Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Kitahara, Ayao , Tamura, Takemitsu and Kon-no, Kijiro(1980) 'Effect of Water on Flocculation of Carbon Black in Nonaqueous Surfactant Solutions', Separation Science and Technology, 15: 3, 249 — 261

To link to this Article: DOI: 10.1080/01496398008068482

URL: http://dx.doi.org/10.1080/01496398008068482

SEPARATION SCIENCE AND TECHNOLOGY, 15(3), pp. 249-261, 1980

EFFECT OF WATER ON FLOCCULATION OF CARBON BLACK IN NONAQUEOUS SURFACTANT SOLUTIONS

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ABSTRACT

The effect of solubilized water on stability or flocculation of four kinds of carbon blacks dispersed in cyclohexane solutions of anionic (AOT) or nonionic (NP-8) surfactants was studied. The stable region (A) appeared at the lower concentration range of water. The stability decreased with increasing concentration of water. An additional increase of water concentration caused marked flocculation (region B) followed by the apparent stable dispersion (region C). The stability of the region A and the transient region to B was elucidated by the interaction of the electric double layers for AOT systems. The flocculation at B may be due to increase of interfacial tension because of the water layer formed on carbon-black particles. The apparent stability of the region C is considered to result from the network structure formed among carbon particles and water-in-oil microemulsion particles for AOT systems. This was suggested from shear rate-stress curves. The appearance of the region C for NP-8 systems is considered to be caused by the viscosity (lamellar structure) of the solution.

INTRODUCTION

Many studies have been done on the dispersibility of carbon black in nonaqueous media (1). The effect of surface charge or surface potential on dispersibility has also been discussed (2). The important role of a small quantity of water had often been indicated in nonaqueous media. For example, the effect of water in the ppm range on the dispersion of TiO_2 in nonaqueous surfactant solutions has been published by Parfitt et al. (3). However, few studies have been carried out on the effect of water on nonaqueous carbon-black dispersions.

One of the authors (A.K.) and collaborators showed the existence of the effect of water on the electrokinetic potential of so-called hydrophobic particles, carbon black, in nonaqueous surfactant solutions. They referred also to the effect of water on the stability of the carbon-black dispersion as well as the zeta-potential (4).

In this paper, the study will be mainly focused on the stability or flocculation of carbon black in nonaqueous surfactant solutions. Additionally, the range of water content in the solubilized state will be much more enlarged than the previous work (4). An interesting dispersibility behavior results from it. The mechanism of the behavior will be discussed from measurements of zeta-potential, viscosity, and water solubilities.

MATERIALS

Four kinds of carbon blacks, shown in Table 1, were used. The mean particle size, surface area, and pH of each kind published by each maker are also indicated in the table. These carbon blacks were washed with aqueous hydrochloric acid, water, methanol, acetone, and finally cyclohexane, successively. This procedure was followed by drying in a vacuum for 6 hr at 150°C.

Sodium bis-(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) and octaoxyethylene nonylphenylether (NP-8) were used as the surfactants. The AOT was purified as follows: the filtrate of methanol solution of AOT from which the residue was filtered was treated with active charcoal, dried, and dissolved in benzene. A small quantity of inorganic electrolytes which affects markedly the solubility behavior of water in nonaqueous media

TABLE 1

Forms of Carbon Black Used and Their Properties

	Particle Size (mμ)	Surface Area (m^2/g)	pH
Sterling MT	238	7	9.5
Sterling R	75	25	8.5
MA 11	29	104	3.2
Special Black 4	26	180	3.0

was extracted from benzene solution with water. Finally, benzene was evaporated from the solution, followed by drying at 80°C and 0.1 mm Hg. Purification of NP-8 was accomplished by using the method described elsewhere (5). Cyclohexane as a solvent was purified as usual, distilled, and dried with Molecular Sieve 4A.

The stability of dispersion was estimated from the sedimentation experiment. The dispersion of particle concentration of 0.1 wt % carbon black was prepared in surfactant solutions solubilizing various amounts of water. The dispersion was shaken in a flask for 15 hr at 30°C and transferred in sedimentation tubes. The whole volume of dispersion had a height of 30 cm in each tube. The height of the sediment was recorded with time after shaking. Figures 1 and 2, made for the estimation of the stability, show the height after 6 hr.

The zeta-potential was calculated from the electrophoretic mobility obtained from microelectrophoresis (4) with the use of Hückel's equation. The dispersion used for microelectrophoresis was diluted to about 0.01% from that of the sedimentation experiment.

Shear rate — shear stress curves were obtained with the use of a double cylindrical rotational viscometer (the Rotovisco RV-3 of

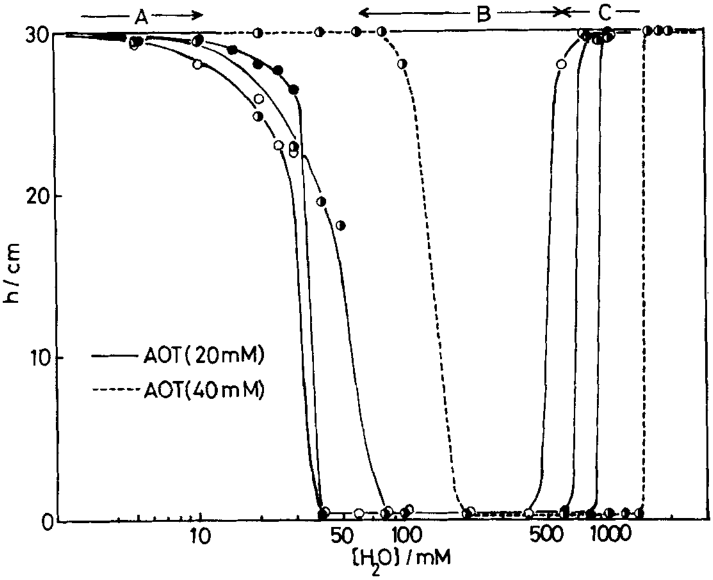

FIGURE 1. Change of sediment height h of carbon blacks with $[H_2O]$ for AOT-cyclohexane solutions (solid lines - 20 mM, dashed line - 40 mM). ◑ - sterling MT, ○ - sterling R, ● - MA 11).

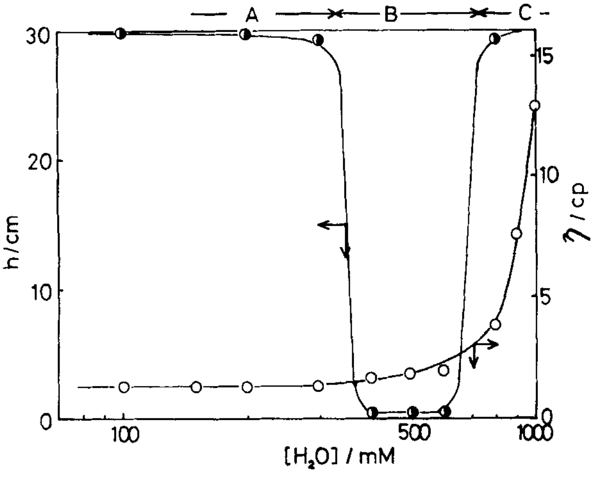

FIGURE 2. Change of sediment height h of carbon black (sterling MT) and viscosity η of dispersion media with $[H_2O]$ for NP-8-cyclohexane solution (0.1 M).

the Haake Company). The measurement was made with 0.1 wt % of carbon-black (Sterling MT) dispersion at 10°C.

The concentration of surfactants adsorbed on carbon black was determined by ultraviolet spectroscopy. The characteristic wave lengths were 210 nm for AOT and 282 nm for NP-8.

The sedimentation and the adsorption experiments were conducted at 30°C.

RESULTS

The sediment height at 6 hr after shaking is shown in Figs. 1 and 2 for AOT and NP-8 systems, respectively. The solid lines in Fig. 1 show the sedimentation curves of three types of carbon for 20 mM of AOT. The dashed curve in Fig. 1 and the sedimentation curve in Fig. 2 show data of Sterling MT in 40 mM of AOT and 100 mM of NP-8 solutions, respectively.

Three different regions in these figures were observed with an increase in water concentration [H_2O]. The region A is the stable and freely sedimenting region. The region B is the rapidly flocculating and sedimenting region, and the region C is the apparently stable and subsiding sedimentation region for both AOT and NP-8 systems. The transient region between A and B is displayed in Fig. 1.

The range of each region was not very different among the different kinds of carbon blacks in 20 mM AOT systems, as seen in Fig. 1. However, the range shifted considerably with the change of the concentration of AOT from 20 to 40 mM, as shown in Fig. 1 for Sterling MT.

The dependence of zeta-potential on [H_2O] in the transient region is depicted in Fig. 3. Each zeta-potential decreased with an increase of [H_2O].

The relation between shear rate and shear stress is shown in Fig. 4 for Sterling MT dispersion. The yield point and faint thixotropy could be observed by lowering the

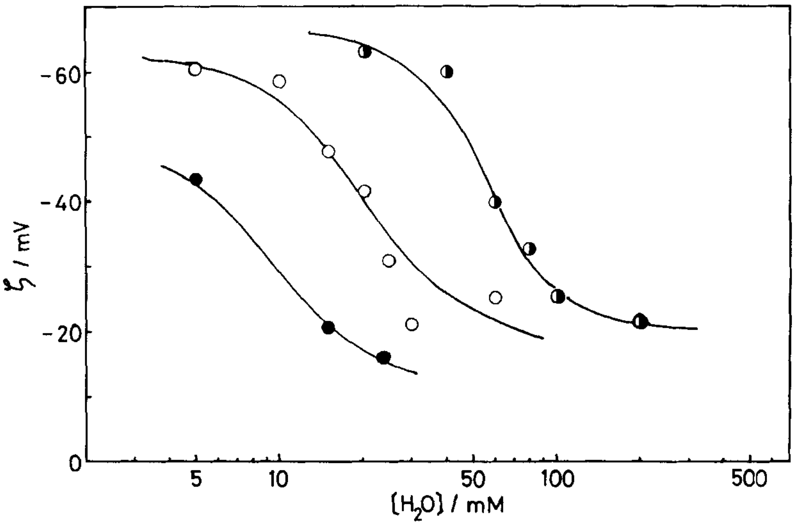

FIGURE 3. Effect of [H_2O] on zeta-potential ζ of carbon blacks dispersed in AOT (20 mM) cyclohexane solutions (◑ - sterling MT, ○ - sterling R, ● - MA 11).

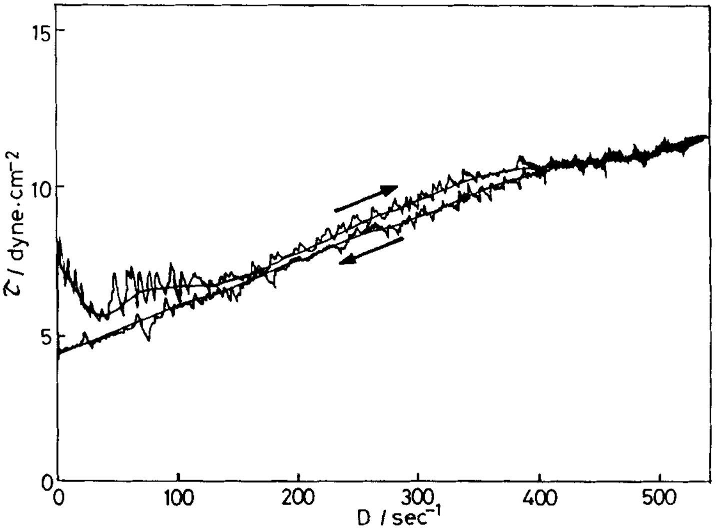

FIGURE 4. Shear rate (D)--stress (τ) curve of the sterling MT (0.1 %)-AOT (20 mM) - H_2O (800 mM) system.

measurement temperature, though the measurement was difficult because of the low concentration of carbon black.

The adsorption isotherms of AOT and NP-8 on carbon black in cyclohexane are shown in Figs. 5 and 6, respectively, in which the amount adsorbed per unit weight of carbon black, Γ, is plotted as a function of concentration C. All of the isotherms followed Langmuir behavior. However, isotherms of AOT had much steeper initial slopes than those of NP-8.

DISCUSSION

The decrease of the stability of the transient region between A and B with increase of water concentration (Fig. 1) corresponds to the decrease of zeta-potential (see Fig. 3). Therefore, the stability of A and transient regions for the AOT systems can be elucidated by the interaction of the electric double layers. The stability in nonaqueous systems due to electric factors has

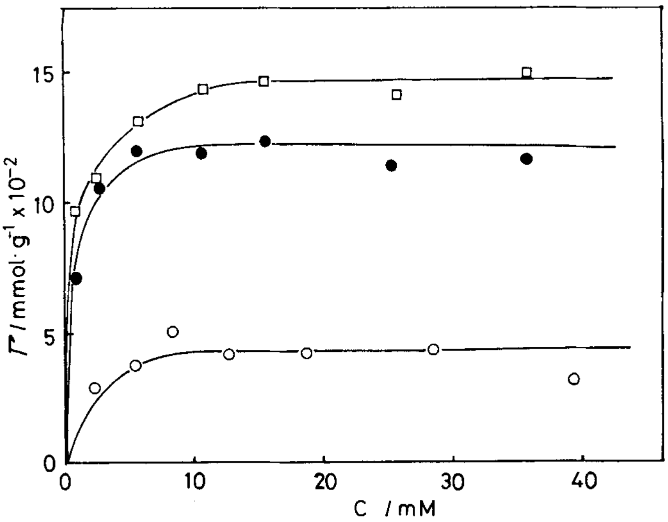

FIGURE 5. Adsorption isotherms of AOT on carbon blacks (○ - sterling R, ● - MA 11, □ - special black 4).

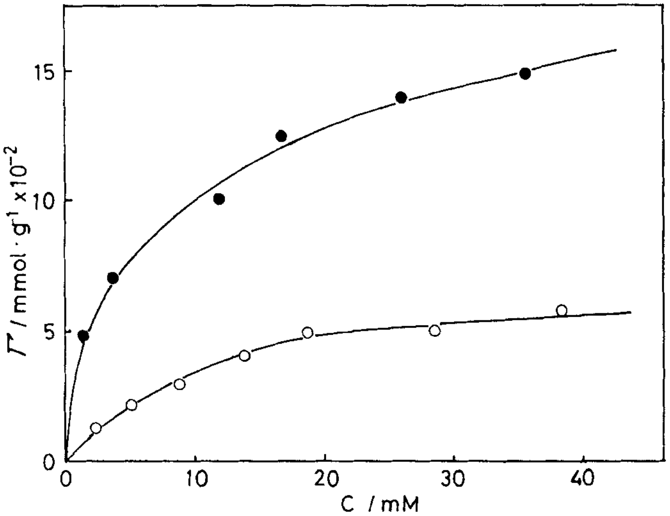

FIGURE 6. Adsorption isotherms of NP-8 on carbon blacks (○-sterling R, ●- MA 11).

been known for TiO_2 dispersion (3). The charge mechanism in nonaqueous systems has been proposed by one of the authors and collaborators (6).

Quantitatively, a considerable difference can be seen in the zeta-potentials of the three different kinds of carbon blacks in Fig. 1. In order to consider the quantitative relation between sedimentation and zeta-potential, it is necessary to calculate sedimentation or flocculating velocity instead of the sedimentation curve at a fixed time. (This remains to be done.)

The dispersion behavior in region A is shown schematically in Fig. 7(a). The decrease of zeta-potential with increase of $[H_2O]$ is considered to result from the transfer of Na^+ from the reversed micelle to the wet surface of carbon black, as shown in Fig. 7(b). This consideration was ascertained by the observation that the saturating amount of adsorption of AOT does not change with $[H_2O]$ in this range. The fast flocculation in the B-region may result from an increase of the interfacial tension between the water

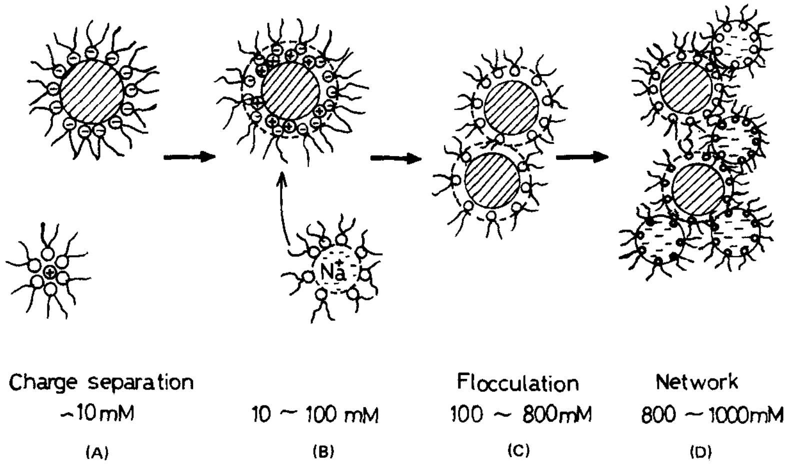

FIGURE 7. Schematic description of reversed micelles and carbon-black surfaces dispersed in AOT-cyclohexane solutions (hatched particles - carbon black, short lines - water).

layer formed on carbon black and the solvent. Here the surface charge seems to be perfectly neutralized, as shown in Fig. 7(c).

Region C is very peculiar. A large amount of water is solubilized in the AOT solution in this region and faint blue scattering light can be observed (7). The solubility region indicated in Ref. 7 has to be corrected because of the marked effect of minor inorganic impurities contained in the AOT sample. The revised solubility diagram of water in AOT-cyclohexane solution (20 and 40 mM) is shown in Fig. 8. The hatched area in this figure shows the area of so-called water-in-oil microemulsion, which swells by the solubilization of a large amount of water. The dispersion prepared by the addition of carbon black into the microemulsion (region C) shows the considerable stability and subsiding sedimentation. This behavior may be elucidated by the network formation among carbon-black particles and microemulsion particles, as shown in Fig. 7(d).

This network structure may be weak, because the particle concentration of carbon black is very low (0.1 wt %). This weak

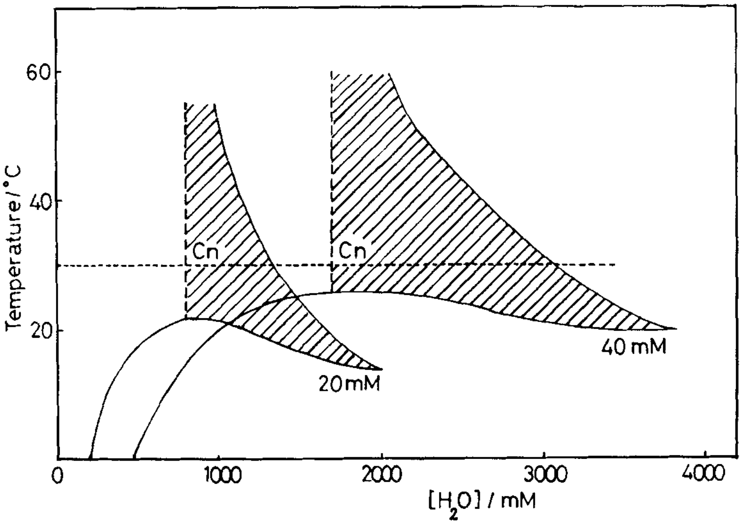

FIGURE 8. Solubility diagram of water in AOT-cyclohexane solutions. (Left region from hatched region is clear solubilization area.)

network can be illustrated from the appearance of the supernatant after standing overnight. The weak network structure can hardly be observed by the usual viscometer. Hysteresis or thixotropy could barely be observed with the use of 0.1% carbon-black dispersion at 10°C, as shown in Fig. 4. The formation of a very weak network structure at 30°C may be suggested from the result at 10°C.

A higher concentration of water may be required for the dispersion in more concentrated AOT solution to decrease its stability and zeta-potential. This factor is shown in Fig. 1 by comparing the sedimentation curve at 40 mM with that at 20 mM.

The behavior of the sedimentation curve of the dispersion in the nonionic surfactant, NP-8, in Fig. 2 is apparently similar to that of Fig. 1 of the AOT system. However, the mechanism is considerably different. The solubility diagram of water in the NP-8 cyclohexane solution is more complex than that of the AOT cyclohexane solution, as shown by the data presented in Fig. 9.

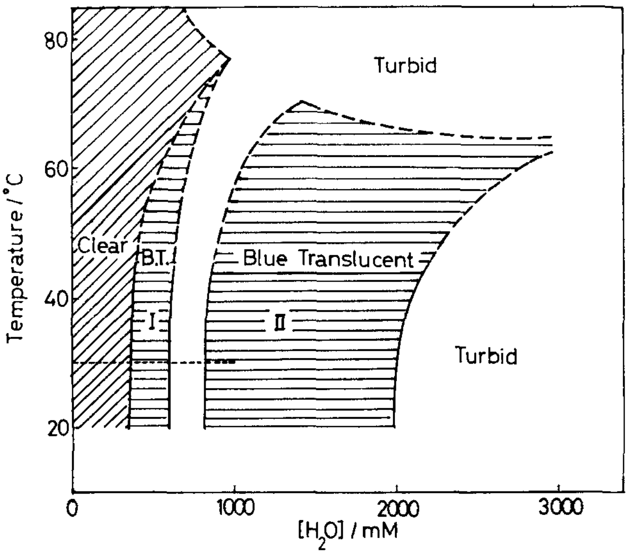

FIGURE 9. Solubility diagram of water in NP-8-cyclohexane solutions.

The first blue translucent regions (B.T.-I) represent a water-in-oil microemulsion and ranged from 400 to 600 mM of $[H_2O]$ at 30°C. This region indicates a low viscosity. The second blue translucent region (II) is suggested to be a lamellar structure region and is very viscous. These solution viscosities have also been described in Fig. 2.

Figure 2 shows that the appearance of water-in-oil microemulsion at 400 mM of $[H_2O]$ does not give rise to apparent stability, which differs from the case of AOT. However, the appearance of lamellar structure at 800 mM of $[H_2O]$ causes the apparent stability, where the increase of the solution viscosity can be observed. Therefore, the apparent stability (region C) of the NP-8 system is considered to result from the hold of carbon black particles in the viscous solution.

The different behavior between AOT and NP-8 can also be illustrated by the adsorption experiment. The area occupied by an adsorbed molecule at saturation (A_m) was calculated on the basis of the specific surface area in Table 1. The required saturation value of adsorption (Γ_m) for NP-8 was obtained from the modified Langmuir equation

$$\frac{C}{\Gamma} = \frac{1}{a\Gamma_m} + \frac{C}{\Gamma_m} . \qquad (1)$$

The results are listed in Table 2. The difference appears among A_m of AOT on three kinds of carbon blacks. However, carbon black particles are not perfectly dispersed in nonaqueous media as the primary particles for which the specific surface area was obtained. This dispersed state can be observed by an optical microscope. Therefore, the real A_m depends on the size of the secondary particles. Hence it is considered that the difference in A_m of AOT and NP-8 in Table 2 should not be emphasized.

Similarly, the use of Eq. (1) also permits values of the parameter a to be obtained from the adsorption data. The results are also listed in Table 2. The values of a in the AOT solutions are larger than those of NP-8. The value of a in the Langmuir equation is related to the value of the heat of adsorption (ΔH_{ad}) by the equation

$$a = K \exp(-\Delta H_{ad}/RT). \qquad (2)$$

Hence the heat of adsorption of AOT (more negative value) is higher than that of NP-8 because the value K is approximately

TABLE 2

Adsorption Data and Langmuir's Constant

	$10^{-2}\Gamma_m$(mmol/g)		A_m(A^2·molecule)		a (mM^{-1})	
	AOT	NP-8	AOT	NP-8	AOT	NP-8
Sterling R	4.1	5.9	100	70	700	70
MA 11	12	17	190	140	4100	180
Special Black 4	15	-	310	-	1500	-

constant. The AOT adsorption isotherm has a steeper slope than NP-8, as shown in Figs. 5 and 6, and AOT is therefore more strongly adsorbed on carbon black than NP-8. Hence AOT adsorbed strongly on carbon black can make a bridge between the carbon-black and microemulsion surfaces. On the other hand, NP-8 cannot make such a bridge in the microemulsion region because of weak adsorption. However, NP-8 in higher concentration (100 mM) can make a viscous solution (lamellar structure) by solubilization of a large amount of water and can hold the carbon-black particles in the very viscous solution.

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