	6.31	15.8	35.3	1.1	6.69	4.0	1.17
C ₁₂ Br–C ₁₂ EBr–Brij30	5.18	12.9	26.0	0.8	4.77	2.9	1.19
C ₁₆ series							
C ₁₆ Br	3.51	8.8	12.0	0.4	3.72	2.2	1.18
C ₁₆ BzCl	3.40	8.5	9.89	0.3	3.19	1.9	1.24
Brij58	5.60	14.0	21.3	0.6	4.98	3.0	1.07
C ₁₆ BzCl–C ₁₆ Br	3.58	8.9	11.2	0.3	3.46	2.1	1.20
C ₁₆ Br–Brij58	6.58	16.5	28.5	0.9	5.98	3.6	1.10
C ₁₆ BzCl–Brij58	6.64	16.6	30.2	0.9	7.38	4.4	1.12
C ₁₆ BzCl–C ₁₆ Br–Brij58	5.82	14.5	24.3	0.7	5.07	3.0	1.13

^a Also included are the I_1/I_3 values of pyrene in given surfactant systems. Error limits in the measurement of K_1 , S^M , and I_1/I_3 are ± 4 , ± 6 , and $\pm 4\%$, respectively.

to be 25 179 Å.³ Incorporation of 16.6 naphthalene molecules in such a micelle would lead to a volume increase of $16.6 \times 126.9 = 2106.5$ Å³, which is just 8.4%. For the other systems, the percentage increase is even smaller. Accordingly, the assumption that incorporation of solubilizates into the micelles is not so large as to change the intrinsic property of micelles is still satisfied.

The K_1 value increases with the number of benzene rings in the PAH in all systems, indicating contribution of all benzene rings to solubilization through hydrophobic interactions. However, the differential change in K_1 values between naphthalene and anthracene with 10 and 14 carbon atoms is greater than that between anthracene and pyrene with 14 and 16 carbon atoms. This may be an indication of the different solubilization sites of anthracene and pyrene.²⁹ Among the cat- and nonionic surfactants in each series, nonionics show a greater magnitude of K_1 values compared to cationics. The values for the cationic surfactants in the C₁₆ series are larger than in the C₁₂ series owing to larger hydrophobic content in the former. However, among the nonionics, Brij30 showed larger values compared to Brij58 even though it had a shorter hydrophobic tail. The ratio K_1/N , which can also be taken as a measure of solubilizing power of a micelle, is found to be greater for Brij58 than for Brij30. However, due to a larger aggregation number of Brij30, K_1 comes out to be larger than in Brij58. Therefore, a different trend in K_1 compared to MSR and K_m is related to the aggregation number of the micelles. A substantial increase in K_1 in both the series of surfactants when a nonionic surfactant is mixed with the cationic indicates increased stability of solubilizates in the mixed cationic–nonionic surfactant systems relative to pure cationics. It has been observed⁵⁸ that, in addition to micellar core solubilization, naphthalene, anthracene, and pyrene are adsorbed at the cationic micelle–water interface due to electrostatic interactions between π -electrons of arenes and the positive charges. In cationics, lower values of K_1 , MSR, and K_m can, therefore, be attributed to limited solubilization at micelle–water interface and micellar core. In the case of nonionics, due to weak interaction of oxygen of POEs with π -electrons of arenes, more of the micellar core solubilization would be prevalent. This therefore explains relatively larger values of K_1 , MSR, and K_m for nonionics. In cationic–nonionic mixed micelles, as only a small mole fraction of cationic (Table

1) is present and also the degree of counterion binding is negligible,⁴⁴ a slight positive charge on mixed micelles facilitates micelle–water interface adsorption in addition to the micellar core solubilization characteristic of nonionics. Consequently, we expect larger values of MSR and K_m than individual surfactants and comparable value of K_1 with nonionics. The mixed cationic–nonionic systems in C₁₆ series exhibited a higher MSR as well as K_m values compared to the C₁₂ series due to their larger hydrophobic chain length that facilitates micellar core solubilization. A similar trend, in general, is observed for K_1 except for the solubilization of anthracene in C₁₂EBr–Brij30 and C₁₂Br–Brij30 systems where the values are slightly larger than in C₁₆BzCl–Brij58 and C₁₆Br–Brij58. This may be due to the difference in aggregation numbers. A similar explanation can be furnished for mixed ternary systems wherein these values are higher than the cationic surfactants. The results of ternary systems also point to the effect of increased hydrophobic chain length on K_1 , MSR, and K_m . Thus, the incorporation of a cationic surfactant into nonionic micelles facilitates the solubilization of arenes due to their additional micelle–water interface adsorption.

The I_1/I_3 ratio of pyrene emission spectra is sensitive to the polarity of the medium sensed by pyrene molecules. For example, these values in cyclohexane, toluene, ethanol, methanol, and water are 0.6, 1.04, 1.23, 1.33, and 1.84, respectively.⁵⁹ Table 3 presents I_1/I_3 ratios of pyrene in single, binary, and ternary mixed systems. The higher values in cationic surfactants of the C₁₆ and C₁₂ series indicate solubilization of pyrene in the palisade layer of the micelles. However, slightly lower values in cationic surfactants of the C₁₆ series indicate somewhat deeper solubilization as reported.⁶⁰ In nonionics, the solubilization site is more toward the micellar core compared to cationics or cationic–cationic binary systems. Among mixed systems, the values are intermediate between the nonionic surfactants and pure cationic or cationic–cationic binary systems indicating some solubilization at micelle–water interface in addition to deeper solubilization. This supports the viewpoint that, in such systems, in addition to micellar core solubilization, micelle–water interface adsorption of pyrene takes place. It may not be out of place to mention that, at very high solubilizate concentrations used in solubilization experiments, micellar core solubilization would be predominant compared to inference that can

be drawn from I_1/I_3 values obtained during determination of N , where a very small concentration of pyrene is employed. This has been observed in the case of benzene at its low and high mole fractions.⁶¹

Mixing Effect of Surfactants on Micelle–Water Partition Coefficient (K_m). On the basis of the regular solution approximation (RSA), Treiner et al.^{38–41} have suggested that the partition coefficient of a neutral organic solute between micellar and aqueous phases in mixed binary surfactant solution can be represented by the relationship

$$\ln K_{m12} = X_1^M \ln K_{m1} + (1 - X_1^M) \ln K_{m2} + BX_1^M(1 - X_1^M) \quad (11)$$

where K_{m12} , K_{m1} , and K_{m2} are the micelle–water partition coefficients of the solute in mixed and single surfactant systems, respectively, and X_1^M (X_2^M) represents the micelle mole fraction of surfactant 1 (2). B has the same origin as β in eqs 1–3 and has no provision for either solute–solute or solute–solvent interactions except through individual K_m values.⁴¹ As per Zhu et al.,^{34,35,37} B is an empirical parameter that incorporates both the surfactant–surfactant (as in the case of β) and surfactant–solute interactions. Thus, for $B = 0$, there would be no mixing effect of surfactants on the partitioning of a solute. Also, $B > 0$ ($B < 0$) implies that K_m in mixed surfactant is larger (smaller) than predicted by the ideal mixing rule. This treatment, at least, can be viewed as a useful empirical method and a convenient and pertinent tool for interpretation of experimental observations.

Table 2 lists the values of B evaluated for various equimolar binary surfactant mixtures. X_1^M values were taken from the Rubingh's formulation given in Table 1 for respective surfactant systems. The values of B are found to be positive except for binary cationic–cationic surfactant mixtures where these are either close to zero or slightly negative, in tune with the slight negative value of β . The binary cationic–nonionic surfactant systems yielded large positive values of B , the magnitude of which increases with the increase in chain length of surfactant used and the increase in K_{OW} of PAH except for the $C_{12}EBr$ –Brij30 system. However, in contrast, large negative β values of these systems indicate that the surfactant–surfactant interaction is not the sole factor that determines their solubilization effect. The stabilization of PAHs by cationic–nonionic surfactant mixtures, therefore, plays a greater role. As mentioned earlier, the slight positive charge on the surface of mixed cationic–nonionic micelles may additionally facilitate micelle–water interface adsorption thereby stabilizing PAHs relative to pure cat- or nonionics or cationic–cationic mixtures.

A generalized multicomponent treatment can be proposed in analogy with the binary surfactant system for evaluation of K_m in multicomponent surfactant systems, which can make an effective use of the net experimental interaction parameter determined from the solubilization measurements on binary systems. As per this proposition, the partition coefficient of a solubilize by a ternary surfactant system, K_{m123} , can be represented by the equation

$$\ln K_{m123} = X_1^M \ln K_{m1} + X_2^M \ln K_{m2} + X_3^M \ln K_{m3} + B_{12}X_1^MX_2^M + B_{13}X_1^MX_3^M + B_{23}X_2^MX_3^M \quad (12)$$

The values of X_i^M can be used from the Rubingh–Holland formulation of ternary systems given in Table 1; B_{12} , B_{13} , and B_{23} , as described above for binary surfactant mixtures, can be used from Table 2. The values predicted for K_{m123} in this way are given in parenthesis for cationic–cationic–nonionic

ternary systems for both the series of surfactants in Table 2 along with the experimentally observed values. It can be seen that the average absolute difference of $\log K_{m123}$ between predicted and experimental values is about 0.1 log unit with a relative percentage deviation of less than 2.5% for all the PAHs used in this study. The only exception is solubilization of pyrene in the $C_{16}BzCl$ – $C_{16}Br$ –Brij58 system where the deviation is more. This is a remarkable result indicating that the experimental interaction parameters of binary surfactant systems may be used along with the micellar mole fraction values from RH treatment, proposed for multicomponent surfactant systems, to predict the K_m values of ternary surfactant systems. Further validation from the literature could not be made because no data presenting solubilization of PAHs in ternary surfactant systems are available.

To determine the mixing effect of surfactant systems on solubilization of PAHs, the deviation ratio (R) between the experimental molar solubilization ratio, MSR_{exp} , and the ideal value, MSR_{ideal} , can be evaluated by $R = MSR_{exp}/MSR_{ideal}$, where $MSR_{ideal} = \sum_i MSR_i \alpha_i$. MSR_i is the experimental MSR value of solubilize in the pure i -th surfactant solution whose bulk mole fraction in the mixture is α_i . Values of R , which characterize the mixture nonideality with respect to solubilization, are also presented in Table 2. $R > 1$ implies a positive mixing effect of surfactants on solubilization.

Except in the case of cationic–cationic binary systems, the values of R for all PAHs are greater than unity in all bi- and ternary surfactant mixtures. Because cationic–cationic binary systems form ideal mixed micelles as reflected in their similar α_i and X_i^M values, no significant gain in solubilizing efficiency is achieved by mixing two cationic surfactants with equal hydrophobic chain length and almost similar cmc values. This is in conformity with the lower values of K_1 , MSR , K_m and B . However, in the systems containing cationic and nonionic surfactants, there is a predominance of nonionic surfactant in the mixed micelles, which carry a slight positive charge due to incorporation of cationic surfactant. This facilitates micelle–water interface adsorption in addition to micellar core solubilization, characteristic of nonionics, resulting in the value of R greater than unity.

There is a great increase in R with the hydrophobicity of PAHs in the $C_{12}EBr$ –Brij30 system than for the $C_{12}Br$ –Brij30 system possibly due to the hydrophobic nature of the ethyl group attached to the head group of $C_{12}EBr$. A similar effect is observed in $C_{16}BzCl$ –Brij58 compared with the $C_{16}Br$ –Brij58 system. However, incorporation of one more cationic surfactant into the cationic–nonionic binary mixture decreases the value of R relative to that in the binary system. Again, R values were found to be greater for the more hydrophobic C_{16} surfactant mixed series compared to the C_{12} series.

$\log K_m$ – $\log K_{OW}$ Correlation. Experimental $\log K_m$ values of PAHs in various surfactant systems are correlated to the logarithm of their corresponding octanol–water partition coefficient, $\log K_{OW}$, according to the linear free-energy relationship,⁶²

$$\log K_m = a \log K_{OW} + b \quad (13)$$

where a and b are correlation constants, relying on the lipophilicity of the solvent. The slope a is a measure of the sensitivity of the solvent system to the changes in lipophilicity of solutes.⁶² $a < 1$ means lower sensitivity of a nonaqueous system to hydrophobicity of hydrophobic solute than in the octanol–water system. The results (Table 4) indicate $a > 1$ for all single, binary, and ternary systems in both the series, the

TABLE 4: Values of a and b Obtained from the Plot of Experimental $\log K_m$ vs $\log K_{OW}$ According to the Linear Free Energy Relationship $\log K_m = a \log K_{OW} + b$ for Single and Equimolar Mixed Surfactant Combinations at 25 °C^a

surfactant system	a	b	r^2
C ₁₂ Br	1.092	0.846	0.983
C ₁₂ EBr	1.119	0.786	0.983
Brij30	1.323	0.827	0.954
C ₁₂ EB–C ₁₂ Br	1.091	0.804	0.985
C ₁₂ Br–Brij30	1.159	0.791	0.956
C ₁₂ EBr–Brij30	1.169	0.796	0.945
C ₁₂ Br–C ₁₂ EBr–Brij30	1.144	0.808	0.955
C ₁₆ BzCl	1.130	0.811	0.984
C ₁₆ Br	1.125	0.757	0.981
Brij58	1.148	0.821	0.968
C ₁₆ BzCl–C ₁₆ Br	1.125	0.801	0.983
C ₁₆ BzCl–Brij58	1.226	0.682	0.971
C ₁₆ Br–Brij58	1.171	0.841	0.963
C ₁₆ BzCl–C ₁₆ Br–Brij58	1.146	0.900	0.962

^a Also shown are corresponding linear regression coefficients (r^2).

value for a single system being greater in the case of nonionics in both the series. Among the binary systems, the cationic–nonionic mixed systems present larger a values in a given series indicating the prevalence of a mixing effect of cat- and nonionic surfactants on the solubilization capacity as discussed earlier. Cationic–cationic mixtures exhibited more or less similar values of a as for individual systems, and ternary surfactant systems showed enhanced values in comparison. In general, single and mixed systems of the C₁₆ series of surfactants have higher values of a than the respective C₁₂ series systems due to larger chain length. The results, in general, show that these systems have superior PAH partitioning efficiency than that of the octanol–water system.

Conclusion

The present study represents a systematic investigation on the effects of hydrophobic chain length and hydrophilic groups of two series of cationic as well as nonionic surfactants with do- and hexadecyl chain lengths on solubilization of pyrene, naphthalene, and anthracene PAHs of increasing hydrophobic character. The solubilization capacity has been quantified in terms of MSR and $\log K_m$ values. In general, cationics, with quaternary ammonium head groups, exhibited lesser solubilization capacity than POE nonionics of the same hydrophobic chain length. Increase in hydrophobicity of head groups by incorporation of ethyl or benzyl groups enhanced the solubilization capacity of cationics. Surfactants with a 12 carbon hydrophobic chain showed a lesser capacity to solubilize PAHs than 16 carbon chain ones for both cationics as well as nonionics. Among equimolar binary combinations in each surfactant series, cationic–nonionic mixtures indicated better solubilization capacity than pure cationics, nonionics, or cationic–cationic mixtures, which in general is increased with increasing hydrophobic character of PAHs. However, cationic–cationic–nonionic ternary mixtures showed lower solubilizing efficiency than their binary cationic–nonionic counterparts, but higher than the cationic–cationic combinations. The study also gives insight into the applicability of RSA as applied to solubilizing efficiency of the binary surfactant system to be extended to multicomponent systems in analogy with its more frequent use to mixed micelle formation. This treatment has led to the prediction of $\log K_m$ values of ternary systems using the experimental interaction parameter B of binary surfactant systems. The analysis has yielded fair results and can, therefore,

provide valuable information for the selection of mixed surfactants for the SER of contaminated solutions.

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