

SPECTROPHOTOMETRIC STUDY OF THE MICELLIZATION OF HIGH MOLECULAR WEIGHT ALKYL BENZENE SULPHONATES AND ALKYLTHIOPHOSPHONATES IN APOLAR MEDIA

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Summary

Micellization of high molecular weight alkylbenzene sulphonates and alkylthiophosphonates was studied in apolar solvents through their solubilizing effect on Rhodamine B. The concentration of the dye was measured at 555.5 nm. Specific concentration range and degree of association of the detergent-dispergant oil additives investigated depended on the quality of the polar and the length of the alkyl groups in the molecule as well as on the size of the cation (Gegenion).

The knowledge of the micellar characteristics of detergent-dispergant lubricant additives dissolved in apolar solvents is an important step in the elucidation of their working mechanism. One of the tools used for this purpose is the measurement of the solubilization of a solid substance — otherwise insoluble in the given solvent — by the detergent investigated [1–3]. With proper choice of the material to be solubilized its concentration in solution may be determined spectrophotometrically.

The detergent additives investigated contained polar sulpho- or thiophosphono-groups and long ($> C_{20}$) alkyl chains to ensure oil-solubility. *i*-Octane or cyclohexane were used as solvents in which the dissolution of a triphenylmethane dye — Rhodamine B — was registered in the presence of different detergents. The solubility of this dye in pure *i*-octane is of the order of 10^{-6} mol/l and the solution is colourless because of the presence of the rigid lactonic form of the dye which absorbs light only in the ultraviolet region.

Figure 1 represents the ultraviolet-visible spectra of Rhodamine B in water and in an alkylbenzene sulphonate-containing *i*-octane. The same concentration of the sulphonate in *i*-octane was used as reference in the latter case (curve 2 in Fig. 1). The difference between the two spectra is due to the different environments. The spectrum of the water solution shows the presence of the ionic form of the dye. The ultraviolet region of the spectrum of the organic solution corresponds to that of the *i*-octane solution of the dye alone containing the lacton form of Rhodamine B. The absorption appearing in the visible region shows the presence of the ionic form and represents the portion of Rhodamine B solubilized by the sulphonate.

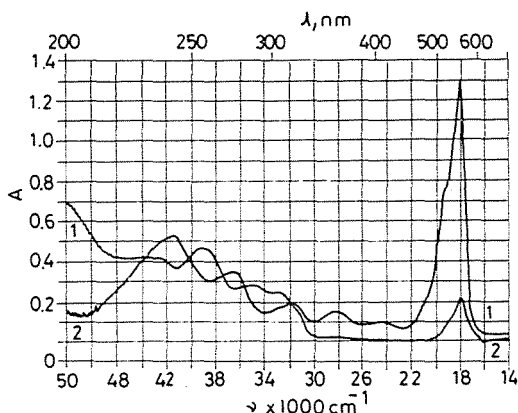


Fig. 1. UV-VIS spectra of Rhodamine B

1. solvent H_2O $C_{\text{Rod}} \leq 1.8 \times 10^{-4} \text{ mol/l}$
2. differential spectrum in i-octane containing barium alkylbenzene sulphonate, $C_{\text{Rod}} \leq 1.8 \times 10^{-4} \text{ mol/l}$

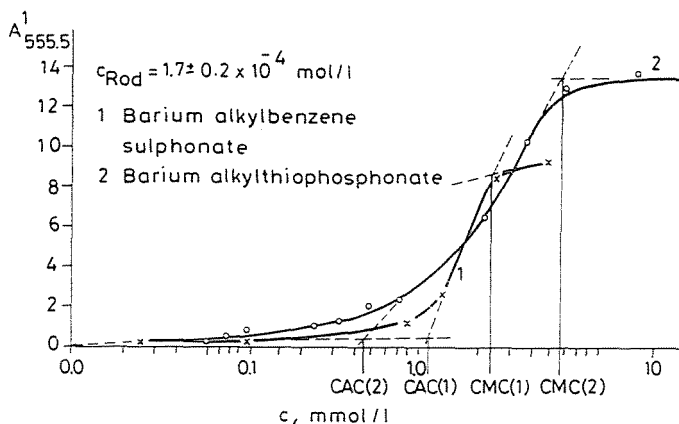


Fig. 2. Effect of the detergent concentration on the solubilization of Rhodamine B in i-octane

In order to investigate micellization equal amounts of Rhodamine B were added to solutions containing a detergent in different concentrations. After thorough mixing the undissolved dye was left to settle down. Absorption of the solution was measured at 555.5 nm. This procedure was repeated in fixed time intervals until the absorbance of the solution — still containing solid dye in excess — became constant. Under these circumstances the equilibrium was reached generally in 8–14 days.

In Figure 2 the results of solubilization of Rhodamine B in i-octane by the barium salts of two different organic acids have been shown. The curves of

absorbances plotted in function of the detergent concentration have break-points indicating the beginning and the end of the association process of soluted molecules: critical association concentration (CAC) and critical concentration of micellization (CMC), respectively [4, 5]. The distance between these two points, the region of micellization is narrower with the sulphonate than in the case of the thiophosphonate.

Significant differences in the critical values of micellization could be observed depending on the quality of the cation (Gegenion) of the detergents. Table 1 shows that in a series of alkali earth salts of an alkylbenzenesulphonic acid, the lower is the concentration range of association the smaller is the diameter of the metal ion present.

Investigating alkylbenzenesulphonic acid, H^+ being the cation, the solubilization took place rapidly but the visible spectrum became complicated indicating the presence of several protonated dye species in solution. This phenomenon made the evaluation of the solubilized amount difficult, so comparison with the data obtained using the salts of the same acid could not be done.

The study of the association of thiophosphonates showed that the length of the alkyl chain has an effect on the critical values of micellization, too.

The degree of the association could be calculated from the data of apparent molecular mass of the detergents in micellar solution determined by vapor pressure osmometry (VPO) [6] and theoretical molecular mass of the monomer. The measurements were performed in cyclohexane and in chloroform. Data in Table 1 show that in cyclohexane the number of molecules

Table 1
Characteristics of the micellization of detergents

Compound	$M_{\text{theor.}}$	CAC 10^{-3} mol/l	CMC 10^{-3} mol/l	$n(60^\circ)$	
				cyclohexane	$CHCl_3$
$(ABS)_2Ba$	369	insol.	insol.	insol.	81
$(ABS)BaOH$	781	1.0	2.3	insol.	24
$(ABS)CaOH$	562	0.16	0.85	59	20
$(ABS)MgOH$	578	0.13	0.70	92	22
	590	0.5	4.3	insol.	insol.
$(ATP)Ba$	750	0.7	2.7	insol.	insol.
	1400	1.0	9.6	40	14

$M_{\text{theor.}}$ = calculated molecular mass of the monomer

CAC = critical concentration of association in *i*-octane at 293 K

CMC = critical concentration of micellization in *i*-octane at 293 K

$n(60^\circ)$ = number of aggregation at 333 K

ABS = alkylbenzenesulphonate anion

ATP = alkylthiophosphonate anion

insol. = insufficiently soluble

associated in micelles increases with the size of the metal ion. In the more polar solvent: chloroform the degree of aggregation seems to depend rather on the molecular mass of the monomer.

Results indicate that both the specific concentration range of association and the degree of association of detergents-dispergants used as lubricating oil additives depend on the quality of the polar and the length of the alkyl groups in the molecule as well as on the size of the Gegenion.

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