

Conductivity and Surface Tension Behavior for Binary Mixtures over a Various Concentration of TTAB

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Abstract : The conductances of trimethyltetradecylammonium bromide (TTAB) plus triphenyltetradecyl phosphonium bromide (TTPB) and TTAB plus trimethylhexadecylammonium bromide (HTAB) over the entire mole fraction range of TTAB were measured in water and in cyclodextrin plus water mixtures at fixed 4 and 8 mM of cyclodextrin at 30°C. The conductivity plot for both binary mixtures shows a single break from which the mixed critical micelle concentration and degree of micelle ionization were computed. From the slope of the conductivity curve, the equivalent ionic conductivities of the monomeric, associated, and the micelle states were calculated and discussed with respect to the surfactant-cyclodextrin complexation in the whole mole fraction range of both surfactant binary mixtures. The association constant *K* between the respective monomeric surfactant and cyclodextrin cavity of fixed 4 mM cyclodextrin was computed by considering 1:1 association from the surface tension measurement. A comparison among the *K* values for HTAB-cyclodextrin, TTAB-cyclodextrin, and TTPB-cyclodextrin shows that the former complexation is significantly stronger in comparison to the other ones due to the longer hydrophobic tail.

Keywords : conductivity, critical micelle concentration, cyclodextrin, surface tension, association.

1. Introduction

Cyclodextrin is an oligosaccharide consisting of seven glucose, and it belongs to a category of macrocyclic compounds which undergo predominantly hydrophobic interaction. The most significant property of cyclodextrin is to form strong inclusion complexes with the hydrophobic tail of amphiphilic molecule such as surface active agents and to impart significant influence on

the micellar properties of surfactants [1-6]. A lot of work has been done to study the inclusion complex formation between a variety of single ionic surfactants and the cyclodextrin cavity [7-10]. The present work deals with the mixed micelle formation by binary cationic surfactants in the presence of cyclodextrin. The mixed micelle formation between two unlike ionic surfactants is considered to be interesting in view of the generally more favorable properties achieved, such as better surface activity and aggregation behavior, in contrast to with individual surfactants in most commercial

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products [11-14]. Mixtures of ionic-nonionic and anionic-cationic surfactants show significant nonideal behavior whereas mixtures of structurally similar surfactants generally exhibit ideal mixing. In the present work, two kinds of binary cationic surfactant mixtures have been selected in view of their identical hydrophobic tails and different polar head groups in TTAB plus TTPB a vice versa in TTAB plus HTAB mixtures. Both binary mixtures are structurally similar and are expected to behave ideally the mixed state. Particularly for single surfactants, it has been observed that the magnitude of the binding constant between surfactant monomer-cyclodextrin cavity depends on the hydrophobicity of the surfactant hydrophobic tail and on the nature substituted cyclodextrin [15-18].

Apart from this, phosphorescence study of 1-bromonaphthalene (1-BrN) in sodium dodecylbenzenesulfonate and cyclodextrin solutions has revealed the formation of a 1:1:1 ternary inclusion complex in which the phenyl of SDBS and resides in the apolar cavity of cyclodextrin whereas the polar head group and a part of the hydrocarbon tail are located outside the cavity. Therefore, in view of the above factors, it is expected that the presence of cyclodextrin may also influence the proposed ideal mixing behavior of TTAB plus TTPB and TTAB plus HTAB mixtures in present work. It has also been observed that the surfactant-cyclodextrin inclusion complex has predominant and sometimes 1:2 stoichiometry rather than 2:1. Therefore it is expected herein that mainly a 1:1 inclusion complex formed between the single surfactant monomer and the cyclodextrin cavity rather than a 2:1 complex in which two monomers are simultaneously inserted into the cyclodextrin cavity. Hence, the association constant between a surfactant monomer and the cyclodextrin cavity has also been computed from the surface tension measurement.

2. Experimental

Cyclodextrin (CD), trimethyltetradecylammonium bromide (TTAB), triphenyltetradecylphosphonium bromide (TTPB) and trimethylhexadecylammonium bromide (HTAB), all reagent from Sigma company were used after purification. Conductivity water was used in the preparation of all solutions. The conductivity measurement at 30°C was carried out at a fixed frequency of 1000 Hz with a digital conductivity meter (Model NDC-732) manufactured by Naina Electronics. A dip-type conductivity cell with double-walled jacket to circulate the thermostatted water was used for all the measurements. Precise conductances of TTAB plus TTPB and TTAB plus HTAB mixtures over the entire mole fraction range in water and cyclodextrin/water containing 4 and 8 mM of cyclodextrin were measured.

Surface tension measurements of TTAB, TTPB, and HTAB in pure water and in the presence of 4 mM of cyclodextrin were carried out by Wilhelmy plate method (Luda surface tensiometer model TD1) with an estimated error of $\pm 0.2 \text{ mNm}^{-1}$. The conductivity (κ) plots for both TTAB plus TTPB and TTAB plus HTAB mixtures show a single break over the whole mole fraction range in pure water and cyclodextrin/water systems, which represents micelle formation by single and mixed surfactants. Since the variation in the κ of the present mixed surfactants in pure water and in different amounts of cyclodextrin are the same, κ plots for only 4 mM cyclodextrin been shown in Fig. 1. From the break in the κ plots, the critical micelle concentration (cmc) was calculated by fitting the linear portions in the premicellar and in the postmicellar regions in a straight line equation with a correlation factor always better than 0.999. The cmc value was obtained from the intersection point of two straight line. Similarly, the surface tension

(v) plots (Fig.2) for single surfactants also show a single break from which the cmc was obtained.

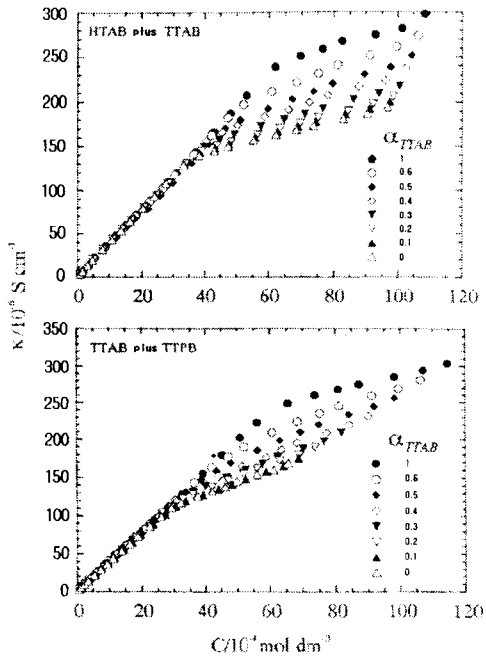


Fig. 1. Plot of κ versus total surfactant concentration (C) for TTAB plus HTAB in aqueous 4 mM cyclodextrin at various mole fractions of TTAB (α TTAB). Plot of κ versus total surfactant concentration (C) for TTAB plus TTPB in aqueous 4 mM cyclodextrin at various mole fraction of TTAB (α TTAB).

3. Results and Discussion

In order to evaluate the conductivity behavior over the whole mole fraction range of the present surfactant mixtures, the equivalent conductance of the monomeric (Λ_m), associated (Λ_{ass}), and the micelle (Λ_{mic}) state were calculated. In the presence of cyclodextrin, the conductivity of the surfactant solution in the associated state of

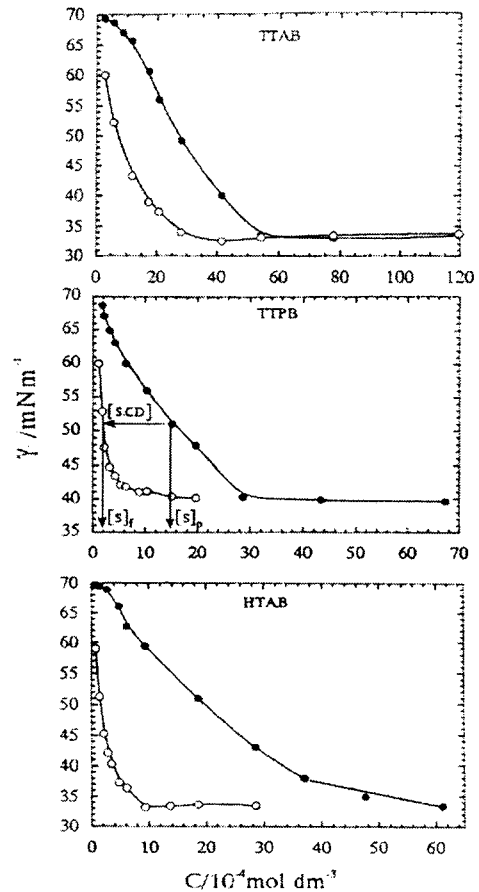


Fig. 2. Plot of surface tension (γ) versus concentration (C) of TTAB, TTPB, and HTAB in pure water (o) and 4 mM aqueous cyclodextrin (●).

the surfactant electrolyte (Λ_{ass}) can be determined from the slope of the κ line in the premicellar region in the presence of cyclodextrin. Similarly, Λ_m can be obtained in the absence of cyclodextrin. On the other hand, since the conductivity of the monomers remains almost constant after the cmc, Λ_{mic} can be calculated from slope of the κ line in the postmicellar region with reference to the monomer conductivity. The Λ values thus obtained for TTAB plus TTPB and TTAB plus HTAB mixtures in different states have been plotted in Fig. 3. The Λ_{mic} values for various colloidal electrolytes have been

mostly in the range $15\text{--}35\text{ S cm}^2\text{ mol}^{-1}$ even in the presence of different kinds of additives. Thus the Λ_{mic} values demonstrated in Fig. 3 for both the binary mixtures seem to be reasonable. These values are somewhat closer to the present $\Lambda_{\text{ass}}=76\text{ S cm}^2\text{ mol}^{-1}$ and $\Lambda_{\text{mic}}=20\text{ S cm}^2\text{ mol}^{-1}$ for the same system with $[\text{CD}]=4\text{ mM}$, but the present values decrease significantly with the increase in $[\text{CD}]$ up to 8 mM . This suggests that at 8 mM of $[\text{CD}]$ apart from 1:1, other stoichiometries of the surfactant-CD inclusion

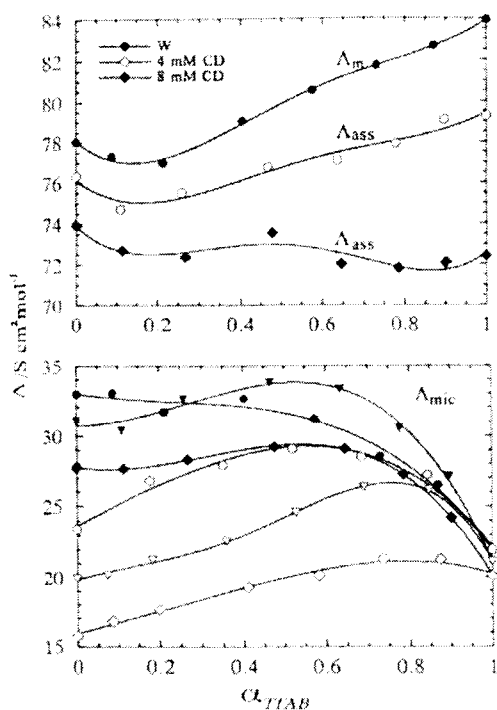


Fig. 3. Plot of equivalent conductivity (Λ) versus α_{TTAB} for TTAB plus TTPB in pure water and aqueous cyclodextrin. Plot of micelle conductivity (Λ_{mic}) versus α_{TTAB} in pure water (circles), 4 mM CD (triangles), and 8 mM CD (rectangles). Filled symbols are for TTAB plus TTPB and open symbols are for TTAB plus HTAB mixtures.

complex may also exist. The values for TTAB plus TTPB mixtures in pure water from κ measurements are listed in Table 1.

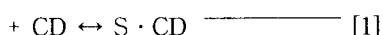
Table 1. Values of $\text{cmc}/10^{-4}\text{ mol}\cdot\text{dm}^{-3}$, χ , and β of TTAB plus TTPB Mixtures in Pure Water at 30°C

$\alpha_{\text{TTAB plus}}$ α_{TTPA}	$\text{cmc}(10^{-4}\text{ mol}\cdot\text{dm}^{-3})$	χ	β
0.0881	11.5 ± 0.3	0.39	-
0.1566	11.45 ± 0.4	-	-
0.2129	13.9 ± 0.5	0.37	-
0.3170	14.4 ± 0.5	-	-
0.4035	15.4 ± 0.7	0.38	0.98
0.4812	15.3 ± 0.2	-	-
0.5750	19.0 ± 0.3	0.36	0.62
0.6500	20.0 ± 0.3	-	0.26
0.7301	24.4 ± 0.4	0.33	0.73
0.8229	25.9 ± 0.5	-	0.17
0.8712	29.9 ± 0.5	0.31	0.67
0.9285	32.1 ± 0.6	0.29	-

A comparison between Λ_{m} and Λ_{ass} shows that Λ_{ass} is always less than Λ_{m} for TTAB plus TTPB and TTAB plus HTAB mixtures over the whole mole fraction range in the premicellar regions (Fig. 3a), and Λ_{ass} further decrease with the increase in the amount of CD from 4 to 8 mM . A similar behavior for Λ_{mic} (Fig. 3b) can also be observed. The small Λ_{ass} values in comparison to Λ_{m} are obviously due to the strong inclusion complex formation between the surfactant monomers and the CD cavity, and Λ_{ass} further decreases with the increase in the amount of

cyclodextrin, since more free monomers are being complexed. On the other hand, the lowest value of Λ_{mic} in comparison to Λ_m and Λ_{ass} is mainly due to the bulkiness of the micell state electrolyte in comparison to the monomer state. It is interesting to observe the variation in different Λ values of the whole mole fraction range. The variation in Λ_m and Λ_{ass} of TTAB plus HTAB with respect to α TTAB is quite constant, suggesting an additive contribution of unlike monomers toward the conductivity in the absence and presence of CD. However, a clear nonlinear variation in Λ_m and Λ_{ass} can be observed for TTAB plus TTPB mixtures (Fig. 3a), and the slope of the perspective curve decreases with the increase in the amount of CD. On the other hand, Λ_{mic} values (Fig. 3b) for TTAB plus TTPB mixtures show a significant fall in comparison to TTAB plus HTAB of the TTAB-rich region of the mixture, which may suggest that the mixed micelles of TTAB plus TTPB are primarily rich in TTPB rather than in TTAB even in the presence of CD.

In order to explore the extent of surfactant-CD interactions, the association constant (K) between the unlike surfactant monomer and CD in the premicellar region has been computed in 4 mM of CD from surface tension data taking into consideration 1:1 association. It can be written as



with the association constant, K , equal to

$$K = \frac{[S \cdot CD]}{[S]_f [CD]_f} \quad [2]$$

where $[CD]_f$ and $[S]_f$ are the free CD and monomeric surfactant concentration, respectively. The total CD concentration can be written as

$$[CD]_0 = [CD]_f + [S \cdot CD] \quad [3]$$

Similarly, the total surfactant concentration can be written as

$$[S]_0 = [S]_f + [S \cdot CD] \quad [4]$$

The following relation can be obtained after combining Eqs. [2]-[4]:

$$K = \frac{[S]_0 - [S]_f}{([CD]_0 - [S]_0 + [S]_f)[S]_f} \quad [5]$$

A rearrangement of Eq. [5] will lead to

$$[S] + [S]_0 - [S]_f = -\frac{1}{K} \left(\frac{[S]_0}{[S]_f} - 1 \right) + [CD]_0 \quad [6]$$

The $[S]_f$ can be calculated from the γ profiles in Fig. 2. The increase in the total monomeric surfactant concentration, i.e., $[S]_0$, at a particular γ value in the premicellar region in the presence of CD is a measure of the amount of surfactant bound ($[S]_0 - [S]_f$) to CD (Fig.2). It follows from Eq. [6] that a plot of $[S]_0 - [S]_f$ versus $[S]_0/[S]_f$ or $[S]_0/[S]_f - 1$ should be a straight line with $-1/K$ as slope. The K values thus computed for TTAB, TTPB, and HTAB are 253, 115, and 481 m^{-1} , respectively. The Largest K value for HTAB can be easily understood from the longest hydrophobic tail in comparison to TTAB or TTPB.

The degree of micelle ionization (α) is closely related to the micellar transitions; therefore, a α value computed by a suitable method can give significant information about the nonideality in the mixed state. In the present work, the choice of TTAB plus TTPB and TTAB plus HTAB mixtures was also due to the common BR⁻ counterion in the mixed state, and hence the mixtures can be treated as a single surfactant solution. The degree of micelle ionization has been calculated by the method suggested by Evans

(20) based upon Stokes' law for the mobility of the micelles, and the micelles are considered to be spherical in shape. It is given by

$$x = (n - m)/n \quad [7]$$

where n is the micelle aggregation number and m is the number of micelle-bound counterions. The n and m are related through the relation

$$1000S_2 = \frac{(n-m)^2}{n^{4/3}}(1000S_1 - \Lambda_{br..}) + \left(\frac{n-m}{n}\right)\Lambda_{br..} \quad [8]$$

where S_1 and S_2 are the slopes of the specific conductivity versus concentration plot in the pre- and the postmicellar regions, respectively. In order to calculate x , an arbitrary value must be given to n .

The value of x is quite insensitive to n . For example, choosing 40, 60, and 80 as the values of n for TTAB, 0.27, 0.28, and 0.29 values, respectively, were obtained for x . Therefore, a value of n is equal to 60 was selected for the present work. The x value of n is equal to 60 was selected for the present work. The x values thus obtained for single surfactants in pure water and in the presence of CD are listed in Table 1, and they have also been compared with those available in the literature from the free electrophoretic method. Good agreement can be observed between the present and the previously reported values. These values for TTAB plus HTAB in pure water, as well as in the presence of CD, predominantly vary linearly over the whole mole fraction range, whereas for TTAB plus TTPB, they pass through a maximum around $\alpha_{TTAB}=0.5$ in pure water (Table 1), as well as in the presence of CD. This suggests that TTAB plus TTPB mixtures undergo stronger structural changes in comparison to TTAB plus HTAB mixtures.

The mixed cmc values for TTAB plus

TTPB and TTAB plus HTAB mixtures in pure water, 4 mM CD, and 8 mM CD are plotted in Fig. 4. The cmc values for both the binary mixtures are significantly higher in the presence of CD than those in pure water, and the values increase with the increase in the amount of CD. Therefore, it can be said that this general behavior for the single ionic surfactants in the presence of CD can also be extended to the binary cationic mixed surfactants. Before discussing the mixing behavior of the present mixtures in the presence of CD, it would be better to evaluate it first in pure water by using the pseudo-phase thermodynamic model. The model relates the ideal mixed cmc(cmc^*) to the cmc of the pure components by the equation

$$\frac{1}{cmc^*} = \frac{\alpha_1}{cmc_1} + \frac{(1-\alpha_1)}{cmc_2} \quad [9]$$

where α_1 is the mole fraction of surfactant 1 (TTAB) in the mixed solute, and cmc_1 and cmc_2 are the critical micelle concentrations of

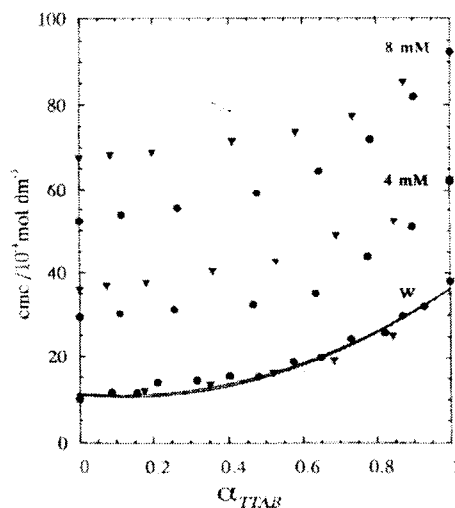


Fig. 4. Plot of cmc versus α_{TTAB} in pure water and aqueous cyclodextrin, experimental data (points) and cmc (solid line). Circles are for TTAB plus TTPB and triangles are for TTAB plus HTAB mixtures.

components 1 and 2, respectively. For the presence structurally similar binary mixtures, the ideal behavior is respected since the interactions between the monomers in the mixed micelles are considered to be similar as in the case of homomicelles, and hence the activity coefficients should be take as unity. The cmc^* values thus calculated using Eq. [9] have also been plotted in Fig. 4. The variation in these values in the case of pure water almost predicts the ideal behavior. This can be further evaluated by considering the regular solution formation based on the phase separation model of micellization which relates the mixed cmc to the individual cmc , i.e., cmc_1 and cmc_2 , by

$$a_1 cmc = x_1 f_1 cmc_1 \quad \text{[10]}$$

and

$$a_2 cmc = x_2 f_2 cmc_2 \quad \text{[11]}$$

where a_1 , a_2 , x_1 , x_2 , and f_1 , f_2 are the mole fractions in the bulk, the mole fractions in the mixed micelle, and the activity coefficients of surfactant 1 (TTAB) and surfactant 2 (HTAB) plus (TPPB), respectively. The value of x_1 can be computed from the following equation [12] :

$$\frac{x_1^2 \ln(cmca_1 / cmc_1 x_1)}{(1-x_1)^2 \ln(cmc(1-a_1 / cmc_2(1-x_1)))} = 1 \quad \text{[12]}$$

Equation [12] can be solved iteratively to obtain the value of x from which the interaction parameter, β , can be computed using Equation [13]:

$$\beta = \frac{\ln(cmca_1 / cmc_1 x_1)}{(1-x_1)^2} \quad \text{[13]}$$

The β value demonstrates the extent of interactions between the two surfactants

which lead to the deviations from the ideal behavior. Within the regular solution approximation, the value should be constant with respect to the change in composition for a given binary surfactant mixture. The average β values computed for TTAB plus TPPB and TTAB plus HTAB mixtures in pure water are 0.53 ± 0.30 and -0.43 ± 0.14 , respectively. As far as the magnitude of these values is concerned, they represent an almost ideal mixing behavior of both binary mixtures. Therefore, keeping in view the ideal mixing of the present surfactant mixtures in pure water, it is possible to determine the CD contribution to the mixed micelle formation (Δcmc) for both mixtures. This is based on the fact that the mixed cmc values for both the binary mixtures be quite close to each other in pure water and are the result of an almost ideal mixing of unlike monomers. The Δcmc can be calculated by subtracting the cmc in pure water from that in the presence of CD (i.e., $\Delta cmc = cmc(cd) - cmc(w)$) at a particular mole fraction.

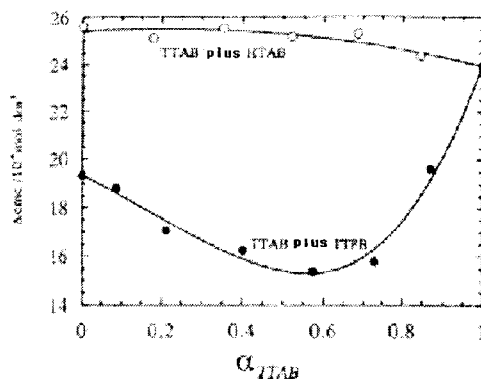


Fig. 5. Plot of Δcmc versus α_{TTAB} .

Fig. 5 shows such a contribution in the presence of 4 mM CD for both the binary mixtures. First of all, the Δcmc values are significantly higher in the HTAB-rich region of TTAB plus HTAB mixtures in comparison

to the TTPB-rich region of TTAB plus TTPB mixtures, indicating a strong association in HTAB-CD rather than in TTPB-CD. Interestingly, the Δc_{mc} curve for TTAB plus HTAB shows a more or less constant variation with the increase in α TTAB, demonstrating an almost equal CD effect over most of the mole fraction range. In contrast, in the case of TTAB plus HTAB mixtures, Δc_{mc} values run through a strong minimum around equimolar proportions. This indicates that the CD contribution decreases with the increase in α TTAB particularly in the TTPB-rich region of the mixture. Thus, a decrease in the CD contribution can only be ascribed on the basis of the participation of TTPB-CD complex in the mixed micelle formation. It is expected that the presence of three phenyl rings in the polar head group region of TTPB may impart additional hydrophobicity to TTPB-CD complex, which may help it undergo mixed micelle formation more favorably.

4. Conclusions

Conductivity and surface tension measurements have been performed on mixed cationic TTAB plus TTPB and TTAB plus HTAB surfactant mixtures in aqueous β -cyclodextrin solutions. It has been observed that TTAB, TTPB, and HTAB undergo 1:1 complexation with the cyclodextrin cavity. This complexation leads to a drastic change in the single and mixed surfactant properties in both the pre- and the postmicellar regions. An analysis of the mixing behavior of both the mixtures in the presence of cyclodextrin shows that the mixing behavior of TTAB plus HTAB mixtures remains close to the ideal state, whereas that of TTAB plus TTPB mixtures deviates from ideality due to the participation of TTPB-CD 1:1 complex in the mixed micelle formation.

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