

## NMR-Studies of the Solubilisation of Aromatic Compounds in Cetyltrimethylammonium Bromide Solution II

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Resonance line shifts and relative line widths of cetyltrimethylammonium bromide (CTAB) hydrogens and aromatic solubilisate hydrogens have been determined at several solubilisate concentrations in 0.1729 M CTAB-solution. The results obtained indicate that for benzene, N,N-dimethylaniline and nitrobenzene, the predominating solubilisation mechanism at low and intermediate solubilisate concentrations involves adsorption at the micelle-water interface whereas isopropylbenzene and cyclohexane preferentially are solubilised in the hydrocarbon part of the micelles. The observed line width effects are compared with viscosity measurements.

In a preceding paper<sup>1</sup> we have given a preliminary report on our NMR-investigations concerning the solubilisation of aromatic compounds in a micellar solution of cetyltrimethylammonium bromide (CTAB). In the present paper a full account of these studies will be given. Resonance line positions and relative line widths have been measured as functions of the solubilisate concentration in a 0.1729 M CTAB-solution at 35°C. The effects of the following solubilisates have been studied: benzene, N,N-dimethylaniline, nitrobenzene, isopropylbenzene, and cyclohexane. Additional experimental information was obtained through viscosity measurements. The present study constitutes an extension of Eriksson's previous work on solubilisation of benzene and bromobenzene in cetylpyridinium chloride solution.<sup>2</sup> According to Lawrence and Stenson<sup>3</sup> the critical micelle concentration of CTAB is  $0.99 \times 10^{-3}$  at 25°C implying that more than 99 % of the CTAB molecules in the investigated solutions are certainly included in the micelles.

### EXPERIMENTAL

The chemicals used in these studies were of *pro analysi* grade and were obtained from KEBO AB, Stockholm, except for CTAB that was a BDH Laboratory Reagent. The CTAB was recrystallized twice from ethanol/acetone. A stock 0.1729 M CTAB-water solution was prepared. By dissolving weighed amounts of the solubilisate, 10 ml samples

of clear CTAB-solubilisate solutions were obtained. The NMR measurements were made at about 35°C on a Varian A-60 spectrometer, equipped with a Hewlett Packard 202A audio oscillator and a Hewlett Packard 5512A electronic frequency counter. In order to let the solutions reach thermal equilibrium, the samples were placed in the probe at least 10 min before measurement. The temperature in the probe was regularly recorded. All resonance line positions of CTAB and solubilisate hydrogens were measured relative to water as an internal standard. The reported chemical shifts are average values of 4–5 separate measurements. The accuracy of the shifts can in general be estimated to be  $\pm 0.1$  c/sec, except for the  $-\text{CH}_2-$  and  $\text{C}-\text{CH}_3$  shifts in the most viscous solutions for which the corresponding resonance peaks are strongly broadened so that the accuracy in the determination of these shifts is only about  $\pm 0.5$  c/sec. For all solutions, the  $\alpha\text{-CH}_2$  shift values reported are rather uncertain since the recording of the small  $\alpha\text{-CH}_2$  peak is often disturbed by the much stronger  $\text{N}-\text{CH}_2$ -resonance occurring at a neighbouring frequency. For dimethylaniline and nitrobenzene, the frequency measurements were made on the most distinct peaks in the *meta* and *ortho-para* multiplets and in the *ortho* and *meta-para* multiplets, respectively. When nitrobenzene was added as solubilisate, the solutions with a mole ratio larger than 1.2 remained cloudy even after extended storage at 35°C. Since this fact may indicate that these solutions are actually two-phase systems, the corresponding curves in Fig. 4 have been drawn with broken lines for mole ratios larger than 1.2. The water resonance line position was determined relative to chloroform as an external standard. For comparison the resonance line positions of the solubilisate molecules in dilute solutions of cyclohexane were determined relative to chloroform as an external reference. The half widths of the peaks were measured relative to the half width of a simultaneously recorded external chloroform signal. The viscosity was measured at 35°C by means of an Ubbelohde viscometer. Every reported value is a mean of 4 or 5 separate readings. With the solutions containing benzene evaporation could not be avoided. The reported viscosities correspond therefore in this case to solutions with a somewhat lower benzene concentration than the original samples. A further indication of this experimental error was that the flow-time decreased with repeated measurements on the same sample when the mole ratio of benzene to CTAB was less than 1.0 and increased when the mole ratio was larger than 1.0.

### SUSCEPTIBILITY CORRECTIONS

From preliminary calculations we could conclude that a negligible error is introduced if it is assumed that the magnetic susceptibility per unit volume of a pure CTAB-solution is equal to the susceptibility of water at the same temperature. Thus, the susceptibility of a solution containing a solubilisate,  $\chi_v^{123}$ , could be evaluated by means of the formula

$$\chi_v^{123} = x_{12}\chi_v^1 + x_3\chi_v^3$$

where  $x_{12}$ ,  $x_3$  are the volume fractions of pure CTAB-solution and solubilisate, respectively, and  $\chi_v^1$  and  $\chi_v^3$  are the volume susceptibilities of water and solubilisate at 35°C. The small upfield shifts of the water peak due to solubilisation as measured against an external  $\text{CHCl}_3$ -reference could generally be attributed to the susceptibility change predicted by the above equation.

Since the water resonance line position is temperature dependent whereas the positions of the other peaks in question do not shift much with temperature variations, chemical shift corrections for the small temperature deviations from 35.0°C were made by using a value equal to 0.5 c/sec, °C for the temperature coefficient of the water resonance line.<sup>4</sup>

When comparing the extrapolated line positions of the solubilisate hydrogens at zero solubilisate concentration in the CTAB-solution and the

corresponding line positions in cyclohexane, the shift values in cyclohexane were corrected for the bulk susceptibility difference, the correction being  $-12.9$  c/sec. In Table 1 the last-mentioned resonance line positions are referred to the water resonance of the pure CTAB-solution.

### RESONANCE LINE SHIFTS

Only one resonance line is found for each kind of the chemically different hydrogens in the CTAB-molecule and the added solubilisate molecule. This fact can be regarded as a consequence of the rather rapid exchange of molecules between the micelles and the surrounding water solution. Due to this exchange, for each kind of hydrogen atoms, an average peak position corresponding to the different sites available to the molecules is observed. However, in the systems studied, the relative population at the micelle sites is much larger than at the water sites. The average peak positions are therefore almost entirely determined by the chemical shifts of the hydrogens of molecules present in the micelles. There is hardly any detectable broadening of the resonance signals of the pure CTAB-solution due to the formation of micelles. It is concluded that the constituent molecules of these micelles are rather loosely coupled having a high degree of relative thermal mobility.

In general, the addition of an aromatic solubilisate to the CTAB-solution causes the resonance lines of CTAB and of the solubilisate itself to shift towards higher applied magnetic fields. The degree of shifting is different for hydrogens at different positions in the CTAB-molecule (Figs. 1, 2, 3, and 4). When, instead, a saturated hydrocarbon like cyclohexane is solubilised, only minor

Table 1.

Resonance line	Line positions at zero solubilisate concentration relative to water (i.s.)		Line position in water (corrected)
	In $C_6H_{12}$ (corrected)	In 0.1729 M CTAB solution	
$C_6H_6$	-147.6	-162.2	-164.7
$\phi$ -CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> aromate H	210.5 -142.7	208.0 -151.0	
$\phi$ -N(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub> <i>ortho</i> -H <i>para</i> -H <i>meta</i> -H	113.5 -116.6 -133.6	105.0 -132.2 -147.9	
$\phi$ -NO <sub>2</sub> <i>ortho</i> -H <i>meta</i> -H <i>para</i> -H	-201.1 -165.7	-214.2 -187.8	-217 ± 2 -187 ± 2
$C_6H_{12}$	197.5	196.5	

shifts of the resonance lines are produced (Fig. 5). It should be noted that the corresponding water peak shifts as measured against an external  $\text{CHCl}_3$  standard are small in all cases.

From studies of homogeneous solutions of aromatic substances it is well known that the aromatic ring usually gives a negative contribution to the local magnetic field, leading to up-field shifts for the hydrogens at neighbouring molecules. The main features of the shift curves can be explained on the basis of this "aromatic" shift. Another process, which also may cause considerable up-field shifts is a change of medium for the studied molecule from a polarizing to a more inert environment.

Useful information may be derived from the solubilisate peak positions at zero solubilisate concentration in the curves of Figs. 1, 2, 3, 4, and 5. If allowance is made for the difference in bulk susceptibility, comparisons between the influence of the micelle medium and other better known media can be made (Table 1). The extrapolated peak positions for all the studied aromatic solubilisates are lower in the CTAB-solution than in the diluted cyclohexane solution. For benzene the value obtained approaches the resonance line position of benzene in water. This observation indicates that at least at low solubilisate contents benzene is solubilised by adsorption at the micelle-water interface. The figures obtained for isopropylbenzene suggest that the first added molecules are adsorbed at the micelle-water interface and that

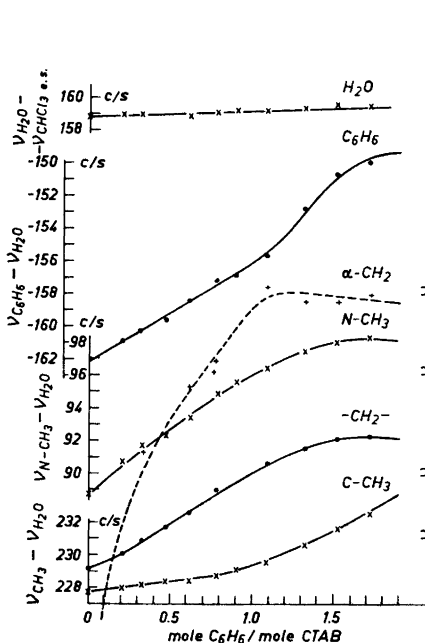


Fig. 1. Resonance line shifts due to solubilisation of benzene in 0.1729 M CTAB-solution.

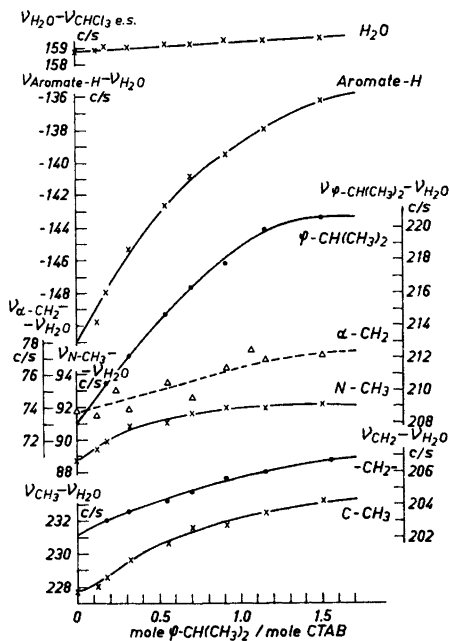


Fig. 2. Resonance line shifts due to solubilisation of isopropylbenzene in 0.1729 M CTAB-solution.

they are orientated in such a manner that the aromatic ring is preferentially directed towards the surrounding water, implying that the isopropyl group is positioned chiefly in a hydrocarbon environment. For nitrobenzene and *N,N*-dimethylaniline the data are also consistent with the assumption of interfacial adsorption of the first solubilise molecules. The figures for cyclohexane show that no solubilisation by interfacial adsorption occurs.

In the cases of benzene and *N,N*-dimethylaniline (Figs. 1 and 3), further addition of solubilise gives rise to a rapid shift of the  $N-CH_3$ ,  $-CH_2-$ , and especially of the  $\alpha-CH_2$ -hydrogen resonance lines towards higher fields. These shifts can be explained if one assumes that adsorption at sites close to the  $\alpha-CH_2$ -groups is the predominating solubilisation mechanism and that this process involves a removal of those water molecules which presumably are present initially at these adsorption sites. The proposed mechanism seems probable since the quite large shifts obtained for the  $\alpha-CH_2$ -hydrogens (26 c/sec) are only expected to result from a combination of interfacial adsorption of benzene and a change of the polarizing ability of the surrounding medium. At a benzene content approximately equal to 1.0 mole  $C_6H_6$ /mole CTAB there is a marked change in slope of the shift curves for  $C_6H_6$  and for the  $\alpha-CH_2$  and  $C-CH_3$  groups that can be interpreted as being due to adsorption saturation and a transition to solubilisation through dissolving of benzene in the central

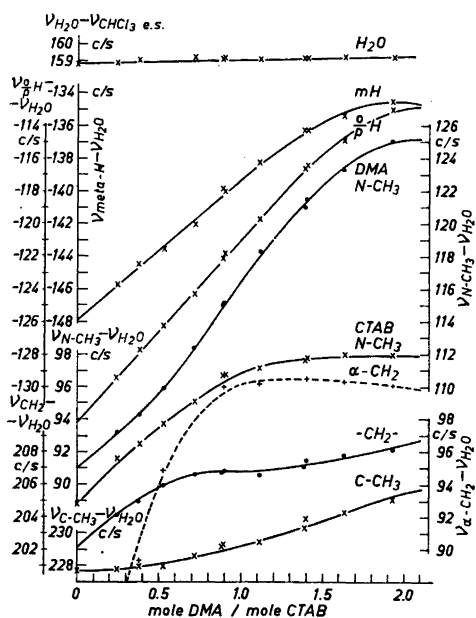


Fig. 3. Resonance line shifts due to solubilisation of *N,N*-dimethylaniline in 0.1729 M CTAB-solution.

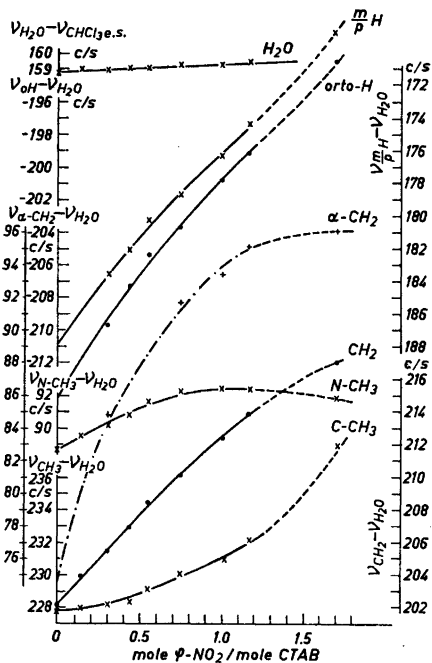


Fig. 4. Resonance line shifts due to solubilisation of nitrobenzene in 0.1729 M CTAB-solution.

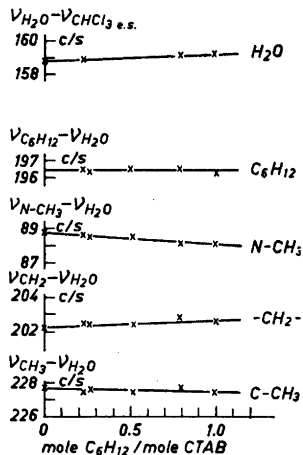


Fig. 5. Resonance line shifts due to solubilisation of cyclohexane in 0.1729 M CTAB-solution.

parts of the micelle. For *N,N*-dimethylaniline this transition occurs at about 0.7 mole  $\phi$ - $N(\text{CH}_3)_2$ /mole CTAB, as is evident from Fig. 3.

In the case of nitrobenzene (Fig. 4) somewhat different shift curves are obtained. The addition of solubilisate causes the  $-\text{CH}_2-$  and the  $\alpha\text{-CH}_2$ -hydrogen signals to shift rapidly towards higher fields leaving, however, the  $\text{N-CH}_3$  hydrogen resonances almost unaffected. If the nitrobenzene molecules are adsorbed at the interface primarily due to interaction between the nitro group and the polar soap molecules and/or the water molecules present, then the aromatic ring will be situated at sites close to the  $\alpha\text{-CH}_2$ -groups. In such case the  $-\text{CH}_2$ -resonance line will be more and the  $\text{N-CH}_3$  resonance line less influenced by the diamagnetic anisotropy of the aromatic ring than in the case of benzene. At a nitrobenzene content of 0.8–0.9 mole  $\phi\text{-NO}_2$ /mole CTAB the change of slope of the shift curves for  $\alpha\text{-CH}_2$  and  $\text{N-CH}_3$  indicates that the solubilisation mechanism is changed to one of dissolution in the interior of the micelle. For isopropylbenzene (Fig. 2) rather different shift curves are obtained. In this case the CTAB-hydrogen resonance positions do not shift much upon addition of the solubilisate, whereas the isopropylbenzene signals move rapidly towards higher field. This behaviour is consistent with the assumption that the isopropylbenzene molecules preferentially gather in the centre of the micelles except at very low solubilisate contents, when probably also the interfacial adsorption mechanism is operative to some extent.

#### LINE WIDTH BROADENING AND VISCOSITY CHANGES

In Figs. 6, 7, 8, and 9 it is shown how the viscosities and the line widths of the resonance peaks vary as functions of the solubilisate content. The plotted relative line width is the ratio of the half intensity widths of the signal in question and of an external  $\text{CHCl}_3$ -signal. When benzene, *N,N*-dimethylaniline or nitrobenzene is solubilised pronounced maxima in the line widths

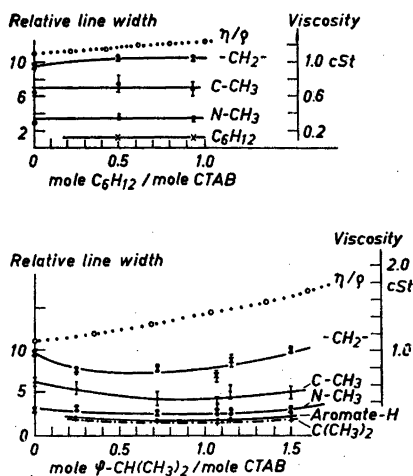


Fig. 6. Line widths and viscosity vs. mole ratio of solubilised isopropylbenzene and cyclohexane in 0.1729 M CTAB-solution.

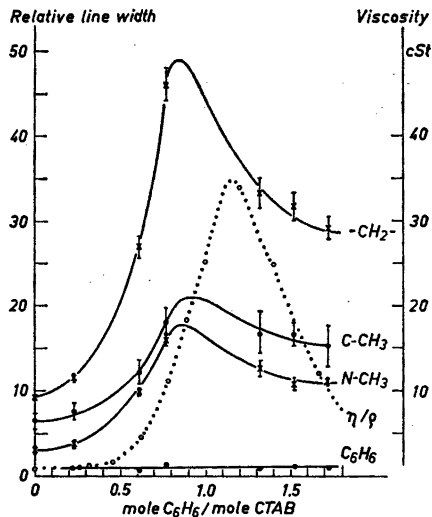


Fig. 7. Line widths and viscosity vs. mole ratio of solubilised benzene in 0.1729 M CTAB-solution.

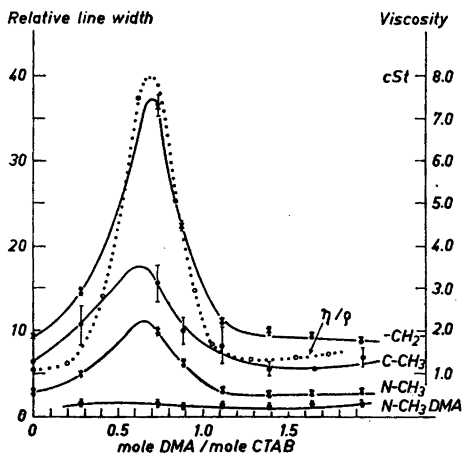


Fig. 8. Line widths and viscosity vs. mole ratio of solubilised N,N-dimethylaniline in 0.1729 M CTAB-solution.

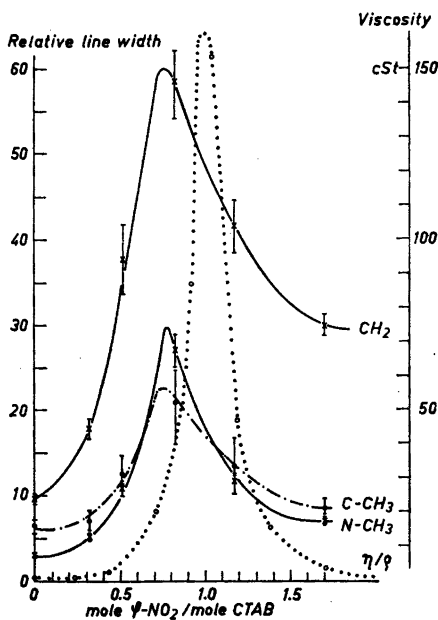


Fig. 9. Line widths and viscosity vs. mole ratio of solubilised nitrobenzene in 0.1729 M CTAB-solution.

of the CTAB-hydrogens are produced, whereas there is no detectable broadening of the solubilisate signal. These line widths changes are accompanied by roughly parallel changes in viscosity. A possible interpretation is as follows. Through the adsorption of, *e.g.*, benzene close to the polar heads and the consequent removal of penetrating water, the hydrocarbon chain distances decrease involving an increased chain interaction and a diminishing thermal chain mobility. Because of the reduced chain mobility the nuclear dipole-dipole interaction gives rise to a line width broadening. The described changes of the micellar structure may promote the formation of large rod-shaped micelles. Such a process would presumably lead to an increase of the viscosity. Above the saturation point, when the benzene molecules preferentially enter into the micelle interior, the line width decrease indicates that the hydrocarbon chains recover their thermal mobility. It can be assumed that benzene then acts similarly as an ordinary solvent. The adsorption saturation point for benzene, *N,N*-dimethylaniline and nitrobenzene is approximately at 1.0, 0.7, and 0.9 mole solubilisate/mole CTAB, respectively. The mole volumes for the same substances are 88.8, 126.8, and 102.6 ml. Adsorption saturation thus occurs when roughly the same volume has been added of the different solubilisates. The relative line widths of the  $-\text{CH}_2-$  peaks at the respective maxima are approximately 50, 40, and 60. The corresponding kinematic viscosities are 35, 8, and 160 cst.

For isopropylbenzene and cyclohexane there are no drastic changes of the line widths and the viscosities. Although isopropylbenzene may be slightly adsorbed at low concentrations, the bulky hydrophobic isopropyl group probably prevents the development of the particular interfacial structure that presumably is a prerequisite for the assumed changes of the structure of the hydrocarbon part of the micelle. The slight increase of the viscosity observed due to the solubilisation of isopropylbenzene and cyclohexane can be attributed to the swelling of the micellar part of the solution.

#### DISCUSSION

Smith and Alexander<sup>5</sup> recorded the sedimentation patterns of micellar solutions of cetylpyridinium chloride containing various amounts of trichlorobenzene, toluene, and methylcyclohexane in the presence of sodium chloride. They concluded that at concentrations below the observed viscosity maximum the addition of an aromatic solubilisate promoted the formation of long rod-shaped micelles leading to increased viscosity. At higher solubilisate contents they found evidence for the appearance of more compact micelles which could account for the decreasing viscosity. Apparently our findings for the benzene, *N,N*-dimethylaniline, and nitrobenzene solubilisate solutions may be regarded as consistent with their conclusions. Götz and Heckmann<sup>6</sup> studied the conductivity anisotropy of more concentrated CTAB-solutions (0.30–0.57 M). They concluded that the CTAB micelle is anisotropic even in the absence of additives and, furthermore, they found that the solubilisation of small amounts of benzene greatly enhances the apparent micelle length.



Reiss-Husson and Luzzati<sup>7</sup> studied the structure of micellar solutions of several amphiphilic substances by means of X-ray diffraction. They could conclude that the micelles in a pure CTAB-solution at 27°C are rod-shaped when the concentration is larger than 5 % by weight.

The phenomenon of solubilisation of aromatic compounds by adsorption at the micelle-water interface can be understood on the basis of thermodynamic arguments. We may suppose that in the pure micellar solution some water molecules penetrate into that hydrocarbon part of the micelle which is close to the polar heads. It is certainly favourable from an energetic point of view that an aromatic like benzene, N,N-dimethylaniline, or nitrobenzene is substituted for this penetrating water because of the high polarizability of the aromatic ring and the bonding abilities of the substituent groups. Thus, by this adsorption, the system can lower its energy in comparison with the case of an even distribution of aromatic molecules within the micelle, and the energy difference in question may more than compensate the associated diminution of entropy. In the case of isopropylbenzene it is not likely that the same solubilisation mechanism is so effective because of the presence of the isopropyl group, which counteracts the effect of the aromatic ring. Instead the dissolution of isopropylbenzene in the central parts of the micelles appears to be energetically advantageous, implying that the particular interfacial structure which promotes a more well-ordered micelle state is never created. It is also fairly probable that a similar solubilisation mechanism is the only operative one in the case of cyclohexane. This solubilisation in the center of the micelle might involve a reorganisation of the micellar structure so that a more spherical micelle is obtained instead of the postulated original rod-shaped micelle.

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