



Study of mixtures of *n*-dodecyl- β -D-maltoside with anionic, cationic, and nonionic surfactant in aqueous solutions using surface tension and fluorescence techniques

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Abstract

Surfactants of practical interest are invariably mixtures of different types. In this study, mixtures of sugar-based *n*-dodecyl- β -D-maltoside with cationic dodecyltrimethylammonium bromide, anionic sodium dodecylsulfate, and nonionic pentaethyleneglycol monododecyl ether in solution, with and without supporting electrolyte, have been studied using surface tension and fluorescence spectroscopic techniques. Interaction parameters and mole fraction of components in mixed micelles were calculated using regular solution theory. The magnitude of interactions between *n*-dodecyl- β -D-maltoside and other surfactants followed the order anionic/nonionic > cationic/nonionic > nonionic/nonionic mixtures. Since all surfactants have the same hydrophobic groups, strengths of interactions are attributed to the structures of hydrophilic headgroups. Electrolyte reduced synergism between *n*-dodecyl- β -D-maltoside and ionic surfactant due to charge neutralization. Industrial sugar-based surfactant, dodecyl polyglucoside, yielded results similar to that with dodecyl maltoside, implying that *tested* commercial alkyl polyglucosides are similar to the pure laboratory samples in synergistic interactions with other surfactants. Fluorescence study not only supported the cmc results using tensiometry, but showed that interfaces of all the above mixed micelle/solution interfaces are mildly hydrophobic. Based on these results, an attempt is made to discover the nature of interactions to be a combination of intermolecular potential energies and free energy due to packing of surfactant molecules in micelles.

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1. Introduction

Alkyl polyglucosides have attracted considerable attention recently [1–7] due to their environmental compatibility [8,9] and outstanding physical properties such as low surface tension [10] and good electrolyte tolerance [11]. They have been successfully utilized for detergency, cosmetic, agriculture, and enhanced oil recovery applications [9,10]. However, polydispersity of alkyl polyglucosides has complicated understanding of the relationship between their structures and performance. *n*-Dodecyl- β -D-maltoside was used as a model substance to represent alkyl polyglucosides in this study.

The micellar size, shape, and aggregation number of dodecyl maltoside have been determined in the past by SANS

[12–14] technique. Other properties such as aggregation [15], adsorption [16], and phase behavior [17–19] have also been under investigation. Industrial surfactant systems are usually mixtures for economical as well as synergetic reasons. To maximize the beneficial synergistic effects, it is useful to understand interactions among surfactants in mixtures. Holland and Roubingh [20,21] have developed the regular solution theory (RST) for binary mixtures in solution with basic assumption that the entropy of mixing is zero and only enthalpy change contributes to nonideality. Interaction parameter β was introduced empirically to measure deviation of molecular interactions from ideality [22]. The regular solution theory approach was also extended to monitor the interactions in mixed monolayers at air/aqueous solution interfaces [23,24].

Research [25–30] on surfactant mixtures has been conducted in the past to study dodecyl maltoside interaction with nonionic [25,27], anionic [28–30], cationic [26], and

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zwitterionic surfactants [28,29]. The objective of this work is to measure interactions of mixtures of sodium dodecylsulfate, *n*-dodecyl trimethylammonium bromide and *n*-dodecyl pentaethylene with dodecyl maltoside with all of them having a 12-carbon chain but with different head groups. Dodecyl polyglucoside was selected for comparing the performance of dodecyl maltoside with industrial products. Thus all changes in the interactions are due to the differences in head groups. Fluorescence technique was used along with surface tension measurements to probe the polarity of the microenvironment of micellar/solvent interface.

2. Materials and methods

2.1. Surfactants

Nonionic *n*-dodecyl- β -D-maltoside of >95% purity from Calbiochem and dodecyl polyglucoside with 1.8 polymerization from Henkel Corp., nonionic ethoxylated surfactant pentaethyleneglycol monododecyl ether of >99% purity from Nikko Chemicals, anionic sodium dodecylsulfate of >99% purity from Fluka Chemicals and cationic dodecyltrimethylammonium bromide of >99% purity from TCI Chemicals were used as received.

2.2. Other chemicals

A.C.S. certified NaCl from Fisher Scientific Co. was used as received. Water used in all the experiments was triple distilled, with a specific conductivity of less than $1.5 \mu\Omega^{-1}$ and tested for the absence of organics using surface tension measurements. Fluorescence probe, pyrene, was obtained from Aldrich Chemicals and used as received.

2.3. Surface tension

The surface tension of nonionic and anionic surfactants and their mixtures was measured at 25 ± 1 °C with the Wilhelmy plate technique using a sandblasted platinum plate as the sensor. For each measurement, the sensor was in contact with surfactant solution for 30 min to allow equilibration. For cationic surfactant and its mixtures, adsorption of the cationic surfactant on platinum plate resulted in nonzero contact angle between plate and air/solution interface. In this case, surface tension was measured by drop volume method.

2.4. Fluorescence spectroscopy

A Photon Technology International PTILS-100 was used for fluorescence experiments. Surfactant solutions were prepared using pyrene saturated triple distilled water. The samples were excited at 335 nm and emission between 365 and 500 nm was recorded. In fluorescence spectroscopy, ratio of relative intensities of I_1 (373 nm) and I_3 (383 nm) peaks

(I_3/I_1) on a pyrene emission spectrum showed the greatest solvent dependency. Polarity at surfactant micelle/water interface [31] was estimated by calculating the polarity parameter I_3/I_1 .

2.5. Molecular modeling

Molecular structures and optimized geometry were constructed using Cache software from Fujitsu.

3. Results and discussions

All surfactants in this study had dodecyl chain as the hydrophobic tail. Any deviation from ideality could be ascribed to the differences between hydrophilic head groups.

3.1. Sugar-based surfactant/anionic surfactant mixtures

Interaction parameter β is a dimensionless parameter. $RT * \beta$ (R is the gas constant and T is the absolute temperature) is the difference in interaction energies between mixed and unmixed systems. Magnitude of β is a measure of the deviation of mixtures from single components. A negative β means synergism, namely, attractive interaction between surfactant molecules in mixed micelles than monomers in the bulk solution. A positive β indicates antagonism or demixing.

To calculate the interaction parameter, one has to solve surfactant micellar mole fraction first by iterative solution of following equation [26]:

$$\frac{X_1^2 \ln(\alpha_1 C_{12}/X_1 C_1^0)}{(1 - X_1)^2 \ln[(1 - \alpha_1)C_{12}/(1 - X_1)C_2^0]} = 1, \quad (1)$$

where X_1 is the mole fraction of surfactant 1 in mixed micelles, α_1 is the mole fraction of surfactant 1 in total concentration, C_1^0 , C_2^0 , and C_{12} are cmcs for surfactant 1, 2, and their mixture.

By introducing X_1 , the interaction parameter can be obtained from equation

$$\beta = \frac{\ln(\alpha_1 C_{12}/X_1 C_1^0)}{(1 - X_1)^2}. \quad (2)$$

Interactions of *n*-dodecyl- β -D-maltoside with a typical anionic surfactant, sodium dodecylsulfate, were studied first. Surface tension data obtained for *n*-dodecyl- β -D-maltoside, sodium dodecylsulfate, and 3:1, 1:1, and 1:3 *n*-dodecyl- β -D-maltoside/sodium dodecylsulfate mixtures at pH 6.5 and 25 °C are shown in Fig. 1 as a function of total concentration. Relevant data such as critical micellar concentrations, mole fractions of *n*-dodecyl- β -D-maltoside in mixed micelles, and interaction parameters of mixtures are given in Table 1. Mole fractions and interaction parameters were calculated using regular solution theory. Interaction parameter at mixing ratio of 0.25 in the literature [28] agrees well with the results obtained in this work. However, interaction parameters at other

Table 1

Results of surface tension data analysis for *n*-dodecyl- β -D-maltoside (DM)/sodium dodecylsulfate (SDS) mixtures without salt at 25 °C

| DM : SDS | 100 : 0 | 75 : 25 | 50 : 50 | 25 : 75 | 0 : 100 |
|-----------------------------|---------|---------|---------|---------|---------|
| cmc (M) | 0.00018 | 0.00020 | 0.00026 | 0.00044 | 0.008 |
| DM mole fraction in micelle | | 0.87 | 0.80 | 0.73 | – |
| Interaction parameter | | –4.00 | –3.77 | –3.25 | |

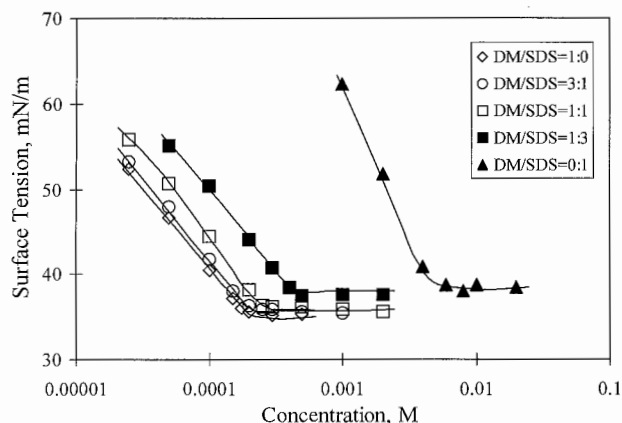


Fig. 1. Surface tension vs. concentration of *n*-dodecyl- β -D-maltoside and sodium dodecylsulfate mixed systems without salt, pH = 6.5, temperature 25 °C. DM and SDS stand for *n*-dodecyl- β -D-maltoside and sodium dodecylsulfate, respectively.

mixing ratios (0.5 and 0.75) differ significantly. pH and sample purity may cause such differences. In this paper, pH is maintained at 6.5 while the pH value is not specified in the literature. cmcs for single surfactants obtained in this study are higher than those in the literature, suggesting that sample used here in this work is possibly purer. Hence cmcs for mixtures are different, yielding different interaction parameters. It can be seen that dodecyl maltoside plays a predominant role in mixed micellization at various mixing ratios. In surfactant mixtures, the component with lower cmc usually is present in micelles and at air–water interface at a higher percentage because of its higher surface activity. These results are in accord with the fact that *n*-dodecyl- β -D-maltoside is much more surface active than sodium dodecylsulfate.

Interaction parameter β is between -4.0 and -3.25 for this system, indicating moderate interaction between *n*-dodecyl- β -D-maltoside and sodium dodecylsulfate. This β value is typical of nonionic–ionic mixed surfactant systems [28–30]. However, it should be noted that the interaction parameter decreases with increase in percentage of *n*-dodecyl- β -D-maltoside. The mixing of an ionic surfactant with the nonionic one can cause a decrease in the surface charge density of the micelles, so that mixed micelles of ionic and nonionic surfactants are more stable than the micelles containing only the ionic surfactant. Higher the mixing ratio with respect to *n*-dodecyl- β -D-maltoside, less is the surface charge density and hence the interaction is stronger. Both the hydrophobic interactions between the hydrocarbon chains and the ion–dipole interactions of the headgroups [32] contribute to the intra-molecular interactions and thus

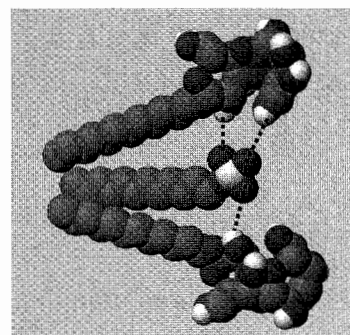


Fig. 2. Schematic of ion–dipole interactions between one sodium dodecylsulfate (middle) and two *n*-dodecyl- β -D-maltoside (top and bottom) molecules. Here blue, white, red, and yellow colors stand for carbon, hydrogen, oxygen, and sulfur atoms, respectively. The black dotted lines indicate the hydrogen bonding.

the interaction is stronger. The ion–dipole interactions of head groups are illustrated in Fig. 2. For simplification purposes, the hydrogen atoms on the hydrocarbon chain are not shown. Three oxygen atoms (except the one connecting with hydrocarbon chain) in the sulfate group of sodium dodecyl sulfate can be expected to interact with the hydrogen atoms in the hydroxyl groups of *n*-dodecyl- β -D-maltoside. Moreover, different surfactant headgroups at the micellar surface can reduce the steric repulsion by adjusting their conformations. Both partial charge neutralization and reduction of steric repulsion favor mixed micellization.

3.2. Sugar-based surfactant/cationic surfactant mixtures

Interactions of sugar-based *n*-dodecyl- β -D-maltoside with the cationic surfactant, dodecyltrimethylammonium bromide, were studied next under different mixing conditions. The surface tension results are exhibited in Fig. 3 as a function of the total concentration. Relevant data for these mixtures are listed in Table 2.

It can be seen from Fig. 3 and Table 2 that a small amount of *n*-dodecyl- β -D-maltoside does affect the surface tension of the mixture to a significant extent. Mole fraction of *n*-dodecyl- β -D-maltoside in micelle is much higher than that in the bulk solution, suggesting that *n*-dodecyl- β -D-maltoside is the dominant component in the micellar phase again due to its higher surface activity in comparison to that of dodecyltrimethylammonium bromide.

Again, the interaction parameter decreases from -1.54 to -0.43 with the increase in percentage of *n*-dodecyl- β -D-maltoside, indicating weak interactions between *n*-dodecyl- β -D-maltoside and dodecyltrimethylammonium bromide.

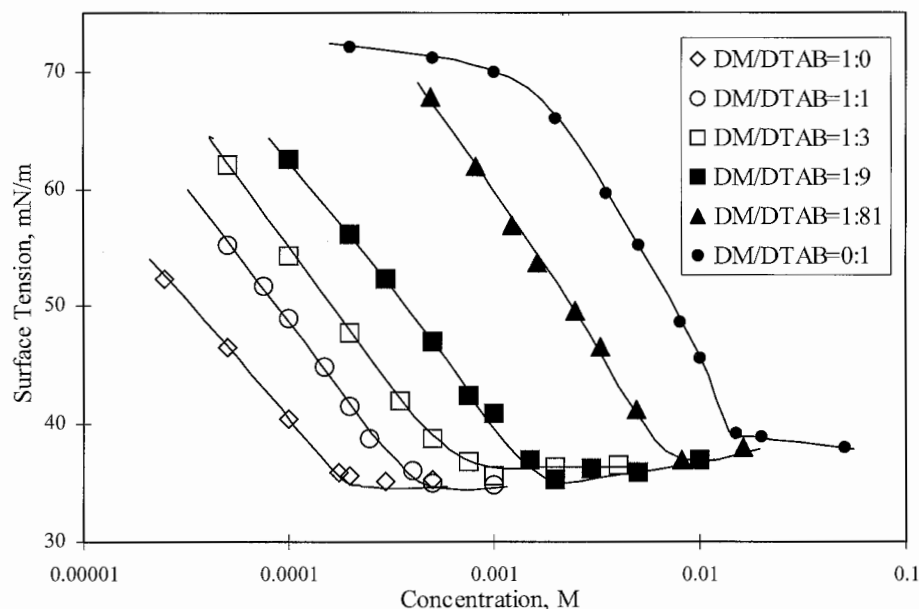


Fig. 3. Surface tension vs. concentration of *n*-dodecyl- β -D-maltoside and dodecyltrimethylammonium bromide mixed systems without salt at pH 6.5 and temperature of 25 °C. DM and DTAB stand for *n*-dodecyl- β -D-maltoside and dodecyltrimethylammonium bromide, respectively.

Table 2

Results of surface tension data analysis for *n*-dodecyl- β -D-maltoside (DM)/dodecyltrimethylammonium bromide (DTAB) mixtures without salt at 25 °C

| DM : DTAB | 1 : 0 | 1 : 1 | 1 : 3 | 1 : 9 | 1 : 81 | 0 : 1 |
|-------------------------------|---------|---------|---------|--------|--------|-------|
| cmc (M) | 0.00018 | 0.00035 | 0.00064 | 0.0015 | 0.0067 | 0.015 |
| DM mole fraction in micelles | | 0.95 | 0.90 | 0.83 | 0.51 | |
| Interaction parameter β | | -1.54 | -1.36 | -0.98 | -0.43 | |

The charge density of micelles is diluted with the addition of *n*-dodecyl- β -D-maltoside, resulting in stable micelles. Interestingly, this interaction, however, was less than that between *n*-dodecyl- β -D-maltoside and sodium dodecylsulfate. The weaker interaction in cationic/nonionic system is attributed to the fact that nitrogen atom in the hydrophilic group of dodecyltrimethylammonium bromide is screened by three methyl groups that hinder formation of ion-dipole interaction [33]. The small residual charge of a dodecyltrimethylammonium bromide micelle (0.23–0.36 [34–36]) supports this suggestion.

3.3. Sugar-based surfactant/nonionic ethoxylated surfactant mixtures

Even though sugar-based surfactants are nonionic, their interfacial properties are found to be quite different from that of the commonly used nonionic ethoxylated surfactants. For example, the sugar-based surfactant adsorbs on alumina but very little on silica [37] while the behavior of nonionic ethoxylated surfactants is an opposite [38,39].

Results obtained for surface tension of *n*-dodecyl- β -D-maltoside mixtures with pentaethylene glycol monododecyl ether are given in Fig. 4 and Table 3. Values obtained for cmcs are in agreement with those reported in the literature [11,13,21]. In these systems, pentaethylene glycol

monododecyl ether is more surface active than sugar-based surfactants, even though both have the same hydrocarbon chain. This suggests a higher hydrophilicity of two sugar groups than that of five ethoxylated groups. For nonionic surfactants, clouding phenomenon could be used to judge the hydrophilic properties. Dissolution of these surfactants in water relies on formation of hydrogen bonds between hydrophilic head and water molecules. *n*-Dodecyl- β -D-maltoside does not exhibit clouding up to 45% concentration [40] while pentaethyleneglycol monododecyl ether solutions clouds at much lower concentrations (0.02%) with a phase transition temperature of around 30 °C [41]. Since hydrophilic materials have high surface tension [42], the surface tension values above cmc are used here to test the above considerations. Experimental results show *n*-dodecyl- β -D-maltoside to have a higher surface tension of 35.5 mN/m than 30.0 mN/m for pentaethyleneglycol monododecyl ether.

Rosen et al. [43] have investigated interaction between *n*-dodecyl- β -D-maltoside and dodecyl hexaethoxyethanol by means of surface tension measurements and determined interaction parameter to be -0.05 . Similar value was determined to be 0.05 for mixtures of *n*-dodecyl- β -D-maltoside and pentaethyleneglycol monododecyl ether, indicating almost ideal mixing in solutions. These low values of interaction parameters are expected since both surfactants are

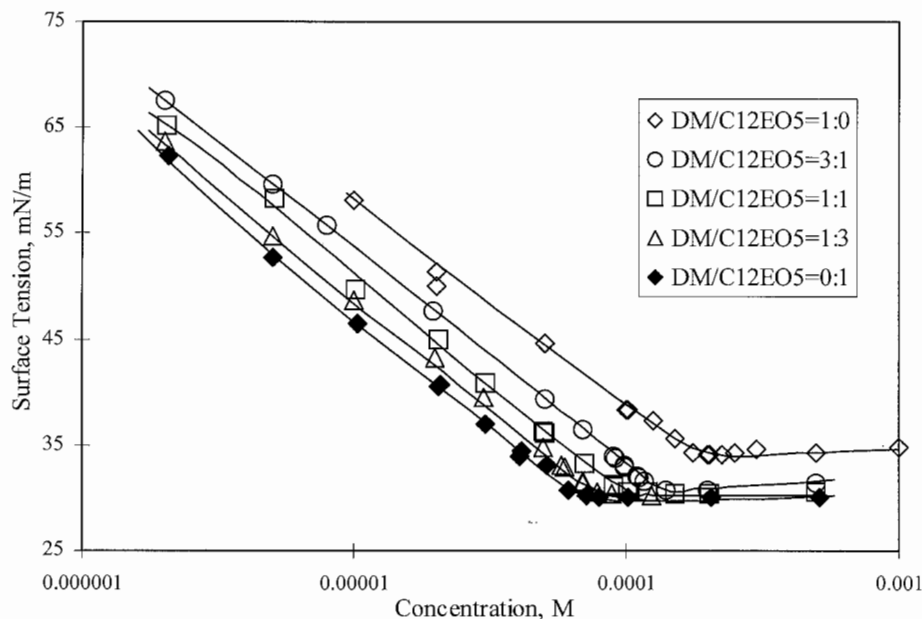


Fig. 4. Surface tension vs. concentration of *n*-dodecyl- β -D-maltoside and pentaethyleneglycol monododecyl ether mixed systems without salt, pH 6.5, temperature 25 °C. In above figure, DM and C12EO5 stand for *n*-dodecyl- β -D-maltoside and pentaethyleneglycol monododecyl ether, respectively.

Table 3

Results of surface tension data analysis for *n*-dodecyl- β -D-maltoside (DM)/pentaethyleneglycol monododecyl ether (C₁₂EO₅) mixtures without salt at 25 °C

| DM : C ₁₂ EO ₅ | 100 : 0 | 75 : 25 | 50 : 50 | 25 : 75 | 0 : 100 |
|--------------------------------------|---------|---------|----------|----------|----------|
| cmc (M) | 0.00018 | 0.00013 | 0.000096 | 0.000078 | 0.000065 |
| DM mole fraction in micelle | | 0.52 | 0.26 | 0.11 | |
| Interaction parameter β | | 0.11 | 0.03 | 0.01 | |

Table 4

Summary of results for sugar-based surfactant in mixtures. DM, SDS, APG, DTAB and C₁₂EO₅ stand for *n*-dodecyl- β -D-maltoside, sodium dodecylsulfate, dodecyltrimethylammonium bromide, and pentaethyleneglycol monododecyl ether, respectively

| Mixtures | Nonionic/anionic | | Nonionic/cationic | | Nonionic/nonionic | |
|--------------------|------------------|-----------|-------------------|------------|--------------------------------------|---------------------------------------|
| | DM : SDS | APG : SDS | DM : DTAB | APG : DTAB | DM : C ₁₂ EO ₅ | APG : C ₁₂ EO ₅ |
| β (w/o salt) | -4 to -3.25 | | -1.54 to -0.43 | | 0.01 to 0.11 | -0.106 |
| β (w/salt) | -2.89 | -3.20 | -0.62 | -0.41 | | |

nonionic. Possible driving forces for interaction can hence be considered to be dipole-dipole, dipole-induced dipole and London dispersion type. These forces are much weaker than the ion-dipole interaction for the ionic-nonionic surfactant mixtures discussed above.

3.4. Effect of salt

To study the effect of salt on surfactant interactions in mixed systems, surface tension of *n*-dodecyl- β -D-maltoside/sodium dodecyl sulfate and *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide mixtures of 1:1 mixing ratio was measured in 0.03 M NaCl solutions and results for interactions are given in Table 4. It is clear that the presence of salt does reduce the synergy between the surfactants. For *n*-dodecyl- β -D-maltoside/sodium dodecyl sulfate mixtures, interaction parameter is reduced from -3.77 to -2.89,

and for *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide system from -1.54 to -0.62. The decrease is mainly due to charge neutralization by sodium counterions for *n*-dodecyl- β -D-maltoside/sodium dodecyl sulfate and chloride ions for *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide mixtures. This also verifies the importance of electrostatic interaction in synergism.

3.5. Alkyl polyglucoside mixtures with other surfactants

To correlate behavior of laboratory dodecyl maltoside sample with that of industrial samples, an alkyl polyglucoside sample, dodecyl polyglucoside mixed with sodium dodecyl sulfate, dodecyltrimethylammonium bromide and pentaethyleneglycol monododecyl ether was studied. Results obtained for these mixtures are given in Table 4. Again, the sugar-based surfactant is the dominant one in alkyl

Table 5

Correlation of polarity parameter with surface tension results for *n*-dodecyl- β -D-maltoside (DM)/sodium dodecyl sulfate (SDS), *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide (DTAB), *n*-dodecyl- β -D-maltoside/pentaethyleneglycol monododecyl ether (C₁₂EO₅)

| Mixtures | Nonionic/anionic | | | Nonionic/cationic | | | Nonionic/nonionic | | |
|-----------------------------|------------------|--------|-------|-------------------|---------|-------|-------------------|--------|---------------------------------|
| | DM | 1 : 1 | SDS | DM | 1 : 1 | DTAB | DM | 1 : 1 | C ₁₂ EO ₅ |
| Cmc by fluorescence (mol/L) | 0.00019 | 0.0003 | 0.008 | 0.00019 | 0.00035 | 0.015 | 0.00019 | 0.0011 | 0.000066 |
| Polarity parameter > CMC | 0.83 | 0.83 | 0.83 | 0.83 | 0.80 | 0.75 | 0.83 | 0.85 | 0.85 |
| DM mole fraction in micelle | 0.801 | | | 0.954 | | | 0.263 | | |

polyglucoside/sodium dodecyl sulfate and alkyl polyglucoside/dodecyltrimethylammonium bromide systems. Interaction parameters for dodecyl polyglucoside/sodium dodecyl sulfate and alkyl polyglucoside/dodecyltrimethylammonium bromide systems are -3.20 and -0.41 , respectively, suggesting moderate synergistic interaction between dodecyl polyglucoside and sodium dodecyl sulfate, and weak interaction between dodecyl polyglucoside and dodecyltrimethylammonium bromide. In the case of dodecyl polyglucoside/pentaethyleneglycol monododecyl ether mixtures, the interaction parameter is -0.11 , close to that for ideal mixing. Similarities in interactions between *n*-dodecyl- β -D-maltoside and dodecyl polyglucoside with other surfactants imply that commercial polyglucosides are similar to the pure laboratory samples in synergistic interfacial interactions with other surfactants.

Surface tension of dodecyl polyglucoside above cmc was lower than that for *n*-dodecyl- β -D-maltoside due to the former being a mixture of surfactants with one and two sugar groups. Alkyl glucoside is hence less hydrophilic and more surface active than the maltoside. Thus, surface tension of decyl glucoside at cmc is 28.1 mN/m compared to 36.9 mN/m for decyl maltoside [43]. Dodecyl glucoside has a low solubility in water. The small negative interaction parameter for industrial sample and pentaethyleneglycol monododecyl ether supports the fact that mixtures of maltoside and polyethylene oxide surfactants have stronger interactions than those of laboratory *n*-dodecyl- β -D-maltoside with ethoxylated surfactants [44].

3.6. Fluorescence spectroscopy

To acquire information on the property of mixed micelles, surfactant mixtures were studied by fluorescence spectroscopic technique. Pyrene was polarity probe and polarity parameter, I_3/I_1 , was used to estimate the polarity at the micelle/solution interface. The polarity parameter of pyrene is determined as a function of concentration for the *n*-dodecyl- β -D-maltoside/sodium dodecyl sulfate, *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide and, *n*-dodecyl- β -D-maltoside/pentaethyleneglycol monododecyl ether mixtures, respectively.

At low surfactant concentrations, value of polarity parameter corresponded to that for water (0.5 – 0.6). Polarity parameter increased around cmc as measured by surface tensiometry. cmc values, polarity parameters of pyrene at concentrations above cmc and mole fraction of dodecyl mal-

toside in mixed micelles are given in Table 5. I_3/I_1 ratio for *n*-dodecyl- β -D-maltoside/sodium dodecylsulfate mixtures above cmc is similar to that for sodium dodecylsulfate and *n*-dodecyl- β -D-maltoside system, suggesting similar hydrophobicity for micelles of *n*-dodecyl- β -D-maltoside, sodium dodecyl sulfate and their mixtures. The polarity parameter number is less than those for hydrocarbons, suggesting that interface, as expected, is a mixture of hydrocarbon chains and small amount of water. The addition of salt increases polarity of the solvent as well as that at interface. For *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide system, I_3/I_1 ratio for *n*-dodecyl- β -D-maltoside above cmc is higher than that for dodecyltrimethylammonium bromide, suggesting that the interface of *n*-dodecyl- β -D-maltoside micelles is more hydrophobic than that of dodecyltrimethylammonium bromide micelles, possibly because of bulky nature of the trimethylammonium head group causing a less dense packing of hydrocarbon chains. In the case of mixtures, the predominance of *n*-dodecyl- β -D-maltoside in mixed micelle increases hydrophobicity for the mixture. Thus polarity parameter of *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide mixed micelle yields a more hydrophobic interface. Polarity parameter of *n*-dodecyl- β -D-maltoside/dodecyltrimethylammonium bromide mixed micelle is only slightly lower than that for *n*-dodecyl- β -D-maltoside. In the case of *n*-dodecyl- β -D-maltoside/pentaethyleneglycol monododecyl ether systems, I_3/I_1 for both *n*-dodecyl- β -D-maltoside and pentaethyleneglycol monododecyl ether are similar at concentrations higher than cmc, indicating similar hydrophobicities for interface of micelles of both surfactants. Since pentaethyleneglycol monododecyl ether is predominant in mixed micelles, polarity parameter of the mixed micelle is close to that for pentaethyleneglycol monododecyl ether. Thus in the case of mixtures of sugar-based surfactant with ionic ones, mixed micelle characteristics could be concluded to be similar to that of nonionic sugar-based surfactant.

4. Nature of interaction

Mixed cmc can also be predicted from phase separation model by assuming ideal mixing of components, that is, micellar activity coefficients of surfactant components are equal to unity [45]:

$$\frac{1}{C_{12}} = \sum \frac{\alpha_i}{C_i} \quad (3)$$

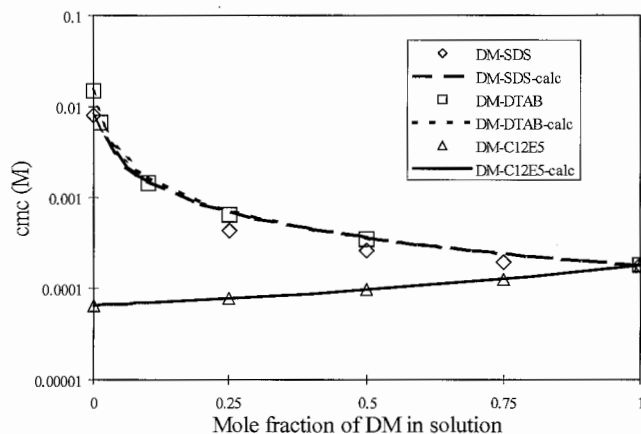


Fig. 5. Comparison of experimental data for *n*-dodecyl- β -D-maltoside, sodium dodecylsulfate, *n*-dodecyl- β -D-maltoside-dodecyltrimethylammonium bromide, *n*-dodecyl- β -D-maltoside-pentaethyleneglycol monododecyl ether with those calculated by assuming ideal mixing of components.

where α_i and C_i are composition and cmc of surfactant component i , respectively.

Cmcs of the three surfactant combinations obtained from theoretical calculations for ideal mixing are compared with those from surface tension measurements in Fig. 5. Calculated cmcs for *n*-dodecyl- β -D-maltoside mixtures with sodium dodecylsulfate obviously deviate from experimental results. A good agreement between theoretical and empirical results is seen in the case of *n*-dodecyl- β -D-maltoside and pentaethylene glycol monododecyl ether.

To understand the magnitude of the interaction parameters of surfactant mixtures, the potential energies for ion-dipole, dipole-dipole, induced dipole-induced dipole interactions are taken into account. Electrostatic interaction is very strong compared to other interactions. Magnitude of the intermolecular interactions follow an order: electrostatic interaction > ion-dipole > dipole-dipole > ion-induced dipole > dipole-induced dipole > London dispersion [46]. Ion-dipole interaction is responsible for properties of sodium dodecylsulfate and dodecyltrimethylammonium bromide mixtures with *n*-dodecyl- β -D-maltoside. Dipole-dipole, dipole-induced dipole, and London dispersion interaction are the main driving forces for pentaethyleneglycol monododecyl ether and *n*-dodecyl- β -D-maltoside mixtures. Since bulky loose structure of the hydrophobic head of dodecyltrimethylammonium bromide will prevent direct contact with hydroxyl groups in *n*-dodecyl- β -D-maltoside, this interaction can be expected to be less than that for sodium dodecylsulfate and *n*-dodecyl- β -D-maltoside.

Interaction parameter of *n*-dodecyl- β -D-maltoside and pentaethyleneglycol monododecyl ether is around zero as shown in Fig. 6. The data for the mixtures of *n*-dodecyl- β -D-maltoside with sodium dodecylsulfate and with dodecyltrimethylammonium bromide [40] are also given in this figure. There are decreasing trends in cationic-nonionic and anionic-nonionic surfactant mixtures. We have proposed these tendencies to be due to the asymmetry of ex-

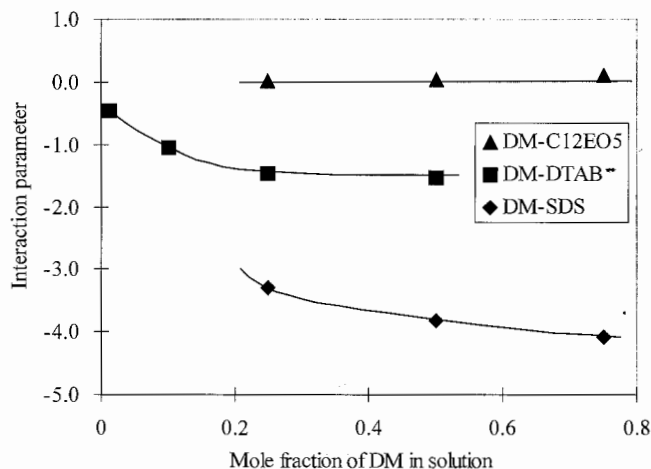


Fig. 6. Interaction parameter of *n*-dodecyl- β -D-maltoside with sodium dodecylsulfate, dodecyltrimethylammonium bromide and pentaethyleneglycol monododecyl ether as a function of mole fraction of *n*-dodecyl- β -D-maltoside in solution.

cess free energies with respect to the micellar compositions [47]. To simplify treatment of regular solution theory, only contribution of electrostatic interaction is considered for ionic/nonionic surfactant mixtures. However, steric interactions between surfactant hydrophilic heads and packing restrictions of the hydrophobic groups in the core can also be expected to contribute in this case. Shah and coworkers have found that maximum performance of surfactant mixtures occurs at a certain mixing ratio in accord with packing of molecules at air/water interface and in micelles [48–50].

5. Summary

Surface tensiometry and fluorescence spectroscopy have been used to study mixtures of sugar-based *n*-dodecyl- β -D-maltoside and dodecyl polyglucoside with cationic, anionic, and nonionic surfactants with and without supporting electrolyte. Interaction parameters estimated from surface tension data suggest interactions between *n*-dodecyl- β -D-maltoside with other surfactants to follow an order anionic/nonionic > cationic/nonionic > nonionic/nonionic. Moderate synergy between sugar-based surfactants with cationic and anionic surfactants is considered to be due to ion-dipole interactions. On the other hand, behavior of mixtures of nonionic surfactants is close to that for ideal mixing, synergistic effects being mainly due to entropic contributions of surfactant headgroups [51].

Presence of salt is found to reduce synergy between surfactants mainly due to charge neutralization by counter ions. Interaction parameter decreases with mole fraction of *n*-dodecyl- β -D-maltoside in dodecyl maltoside/sodium dodecylsulfate and dodecyl maltoside/dodecyltrimethylammonium bromide systems.

Polarity parameter, as determined by fluorescence, shows interfacial region of all mixed micelles/solution to be mildly

hydrophobic. Industrial dodecyl polyglucoside dodecyl polyglucoside yielded results similar to those for dodecyl maltoside, with similar synergistic interactions.

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