

und vollständig in weniger als 10 min. Von den Diffusionskoeffizienten von Ag^+ in festem AgJ und aus der Diffusionstheorie folgt, daß die Teilchen kubisch sind.

Frische Fällprodukte tauschen bei pAg 3 schneller als gealterte aus. Bei pAg 4 ist die Austauschgeschwindigkeit unabhängig vom Alter des Gefällten. Die Partikelgröße bei pAg 3 und pAg 4, berechnet auf Grundlage des Ag^+ -Diffusionskoeffizienten, stimmt für hexagonale Modifikation mit derjenigen überein, die aus Elektronenabbildungen folgt; daher sind die Teilchen hexagonal.

Der Silberjodid/Silber-Austausch im Bereich zwischen pAg 2 bis 4 ist immer vollständig, d. h. der Austauschanteil wird in relativ kurzen Austauschzeiten gleich 1, während der geschwindigkeitsbestimmende Prozeß die Diffusion in der festen Substanz ist. Das Gleichgewicht AgJ/Ag^+ auf der Oberfläche ist ein dynamisches.

Bei Alterung von AgJ/Ag^+ -Fällprodukten bleibt der Austauschwert niemals in der Größenordnung von nur mehreren Prozent, welche letztere Beobachtung in

der Literatur für einige Systeme beschrieben ist, auch für Ag-Halogenid/Halogenidionsysteme. Die Einbettung des Austauschs in die feste Phase wird durch Rekristallisationen verursacht, wie eben durch die Alterungsprozesse, und das Gleichgewicht ist nicht dynamisch. Möglicherweise verhindert die Doppelschicht den Übergang des konstituierenden Ions aus der Flüssigkeit in die feste Phase und umgekehrt.

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Temperature Dependence of Micellar Weight of Non-Ionic Surfactant in the Presence of Various Additives

Part I. Addition of n-Decane or n-Decanol

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With 15 figures and 3 tables

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Introduction

In recent years *Debye* and others (1, 2) have applied light scattering techniques to the determination of the molecular size of micelles. However, little work has been directed toward studying the effect of temperature on the micellar size. For n-dodecyl trimethylammonium bromide in 0.03403 M KBr, *Debye* (1b) found that the micellar weight slightly decreased with increase in temperature. In contrast to ionic detergents, where the solubility in water increases with increasing temperature, the non-ionic detergents with a polyoxyethylene tail as the hydrophilic portion are completely miscible with water at moderate temperature, but as temperature is raised a dilute aqueous solution becomes turbid at a definite temperature known as the cloud point and at somewhat higher temperature separates into two phases, presumably as the result of dehydration of the hydrophilic ether linkages in the chain. Therefore, it is of interest to study how the size of micelle varies with temperature elevation. In order to clarify the mechanism of solubilization, it seems instructive to study the influence of tempera-

ture on micellar size in the presence of added solubilize.

In the present investigation, therefore, the micellar weight of methoxy-polyoxyethylene decyl ether in the absence and the presence of added n-decane or n-decanol has been measured by the light scattering method as a function of temperature. Similar experiments were also performed on sodium dodecyl sulfate for comparison.

Experimental

Materials

The sample of methoxy-polyoxyethylene decyl ether $\text{C}_{10}\text{H}_{21}(\text{OC}_2\text{H}_4)_{12}\text{OCH}_3$ (MPd-12) was synthesized by the same procedure as described in the previous paper (2, 3). That the purified sample contained no detectable methoxy-polyethylene glycol and decyl-alcohol was verified by paper chromatography (5) and gas chromatography. The analytical value, average molecular weight and cloud point of the purified sample are as follows. Anal. Calcd. for $\text{C}_{10}\text{H}_{21}(\text{OC}_2\text{H}_4)_{12}\text{OCH}_3$, C: 59.97, H: 10.35; Found, C: 59.82, H: 10.39. Av. mol. wt. 705 by depression of freezing point of benzene solution. Cloud point, 75.5° C (2% aq. soln.).

Sodium dodecyl sulfate (SDS) was a commercial sample obtained from Nihon Yushi Co., Ltd. and was purified by repeated recrystallization from the ethanol solution. Anal. Calcd. for $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, C: 49.98, H: 8.74, Na: 7.97; Found, C: 50.35, H: 8.99, Na: 7.86.

The n-decane and n-decanol used were "guaranteed reagent grade".

Refractive Index Increment

The refractive index increment, dn/dc , at 546 $m\mu$ was determined at 20°, 30° and 40° C on a differential refractometer (Shimadzu Instr. Co.) similar to the one described by *Debye*. The values of the refractive index increment at higher temperatures exceeding 40° C were obtained by extrapolation of the values of dn/dc below 40° C. Because, with our present refractometer, it was impossible to measure the increment at higher temperatures.

Light Scattering

All light scattering measurements were made with the green mercury line, $\lambda = 5461 \text{ \AA}$, using a light scattering photometer equipped with a temperature regulating attachment (4). The attachment is a water-jacket consisting of two concentric cylinders with a 180° "window", slightly larger than the height of the light beam. It is tightly fixed on the shaft inside the photometer, in place of the ordinary cell-holder. A slit system (4 mm wide and 12 mm high) mounted in front of the attachment minimizes the diffused light of the incident beam.

The cylindrical cell can be set in the center cavity of the attachment. The cell is mounted on a circular stainless-steel base, from which four pins protrude downward. Four holes on the floor of the attachment serve to fix the cell at the right position. The cell has two specially ground flats at the 0° and 180° faces, and is frosted on the inside surface of the backwall to minimize stray light. It is 7 cm tall, the inner diameter is 3.7 cm.

Water controlling the temperature in the attachment is forced by a gear pump from a large thermostat, the temperature of which is controlled within $\pm 0.01^\circ \text{C}$, through rubber tubing to the attachment. The actual fluctuation of temperature in the cell was within $\pm 0.1^\circ \text{C}$ at moderate temperatures, but becomes worse with the temperature rise, and reached $\pm 0.2^\circ \text{C}$ at the highest temperature examined.

The instrument with the above mentioned cell and attachment was calibrated by comparing the excess scattering over solvent of a polystyrene solution observed in a semi-octagonal cell at 90° with that observed in the cylindrical cell. In addition, the angular envelope of the cell was checked by measuring the fluorescence of a very dilute fluorescein solution. It was found that the observed intensity was independent of angle (from 30 to 135°) after the correction for the volume viewed has been made.

Distilled water was used as solvent for the MPd-12 in the absence and the presence of added solubilize. In the case of SDS, 0.1 m sodium chloride solution was used in order to eliminate the charge effect. A master solution containing about 6 g. of surfactant in 100 ml. of solution was prepared, and a series of solutions of the desired surfactant concentration was prepared from the respective master solution by diluting with the solvent. Each solution was made dust-free by filtering under pressure directly in the clean cell, immediately before the measurement, through "Cella-filter fein" of the Membranfiltergesellschaft, Göttingen.

When the amount of solubilize is within the solubilizing power of the surfactant, a master solution containing about 6 g. of a mixture of surfactant and solubilize in 100 ml. of solution was prepared and shaken for one day. After equilibrium was attained, a

series of solutions of the desired concentration was prepared from the master solution by dilution with distilled water.

To prepare the saturated solution with reference to the n-decane, an excess of n-decane was added to the aqueous solution of MPd-12 (about 2 wt. %), and shaken for 2 days vigorously with a mechanical shaker in a thermostat. After equilibrium was attained, the mixture was allowed to settle quietly for a day or more. The lower transparent aqueous phase saturated with the n-decane was used as the master solution, the concentration of which was determined by weighing the solute after freeze-drying. A 60 ml. of the solution was filtered under pressure directly in the clean cell through "cella-filter fein" at the temperature of the measurement. After the temperature equilibrium was attained (after about 1 hr.), the reduced intensity of scattered light, R_0 , was determined. Then a 10 ml. of solution was withdrawn with a pipet and a 10 ml. of water cleaned by filtration was added with the same pipet. After temperature equilibrium was attained, measurement was made again. This procedure was repeated and measurements were made for various concentrations. The reduced intensity of the pure solvent was determined at all temperatures and subtracted from that of solutions.

The dissymmetry corrections were not applied in micellar weight determinations, because I_{45}/I_{135} observed did not significantly deviate from 1 in all cases.

Cloud Point

To a series of test tubes, various amounts of each solubilize were weighed in each tube, and 10 ml. of 2% aqueous MPd-12 solution was added. After sealing, the tubes were heated over cloud point, shaken vigorously, cooled rapidly, and then shaken again. They were placed side by side in a temperature-controlled bath. The regulator was adjusted manually until a temperature just below the cloud point was reached. A slow careful increase in temperature then permitted accurate observation of the point of clouding.

Results and Discussion

Fundamental interpretation of light scattering data for dilute colloidal solutions is based on the following relationship.

$$K C m / R_{90} = 1/M + 2 B C m \quad [1]$$

$$K = \frac{2 \pi^2 n_0^2 (dn/dc)^2}{\lambda_0^4 N} \quad [2]$$

where R_{90} is the reduced intensity at 90° of the solution minus that of the solvent, n_0 and n are the refractive indices of the solvent and the solution, respectively, Cm is the concentration of micelles in g/ml. and is assumed to be equal to $C - C_0$, where C is the stoichiometric concentration and C_0 is the monomer concentration (the critical micelle concentration), λ_0 is the wave length of incident light in vacuum, N is *Avogadro's* number, M is the micellar weight and B is the apparent second virial coefficient.

Fig. 1 and 2 illustrate the reduced intensity vs. concentration curves for MPd-12 and SDS at several temperatures. The critical

micelle concentration, C_0 , was estimated by extrapolating each curve smoothly from higher concentration region to the abscissa.

In fig. 3 and 4 are shown typical plots of $K C m / R_{90}$ as a function of $C m$ at various temperatures for MPd-12 and SDS, respectively. The micellar weights are calculated by extrapolating these straight lines to zero concentration and the apparent second virial coefficients are calculated from the slope of these lines. The results obtained are summarized in table I. In the MPd-12 solution at above 60°C , a slight curvature

of the plots of $K C m / R_{90}$ vs. $C m$ is observable. This curvature could be caused either by the quadratic term of the light scattering equation or also by an effect of concentration on aggregation. In the present case it is questionable that the quadratic term takes a significant value, because the upward slope is not observed. The fact that the cloud point of the MPd-12 solution rises at concentration range lower than 0.6 g/dl. may reflect any dependency of the aggregation on concentration. The extrapolation of $K C m / R_{90}$ at low concentration is, therefore, rather

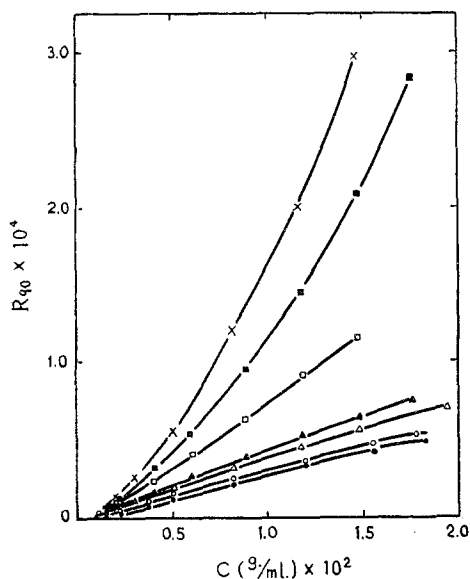


Fig. 1. Variation of R_{90} with concentration of aqueous solutions of MPd-12 at various temperature: ● 9.7° , ○ 29° , △ 50.7° , ▲ 58.5° , □ 69.7° , ■ 73.4° , × 75°

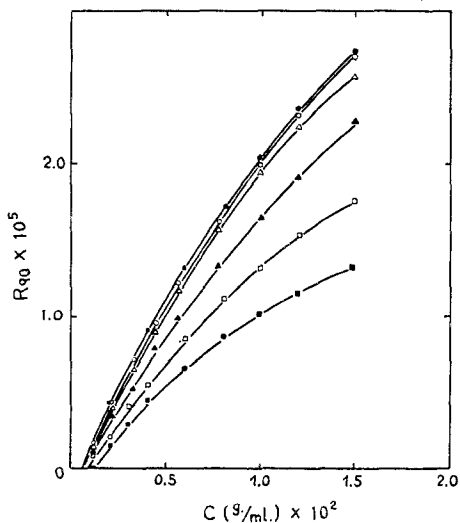


Fig. 2. Variation of R_{90} with concentration of sodium dodecyl sulfate in 0.1 m. NaCl at various temperature. ● 17° , ○ 18° , △ 20° , ▲ 30° , □ 50.2° , ■ 69.8°C

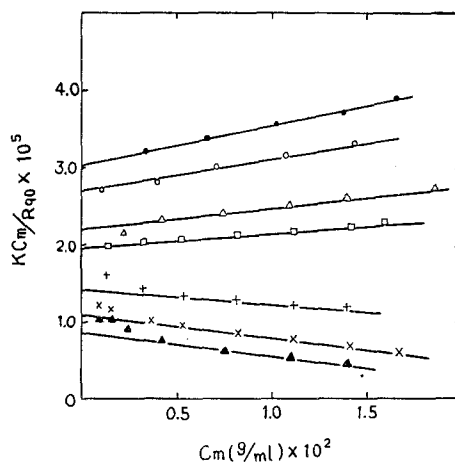


Fig. 3. Variation of $(K C m / R_{90})$ with concentration of MPd-12 in water: ● 9.7° , ○ 29° , △ 50.7° , □ 58.5° , + 69.7° , × 73.4° , ▲ 75°C

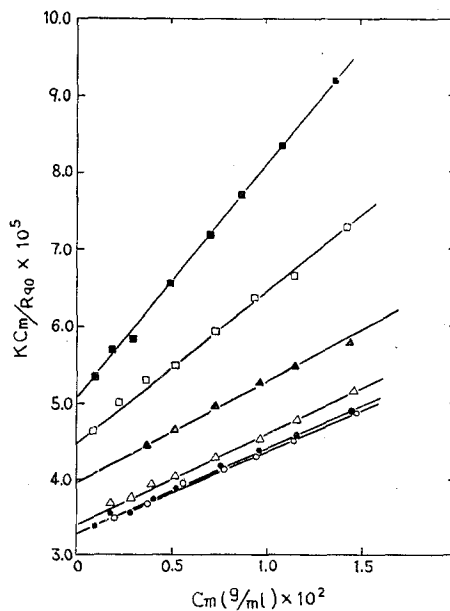


Fig. 4. Variation of $(K C m / R_{90})$ with concentration of sodium dodecyl sulfate in 0.1 m. NaCl : ○ 17° , ● 18° , △ 20° , ▲ 30° , □ 50.2° , ■ 69.8°C

Table 1

Light scattering results on MPd-12 in water and sodium dodecyl sulfate in 0.1 m NaCl at various temperature

| Temp. °C | dn/dc | Monomer conc. $C_0 \times 10^2$ (g/ml.) | Micellar weight $M \times 10^{-4}$ | No. soap molecules per micelle | Second virial coeff. $B \times 10^4$ | Micellar charge p | Degree of dissoc. p/n |
|-------------------|--------------------|---|---------------------------------------|-----------------------------------|---|------------------------|----------------------------|
| MPd-12 in water | | | | | | | |
| 9.7 | 0.131 ₅ | 0.17 ₀ | 3.29 | 47 | 2.55 | | |
| 29.0 | .128 ₆ | .11 ₁ | 3.71 | 53 | 2.06 | | |
| 50.7 | .125 ₄ | .07 ₃ | 4.55 | 65 | 1.36 | | |
| 58.5 | .124 ₂ | .07 ₀ | 5.15 | 73 | 1.01 | | |
| 69.7 | .122 ₅ | .06 ₂ | 7.09 | 101 | — 0.85 | | |
| 73.4 | .122 ₀ | .06 ₀ | 9.26 | 131 | — 1.50 | | |
| 75.0 | .121 ₇ | .06 ₀ | 11.6 | 165 | — 1.51 | | |
| SDS in 0.1 m NaCl | | | | | | | |
| 17.0 | 0.117 ₇ | 0.04 ₀ | 3.04 | 106 | 5.40 | 14.2 | 0.133 |
| 18.0 | .117 ₇ | .04 ₀ | 3.03 | 105 | 5.47 | 14.3 | .136 |
| 20.0 | .117 ₇ | .04 ₁ | 2.92 | 101 | 5.90 | 14.3 | .141 |
| 30.0 | .117 ₇ | .04 ₃ | 2.52 | 88 | 6.55 | 13.0 | .148 |
| 50.2 | .117 ₇ | .07 ₂ | 2.24 | 78 | 9.85 | 14.2 | .182 |
| 69.8 | .117 ₇ | .11 ₀ | 1.97 | 68 | 15.7 | 15.9 | .234 |

difficult owing to the curvature of the plots, and the limiting molecular weight determined by this method includes unavoidable uncertainty. However, the substantial differences between the micellar weights at different temperatures are greater than can be accounted for by experimental shortcomings.

Fig. 5 shows how micellar weight and critical micelle concentration vary with temperature. From fig. 5 it is clear that in aqueous solution of MPd-12 the micellar weight increases with increase in temperature, especially rapidly with the approach of the cloud point, and CMC decreases with increasing temperature. As shown in table 1, the apparent second virial coefficient, B , has a negative temperature coefficient, which suggests that with rise in temperature the hydration will decrease. When the hydrophilicity of the ethylene oxide chain is decreased by the elevation of temperature, the cohesive force between hydrocarbon chains, which hitherto counterbalanced the hydration effect, becomes predominant, thus causing lower CMC and higher micellar weight. *McBain* and *Marsden* (6) found that the aqueous solutions of diethylene glycol monolaurate and glycerol monolaurate formed two phases, one of which was isotropic and gave no long spacing and the other was liquid crystal and gave a long spacing which varied as the reciprocal of the concentration. This fact may suggest that in liquid crystal

lamellar micelles exist. Also the above mentioned two phase separation is considered to be equivalent to phase separation of an aqueous solution of non-ionic surfactants at higher temperatures than the cloud point. A possible interpretation for clouding formation is that the micelle grows larger and larger with the elevation of temperature and at cloud point its opalescence becomes perceptible even with the naked eye. At a higher temperature the micelle cannot move about in its solution, because of the buoyancy overwhelming the *Brownian* motion or the local convection, and floats up or sinks down thus causing the phase separation into two layers.

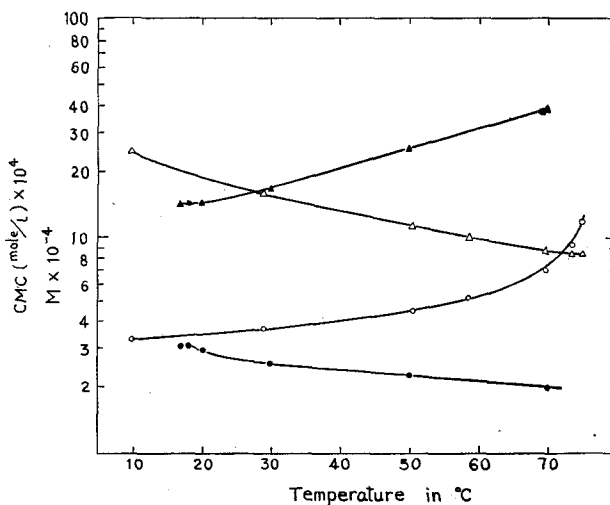


Fig. 5. Temperature-dependence of micellar weight and critical micelle concentration for MPd-12 in water and sodium dodecyl sulfate in 0.1 m. NaCl. ○ MPd-12, ● SDS for micellar weight, △ MPd-12, ▲ SDS for CMC

On the other hand, in the solutions of SDS in 0.1 M NaCl the micellar weight decreases slightly with increase in temperature, and CMC increases with increasing temperature. The micellar weight of the ionic surfactants is controlled mainly by three forces, namely the electrical repulsive forces of the ionized groups, the *van der Waals* attractive forces between the long hydrocarbon chains, and the thermal forces. Since the direct effect of the temperature rises on the ionization and its secondary effect brought about by the lowering of the dielectric constant of water approximately cancels each other (7), its over-all effect on the electrical forces should be small. Since the *van der Waals* forces are also independent of temperature, the decrease in micellar weight is most likely due to the increased thermal forces.

According to *Myself* (8), the initial slope of $K C m / R_{90}$ vs. $C m$ plots is related to the micellar charge, p , by the following equation.

$$\left[\frac{\partial (K C m / R_{90})}{\partial C m} \right]_{C m = 0} = \frac{p^2}{2 \kappa M^2},$$

where κ is the concentration of simple electrolyte at CMC in equiv./ml. and M is the micellar weight. The equation is precise at low $C m$ values, but errors in $K C m / R_{90}$ in

this region are the largest, owing to uncertainties in the correct value of CMC and to the very low turbidities observed. Therefore, the micellar charge, p , was calculated using the micellar weight and the slope obtained from the measurements at higher concentration regions. The results are given in table 1. The micellar charge, p , of about 14 estimated for SDS is very close to the value obtained by other workers (1c, 9, 10) and seems to be independent of temperature. It seems to be evident that the apparent degree of electrolytical dissociation, p/n , increases with increasing temperature.

In the presence of solubilized n-decane or n-decanol, the plots of R_{90} as a function of the total solute concentration (surfactant plus solubilize, g/ml.) at various temperatures show a very high and sharp peak below a certain concentration, as described in a previous paper (2), and above this concentration the curves resemble typical R_{90} vs. C plots for polymer solutions, as the solubilize is fully solubilized by the micelles. However, it is expected that the composition of micelle changes in lower concentration range where mono-molecularly dispersed surfactant occupies a large portion of total surfactant. Therefore the critical micelle concentration, C_0 , is given as the concentration where the

Table 2
The micellar weight of MPd-12 with solubilize

| Solubilize MPd-12 (wt. %) | Monomer conc. $C_0 \times 10^2$ (g/ml.) | Micellar weight $M \times 10^{-4}$ | No. MPd-12 molecules per micelle | No. oil molecules per micelle | Second virial coeff. $B \times 10^4$ |
|---|---|--|--|-------------------------------------|--|
| at 30° C, $(dn/dc) = 0.128_5$ solubilized n-decanol | | | | | |
| 0 | 0.105 | 3.72 | 53 | 0 | 2.06 |
| 1.87 | .105 | 4.31 | 60 | 5 | 1.97 |
| 4.56 | .099 | 5.05 | 69 | 14 | 1.96 |
| 7.75 | .092 | 6.00 | 79 | 27 | 1.84 |
| 9.17 | .088 | 6.42 | 83 | 33 | 1.81 |
| 11.10 | .085 | 8.75 | 112 | 55 | 0.70 |
| 19.08 | .070 | 25.0 | 298 | 250 | 0.46 |
| at 45° C, $(dn/dc) = 0.126_5$ solubilized n-decanol | | | | | |
| 0 | 0.082 | 4.30 | 61 | 0 | 1.40 |
| 5.37 | .078 | 7.17 | 97 | 23 | 0.52 |
| 9.17 | .075 | 9.00 | 117 | 48 | 0.52 |
| 10.68 | .074 | 18.2 | 233 | 110 | 0.0 |
| 12.75 | .073 | 22.7 | 286 | 161 | 0.0 |
| 17.31 | .069 | 30.7 | 371 | 283 | 0.0 |
| at 50° C, $(dn/dc) = 0.125_5$ solubilized n-decanol | | | | | |
| 0 | 0.078 | 4.55 | 65 | 0 | 1.36 |
| 1.86 | .078 | 5.10 | 71 | 6.5 | 1.36 |
| 2.23 | .076 | 5.14 | 71 | 7 | 1.33 |
| 3.53 | .075 | 5.37 | 74 | 13 | 1.24 |
| 5.58 | .073 | 5.99 | 80 | 22 | 0.81 |
| 7.52 | .071 | 6.27 | 83 | 30 | 0.78 |
| satd. (8.7) | .070 | 7.41 | 97 | 41 | 0.65 |

abscissa crosses with R_{90} vs. C curve extrapolated smoothly from higher concentration region.

In order to analyse the light scattering data obtained, we have assumed the following two conditions, i. e., (a) as in the solvent with regard to micelles, there exists a solution having a definite concentration C_0 , at each

inclination of lines. The numbers of surfactant and solubilize molecules constituting one micelle were calculated from micellar weight and mixing ratio.

The data from light scattering measurements for various solubilize/MPd-12 ratios are summarized in table 2, and the micellar weight as a function of solubilize/MPd-12

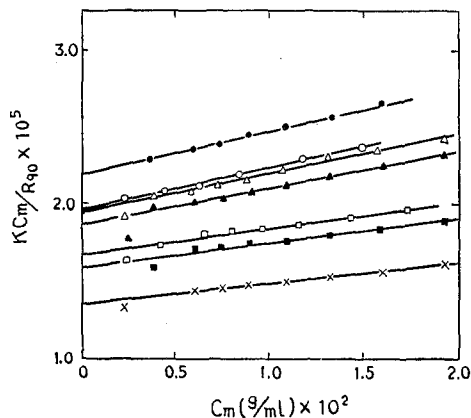


Fig. 6. Variation of KCM/R_{90} with concentration at various n-decane/MPd-12 ratios at 50° C. n-decane/MPd-12 ratio = ● 0%, ○ 1.86%, △ 2.23%, ▲ 3.53%, □ 5.58%, ■ 7.52%, × satd. (8.7%)

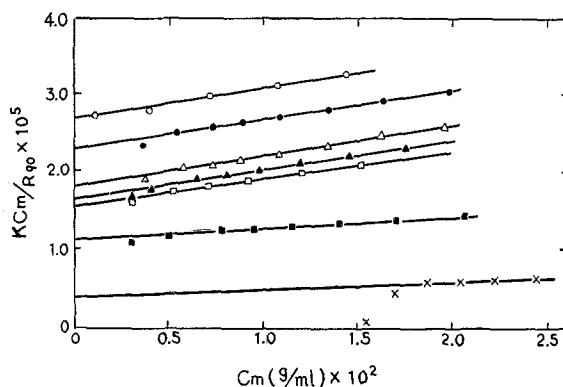


Fig. 7. Variation of (KCM/R_{90}) with concentration at various n-decanol/MPd-12 ratios at 30° C. n-decanol/MPd-12 ratio = ○ 0%, ● 1.87%, △ 4.56%, ▲ 7.75%, □ 9.17%, ■ 11.10%, × 19.08%

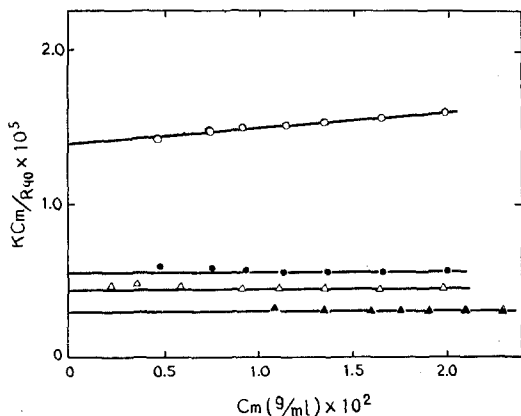


Fig. 8. Variation of (KCM/R_{90}) with concentration at various n-decanol/MPd-12 ratios at 45° C. n-decanol/MPd-12 ratio = ○ 5.37%, ● 10.68%, △ 12.75%, ▲ 17.31%

solubilize/surfactant ratio, and (b) the composition of the micelle is not affected by the concentration of solution. And the equation [1] is applied. Since the plots of KCM/R_{90} as a function of C_m at various temperatures, as shown in figs. 6–11, were linear except in the lower concentration region, the values of the micellar weight, M , were calculated from the reciprocal of the extrapolated values. The apparent second virial coefficients were estimated from the

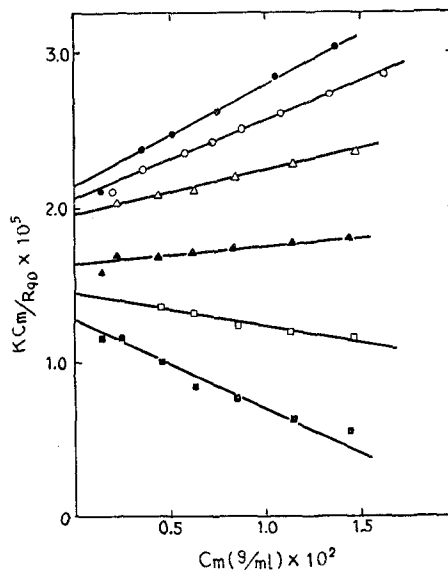


Fig. 9. Variation of (KCM/R_{90}) with concentration at n-decane/MPd-12 ratio of 0.0186 at various temperature. ● 9.6°, ○ 30°, △ 50°, ▲ 60°, □ 66.6°, ■ 69° C

ratio is shown in fig. 12. It is seen from fig. 12 the micellar weight increases steadily with increasing solubilization of n-decane up to saturation and does not increase with further addition of hydrocarbon exceeding the saturation. This result agrees with the

Table 3
The effect of temperature on the micellar weight of MPd-12 solubilizing n-decane or n-decanol

| Temperature t °C | dn/dc | Monomer conc. $C_0 \times 10^2$ (g/ml.) | Micellar weight $M \times 10^{-4}$ | No. MPd-12 molecules per micelle | No. oil molecules per micelle | Second virial coeff. $B \times 10^4$ | |
|--|-------------------------------|---|--|--|-------------------------------------|--|------|
| n-decane/MPd-12 = 1.86×10^{-2} g/g | | | | | | | |
| 9.6 | 0.131 ₅ | 0.165 | 4.67 | 65 | 5.9 | 3.20 | |
| 30.0 | .128 ₅ | .105 | 4.83 | 67 | 6.1 | 2.33 | |
| 50.0 | .125 ₅ | .078 | 5.10 | 71 | 6.5 | 1.36 | |
| 60.0 | .124 ₀ | .070 | 6.12 | 85 | 7.8 | 0.57 | |
| 66.6 | .123 ₀ | .062 | 6.90 | 96 | 8.8 | -1.10 | |
| 69.0 | .121 ₀ | .062 | 7.87 | 110 | 10 | -2.88 | |
| n-decanol/MPd-12 = 9.17×10^{-3} g/g | | | | | | | |
| 10.0 | 0.131 ₅ | 0.145 | 5.62 | 73 | 30 | 2.37 | |
| 29.9 | .128 ₅ | .088 | 6.42 | 83 | 33 | 1.81 | |
| 43.4 | .126 ₅ | .076 | 8.45 | 110 | 44 | 0.54 | |
| 49.7 | .125 ₅ | .070 | 10.75 | 140 | 57 | 0.18 | |
| 55.4 | .124 ₇ | .066 | 14.3 | 186 | 76 | -0.36 | |
| 61.4 | .123 ₈ | .062 | 31.1 | 404 | 163 | -0.45 | |
| MPd-12 saturated with n-decane | | | | | | | |
| | n-decane MPd-12 (wt. %) | | | | | | |
| 10.0 | 2.6 | 0.131 ₅ | 0.163 | 5.67 | 78 | 10 | 4.00 |
| 30.0 | 4.4 | .128 ₅ | .102 | 6.27 | 85 | 18 | 2.20 |
| 50.0 | 8.7 | .125 ₅ | .070 | 7.41 | 97 | 41 | 0.65 |
| 60.0 | 13.5 | .124 ₀ | .068 | 10.20 | 127 | 84 | 0.00 |

conclusion given by *Mattoon* et al. (11) from the analysis of X-ray pattern. When n-decanol is solubilized into the MPd-12 solutions, as shown in fig. 12, the micellar weight increases linearly with increasing n-decanol/MPd-12 ratio until a ratio of approximately 0.1 is reached, from whence an abrupt increase in micellar weight occurs.

The marked change may be ascribable to the change of micelle structure, e. g. from a nearly spherical micelle to a disklike micelle, although the dissymmetry was scarcely altered. As shown in table 2, the increase in micellar weight due to solubilization does not only originate from the simple incorporation of solubilize molecules into

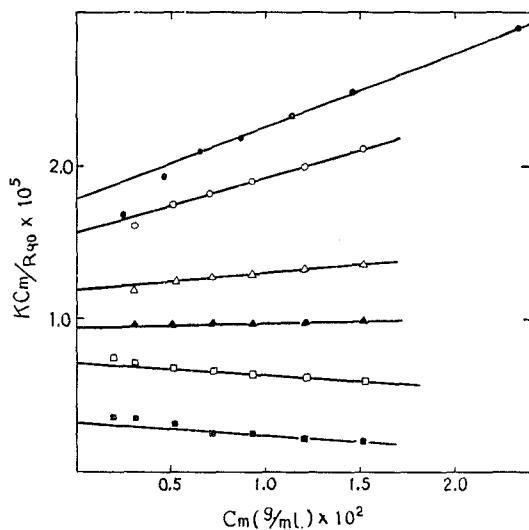


Fig. 10. Variation of (KCm/R_{90}) with concentration at n-decanol/MPd-12 ratio of 0.0917. ● 10°, ○ 29.9°, △ 43.4°, ▲ 49.7°, □ 55.4°, ■ 61.4° C

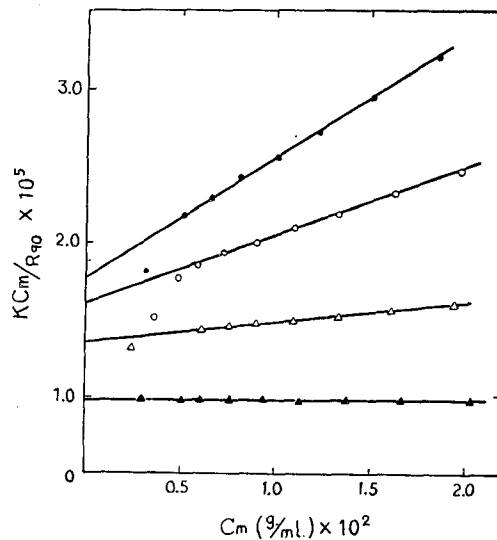


Fig. 11. Variation of KCm/R_{90} with concentration in aq. soln. of MPd-12 saturated with n-decane at various temperatures. ● 10°, ○ 30°, △ 50°, ▲ 60° C

the existing micelle but also from the increase of the number of surfactant molecules, which are in the micelle, with the added solubilizate. Thus the solubilization process is accompanied by the reconstitution of the micelles. The monomer concentration, C_0 , and the apparent second virial coefficient, B , decrease with the increase of solubilizate.

The data from light scattering measurements at various temperatures for the solutions at the n-decane/MPd-12 ratio of

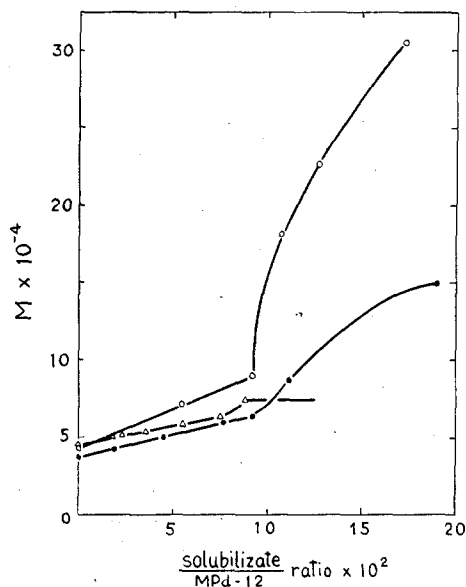


Fig. 12. Variation of the micellar weight with solubilizate/MPd-12 ratio. ● at 30°, ○ at 45° for MPd-12 ~ n-decanol system, △ at 50° C for MPd-12 ~ n-decane system

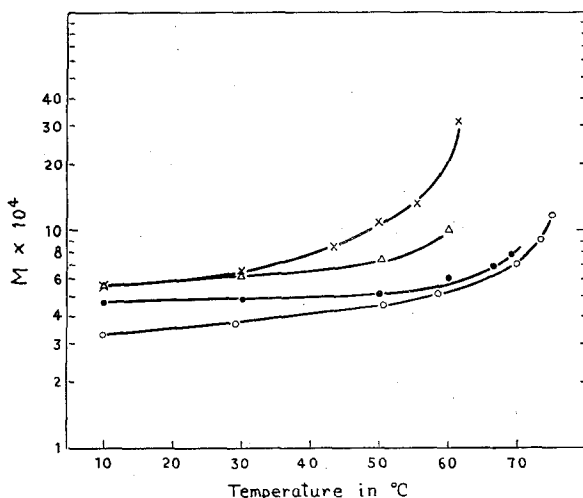


Fig. 13. Temperature-dependence of micellar weight in aqueous solution of MPd-12 solubilizing n-decane or n-decanol. ○ MPd-12 alone, ● n-decane/MPd-12 ratio of 0.0186, △ MPd-12 saturated with n-decane, × n-decanol/MPd-12 ratio of 0.0917

0.0186, n-decanol/MPd-12 ratio of 0.0917, and MPd-12 saturated with n-decane are summarized in table 3. The logarithm of these micellar weights as a function of temperature is shown in fig. 13 together with that of MPd-12 alone.

The micellar weights described in table 3 for the aqueous solution of MPd-12 saturated with n-decane are given in order to show qualitative tendency. This is because when the aqueous solution of MPd-12 saturated with n-decane is diluted with distilled water, it may be expected that some of the surfactant molecules in micellar state will dissociate to monomolecular state, and the n-decane molecules hitherto solubilized will be released from micelles to the aqueous medium, and there form large particles. The reduced intensity, R_{90} , therefore, will be somewhat larger than the expected value in lower concentration, and thus the slope of the plots of $K C m_i / R_{90}$ vs. $C m_i$ tends to enlarge and the micellar weight obtained will be larger than the true value. But the growing in micellar weight due to the temperature elevation may be pointed out clearly.

In order to make clear the effect of solubilizate on the cloud point, the solubilization and cloud point curves are illustrated in figs. 14 and 15 according as the solubilizate is n-decane or decanol. In the domain lying under the cloud point curve and at left side to the solubilization curve, only one phase does exist. The numbers in each point express the micellar composition (aggregation numbers of MPd-12 and solubilizate) and the concentration of molecularly dispersed species in millimole per liter. The values are quoted from table 2 and 3. As shown in figs. 13-15, it is common to all systems that the micellar weight increases with increasing temperature, especially rapidly near the cloud point. However, there is a difference in the way of the increase of the micellar weight between the solubilization of n-decane and n-decanol. The micellar weight of the aqueous solution of MPd-12 at the n-decane/MPd-12 ratio of 0.0186 at 10° C is close to that for MPd-12 saturated with n-decane on account of the amount solubilized near the saturation. With increasing temperature the micellar weight of the former approaches gradually to that for MPd-12 without added solubilizate, because the amount solubilized becomes progressively smaller as compared with the saturation amount. From the data in the aqueous solution of MPd-12 saturated with n-decane, it is expected that the rate

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Wissenschaftliche Kurzberichte

Kurz-Mitteilungen sichern rasch die Priorität. Die Verantwortung für den Inhalt trägt der Autor. Erscheinungstermin ca. innerhalb 2–6 Wochen nach Einreichung. Umfang der deutlich (Formeln!) geschriebenen Manuskripte bis zu 2 Maschinenseiten. Abbildungen vermeiden. Sonst klischierfähige Zeichnungen mit Beschriftung in weichem Blei. Sonderdruckfreiemplare wie bei Originalarbeiten. Manuskripte an: Prof. F. H. Müller, Marburg/L., Georg-Voigt-Str. 5. Herausgeber und Verlag

Aus dem Deutschen Kunststoff-Institut, Darmstadt

ESR-Untersuchungen an bestrahlten aromatischen Verbindungen

Von H. Fischer

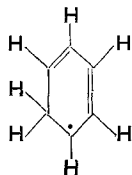
Mit 1 Abbildung in 2 Einzeldarstellungen

(Eingegangen am 6. November 1961)

Zur Identifizierung von langlebigen Radikalen, die als Teilnehmer an durch die Bestrahlung ausgelösten Reaktionen in aromatischen Verbindungen auftreten, wurden ESR-Untersuchungen an bestrahltem Benzol, Toluol, Äthylbenzol, Cumol, Fluorbenzol, Chlorbenzol und Polystyrol durchgeführt. Die Substanzen wurden bei 77 °K, Polystyrol auch bei Zimmertemperatur, dem Elektronenstrahl eines 1 MeV *van de Graaff*-Generators ausgesetzt. Anschließend wurden die ESR-Spektren mit einem Varian-Spektrometer mit 100 kHz-Modulation des Magnetfeldes aufgenommen. Die Temperatur der Proben während der Messung konnte von 100 bis 400 °K variiert werden.

Im Prinzip bestehen die Spektren aller untersuchten aromatischen Verbindungen aus einem Triplett, dessen Komponenten um $\Delta H \approx 50$ Oe getrennt liegen und in jeweils mehrere Einzellinien aufgespalten sind. Diese Triplettstruktur erscheint, auch nach Ergebnissen anderer Autoren (1, 2) an weiteren Substanzen, für Radikale in bestrahlten aromatischen Verbindungen charakteristisch. Damit treten hier stets Radikale des gleichen Typs auf. In diesen Radikalen muß weiterhin das unpaarige Elektron Valenzelektron von Ringkohlenstoffatomen sein.

Als Modellfall wird zur Bestimmung des Radikaltyps bestrahltes Benzol herangezogen, da dessen ESR-Spektrum auf Grund der guten Auflösung in Einzellinien sicher interpretiert werden kann. Im Temperaturbereich von 100–200 °K ist das Spektrum ein Triplett mit einer Aufspaltung $\Delta H_1 = 50 \pm 2$ Oe, dessen Komponenten jeweils aus einem Quartett mit einer Aufspaltung $\Delta H_2 = 10,6 \pm 0,5$ Oe bestehen. Dies ist auch von anderen Autoren (1) festgestellt worden. Die Auflösung steigt mit wachsender Temperatur. Bei einer Erwärmung der Probe auf 220 °K zeigt sich eine weitere dritte Aufspaltung aller Linien in vermutlich je drei Komponenten mit $\Delta H_3 = 2,6 \pm 0,2$ Oe (Abb. 1a).



Im Gegensatz zu anderen Deutungsversuchen (1), mit denen die jetzt gefundene dritte Aufspaltung ΔH_3 nicht befriedigend interpretiert werden kann, wird an-

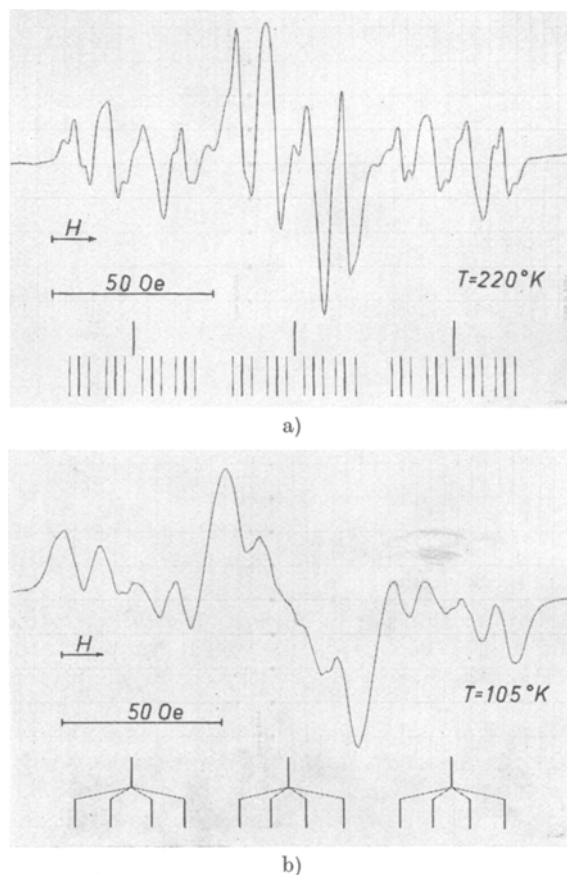


Abb. 1. ESR-Spektrum von Benzol, bestrahlt bei 77 °K. a) Meßtemperatur 220 °K. b) Meßtemperatur 105 °K; Probe $\frac{1}{2}$ h bei 220 °K getempert