

A Comparison between the Organic Solution Phases Containing Hexanol, Water and Hexadecyltrimethylammonium Bromide or Sulphate

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The existence region of the organic solution phase L_2 containing hexanol, water and hexadecyltrimethylammonium sulphate (CTAS) has been determined. The extension of the solution phase is smaller and the ability to dissolve water is smaller than in the corresponding hexadecyltrimethylammonium bromide (CTAB) system. From ^{14}N NMR relaxation data, it is argued that it is mainly the region containing larger aggregates that is affected. The water self-diffusion coefficient decreases rapidly when diluting a water-rich sample in the ternary CTAB system with decane, indicating that well-defined water-in-oil aggregates are formed at a high hydrocarbon content.

The work of Ekwall and coworkers on phase equilibria in multicomponent systems containing water, surfactant, and aliphatic alcohols^{1,2} has offered a natural starting point for many investigations of the aggregation phenomena in these complex systems. The phase diagrams are of great value, e.g., in the studies of ionic microemulsion systems since quaternary ionic microemulsions can be regarded as extensions of the isotropic solution phases in the ternary system without hydrocarbon.^{3–5} Hexadecyltrimethylammonium bromide (CTAB)/hexanol/water is one of the comparatively few systems containing a cationic surfactant system for which a detailed phase diagram has been determined.⁶ The hexanol-rich solution phase L_2 (Fig. 1b) has been studied with viscosity measurements⁷, counterion NMR relaxation⁸ and ^{14}N NMR relaxation of the surfactant as well as by light scattering⁹. In the last-named investigation, the effect of adding decane to the ternary solution has also been studied.

The present study can be seen as a continuation of the previous work⁹ by applying the FT–NMR pulsed gradient spin echo method for measuring self-diffusion coefficients¹⁰ and also by studying the effects of the valency of the counterion by exchanging bromide for sulphate. The existence region of the alcohol-rich solution phase has been tentatively determined for the hexadecyl-trimethylammonium sulphate (CTAS)/hexanol/water system, measurements of surfactant ^{14}N relaxation and of self-diffusion coefficients for the different components have been performed, and the results compared with those from the CTAB system. The self-diffusion method has been extremely fruitful in the investigation of microemulsions, stressing the difference between the microemulsions with short chain alcohols like butanol or pentanol as cosurfactants and those with long chain alcohols like octanol or decanol as cosurfactant. While the latter systems can be readily regarded as composed of closed water droplets dispersed in a hydrophobic continuous phase, the former are effectively bicontinuous for the water and the oil on the time scale of the diffusion measurements, i.e., 100 ms^{11–14}.

Dedicated to Professor Per Ekwall on his 90th birthday.

Experimental

Chemicals. Hexanol (Fluka, >99 %), heavy water (Merck, >99.75 % ^2H) and decane (Fluka, >99.5 %) were used as received. CTAB (Merck) was recrystallized from methanol/acetone (1:1). CTAS was prepared by ion exchange with solid silver sulphate in an ethanolic CTAB solution¹⁵. The solution was sonicated for 30 min, alternately stirred for several hours in the dark. After filtering, the ethanol was evaporated, and the residue, solid CTAS, was recrystallized twice from methanol/acetone (1:1) and dried *in vacuo* at 80 °C. Elementary analysis of the salt gave the following results: C: 68.35 % (theor.: 68.62 %), H: 13.75 % (theor.: 12.73 %), N: 4.25 % (theor.: 4.21 %), S: 4.50 % (theor.: 4.82 %). The Br analysis showed that the CTAB content was less than 2%. Water was twice distilled. Samples for the self-diffusion measurements were prepared with D_2O instead of H_2O .

NMR measurements. The measurements were performed on a Bruker CXP-100 spectrometer, at 6.50 and 90 MHz for ^{14}N and ^1H , respectively, at the ambient probe temperature, 26.5 ± 0.5 °C. The spin-lattice relaxation time T_1 was measured using the fast inversion recovery technique,¹⁶ while the spin-spin relaxation time T_2 was obtained from the experimental line widths corrected for field nonhomogeneities. The accuracy was estimated to be better than 3 % and 10 %, respectively. The measurements of the self-diffusion coefficients were performed by the FT-NMR pulsed gradient spin-echo method.¹⁰ The evaluation of the data was performed as described previously.¹⁴ A normal standard deviation percentage for a diffusion coefficient was 3 %. The peaks from the α -methylene protons of the alcohol and the N-methyl protons of the surfactant were sometimes difficult to separate in spite of the rather large difference in chemical shifts due to line broadening and poor line shape in the home-built gradient probe head. At high hydrocarbon content, it was possible to obtain rough values of the decane self-diffusion coefficient by subtracting the estimated intensity of the slowly diffusing components from the unresolved methylene peak.¹²

Phase diagrams. The existence region of the alcohol-rich isotropic solution phase in the CTAS

system was determined by titration with hexanol or water. The samples were examined between crossed polarizers in a thermostatted bath at 25 ± 0.2 °C.

Results and discussion

The existence region of the organic solution phase in the system water/hexanol/CTAS is shown in Fig. 1a, and can be compared with the corresponding phase in the water/hexanol/CTAB system (Fig. 1b). Regardless of whether the comparison is made on a weight basis, as in Fig. 1, or on a molar basis, some significant differences emerge: the extension of the solution phase towards the water-surfactant axis has decreased and the protrusion towards the water corner is less predominant. In addition, CTAS is more effective than CTAB in reducing the hexanol/water miscibility gap.

These findings can be seen in the light of the important work of Khan et al.¹⁷⁻¹⁹ where the complete phase diagrams were determined for the systems water/decanol/Mg- or Ca-octylsulphate. The extension of the lamellar phase towards the water corner is drastically reduced when exchanging Na-octylsulfate for the corresponding calcium or magnesium salt. This can be understood from simple considerations of the stability of the lamellar phase for which the maximum swelling is determined by the balance between the attractive van der Waals forces and the repulsive electrostatic forces. Divalent counterions screen the electrostatic repulsion more efficiently than univalent ions, resulting in a reduced maximal water uptake. It was also found that the other phases were considerably less affected than the lamellar phase. However, the alcohol-rich solution phase increased somewhat in size.

Jönsson and Wennerström have demonstrated that most features of the phase diagrams for three-component surfactant systems can be reproduced from some concise assumptions and if the electrostatic part of the free energy is calculated from the Poisson-Boltzmann (PB) equation²⁰⁻²². However, from Monte Carlo simulations²⁴ and from analytical theories which take ion-ion correlations into account,^{25,26} it is clear that the PB equation considerably overestimates

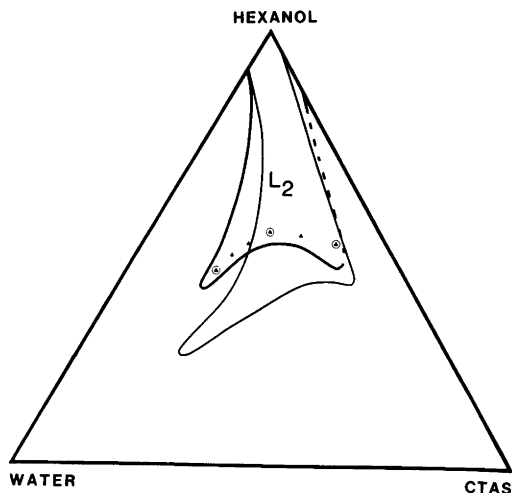


Fig. 1a. The extension of the alcohol-rich isotropic solution phase L_2 in the system water/hexanol/hexadecyltrimethylammonium sulphate (CTAS) at 25°C. The boundary between the L_2 phase and solid surfactant is not accurately determined. The extension of the L_2 phase in the system water/hexanol/hexadecyltrimethylammonium bromide (CTAB) is included in the figure (thin solid line) to facilitate a comparison.

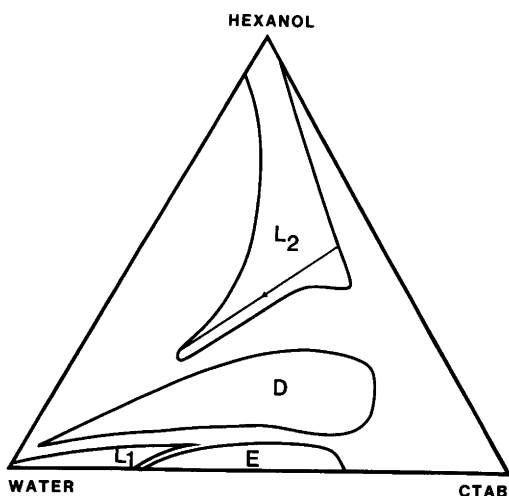


Fig. 1b. The phase diagram of the system water/hexanol/hexadecyltrimethylammonium bromide (CTAB) at 25°C. L_1 and L_2 denote the isotropic solution phases; D and E denote the lamellar and hexagonal liquid crystalline phases, respectively. From Ref. 6.

the repulsion between charged surfaces for the case of divalent counterions. Thus, the PB equation predicts a larger swelling for a lamellar liquid crystalline phase than the one found experimentally.¹⁷⁻¹⁹

Assuming that the L_2 phase contains some kind of inverse aggregates, the extension of the existence region can be qualitatively understood from the arguments put forth in a quantitative form by Jönsson.²⁰⁻²² The area per head group is very small in reverse phases, and the lateral repulsion between the head groups is moderated by the presence of alcohol hydroxylic groups at the aggregate surface. The capacity for dissolving water and the size of the aggregates present depend on the availability of alcohol molecules that can be incorporated into the interfacial region. When very little alcohol remains, phase separation occurs. Evidently, at a constant ratio water/surfactant, more alcohol is needed for keeping the water in solution in the CTAS system. This can be seen as an indication that the difference in the electrostatic interaction when Br^- is exchanged for SO_4^{2-} causes a reduction in aggregate size with an accompanying increase in the total interfacial area. If the amount of alcohol available is insufficient, this will lead to phase separation.

The question whether aggregates are present at all in the system can be partially answered by NMR relaxation measurements. For surfactants containing a quaternary ammonium group the ^{14}N nucleus offers a convenient tool for this purpose. For a nucleus with spin quantum number $I = 1$, like ^{14}N , the quadrupolar relaxation rates R_1 and R_2 are²⁷:

$$R_1 = 1/T_1 = \frac{3\pi^2}{40} \chi^2 [2J(\omega_0) + 8J(2\omega_0)], \quad (1)$$

$$R_2 = 1/T_2 = \frac{3\pi^2}{40} \chi^2 [3J(0) + 5J(\omega_0) + 2J(2\omega_0)], \quad (2)$$

where χ is the quadrupolar coupling constant, $J(\omega)$ is the spectral density function and ω_0 is the Larmor frequency. In eqs. (1) and (2), it is assumed that the asymmetry parameter of the electric field gradient tensor is zero. Recent work²⁸⁻³² has shown that in order to obtain detailed infor-

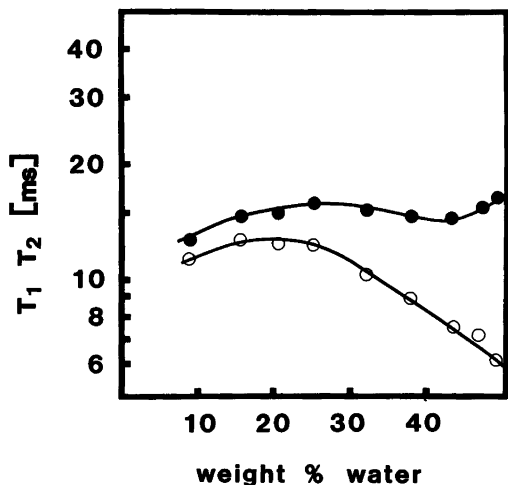


Fig. 2a. ^{14}N relaxation data in the CTAB-system for samples along the dilution line in Fig. 1b. From Ref. 9. (●) T_1 and (○) T_2 .

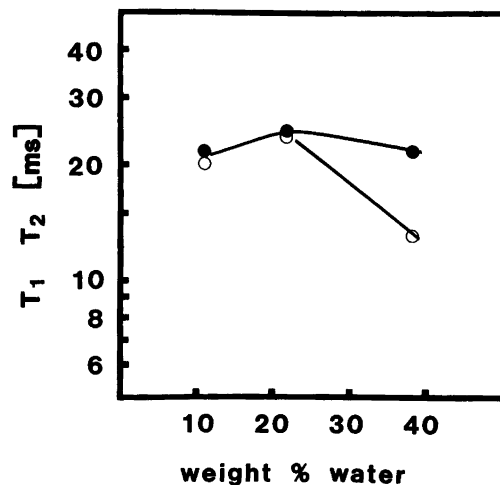


Fig. 2b. ^{14}N relaxation data in the CTAS system for the samples marked with circles in Fig. 1a. (●) T_1 and (○) T_2 .

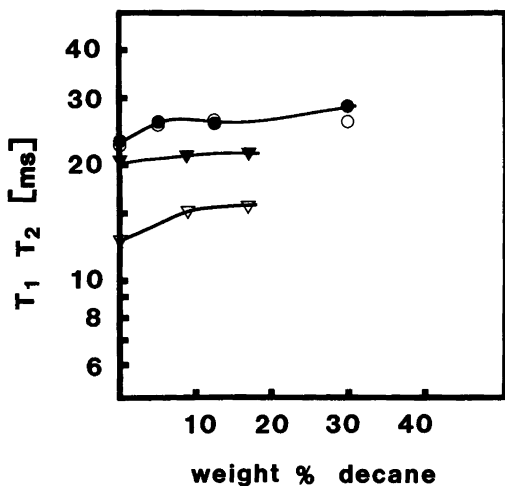


Fig. 2c. ^{14}N relaxation data for two samples in the CTAS system (marked with circles in Fig. 1a) diluted with decane. (●) T_1 and (○) T_2 , sample containing 23% H_2O without added decane. (▼) T_1 and (▽) T_2 , sample containing 38% H_2O without added decane.

mation about the molecular dynamics and aggregation behaviour in surfactant systems it is necessary to measure the relaxation rates at different magnetic field strengths. The so-called "two-step model" which considers uncorrelated

fast local motion and slow aggregate motions has been applied in several studies of relaxation in surfactant systems. From the field dependence of the relaxation rates, it is verified that this model properly describes the dynamics of spherical micelles in an aqueous surrounding^{29,31}. For microemulsions containing SDS, toluene and alcohols of different chain length, the multifield relaxation gives a more complicated picture of the dynamics in these systems.³² For the short chain alcohols (C_3 – C_4) only small aggregates or aggregates with very flexible hydrophobic/hydrophilic interfaces are present. For the long chain alcohols (C_5 – C_{10}), the shape fluctuations of the interface become slower and the amplitude is reduced so that the reorientation of the whole aggregate also contributes to R_2 through the $J(0)$ term in eq. (2).

It is clear from the discussion above that ^{14}N T_1 and T_2 measured at one magnetic field strength cannot give a detailed picture of the dynamics in the systems studied. However, it is possible to use the relaxation data in a more qualitative way since T_2 is more sensitive to the slow motions due to the term $J(0)$ in eq. (1). From eqs. (1) and (2), it is clear that if the extreme narrowing condition $T_1 = T_2$ is fulfilled, slow motions of aggregated surfactant on the time scale $>1/\omega_0$ do not contribute to the relaxation while $T_2 < T_1$ when such mo-

tions are present. In the CTAB system, the ^{14}N data fully confirm the presence of aggregates along the dilution line (Fig. 2a). This seems to be the case also for the CTAS system, where $T_2 < T_1$ for the highest water content (Fig. 2b). It is notable that the dilution with decane does not affect the ^{14}N relaxation very much neither in the CTAB⁹ nor the CTAS system (Fig. 2c). Two more facts are worth noting about the ^{14}N relaxation data: the relaxation times are generally longer in the CTAS system at comparable compositions of the solution and the region where $T_2 < T_1$ has decreased significantly.

The self-diffusion data furnish some additional information on the microstructure in the CTAB and the CTAS systems, respectively. The water self-diffusion coefficient rises appreciably when diluting the system with water at a fixed ratio hexanol/CTAB (Fig. 3a). The corresponding results for the CTAS system show slightly lower values and a less accentuated increase (Fig. 4a). However, these samples have a higher hexanol content, and the difference most likely reflects

this fact. The drastic reduction of the water self-diffusion coefficient, when diluting a water-rich sample in the CTAB system with decane (Fig. 3b), deserves to be stressed. The decrease is approximately ten-fold. At concentrations of decane $>20\%$ the water self-diffusion is very slow while the decane self-diffusion is quite rapid (estimated to $10^{-9} \text{ m}^2 \text{ s}^{-1}$). This is in contrast to the hydrocarbon-free solution, where the difference between the self-diffusion coefficients of the hydrophobic component (hexanol) and water is small.

A similar diffusion behaviour has been found for the anionic microemulsions water/oleate/pentanol/hydrocarbon where the water diffusion also becomes considerably slower upon dilution with hydrocarbon. This is explained in terms of a redistribution of alcohol from the interfacial region and the hydrophilic domains to the continuous hydrocarbon domains.³³ This results in a more rigid interfacial membrane; the increased head group-head group repulsion causing a closer counterion binding, as probed by ^{23}Na NMR.³⁴

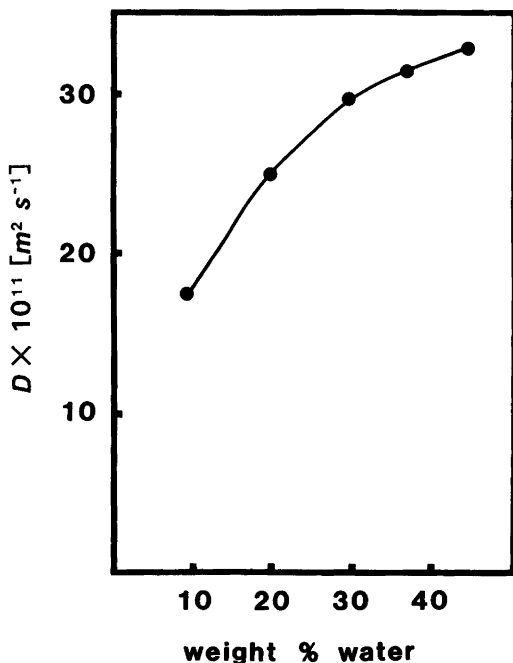


Fig. 3a. Water self-diffusion coefficient in the CTAB system for samples along the dilution line in Fig. 1b.

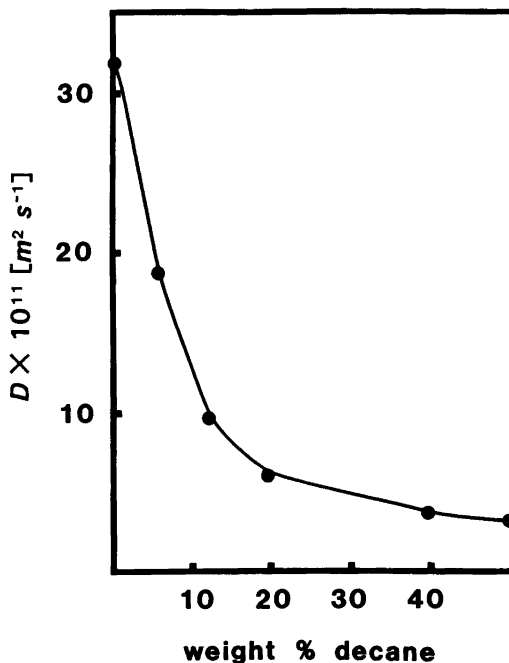


Fig. 3b. Water self-diffusion coefficients for a sample in the CTAB system (weight ratio water/hexanol/CTAB 45/32/23), diluted with decane.

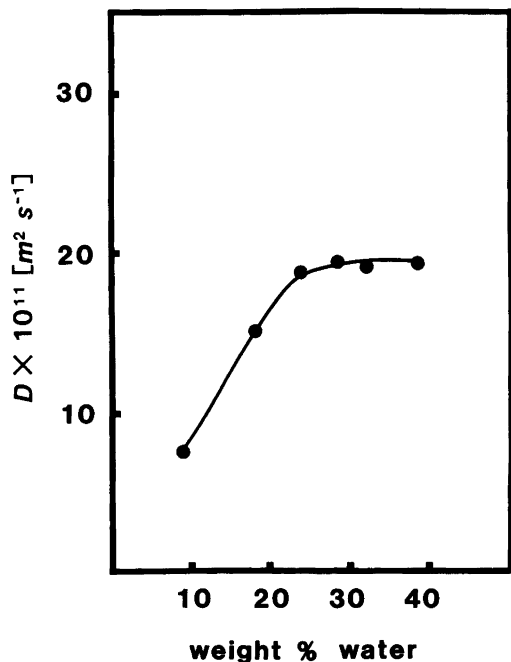


Fig. 4a. Water self-diffusion coefficients in the CTAS system for the samples marked with triangles in Fig. 1a.

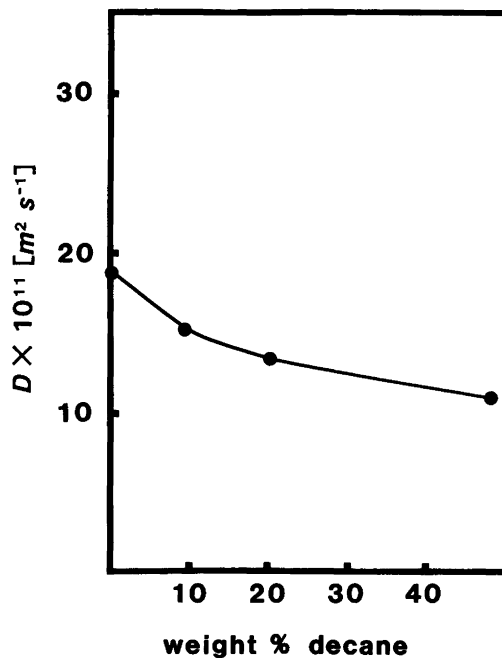


Fig. 4b. Water self-diffusion coefficients for one of the samples marked with a circle in the CTAS system (Fig. 1a) diluted with decane containing 23% water without added decane).

In the CTAS system the decrease in water self-diffusion coefficients upon dilution with decane is less drastic. However, it is also possible to link this to the lower water and higher hexanol content in the CTAS sample diluted with hydrocarbon (Fig. 4b).

The question remains how to reconcile the rather dramatic decrease in the water self-diffusion coefficient upon dilution with decane with the practically unaffected ^{14}N relaxation rates. In the quaternary CTAB microemulsions at a decane content $>20\%$, the water self-diffusion is sufficiently slow and the hydrocarbon self-diffusion sufficiently rapid to be consistent with closed w/o aggregates. This conclusion is supported by the measured value of the surfactant self-diffusion coefficient for these samples, $3 \pm 1 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$, which within the errors of measurements is equal to the water self-diffusion coefficient. For such aggregates it is expected that the $^{14}\text{N } T_2 < T_1$ in agreement with the experimental results.⁹

In the water-rich ternary CTAB system, the water diffusion is considerably faster than the

surfactant diffusion ($D_{\text{H}_2\text{O}} \sim 3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{CTA}^+} \sim 5 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 45% water). The rapid water diffusion, which is of the same magnitude as for water dissolved in hexanol, shows that the mechanism for transport of water in these solutions can not be translational motion of aggregates. On the other hand, the ^{14}N relaxation data show that the surfactant molecules are aggregated in some kind of interface between hydrophilic and hydrophobic domains where they undergo slow motions with a correlation time 10 ns.⁹ Taking the diffusion results into account, it must be concluded that these slow motions do not originate in the motion of well-defined aggregates but rather in the shape changes of a flexible hydrophilic/hydrophobic interface. The high water diffusion rate indicates that on the time scale of the measurement (100 ms), the water molecules are not much hampered in their movement by the interfacial film but are allowed to diffuse rather freely over considerable distances.

It should be noted that in the discussion above quite different molecular motions have been pro-

posed to be responsible for the ^{14}N relaxation: high amplitude shape fluctuations of the interface in the ternary system and aggregate rotation and monomer diffusion over the curved surface of small rather well-defined aggregates in the hydrocarbon-rich solutions. It must be considered as a coincidence that these two mechanisms give practically the same ^{14}N T_1 and T_2 for the two solutions. Multifield relaxation data are obviously needed to determine the detailed form of the spectral density functions in the different cases.

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