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Partition constants of alcohols and surfactants in mixed alcohol/10-carbon dimeric amphiphile aggregates from NMR-diffusion experiments

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The partition constants (*p*-values) of primary alcohols in solutions containing aggregates of some symmetric dimeric (gemini) surfactants *N*,*N*′-dimethyl,*N*-*N*′-didecyl-α,ω-alkanediammonium dibromide (10-*s*-10 gemini surfactants) have been computed from the diffusion coefficients *via* NMR spectroscopy. From the partition constants, thermodynamic partition coefficients and Gibbs energies of transfer for the alcohols from the bulk D_2O phase to the dimeric aggregate phase have been calculated. For 10-6-10 and 10-8-10 surfactants, the partition constants for two primary alcohols, 1-butanol (C_4OH) and 1-pentanol (C_5OH), increased with increasing the amount of the surfactant in the solution, while the thermodynamic partition coefficients and the calculated Gibbs transfer energies were constant with increasing surfactant concentration. The partition constants and the thermodynamic partition coefficients for a series of homologous alcohols in the 10-series dimerics were determined at a surfactant concentration corresponding to 100 mg mL^{-1}; the Gibbs energy of transfer (obtained from the thermodynamic partition coefficients) decreased linearly with the alcohol carbon length for each of the primary alcohol/gemini amphiphile series studied. Finally, the diffusion coefficients for the surfactants were used along with the diffusion coefficients of the aggregates to obtain partition constants of the dimeric surfactants in mixed aggregates composed of C_4OH and C_5OH in both 10-6-10 and 10-8-10; our results indicated the surfactant partition constants increased with increasing surfactant concentration in excellent agreement with our previous work and the literature. All these results were used to obtain a comprehensive description of the alcohol/surfactant mixed micelles as a function of the composition of the system, and to examine the applicability of the pseudo-phase separation model to describe the phenomenon of solubilization in the formation of mixed micelles.

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Introduction

Surfactant aggregates can be used to solubilize substances that are otherwise sparingly soluble or insoluble in water, resulting in the formation of mixed aggregates in solution.[1–7] The solubilization, or partitioning of these neutral molecules (*e.g.*, *n*-alcohols, amines, ketones) can be described in terms of a thermodynamic partition coefficient (either mole-fraction based – K_X or concentration based – K_C).[1,8–17] In the context of the simple phase separation model of micelle formation, this partitioning is best described as an equilibrium of the solubilizate between the "aggregate phase" and the bulk aqueous solution. Hence, K_X values for partitioning of neutral solubilizates (additives) can be calculated as follows

$$K_X = \frac{X_{a,agg}}{X_{a,aq}} \quad (1)$$

where $X_{a,agg}$ and $X_{a,aq}$ are the mole fractions of the additives (solubilizates) in the aggregate phase and aqueous phases, respectively. In terms of molar concentration, the partition coefficient K_C is calculated by dividing the amount of additive in the aggregate phase $C_{a,agg}$ by the amount of the solubilizate in the aqueous phase, $C_{a,aq}$,

$$K_C = \frac{C_{a,agg}}{C_{a,aq}} \quad (2)$$

It is readily apparent that determining the amount of solubilizate that "partitions" into the micellar phase is key in understanding the fundamental effects these neutral

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solubilizates have on the formation of mixed micelles in solution. The partition constant (p-value) of the solubilizate is defined as follows

$$p = \frac{c_{a,mic}}{c_{a,t}} \quad (3)$$

where $c_{a,mic}$ is the concentration of solubilizate (additive) in the aggregates and $c_{a,t}$ represents the total concentration of additive. The partitioning of additives in micellar systems can be obtained *via* several techniques;[18] in our lab, we have focussed on using NMR measurements of solubilization to study partitioning *via* the nuclear magnetic resonance (NMR) paramagnetic relaxation experiment,[19–21] or the measurement of diffusion coefficients.[22–24]

Dimeric surfactants have two head groups connected by a linking chain, known as the spacer group.[25–33] The most commonly studied dimeric surfactants are the dicationic gemini amphiphiles of the type *N*,*N*′-bis (dimethylalkyl)-α,ω-alkanediammonium dibromide (m-*s*-m), an example of which is *N*,*N*′-bis (dimethyldecyl)-α,ω-hexanediammonium dibromide (10-6-10).[32,34–40] Dimeric surfactants are superior to conventional single-headed, single-tailed surfactants with respect to a number of aggregate properties (*e.g.*, critical micelle concentrations, surface activity, cold-water solubility and hard-water tolerance) when compared to conventional surfactants.[25–28,41,42] Despite the fact that surfactants are heavily used commercially as solubilizing and emulsifying agents, few studies concerning the solubilizing power of dimeric surfactants exist in the literature.[43–50] In our previous paper,[23] we examined the partitioning of primary alcohols in a number of symmetric cationic dimeric surfactants and concluded that the partitioning of the alcohol between the aqueous phase and the aggregate phase was mostly dependent on the inherent hydrophobicity of the alcohol, *i.e.*, the calculated thermodynamic partition coefficients were independent of both the chain length and the spacer length of the dimeric surfactant. In this paper, we further explore the solubilization of primary alcohols by the aggregates comprised of a series of 10-carbon symmetric gemini surfactants as a function of the spacer length of the surfactant, the surfactant concentration, and the amount of alcohol added to the system. The surfactants chosen specifically for this work were some members of the 10-series gemini surfactants, namely 10-4-10, 10-6-10, 10-8-10, and 10-10-10. The partition constants of primary alcohols in these surfactants have been determined from diffusion NMR experiments and these values were used to obtain both mole-fraction and concentration based thermodynamic partition coefficients. Gibbs transfer energies ($\Delta_{tr}G^0$ values) of the alcohol from the aqueous phase (in this case D_2O) to the aggregate phase of the symmetric gemini amphiphiles were calculated from the distribution coefficients. The partition constants of the surfactants in a series of mixed aggregates composed of various concentrations of C_4OH and C_5OH were also determined by applying eqn (3) to the surfactant diffusion data. The results are discussed in terms of the solubilization of the alcohol molecules as a function of the concentration of both the surfactants and the alcohols in the system, as well as the applicability of the simple two-site model as an appropriate description for the partitioning of solubilizates in these 10-series dimeric surfactants, and the change in the composition of the mixed aggregates as a function of the system composition.

Experimental section

Materials

The symmetric m-s-m gemini surfactants were synthesized using the recently developed microwave method of Singer *et al.*[51] The structures for the gemini surfactants used in the work are given in Table 1. All the reagents used to prepare the surfactants were obtained from either Sigma or TCI America and were the highest quality available (≥95%); no efforts were made to additionally purify the synthetic reagents.

The alcohols used in the present work were obtained from Sigma or TCI America and were the highest quality available (≥98%); no efforts were made to further purify the alcohols. D_2O (99.9 atom% D) was obtained from CDN Isotopes and was used as received.

NMR-diffusion measurements

The diffusion coefficients for the alcohols in both D_2O and the aggregates were obtained on a Bruker Advance II NMR spectrometer, operating at 400.13 MHz for protons, using the standard-issue Bruker gradient probe. Stock solutions of the surfactants (100 mg mL^{-1}) were prepared in D_2O; the different concentrations of the surfactants were prepared directly in the NMR tubes by diluting the appropriate amount of the stock solutions to the final specified concentration with D_2O; the alcohols were injected directly in the NMR tubes using calibrated micropipettes.

The pulse sequence used for the determination of the D values was the longitudinal eddy current delay bipolar gradient pulse (ledbpgp2s) from the standard Bruker software library in conjunction with the standard Bruker program, DOSY. For these systems, we used 16 or 32 scans to obtain the spectra at each gradient value and a total of 16 FID's per experiment were collected. The diffusion time and the gradient length for the experiments were optimized as we had described previously.[23,52] The diffusion coefficients were obtained from the signal decay

Table 1 Structures, names, and abbreviations of the of the *m-s-m* dimeric amphiphiles used in the present paper

Name	Structure	Abbreviation
N,*N*′-didecyl-*N*,*N*,*N*′,*N*′-tetramethylbutane-1,4-diaminium dibromide	$C_{10}H_{21}N(CH_3)$–$(CH_2)_4$–$N(CH_3)_2C_{10}H_{21}Br_2$	10-4-10
N,*N*′-didecyl-*N*,*N*,*N*′,*N*′-tetramethylhexane-1,4-diaminium dibromide	$C_{10}H_{21}N(CH_3)_2$–$(CH_2)_6$–$N(CH_3)_2C_{10}H_{21}Br_2$	10-6-10
N,*N*′-didecyl-*N*,*N*,*N*′,*N*′-tetramethyloctane-1,4-diaminium dibromide	$C_{10}H_{21}N(CH_3)_2$–$(CH_2)_8$–$N(CH_3)_2C_{10}H_{21}Br_2$	10-8-10
N,*N*′-didecyl-*N*,*N*,*N*′,*N*′-tetramethyldecane-1,4-diaminium dibromide	$C_{10}H_{21}N(CH_3)_2$–$(CH_2)_{10}$–$N(CH_3)_2C_{10}H_{21}Br_2$	10-10-10

curves using the standard Bruker T_1/T_2 software. It has been well established in the literature that for these systems, the exchange of the alcohol between the aqueous and aggregates phases is fast on the NMR timescale;[53–57] hence, the diffusion coefficients were extracted from the mono-exponential decay curves collected *via* the Bruker software. All the NMR experiments were run at a controlled, fixed temperature of 298.2 K. It is well-known that the viscosity of the medium can affect the mass-transport of the solubilizates, which can, in turn affect the calculation of the partition constants.[58] Although the viscosities of the solution were not measured as part of this work, the fact that did not observe any visible thickening of the solutions with either increasing the surfactant or alcohol concentration indicates the medium viscosity is little changed and that any change in the measured diffusion coefficients results from the incorporation of the solubilizates into the dimeric aggregates. The errors in the D values, estimated from reproducibility of the data in separate trials, were used to obtain the error estimates in the calculated partition constants, distribution coefficients, and Gibbs energies.

Results and discussion

Alcohol solubilization as a function of changing surfactant and alcohol concentrations

The degrees of solubilization, (the partition constants or the *p*-values), of the primary alcohols in 10-*s*-10 gemini amphiphiles were obtained from the NMR-diffusion experiments as follows[59]

$$\text{Partition constant} = p = \frac{D_{\text{alc}}(\text{aq}) - D_{\text{alc}}(\text{obs})}{D_{\text{alc}}(\text{aq}) - D_{\text{alc}}(\text{agg})} \qquad (4)$$

where D_{alc}(obs) and D_{alc}(aq) are the measured diffusion coefficients of the primary alcohols in a aggregate solution and the aqueous phase, respectively; as in previous papers, D_{alc}(agg) was obtained by measuring the diffusion coefficient for 1-decanol in the different concentrations of surfactants.[22,23] Here, we assume that the diffusion coefficient of the alcohols in the micelles (or aggregates) is the same as the diffusion coefficients for the micelles themselves, *i.e.*, $D_{\text{alc}}(\text{agg}) = D_{\text{mic}} = D_{\text{agg}}$. This means eqn (4) can be re-written:

$$p = \frac{D_{\text{alc}}(\text{aq}) - D_{\text{alc}}(\text{obs})}{D_{\text{alc}}(\text{aq}) - D_{\text{agg}}} \qquad (5)$$

Although it has been suggested in the literature the diffusion coefficients of the primary alcohols in the aggregate solution should be corrected for the obstructing effects of the aggregates in solution,[56,60] since the composition and sizes (and the morphology) of the dimeric aggregates are unknown, we have neglected the contribution of the aggregates to solubilizate diffusion, in agreement with our previous paper.[23]

The advantage of NMR-diffusion experiments is that, in a multicomponent system, the diffusion coefficients for the different components of the systems can be obtained in a single experiment, if there is sufficient separation between the ^{1}H resonances for the surfactant and solubilizate, and their diffusion coefficients do not substantially differ (*e.g.*, by more than an order of magnitude). In Fig. S1, we present the NMR spectrum for 6 μL of the medium chain length alcohol, 1-butanol, dissolved in 50 mg mL^{-1} of the symmetric gemini surfactant 10-6-10; the ^{1}H spectra are referenced to the HOD peak (δ = 4.700 ppm) as suggested by Söderman and Guering.[61] We observe excellent separation between the ^{1}H signals for the α-CH_2 resonance of 1-butanol (at ∼3.53 ppm) and the spacer CH_2's of the surfactant (at ∼3.23 ppm); hence, we have used the α-CH_2 resonances on the alcohols to obtain the *D* values of the solubilizates in the aggregate solutions. In Fig. S2, we show the stack plot of the spectra from the NMR diffusion experiment for the same system. The stack plot shows significant signal attenuation for HOD, moderate attenuation for the α-CH_2 resonance of the C_4OH, and substantially less signal decay for the surfactant resonances. This means we expect the diffusion coefficients to decrease in the order D(HOD) > D(C_4OH) > D(10-6-10). In the presence of the surfactant, the signal attenuation for the α-CH_2 peak yields an observed diffusion coefficient, D_{alc}(obs) that is substantially lower than the value obtained in free solution, D_{alc}(aq), as a portion of the alcohol molecules are now incorporated in the aggregate pseudo-phase;[56,57,62] as the exchange of the alcohol between the D_2O phase and the aggregate phase is fast, the observed signal attenuation for the alcohol (and surfactant) represents the average of those molecules we consider to be "free" (in the bulk aqueous phase) and "bound" (associate with the aggregates). Using the two-site model for the partitioning of the alcohol, the observed diffusion coefficients are related to the diffusion coefficients amount of bound solubilizate *via* the partition constant as follows:

$$D_{\text{alc}}(\text{obs}) = pD_{\text{agg}} + (1 - p)D_{\text{alc}}(\text{aq}) \qquad (6)$$

which readily rearranges to eqn (4).

Table 2 presents the diffusion coefficients and the calculated partition constants (*p*-values) for two medium chain length alcohols, C_4OH and C_5OH as a function of the surfactant concentration in solution for two dimeric surfactants, namely 10-6-10 and 10-8-10. The diffusion data are plotted in Fig. 1 and Fig. 2 for the 10-6-10 surfactant and 10-8-10 surfactants, respectively where we have changed the concentration of the dimeric amphiphile at a constant amount of alcohol. Also, in Table 2, we have the diffusion data for a single amount of 10-6-10 and 10-8-10 (50 mg mL^{-1} each) with increasing amounts of added C_4OH and C_5OH (not plotted in the above figures).

The data in Table 2 for C_4OH and C_5OH in the 10-6-10 system are in excellent agreement with our previous paper.[23] When we examine Table 2 (and the associated Fig. 1 and 2), several trends are immediately apparent. Firstly, as expected, the diffusion coefficients for both alcohols decrease as the amount of the surfactant is increased, indicative of increased partitioning of both alcohols in the micelles (or aggregates) when the concentration of the surfactant is increased. Secondly, as the concentration of alcohol is increased at a constant surfactant concentration (50 mg mL^{-1} of both dimeric surfactants), the partition constants of the alcohols in both cases exhibit little (if any) variation in a systematic way, indicating

Table 2 Diffusion coefficients for the alcohols, surfactant, and the micelles for different concentrations of 10-6-10 and 10-8-10 and varying amounts of the alcohols in a single surfactant concentration

Amount of 10-6-10/mg mL^{-1}	C_t(C_4OH) (M)	D_{alc}(obs) (m^2 s^{-1})	D_{mic} (m^2 s^{-1})	p(C_4OH)
20	0.0656	7.13	0.80	0.10 ± 0.02
30	0.0656	6.92	0.76	0.13 ± 0.02
40	0.0656	6.43	0.73	0.19 ± 0.03
50	0.0656	6.28	0.70	0.21 ± 0.03
60	0.0656	5.74	0.67	0.29 ± 0.03
70	0.0656	5.30	0.69	0.35 ± 0.04
80	0.0656	5.13	0.67	0.37 ± 0.04
90	0.0656	4.93	0.65	0.40 ± 0.04
100	0.0656	5.04	0.63	0.39 ± 0.04
50	0.0328	6.03	0.70	0.25 ± 0.03
50	0.0984	6.30	0.70	0.21 ± 0.02
50	0.1311	6.01	0.70	0.25 ± 0.03
50	0.1639	5.92	0.70	0.27 ± 0.03
Amount of 10-6-10/ mg mL^{-1}	C_t(C_5OH) (M)	D_{alc}(obs) (m^2 s^{-1})	D_{mic} (m^2 s^{-1})	p(C_5OH)
20	0.0558	5.43	0.80	0.29 ± 0.03
30	0.0558	4.94	0.83	0.36 ± 0.04
40	0.0558	4.64	0.80	0.41 ± 0.04
50	0.0558	4.24	0.59	0.46 ± 0.04
60	0.0558	3.78	0.58	0.53 ± 0.05
70	0.0558	3.34	0.64	0.60 ± 0.05
80	0.0558	3.18	0.64	0.62 ± 0.05
90	0.0558	3.06	0.67	0.64 ± 0.05
100	0.0558	2.97	0.65	0.65 ± 0.05
50	0.0279	4.20	0.59	0.47 ± 0.04
50	0.0837	3.57	0.59	0.56 ± 0.05
50	0.1116	3.44	0.59	0.58 ± 0.05
50	0.1395	3.28	0.59	0.60 ± 0.05
Amount of 10-8-10/ mg mL^{-1}	C_t(C_4OH) (M)	D_{alc}(obs) (m^2 s^{-1})	D_{mic} (m^2 s^{-1})	p(C_4OH)
20	0.0656	7.23	0.80	0.08 ± 0.02
30	0.0656	6.89	0.76	0.13 ± 0.02
40	0.0656	6.70	0.80	0.16 ± 0.03
50	0.0656	6.35	0.59	0.20 ± 0.02
60	0.0656	5.78	0.64	0.28 ± 0.03
70	0.0656	5.53	0.63	0.32 ± 0.03
80	0.0656	5.20	0.64	0.36 ± 0.03
90	0.0656	5.05	0.61	0.38 ± 0.04
100	0.0656	5.03	0.65	0.39 ± 0.04
50	0.0328	5.90	0.61	0.26 ± 0.03
50	0.0984	6.01	0.59	0.25 ± 0.02
50	0.1311	5.87	0.61	0.27 ± 0.03
50	0.1639	5.94	0.59	0.26 ± 0.03
Amount of [10-8-10]/ mg mL^{-1}	C_t(C_5OH)	D_{alc}(obs) (m^2 s^{-1})	D_{mic} (m^2 s^{-1})	p(C_5OH)
20	0.0558	5.43	0.79	0.29 ± 0.04
30	0.0558	4.94	0.78	0.36 ± 0.05
40	0.0558	4.64	0.74	0.41 ± 0.05
50	0.0558	4.21	0.68	0.47 ± 0.05
60	0.0558	3.78	0.67	0.53 ± 0.06
70	0.0558	3.34	0.63	0.60 ± 0.06
80	0.0558	3.18	0.65	0.62 ± 0.06
90	0.0558	3.06	0.63	0.64 ± 0.06
100	0.0558	2.97	0.60	0.65 ± 0.06
50	0.0279	4.20	0.61	0.47 ± 0.05
50	0.0837	3.57	0.59	0.56 ± 0.05
50	0.1116	3.44	0.61	0.58 ± 0.06
50	0.1395	3.28	0.59	0.60 ± 0.06

the overall partitioning of the alcohol does not possess a strong dependence on the quantity added and will distribute between

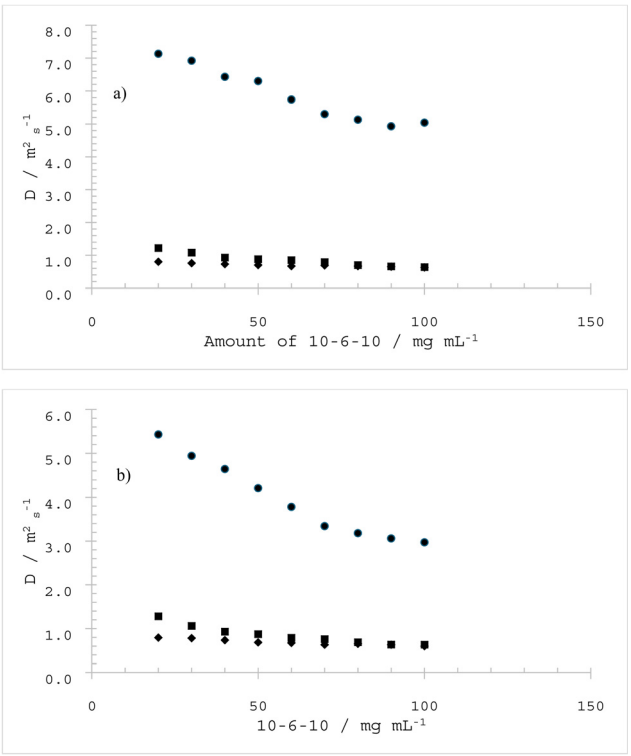

Fig. 1 Diffusion coefficients for alcohol (●), surfactant (■), and the micelles (⧫) for the system (a) C_4OH/10-6-10 and (b) C_5OH/10-6-10 as a function of the concentration of the surfactant.

the aqueous phase and the aggregate phase as long as the amount of the alcohol in the aqueous phase upon partitioning does not exceed its intrinsic aqueous solubility. This is a possible reason why in some publications in the literature, a dependence on the partitioning of hydrophobic, aromatic based solubilizates has exhibited a dependence on the structure of certain dicationic dimeric surfactants.[6,45,46]

In terms of the surfactant diffusion data, at the lowest amphiphile concentrations investigated, the differences between D_{surf}(obs) and D_{agg} (as measured by the solubilization of 1-decanol at each concentration) is significant and decreases as more surfactant is added to the system. This is consistent with the fraction of monomer in solution decreasing as we add more surfactant to the solution, in excellent agreement with our previous paper[52] and the results of Lindman and Stilbs.[63] We will return to the use of this data to obtain the partition constants for the surfactant in the mixed aggregates below.

A clearer picture of any possible dependence of solubilizate partitioning on the amount of dimeric surfactant or alcohol in solution emerges when the thermodynamic partition coefficients and Gibbs transfer energies are obtained. For K_X values, the mole fractions of the solubilizate in the aggregate interior and the aqueous phase are obtained as follows:

$$X_{alc,agg} = \frac{pc_{alc,t}}{pc_{alc,t} + \left(c_{surf,t} - c_{surf,mon}\right)} \quad (7)$$

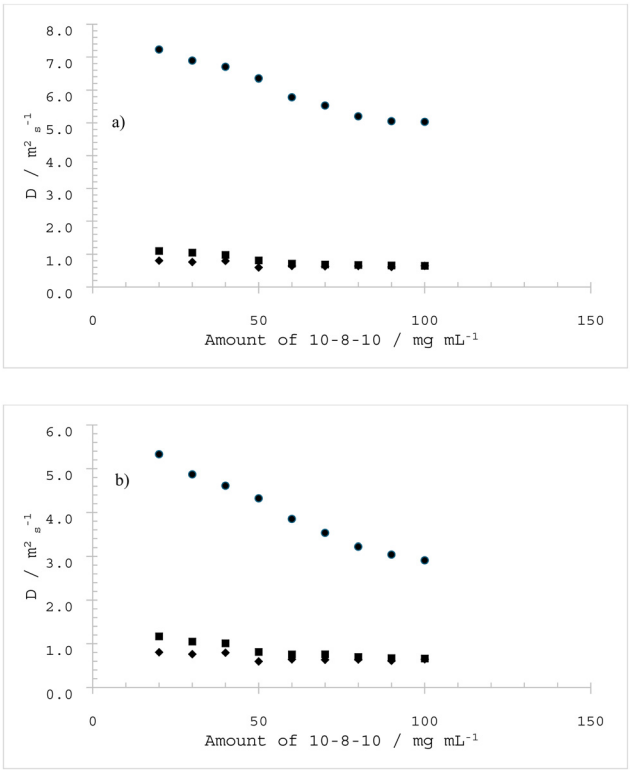

Fig. 2 Diffusion coefficients for alcohol (●), surfactant (■), and the micelles (♦) for the system (a) C_4OH/10-8-10 and (b) C_5OH/10-8-10 as a function of the concentration of the surfactant.

$$X_{alc,aq} = \frac{(1-p)c_{alc,t}}{c_{D_2O}} \quad (8)$$

here $c_{surf,t}$ and $c_{surf,mon}$ are the total and the monomeric concentrations of surfactant, respectively; c_{D_2O} is the solvent concentration and $c_{alc,t}$ is the alcohol concentration in molar units. The Gibbs energy of transfer of the alcohol from the aqueous phase to the micellar phase (the $\Delta_{tr}G^\circ$ value) is obtained from the standard thermodynamic relationship.

$$\Delta_{tr}G^\circ(K_X) = -RT\ln K_X \quad (9)$$

For the concentration-based thermodynamic partition coefficients

$$K_C = \frac{C_{alc,agg}}{C_{alc,aq}} = \frac{p}{1-p} \times \frac{V_{aq}}{V_{agg}} \quad (10)$$

where $C_{alc,agg}$ and $C_{alc,aq}$ are the concentrations of the alcohols in the aggregate and aqueous phases, respectively, V_{aq} and V_{agg} represent the volumes of the aqueous and aggregate phases, respectively. In this paper, we have used the approximate form of K_C suggested by Stilbs[57] derived from the partition constants and the concentration of surfactant in micellar form.

$$K_C = \frac{p}{1-p} \times \frac{1}{(c_{surf,t} - c_{surf,mon})} \quad (11)$$

The Gibbs energy of transfer of the alcohol from the aqueous phase to the micellar phase, $\Delta_{tr}G^0(K_C)$, is obtained by substituting the value of K_C for K_X in eqn (9).

$$\Delta_{tr}G^\circ(K_C) = -RT\ln K_C \quad (12)$$

The partition constants and the calculated Gibbs transfer energies are given in Table 3; it is remarkable that for all the combinations of differing alcohol and surfactant combinations, encompassing almost an order of magnitude in surfactant concentration, the thermodynamic partition coefficients for both alcohols are consistent in both surfactants. The averaged K_X values for the two alcohols in both surfactants (with standard deviations) are as follows: C_4OH in 10-6-10, K_X = 166 ± 22, *C_4OH* in 10-8-10, K_X = 162 ± 26, C_5OH in 10-6-10, K_X = 454 ± 39, C_5OH in 10-8-10, K_X = 456 ± 41. Barring specific interactions between the solubilizate and the surfactant (which has been observed with aromatic solubilizates and cationic surfactants like DTAB[64,65]), the data presented here, along with previous literature[18,20,22–24,57,66–70] suggest that the simple two-site model gives a very good quantitative description of solubilization phenomena data in micelles and other aggregated systems. This is also in excellent agreement with Almgren and Swarup[71] where they stated that partitioning and hence the composition of alcohol-surfactant mixed micelles is well described by a distribution equilibrium between the micelle and water ''pseudo phases.'' Almgren and Swarup also stated that the ''...details of this distribution equilibrium, *i.e.*, the dependence of the distribution coefficient on the composition of the pseudo-phases are, however, far from settled''.[71] Clearly, for the systems we have investigated here the distribution coefficients (and the calculated Gibbs transfer energies) are very consistent over a wide range of micellar compositions.

In measuring partitioning for a complicated process such as the solubilization of water-soluble, neutral molecules in surfactant aggregates, many (if not all) experimental techniques require assumptions; these are well covered in several excellent papers and articles.[1,72–76] NMR data (diffusion coefficients, chemical shifts, and relaxation times) should provide an excellent, quantitative description of micellar solubilization as the NMR observables listed above are directly related to the number of molecules residing in various states. In a review of different methods for measuring solubilization of alcohols in SDS and DTAB, Marangoni and Kwak stated the measurement of the thermodynamic partition coefficients is not straightforward,[18] and that the numerical values of the thermodynamic partition coefficients of alcohols in SDS and DTAB micelles depend on the methods used to obtain them. As an example, for C_4OH and C_5OH in SDS the values of K_X collected by these authors differ by a factor of 10! In their review, they postulated that some of this variation may be due to a dependence of the thermodynamic partition coefficients K_X on the solubilizate concentration,[3,72,77–80] however, we have clearly

Table 3 Thermodynamic partitioning data for C_4OH in two 10-carbon dimeric surfactants

Amount of dimeric surfactants (mg mL^{-1})	Ca,t (mol L^{-1})	K_X	K_C	$\Delta_{tr}G^\circ(K_X)$	$\Delta_{tr}G^\circ(K_C)$
C_4OH/10-6-10					
20	0.0656	142 ± 23	5 ± 1	−12.3 ± −0.9	−3.8 ± −0.6
30	0.0656	130 ± 15	4 ± 1	−12.1 ± −0.6	−.2 ± −0.4
40	0.0656	151 ± 12	4 ± 1	−12.4 ± −0.7	−3.5 ± −0.5
50	0.0656	140 ± 15	4 ± 1	−12.2 ± −0.6	−3.2 ± −0.4
60	0.0656	175 ± 15	5 ± 1	−12.8 ± −0.5	−3.8 ± −0.4
70	0.0656	196 ± 20	5 ± 1	−13.1 ± −0.6	−4.0 ± −0.4
80	0.0656	190 ± 19	5 ± 1	−13.0 ± −0.5	−3.9 ± −0.4
90	0.0656	193 ± 18	5 ± 1	−13.0 ± −0.5	−3.9 ± −0.4
100	0.0656	170 ± 16	4 ± 1	−12.7 ± −0.5	−3.5 ± −0.4
50	0.0328	186 ± 16	5 ± 1	−13.0 ± −0.5	−3.8 ± −0.4
50	0.0656	140 ± 10	4 ± 1	−12.2 ± −0.4	−3.2 ± −0.3
50	0.0984	157 ± 16	5 ± 1	−12.5 ± −0.6	−3.8 ± −0.4
50	0.1311	158 ± 17	5 ± 1	−12.6 ± −0.6	−4.0 ± −0.4
50	0.1639	164 ± 19	6 ± 1	−12.6 ± −0.6	−4.4 ± −0.4
C_4OH/10-8-10					
20	0.0656	119 ± 23	4 ± 1	−11.9 ± −1.1	−3.3 ± −0.7
30	0.0656	135 ± 15	4 ± 1	−12.2 ± −0.6	−3.4 ± −0.4
40	0.0656	131 ± 18	4 ± 1	−12.1 ± −0.7	−3.1 ± −0.6
50	0.0656	137 ± 10	4 ± 1	−12.2 ± −0.4	−3.2 ± −0.3
60	0.0656	174 ± 15	5 ± 1	−12.8 ± −0.5	−3.8 ± −0.4
70	0.0656	181 ± 14	5 ± 1	−12.9 ± −0.4	−3.8 ± −0.3
80	0.0656	190 ± 14	5 ± 1	−13.0 ± −0.4	−3.9 ± −0.3
90	0.0656	186 ± 18	5 ± 1	−12.9 ± −0.5	−3.8 ± −0.4
100	0.0656	176 ± 16	4 ± 1	−12.8 ± −0.5	−3.6 ± −0.4
50	0.0328	203 ± 18	5 ± 1	−13.2 ± −0.5	−4.0 ± −0.4
50	0.0656	137 ± 10	4 ± 1	−12.2 ± −0.4	−3.2 ± −0.3
50	0.0984	163 ± 11	5 ± 1	−12.6 ± −0.4	−3.9 ± −0.3
50	0.1311	163 ± 18	5 ± 1	−12.6 ± −0.6	−4.1 ± −0.4
50	0.1639	146 ± 18	5 ± 1	−12.3 ± −0.7	−4.0 ± −0.4
C_5OH/10-6-10					
20	0.0656	419 ± 41	17 ± 1	−15.0 ± −1.0	−7.0 ± −0.5
30	0.0656	408 ± 30	14 ± 1	−14.9 ± −0.7	−6.5 ± −0.4
40	0.0656	394 ± 31	12 ± 1	−14.8 ± −0.8	−6.2 ± −0.5
50	0.0656	397 ± 29	12 ± 1	−14.8 ± −0.7	−6.1 ± −0.5
60	0.0656	443 ± 38	13 ± 1	−15.1 ± −0.8	−6.3 ± −0.6
70	0.0656	508 ± 44	14 ± 1	−15.4 ± −0.9	−6.6 ± −0.6
80	0.0656	494 ± 43	13 ± 1	−15.4 ± −0.9	−6.4 ± −0.6
90	0.0656	487 ± 42	13 ± 1	−15.3 ± −0.9	−6.3 ± −0.6
100	0.0656	466 ± 40	12 ± 1	−15.2 ± −0.8	−6.2 ± −0.7
50	0.0328	469 ± 24	12 ± 1	−15.2 ± −0.5	−6.2 ± −0.4
50	0.0656	412 ± 30	12 ± 1	−14.9 ± −0.7	−6.2 ± −0.5
50	0.0984	496 ± 44	17 ± 1	−15.4 ± −0.9	−7.1 ± −0.5
50	0.1311	472 ± 48	19 ± 1	−15.3 ± −1.0	−7.3 ± −0.5
50	0.1639	454 ± 53	20 ± 1	−15.2 ± −1.2	−7.5 ± −0.5
C_5OH/10-8-10					
20	0.0656	465 ± 46	20 ± 1	−15.2 ± −1.0	−7.4 ± −0.5
30	0.0656	437 ± 41	15 ± 1	−15.1 ± −0.9	−6.8 ± −0.5
40	0.0656	423 ± 34	13 ± 1	−15.0 ± −0.8	−6.4 ± −0.5
50	0.0656	398 ± 24	12 ± 1	−14.8 ± −0.6	−6.1 ± −0.4
60	0.0656	443 ± 32	13 ± 1	−15.1 ± −0.7	−6.3 ± −0.5
70	0.0656	472 ± 40	13 ± 1	−15.3 ± −0.8	−6.4 ± −0.6
80	0.0656	494 ± 42	13 ± 1	−15.4 ± −0.8	−6.4 ± −0.6
90	0.0656	506 ± 44	13 ± 1	−15.4 ± −0.9	−6.4 ± −0.6
100	0.0656	505 ± 51	13 ± 1	−15.4 ± −1.0	−6.4 ± −0.8
50	0.0328	506 ± 33	13 ± 1	−15.4 ± −0.6	−6.4 ± −0.5
50	0.0656	398 ± 24	12 ± 1	−14.8 ± −0.6	−6.1 ± −0.4
50	0.0984	419 ± 36	14 ± 1	−15.0 ± −0.8	−6.6 ± −0.5
50	0.1311	376 ± 36	14 ± 1	−14.7 ± −0.9	−6.6 ± −0.5
50	0.1639	467 ± 67	22 ± 1	−15.2 ± −1.4	−7.6 ± −0.6

shown above that this is not the case for the surfactant concentrations investigated here. When these authors compared the K_X values from the myriad of techniques available, their analysis indicated that direct concentration methods (*e.g.*, NMR techniques), and direct activity methods (vapor pressure techniques) gave relatively comparable results, and that data derived from

Table 4 Diffusion coefficients from ^{1}H diffusion NMR experiments, partition constants, and thermodynamic partition coefficients for 6 μL of primary alcohols into the interior of symmetric and dissymmetric gemini surfactants[a]

Alcohol	D_{obs} (10^{-10} m^2 s^{-1})	p	K_X	K_C
10-4-10 (100 mg mL^{-1})				
C_3OH	6.09	0.31 ± 0.01	120 ± 20	3 ± 1
C_4OH	4.91	0.40 ± 0.02	180 ± 20	4 ± 2
C_5OH	2.80	0.66 ± 0.03	480 ± 30	12 ± 3
C_6OH	1.59	0.82 ± 0.03	1200 ± 200	30 ± 8
C_7OH	0.91	0.90 ± 0.02	2900 ± 600	70 ± 20
C_8OH	0.58	0.98 ± 0.02	9900 ± 3300	240 ± 70
10-6-10 (100 mg mL^{-1})				
C_3OH	5.96	0.33 ± 0.02	140 ± 20	3 ± 2
C_4OH	5.03	0.44 ± 0.02	180 ± 20	4 ± 2
C_5OH	3.40	0.62 ± 0.03	360 ± 40	9 ± 3
C_6OH	1.70	0.79 ± 0.02	1100 ± 50	28 ± 10
C_7OH	0.76	0.90 ± 0.02	4900 ± 1400	120 ± 30
C_8OH	0.57	0.97 ± 0.02	13 000 ± 5100	320 ± 90
10-8-10 (50 mg mL^{-1})				
C_3OH	7.62	0.30 ± 0.01	94 ± 17	2 ± 1
C_4OH	4.21	0.43 ± 0.01	487 ± 57	14 ± 1
C_5OH	3.66	0.66 ± 0.02	602 ± 64	17 ± 1
C_6OH	1.39	0.76 ± 0.01	3194 ± 1009	99 ± 19
C_7OH	0.98	0.95 ± 0.02	6520 ± 2704	198 ± 52
C_8OH	0.75	0.98 ± 0.02	16 671 ± 16 997	515 ± 328
10-8-10 (100 mg mL^{-1})				
C_3OH	6.22	0.3 ± 0.01	123 ± 10	4 ± 1
C_4OH	4.65	0.43 ± 0.01	213 ± 7	5 ± 2
C_5OH	2.82	0.66 ± 0.02	516 ± 21	12 ± 4
C_6OH	2.07	0.76 ± 0.01	842 ± 26	27 ± 8
C_7OH	0.78	0.95 ± 0.02	4602 ± 674	134 ± 41
C_8OH	0.58	0.98 ± 0.02	10 542 ± 3653	247 ± 75
10-10-10 (100 mg mL^{-1})				
C_3OH	5.85	0.28 ± 0.02	150 ± 10	4 ± 2
C_4OH	4.58	0.43 ± 0.02	230 ± 20	6 ± 2
C_5OH	2.97	0.77 ± 0.04	470 ± 60	12 ± 5
C_6OH	1.81	0.91 ± 0.02	1000 ± 350	26 ± 10
C_7OH	0.71	0.95 ± 0.02	5100 ± 1900	130 ± 40
C_8OH	0.55	0.98 ± 0.02	10 900 ± 3200	280 ± 80

[a] Data for the alcohols in the aqueous phase is taken from ref. 23.

model-dependent techniques (*e.g.*, calorimetric, volumetric, conductometric methods) and total solubility methods yielded K_X values that are higher and lower, respectively. Given all the considerations in using NMR-diffusion techniques for measuring partitioning (*i.e.*, a simple two-site distribution neglecting multi-site solubilization, and a relatively consistent micelle morphology upon solubilization), the results we obtain are reassuringly consistent.

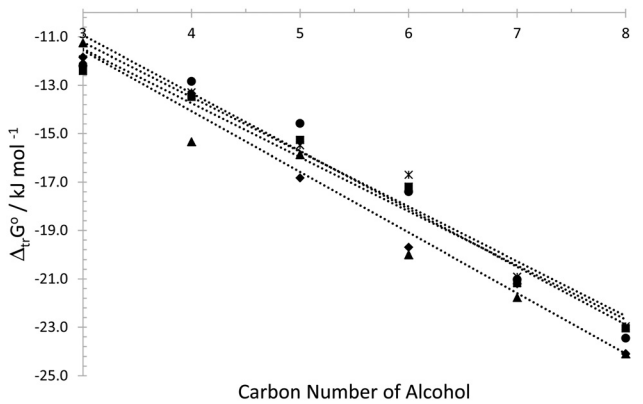

Fig. 3 Plot of the Gibbs transfer energies of the alcohols (kJ mol^{-1}) from D_2O to the interior of dimeric aggregates (mg mL^{-1}). ● 10-4-10 (100 mg mL^{-1}) ■ 10-6-10 (100 mg mL^{-1}) ▲ 10-8-10 (50 mg mL^{-1}) 10-8-10 (100 mg mL^{-1}) ♦ 10-10-10 (100 mg mL^{-1}).

Partitioning of a homologous series of alcohols in 10-carbon dimeric surfactants

In our previous paper, we presented the diffusion coefficients for a series of linear alcohols (C_3–C_8 primary alcohols) in solutions of 50 mg mL^{-1} of 10-4-10, 10-6-10, and 10-10-10 dimeric cationic aggregates. Our results suggested that for all the symmetric dimeric surfactants investigated, the thermodynamic partitioning data for the alcohols was independent of the both the main chain length (m) and the spacer length (s) of the dimeric amphiphiles. In this paper, we have examined this same series of alcohols in 100 mg mL^{-1} solutions of 10-series dimeric surfactants and solutions of 50 and 100 mg mL^{-1} of 10-8-10; Table 4 also gives the thermodynamic partition

Table 5 Diffusion coefficients for the surfactants, and the micelles for different concentrations of 10-6-10 and 10-8-10 and varying amounts of the alcohols in a single surfactant concentration

Amount of 10-6-10/mg mL^{-1}	C_t(C_4OH) (M)	D_{surf}(obs) (m^2 s^{-1})	D_{agg} (m^2 s^{-1})	p (10-6-10)
20	0.0656	1.22	0.80	0.83 ± 0.04
30	0.0656	1.08	0.76	0.88 ± 0.04
40	0.0656	0.93	0.73	0.92 ± 0.04
50	0.0656	0.88	0.70	0.93 ± 0.04
60	0.0656	0.85	0.67	0.94 ± 0.04
70	0.0656	0.79	0.69	0.97 ± 0.04
80	0.0656	0.70	0.67	0.99 ± 0.04
90	0.0656	0.66	0.65	1.00 ± 0.04
100	0.0656	0.64	0.63	1.00 ± 0.04
50	0.0328	0.91	0.70	0.92 ± 0.04
50	0.0984	0.88	0.70	0.93 ± 0.04
50	0.1311	0.85	0.70	0.94 ± 0.04
50	0.1639	0.82	0.70	0.95 ± 0.03
Amount of 10-6-10/mg mL^{-1}	C_t(C_5OH) (M)	D_{surf}(obs) (m^2 s^{-1})	D_{mic} (m^2 s^{-1})	p (10-6-10)
20	0.0558	1.28	0.80	0.81 ± 0.05
30	0.0558	1.06	0.83	0.89 ± 0.05
40	0.0558	0.93	0.80	0.93 ± 0.04
50	0.0558	0.87	0.59	0.93 ± 0.04
60	0.0558	0.79	0.58	0.96 ± 0.04
70	0.0558	0.76	0.64	0.95 ± 0.04
80	0.0558	0.69	0.64	0.99 ± 0.04
90	0.0558	0.64	0.67	1.00 ± 0.04
100	0.0558	0.63	0.65	1.00 ± 0.04
50	0.0279	0.91	0.59	0.89 ± 0.03
50	0.0837	0.75	0.59	0.94 ± 0.03
50	0.1116	0.69	0.59	0.97 ± 0.04
50	0.1395	0.62	0.59	0.99 ± 0.04
Amount of 10-8-10/mg mL^{-1}	C_t(C_4OH) (M)	D_{surf}(obs) (m^2 s^{-1})	D_{mic} (m^{2}s^{-1})	p (10-8-10)
20	0.0656	1.10	0.80	0.88 ± 0.05
30	0.0656	1.05	0.76	0.88 ± 0.05
40	0.0656	0.98	0.80	0.92 ± 0.05
50	0.0656	0.81	0.59	0.92 ± 0.04
60	0.0656	0.72	0.64	0.97 ± 0.04
70	0.0656	0.69	0.63	0.98 ± 0.04
80	0.0656	0.67	0.64	0.99 ± 0.04
90	0.0656	0.66	0.61	0.98 ± 0.04
100	0.0656	0.65	0.65	1.00 ± 0.04
50	0.0328	0.91	0.61	0.89 ± 0.04
50	0.0984	0.84	0.59	0.90 ± 0.04
50	0.1311	0.80	0.61	0.93 ± 0.04
50	0.1639	0.78	0.59	0.93 ± 0.04
Amount of [10-8-10]/mg mL^{-1}	C_t(C_5OH)	D_{surf}(obs) (m^2 s^{-1})	D_{mic} (m^2 s^{-1})	p (10-8-10)
20	0.0558	1.28	0.79	0.85 ± 0.05
30	0.0558	1.06	0.78	0.88 ± 0.05
40	0.0558	0.93	0.74	0.91 ± 0.05
50	0.0558	0.87	0.68	0.92 ± 0.04
60	0.0558	0.79	0.67	0.96 ± 0.04
70	0.0558	0.76	0.63	0.95 ± 0.04
80	0.0558	0.69	0.65	0.98 ± 0.04
90	0.0558	0.64	0.63	0.98 ± 0.04
100	0.0558	0.63	0.60	0.99 ± 0.04
50	0.0279	0.91	0.61	0.89 ± 0.04
50	0.0837	0.75	0.59	0.93 ± 0.04
50	0.1116	0.69	0.61	0.95 ± 0.04
50	0.1395	0.62	0.59	0.95 ± 0.04

coefficients (K_X and K_C), and the Gibbs transfer energy of these alcohols. Again, we clearly see that for each of the primary alcohols investigated, the partition constants of the alcohols, and their subsequent K_X and K_C values increase as the chain length of the alcohols is increased, in excellent agreement with the literature.[18,23,54–56,62,67,68] This is, of course, expected as the hydrophobicity of the alcohol is increased as its carbon chain length increases, which would increase the driving forces for solubilization of the alcohol in the aggregate interior. When we examine the trends in the partition constants of a specific

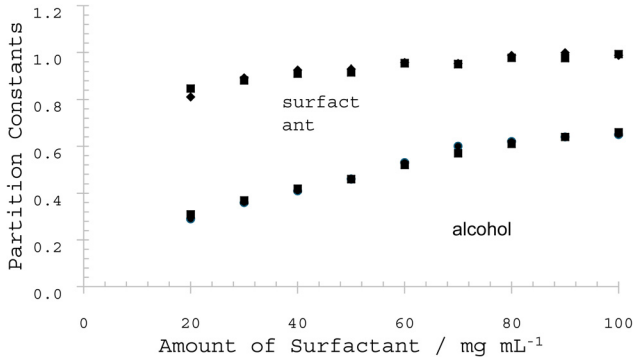

Fig. 4 Partition constants for C_4OH and the amphiphile as a function of the total surfactant concentration in ♦ 10-6-10 and ■ 10-8-10 dimeric surfactants.

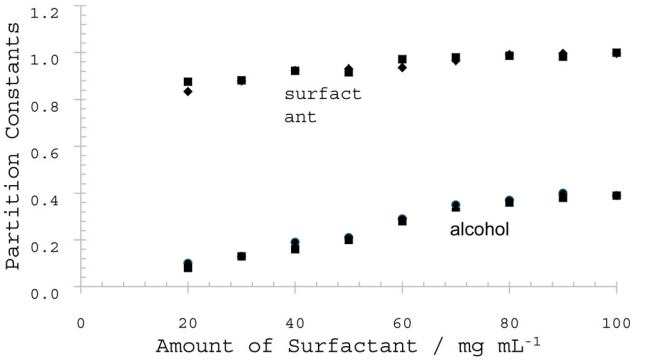

Fig. 5 Partition constants for C_5OH and the amphiphile as a function of the total surfactant concentration in ♦ 10-6-10 and ■ 10-8-10 dimeric surfactants.

alcohol in the 10-series gemini surfactants, the partition constants and the calculated distribution coefficients are essentially identical, indicating the individual alcohols have a similar preference for the interior of 10-series gemini surfactants as a function of the spacer length, both at 100 mg mL^{-1} and 50 mg mL^{-1} (ref. 23) of surfactant. The $\Delta_{tr}G^0$ values for the alcohols between the aqueous phase and the respective gemini aggregate are plotted as a function of the alcohol chain length in Fig. 3; it is clear the alcohol partitioning displays the same linear dependence of the Gibbs transfer energy *versus* carbon number seen previously.[18,20,23,56,67,68] The slope of each plot represents the transfer Gibbs energy of the alcohol CH_2 group from the aqueous phase to the gemini aggregate phase; its averaged value for all the dimeric surfactants investigated here is -2.4 ± 0.2 kJ mol^{-1}, in excellent agreement with values of -2.4 ± 0.4 kJ mol^{-1} for a host of symmetric cationic dimeric surfactants,[23] -2.6 ± 0.3 kJ mol^{-1} for SDS micelles, -2.3 ± 0.1 kJ mol^{-1} for sodium pefluorooctanote (SPFO) micelles,[81] -2.8 ± 0.1 kJ mol^{-1} for sodium decanoate (SD) micelles,[62] -2.7 ± 0.2 kJ mol^{-1} for dodecyltrimethylammonium bromide (DTAB) micelles,[68] -2.6, -2.8, and -2.6 kJ mol^{-1} in DTAB, teteramethyltrimethylammonium bromide, and cetyltrimethylammonium bromide micelles, respectively.[82]

Calculation of the surfactant monomer concentrations in alcohol/surfactant mixed micelles

The diffusion data presented for the amphiphiles above (Table 2, Fig. 1, and Fig. 2) decrease as the concentration of the surfactant is increased, indicating the amount of surfactant existing as monomers in the solution decreases with increasing concentration, in excellent agreement with the literature.[52,63] Using surfactant diffusion data above and re-writing eqn 4 for the amphiphiles, we obtain an expression for calculating the partition constants of the surfactants in the mixed micelles as shown below

$$p_{\mathrm{Surf}} = \frac{D_{\mathrm{Surf}}(\mathrm{aq}) - D_{\mathrm{Surf}}(\mathrm{obs})}{D_{\mathrm{Surf}}(\mathrm{aq}) - D_{\mathrm{agg}}} \qquad (13)$$

The D_{aq} value is obtained for both surfactants at a concentration far below their respective CMC values in solution (*i.e.*, in this case at 1.0 mM concentration); these values are 3.37×10^{-10} m^2 s^{-1} and 3.20×10^{-10} m^2 s^{-1}, respectively for 10-6-10 and 10-8-10. As we have noted above, the differences between the D_{surf}(obs) and D_{agg} become smaller as the surfactant concentration is increased, indicating increased amphiphile partitioning in the mixed aggregates at higher concentrations. The calculated partition constants for both surfactants are also presented in Table 5 and plotted along with the partition constants of the alcohols in Fig. 4 (C_4OH) and Fig. 5 (C_5OH), respectively.

At the highest concentrations of the surfactant investigated, a relatively small amount of the surfactant resides in the aqueous phase. If we look at a constant concentration of surfactant (in this case 50 mg mL^{-1} of the amphiphile), the addition of alcohol molecules induces more of the surfactant molecules to aggregate, with the amount of free surfactant in solution steadily decreasing. It is well known in the literature that the presence of alcohols decreases the CMC values of surfactants,[83] meaning the addition of alcohols reduces the amount of free surfactant in solution that exists in equilibrium with aggregates in the regions where the micelles are just beginning to form in solution. Clearly at a concentration above the CMC, addition of alcohols has a similar effect on the amount of monomer in equilibrium with the aggregates, as evidenced by the increase in the partition constants of both surfactants.

In the case of the mixed micelles, the addition of alcohols to surfactant solutions results in a decrease in the surfactant aggregation number,[71] indicating the mixed micelles are being depleted in surfactant molecules. This appears to contrast with the data presented here where the increase in the partition constants of the surfactants indicates that more surfactant molecules are incorporated into the mixed micelles. It is well known that alcohols induce the formation of more aggregates.[69,71,83] According to Almgren and Swarup,[71] the size of the mixed aggregates micelles is determined by the balance between repulsive electrostatic interactions and the hydrophobic tendencies to reduce the interfacial area. The importance of the balance between those effects on the size and shape of micelles was recognized very early on by Hartley.[84] According to Almgren *et al.*[71] and Marangoni *et al.*,[69] when the aggregation numbers determined by fluorescence quenching are combined with NMR partitioning data, the total aggregation numbers of mixed aggregates of SDS with alcohols and alkoxyethanols (the

sum of the surfactant and alcohol aggregation numbers) increase as the amount of alcohol increases. For the systems investigated here, the increased surfactant partition constants correlate with a higher proportion of the amphiphile molecules in the aggregates as the concentration of surfactant increases, consistent with micelle growth. At a constant concentration of surfactant, adding alcohol to the system also increases the surfactant partition constants, but as alcohols are known to decrease the surfactant aggregation numbers,[69,71] the increased partition constants mean an increase in the number of aggregates induced by these additives, and/or the changes to the morphology of the aggregates.

It is clear from our work here, our previous papers,[18,68] and the extensive work by Stilbs and co-workers,[56–58,62,81] the partitioning of *n*-alcohols in a host of micellar systems yields very consistent results for the thermodynamics of transfer. The consistency amongst the data is remarkable as in many cases, the actual molar amounts of the ''aggregate phase'' available to the solubilizate can span an order of magnitude, as well as differing micellar morphologies. The partitioning of alcohols into surfactant micelles is a complex process that, like surfactant amphiphiles, is critically dependent on the amphipathic properties of the alcohols. Depending on the concentration and the chain length of the alcohol, they can act as cosolvents or as co-surfactants that preferentially localize into the micellar aggregates. If we examine the common picture of alcohol solubilization, we expect the neutral alcohol molecule to be solubilized in the aggregates with the polar head groups intertwined within the palisade layer and the alcohol alkyl chain oriented towards the hydrocarbon core. The series of interactions that drive the transfer process are alcohol hydrophobic effects, the ability of the hydroxyl group to maintain favourable hydrogen-bond interactions with water, and favourable pairwise interactions in the micellar core; there would also be electrostatic contributions stabilizing the mixed systems as the polar alcohol headgroups would effectively screen the repulsive electrostatic interactions between the headgroups. For the transfer process, the hydrophobic effects of the alcohol would give the initial strong push to move the molecules to a more hydrophobic region, so long as the amount of alcohol in the solvent is lower than its intrinsic aqueous solubility. The Gibbs transfer energy encompasses contributions from hydrophobic effects, hydrophobic and electrostatic interactions, and the ability of the alcohol polar head groups to maintain some hydrogen bonding contacts with water. From an energetics standpoint, the largest two contributions would be the hydrophobic effects of the alcohols (which is chain length dependent) and the ability of the hydroxyl group to maintain the hydrogen bonding contacts, and these contributions would be independent of the nature of the surfactant aggregate available. If the pairwise dispersive interactions and the reduction of the electrostatic repulsions are smaller in magnitude *versus* the energetic contributions from the alcohol molecules themselves, then the major driving force for alcohol transfer is limited mostly to the contributions to the alcohol hydrophobic effects and favourable hydrogen-bonding interactions between the polar groups and water molecules. The fact that the partition coefficients for the *n*-alcohols are the same in SDS aggregates, SD aggregates, SPFO aggregates (and their mixtures), and all the cationic and dicationic surfactant aggregates investigated is consistent with the inherent solubility of the alcohols being the main factor controlling the partitioning process. This is especially apparent in the transfer of the alcohols to the interior of SPFO micelles, where the interactions between the alkyl chains and the perfluoro chains are not favourable, yet the alcohol partition coefficient is little changed from its value in typical hydrocarbon aggregates.

Conclusions

From the thermodynamic partition coefficients obtained *via* diffusion-NMR experiments, we conclude the partitioning of an *n*-alcohol in the aggregates of both 10-6-10 and 10-8-10 dimeric surfactants increase as the concentration of the surfactant is increased; when the surfactant concentration is kept constant, we do not observe any differences in the partition constants of the two alcohols with increasing alcohol concentration. The thermodynamic partition coefficients (K_X values) calculated from the partition constants are essentially constant as a function of changing alcohol and surfactant concentration. When we examine a series of *n*-alcohols in solutions containing 100 mg mL^{-1} of these gemini amphiphiles, we see enhanced partitioning of the alcohols based on their carbon chain length; however, the partitioning of a single alcohol (*e.g.*, C_5OH) does not depend on spacer length for the 10-carbon main chain dimeric surfactants, and is identical to the partitioning data for the alcohols in other dimeric surfactants[23] and typical surfactants like SDS,[56] DTAB,[57] and sodium decanoate.[62] Finally, we have used the observed diffusion coefficients to obtain how the composition of the alcohol/surfactant mixed aggregates changes as a function of both the alcohol and surfactant concentration. With increasing amphiphile concentration at a constant alcohol concentration, our results indicate that a substantial reduction in the amount of free surfactant occurs in solution as more amphiphile ions partition into aggregates. At a constant surfactant concentration, adding alcohol to the aggregates also yields a reduction in the amount of free surfactant. These results provide important, fundamental information on how the mixed aggregate compositions vary with both alcohol and surfactant concentrations.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

All relevant data is given in the tables and figures in the manuscript.

Supplementary information is available: The Supplementary Information associated with this article includes Supplementary Fig. S1 and S2. See DOI: **https://doi.org/10.1039/d5cp01361e**

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