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The Behavior of Carbon Black in a Detergent Solution

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The behavior of carbon black (CB) in a detergent (sodium dodecyl sulfate (SDS): 20%, zeolite: 20%, sodium silicate: 5%, sodium carbonate: 3%, sodium (carboxylatomethyl)cellulose (CMC): 1%, sodium sulfate: 51%) solution is discussed in terms of the ζ-potential and potential energy of interaction. The ζ-potential of CB in each solution of SDS, various builders, and the detergent was measured by microelectrophoresis. The potential energies between CB and fabrics (nylon and cellulose), between CB and clay, and between CB and zeolite were calculated by the use of the theory of heterocoagulation. The potential energy between one CB particle and another CB particle was calculated by the use of D-L-V-O theory. The ζ-potential was increased by the addition of builders, except sodium sulfate. The high negative ζ-potential of CB in the detergent solution resulted from the effect of builders. From the potential energies, it became evident that 1) CB in the detergent solution deposits with difficulty onto fabrics; 2) The CB coagulates with zeolite only with difficulty; 3) The CB coagulates with clay or CB.

The builder for a detergent should have the following effects: (1) Sequestration for Ca^{2+} and Mg^{2+}; (2) Buffer for a detergent solution at pH 9.0—10.5; (3) Dispersion of soils. Sodium triphosphate has the above effects and had been used as the main builder in detergents. However, in recent years, the sodium triphosphate levels in detergents have been reduced significantly because it accelerates the eutrophication of lakes and rivers. In the many detergents which have no sodium triphosphate, sequestration for Ca^{2+} and Mg^{2+} is performed by zeolite, sodium carbonate, and sodium silicate. On the other hand, the detergent solution is buffered by sodium silicate and sodium carbonate. The question has been raised whether the dispersion of soils in the detergent solution is satisfied or not. In previous work,[1] it was shown that the deposition of the particle soil, clay (Kanto loam), onto fabrics can be depressed by the coagulation of the particle soil with zeolite. Generally, particle soil contains 1.5% carbon black. In this study, carbon black was used as another particle soil. The behavior of carbon black in the detergent solution was discussed in terms of the D-L-V-O theory and the heterocoagulation theory.

Experimental

Materials. Carbon black (DIABLACK-G, Mitsubishi Chemical Indiustries Ltd." were used as a particle soil model. The particle radii of carbon black are 24.5—30 nm.[2] In this study, the radius was assumed to be 27.5 nm. Sodium dodecyl sulfate (SDS) which was extracted with diethyl ether and recrystallized from ethanol was used for a surface active agent in a detergent. The other chemicals used for builders, such as sodium triphosphate, sodium slicate, sodium carbonate, sodium (carboxylatomethyl)cellulose (CMC), and sodium sulfate, were of reagent grade. The detergent composition is shown in Table 1. Doubly-distilled water was used.

Table 1. Detergent composition

Materials	Compositional level wt%
SDS	20
Zeolite	20
Sodium silicate	5
Sodium carbonate	3
CMC	1
Sodium sulfate	51

Measurement of ζ-Potential. The ζ-potential was measured with an electrophoretic mass-transport analyzer in the previous work. The principle of this apparatus utilizes the difference between the density of particles and that of the solution. The surface of carbon black (CB) has many pores and is hydrophobic. The density was measured by a picnometer with hydrocarbon, methanol, or surfactant solution, and is about 1.8 g cm^{-3}.[2] The densities in aqueous solution used in this work seem to be lower than 1.8 g cm^{-3}, and to be changed by the kind of aqueous solution. Therefore, electrophoretic mass-transport analyzer is not well fitted for the measurement of the ζ-potential of CB. In this work, the ζ-potential of CB was measured with an LASER ZEE™ model 500 (PEN KEM Inc.). This apparatus uses microelectrophoresis, and is well fitted for the measurement of the ζ-potential of CB. The measurement was carried out with an applied potential gradient of 10 V cm^{-1} at 25 °C. The 0.0018 wt% suspension for ζ-potential measurement were prepared with an ultrasonic mixer for 10 min and allowed to stand for 12 h. The suspension were dispersed again with an ultrasonic mixer for 5 min before use. In some cases, the pH of the suspension was adjusted to the desired value by using dilute sodium hydroxide solution while stirring. The pH of the suspension was measured by a pH meter (HM-5A, TOA Electronics Ltd.).

Calculation of the Total Potential Energy. The potential energy for interaction between a spherical particle and a flat plate due to an electrical double layer is given by[3]

$$V_{E,S/P} = \frac{aD}{4kT}\left[(\psi_1^2+\psi_2^2)\ln\left\{\frac{\exp(2\kappa H_0)-1}{\exp(2\kappa H_0)}\right\} + 2\psi_1\psi_2\ln\left\{\frac{\exp(\kappa H_0)+1}{\exp(\kappa H_0)-1}\right\}\right], \tag{1}$$

where a is the radius of the sperical particle, k is Boltzmann's constant, T is the absolute temperature, H_0 is the distance between the surfaces, ψ_1 and ψ_2 are the surface potentials of materials 1 and 2, κ is Debye-Hückel reciprocal length parameter,[4]

$$\kappa = \sqrt{\frac{4\pi e^2(n_+Z_+^2+n_-Z_-^2)}{DkT}}. \tag{2}$$

$Z_{+\mathrm{or}-}$ is the valence of the ionic species in solution, $n_{+\mathrm{or}-}$ is the concentration (ions cm^{-3}) of the same species in solution, and e is the electronic charge.

The potential energy for interaction between a spherical particle and a flat plate due to van der Waals forces is given by[5,6]

$$V_{\mathrm{A,S/P}} = -\frac{A_{12/3}}{6kT}\left[\frac{2a(H_0+a)}{H_0(H_0+2a)} - \ln\frac{H_0+2a}{H_0}\right], \tag{3}$$

$$A_{12/3} = \sqrt{A_{11/3}\cdot A_{22/3}}. \tag{4}$$

$A_{11/3}$ and $A_{22/3}$ are Hamaker's constants for interaction between materials 1, 1 and materials 2, 2 in the separating medium 3.

The total potential energy for interaction between a spherical particle and a flat plate is given by the sum of $V_{\mathrm{E,S/P}}$ and $V_{\mathrm{A,S/P}}$:

$$V_{\mathrm{T,S/P}} = V_{\mathrm{E,S/P}} + V_{\mathrm{A,S/P}}. \tag{5}$$

The total potential energies for interaction between CB and nylon, between CB and cellulose were calculated from Eqs. 1—5.

It has been shown by Hogg *et al.*[7] that the potential energy for interaction between two spherical particles of radii a_1 and a_2 and surface potentials ψ_1 and ψ_2 is given by

$$V_{\mathrm{E,S/S}} = \frac{a_1a_2D}{4(a_1+a_2)kT}\left[(\psi_1{}^2+\psi_2{}^2)\ln\left\{\frac{\exp(2\kappa H_0)-1}{\exp(2\kappa H_0)}\right\} + 2\psi_1\psi_2\ln\left\{\frac{\exp(\kappa H_0)+1}{\exp(\kappa H_0)-1}\right\}\right] \tag{6}$$

The potential energy for interaction between two spherical particles due to van der Waals forces is given by Hamaker[8]

$$V_{\mathrm{A,S/S}} = -\frac{A_{12/3}}{12kT} \times\left\{\frac{y}{x^2+xy+x} + \frac{y}{x^2+xy+x+y} + 2\ln\frac{x^2+xy+x}{x^2+xy+x+y}\right\}, \tag{7}$$

where $x=H_0/2a_1$ and $y=a_2/a_1$. The total potential energies for interaction between CB and clay, and between CB and zeolite were calculated from Eqs. 6—7.

Verwey and Overbeek[9] have shown that the potential energies of interaction between two spherical particles are given by

$$V_{\mathrm{E}} = \frac{aD\psi^2}{2kT}\ln[1+\exp(-\kappa H_0)], \tag{8}$$

$$V_{\mathrm{A}} = -\frac{A}{6kT}\left(\frac{2}{S^2-4} + \frac{2}{S^2} + \ln\frac{S^2-4}{S^2}\right), \tag{9}$$

where $S=(2a+H_0)/a$. Equations 8 and 9 were used for calculation between one CB particle and another CB particle.

The above equations were expressed in kT units. Since the evaluation of surface potential involves some difficulties, the surface potentials were taken as the ζ-potentials. For the computation, the ζ-potentials of nylon, cellulose, clay, and zeolite in the previous paper were used. The Hamaker's constants for nylon and cellulose in water were estimated to be 5×10^{-14} erg from those for polyethylene and polystyrene.[10] The Hamaker's constants for zeolite and clay in water were estimated to be 4.4×10^{-13} erg from that for kaolinite.[11] The Hamaker's constant for CB in water was estimated to be 5×10^{-13} erg from that for graphite.[10] The radii of clay and zeolite were assumed to be 1×10^{-5} cm. The calculations of potential energies as a function of the distance between the surfaces were performed on an IBM 370 computer.

Results and Discussion

ζ-Potential of CB and the PH-Dependence. The water-soluble builders such as sodium triphosphate, sodium carbonate, and sodium silicate are added to water, and the pH of the solution is shifted to the alkali side. For this reason, the ζ-potentials of CB were measured in solutions of various pH (Fig. 1). The ζ-potential of CB is about −22 mV at pH 7, increased with increase of pH, and reached about −46 mV at pH 11. The structure of carbon black was reported by many investigators. Boehm[12] shows the surface structure model (Fig. 2). Murata and Imagawa[13] reported that the negative ζ-potential of carbon black results from the following mechanisms: (i) Ionization of –COOH and –OH or (ii) Adsorption of OH^- on the surface.

The Effect of Sodium Dodecyl Sulfate (SDS) on the ζ-Potential of CB and the Potential Energy. Figure 3 shows the effect of the concentration of SDS on the ζ-potential of CB. The negative ζ-potential of CB increased with increasing the concentration of SDS. The increase in the negative ζ-potential results from adsorption of dodecyl sulfate anion onto CB with some interactions such as van der Waals forces. Since the surface of CB is hydrophobic, the hydrophobic group of dodecyl sulfate anion are adsorbed directly to the surface of CB.

The ideal concentration of detergent is generally 0.2 wt% in washing process. Assuming the formulation of detergent shown in Table 1, the concentration of SDS in the 0.2 wt% detergent solution is 1.387×10^{-3} mol dm^{-3}. The ζ-potential of CB at this concentration was read from Fig. 3. The ζ-potentials of nylon, cellulose, zeolite, and clay in this concentration were −107,

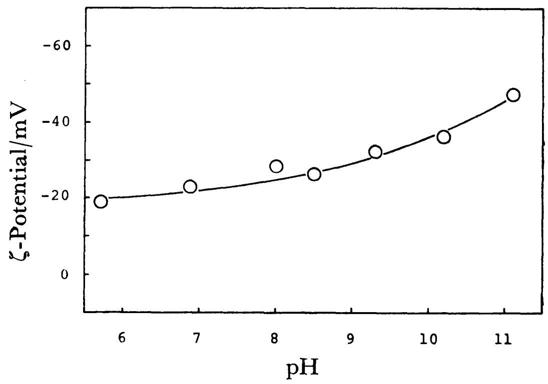

Fig. 1. Effect of the pH of suspension on ζ-potential of CB at 25 °C.

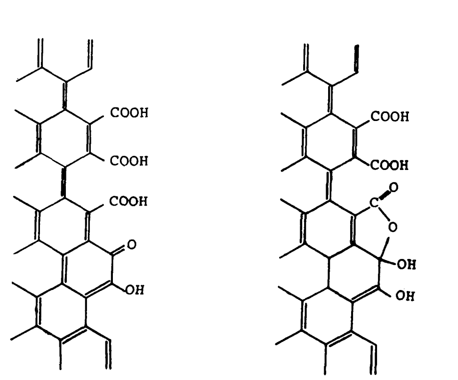

Fig. 2. Surface structure model of carbon black.

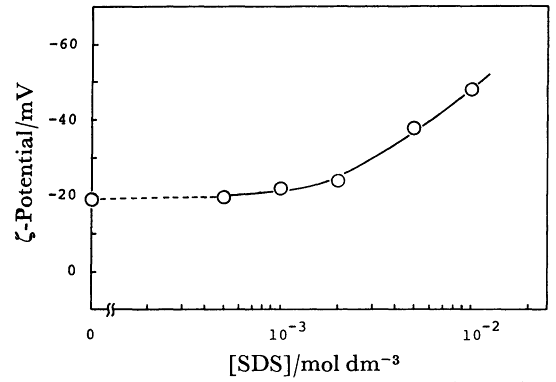

Fig. 3. Effect of the concentration of sodium dodecyl sulfate (SDS) on ζ-potential of CB at 25 °C.

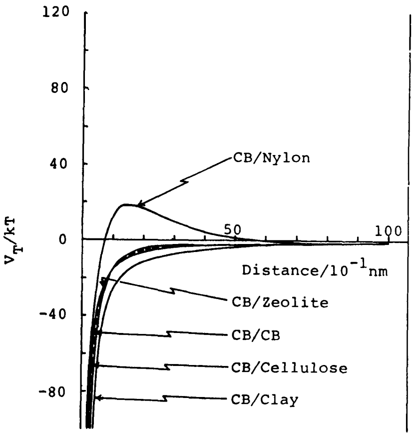

Fig. 4. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 1.387×10^{-3} mol dm^{-3} sodium dodecyl sulfate solution at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^{6} cm^{-1}.

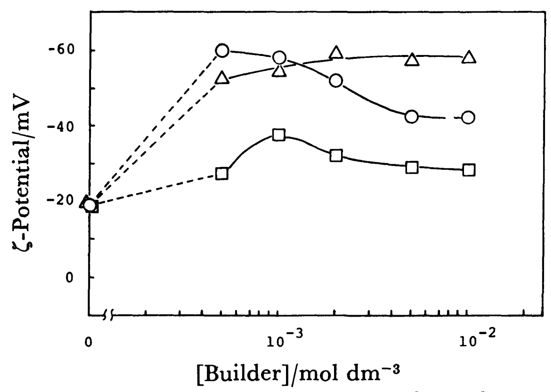

Fig. 5. Effect of the concentration of builder on ζ-potential of CB at 25 °C.
○: Sodium triphosphate, △: sodium carbonate, □: sodium sulfate.

−3, −53, and −17 mV respectively.[1] The total potential energies, V_T, for interactions between CB and nylon, between CB and cellulose, between CB and zeolite, between CB and clay, and between CB and CB were calculated using the ζ-potentials of nylon, cellulose, zeolite, and clay. The results are shown in Fig. 4. Assuming that the electrolyte added is completely ionized, the Debye-Hückel reciprocal length parameter in the 0.2 wt% detergent solution was calculated to be 7.115×10^{6} cm^{-1}. Since the ζ-potential is related to the ionic strength, it is desirable that the ζ-potential be measured in the SDS solution in which κ is controlled to be 7.115×10^{6} cm^{-1} by the addition of an electrolyte, for example potassium chloride. However, if κ in the SDS solution is controlled by the addition of an electrolyte, the solution is different from the detergent solution. Therefore, the ζ-potential obtained by such an operation seems not to be assigned a significance purely in terms of the effect of SDS in the detergent solution. For this reason, the addition of an electrolyte to control κ was not carried out. Thus we consider that the total potential energies, V_T, shown in Fig. 4 mean the behavior of CB under only the effect of SDS in the detergent solution.

A maximum total potential energy, $V_{T,max}$, suggests a repulsive force, and is related with the stability of the hydrophobic colloid. It is said that $V_{T,max}$ has to be about 15 kT to ensure a stability sufficient for all practical purposes.[9] If there is no maximum, rapid coagulation takes place. Similarly to the previous work, the coagulation or deposition was judged to take place with difficulty if $V_{T,max}$ is more than 15 kT, to take place easily if $V_{T,max}$ is less than 15 kT, and not to take place if $V_{T,max}$ is more than 100 kT.[14] On the basis of such criteria, it is clear from Fig. 4 that the deposition of CB onto nylon takes place with difficulty, and the deposition of CB onto cellulose and the coagulations between CB and clay, between CB and zeolite, and between CB and CB take place rapidly.

The Effect of Water-soluble Builder on the ζ-Potential of CB and the Potential Energy. The effects of sodium triphosphate, sodium silicate, sodium carbonate, sodium (carboxylatomethyl)cellulose(CMC), and sodium sulfate on the ζ-potential of CB are shown in Figs. 5—7.

As shown in Fig. 5, the negative ζ-potential of CB was increased with addition of sodium triphosphate. However, the negative ζ-potential decreased with increasing concentrations of sodium triphosphate. The ζ-potential of CB in sodium triphosphate solution was higher than the ζ-potential at the pH of suspension, pH 9.4—9.7. The increase of the negative ζ-potential results from the adsorption of triphosphate anion. The ζ-potential is

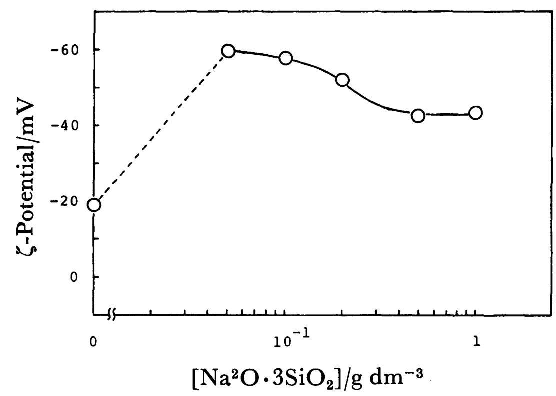

Fig. 6. Effect of the concentration of sodium silicate on ζ-potential of CB at 25 °C.

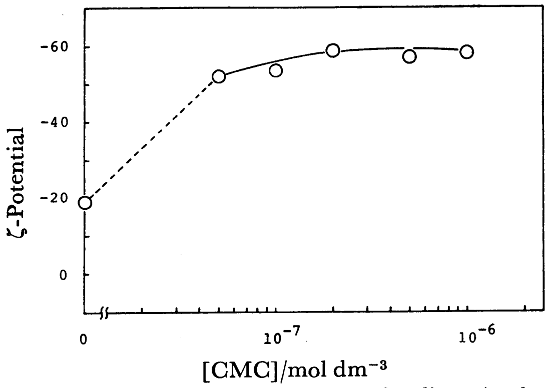

Fig. 7. Effect of the concentration of sodium (carboxylatomethyl)cellulose (CMC) on ζ-potential of CB at 25 °C.

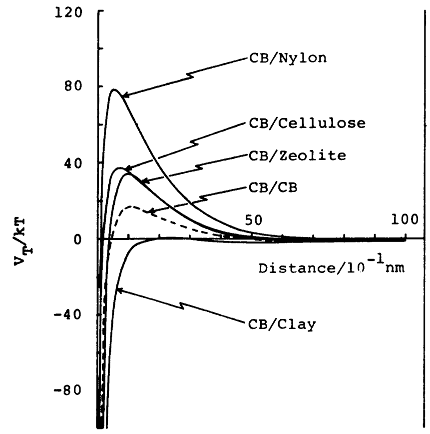

Fig. 8. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 1.190×10^{-3} mol dm^{-3} sodium triphosphate solution at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^6 cm^{-1}.

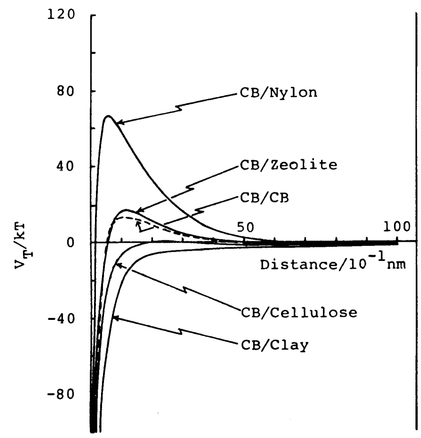

Fig. 9. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 0.1 g dm^{-3} sodium silicate solution at 30 °C. The Debye-Hückel reciprocal length parammeter is assumed to be 7.115×10^6 cm^{-1}.

related to the ionic strength. The decrease of negative ζ-potential with increasing concentration of sodium triphosphate seems to result from the increase of the ionic strength.

In the addition of sodium silicate, the negative ζ-potential of CB increased significantly (Fig. 6). The increase was similar to that which occurred in the addition of sodium triphosphate. The ζ-potential was higher than that at the pH of suspension, pH 10.2—11.4. The increase was larger than that of clay.[1] Since the increase results from the adsorption of silicate anions, the adsorption of silicate anion on CB is more than that on clay.

In the addition of sodium carbonate, the negative ζ-potential increased (Fig. 5). The ζ-potential was higher than that at the pH of suspension, pH 10.3—11.4. As described above, the results are attributed to the effect of pH and/or the adsorption of carbonate anion.

The pH of the suspension did not increase due to the addition of CMC and sodium sulfate. Though the concentration of CMC was low, the negative ζ-potential increased significantly (Fig. 7). This suggests that CMC is useful to disperse CB. On the other hand, the increase of ζ-potenti al in the addition of sodium sulfate was slight (Fig. 5).

As done for SDS, the concentrations of these water-soluble builders in the 0.2 wt% detergent solution were calculated. These ζ-potentials at the concentrations were read from Figs. 5—7. The ζ-potentials of nylon, cellulose, zeolite, and clay and their concentrations are shown in Table 2. The V_T between each pair of materials were calculated with this ζ-potential. The results are shown in Figs. 8—12. The $V_{T,max}$ values in each solution are listed in Table 3. The V_T between CB and nylon in various builders' solutions have maxima: 78.3—14.4 kT. All of these values, except sodium sulfate, were more than the value in SDS solution, and more than 15 kT. CB deposits with difficulty onto nylon fabrics. Though the V_T between CB and cellulose in SDS solution was negative, the V_T in each solution of various builders had maxima. However, the $V_{T,max}$ in the solutions of sodium slicate, sodium carbonate, and sodium sulfate were less than 15 kT. Sodium triphosphate and CMC are useful for prevention of the

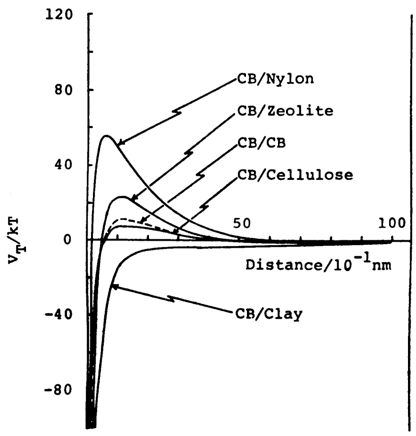

Fig. 10. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 5.661×10^{-4} mol dm^{-3} sodium carbonate solution at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^6 cm^{-1}.

Table 2. ζ-Potentials of nylon, cellulose, zeolite, and clay in the solutions of various builders at 30 °C[1)]

Builder	Concentration / mol dm^{-3}	ζ-Potential/mV			
		Nylon	Cellulose	Zeolite	Clay
$Na_5P_3O_{10}$	1.190×10^{-3}	−64	−40	−67	−28
$Na_2O\cdot3SiO_2$	0.1(g dm^{-3})	−59	−13	−52	−18
Na_2CO_3	5.661×10^{-4}	−55	−22	−61	−21
CMC	1.653×10^{-7}	−51	−32	−61	−17
Na_2SO_4	7.181×10^{-3}	−50	−23	−51	−29

Table 3. Maximum total potential energies, $V_{T,max}$, in the solution of SDS, various builders or detergent at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^{6} cm^{-1}

Electrolyte	Concentration / mol dm^{-3}	$V_{T,max}/kT$				
		CB/Nylon	CB/Cellulose	CB/Zeolite	CB/Clay	CB/CB
SDS	1.387×10^{-3}	18.8	*	*	*	*
$Na_5P_3O_{10}$	1.190×10^{-3}	78.3	37.4	34.1	*	16.4
$Na_2O\cdot3SiO_2$	0.1(g dm^{-3})	66.8	0.5	17.9	*	14.0
Na_2CO_3	5.661×10^{-4}	55.9	8.3	22.9	*	10.7
CMC	1.653×10^{-7}	56.7	24.1	28.2	*	16.4
Na_2SO_4	7.181×10^{-3}	14.4	1.1	*	*	*
Detergent	0.2 (wt%)	84.8	16.3	16.6	*	9.7

* The total potential energy was negative for every distance between two materials.

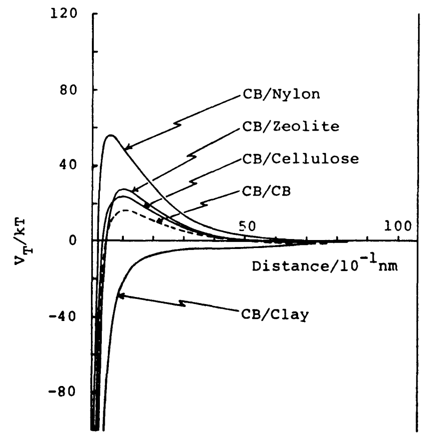

Fig. 11. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 1.653×10^{-7} mol dm^{-3} sodium (carboxylatomethyl)cellulose solution at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^{6} cm^{-1}.

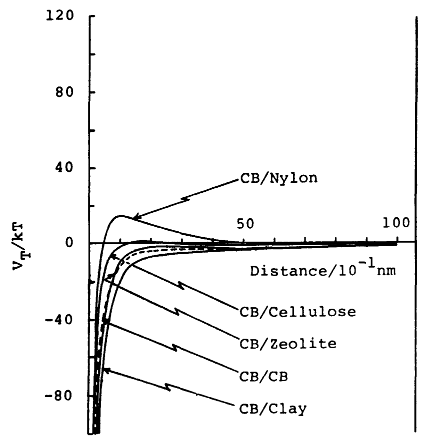

Fig. 12. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 7.181×10^{-3} mol dm^{-3} sodium sulfate solution at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^{6} cm^{-1}.

deposition of CB onto cotton fabrics. The V_T between CB and zeolite in the solutions of various builders, except sodium sulfate, had large maxima of 34.1—17.9 kT. The coagulation between CB and zeolite in these builders takes place with difficulty. Though the V_T between CB and CB in the solutions of sodium triphosphate and CMC had maxima of $\geq15\ kT$, the V_T in the solution of the other builders were negative or had small maxima. The V_T values between CB and clay in the solutions of various builders were negative. The coagulation between CB and clay in the various builders' solutions also takes place easily.

The Behavior of CB in the Detergent Solution. The effect of the detergent concentration on the ζ-potential

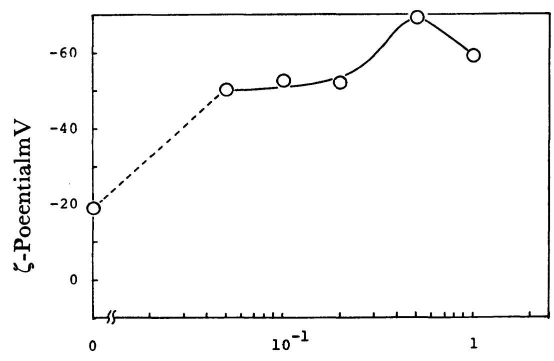

Fig. 13. Effect of the concentration of detergent on ζ-potential of CB at 25 °C.

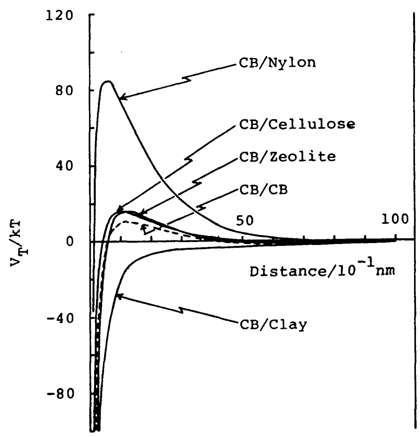

Fig. 14. Total potential energies, V_T, for the interactions between CB/nylon, CB/cellulose, CB/clay, CB/zeolite, and CB/CB in a 0.2 wt% detergent solution at 30 °C. The Debye-Hückel reciprocal length parameter is assumed to be 7.115×10^6 cm^{-1}.

of CB is shown in Fig. 13. The ζ-potential had a maximum at 0.5 wt%. The reason why the maximum existed at this concentration may be interesting; however, since the 0.5 wt% detergent solution is not for practical use, the discussion is excluded from this paper. The ζ-potential of CB at 0.2 wt% was read from Fig. 13. The ζ-potentials of nylon, cellulose, zeolite, and clay in 0.2 wt% detergent solution were −79.9, −28.7, −54.4, and −17.8 mV respectively.[1] The V_T values between each pair of materials in the 0.2 wt% detergent solution were calculated, and are shown in Fig. 14. The $V_{T,max}$ is shown in Table 3. From these results, we can see that CB in the detergent solution deposits with difficulty onto fabrics, coagulates with difficulty with zeolite, and coagulates easily with clay or CB. Consequently, when a detergent which is composed without sodium triphosphate is used, the ζ-potential of CB is increased by the effect of the builders, and the deposition of CB onto fabrics is prevented. Since CB in the detergent solution coagulates easily with clay, the behavior of this coagulated substance in the detergent solution will be discussed in the near future.

References

1) Y. Yoneyama and K. Ogino, *Tenside Deterg.*, **19**, 197 (1982).

2) J. B. Donnet and A. Voet, "Carbon Black," Marcel Dekker, Inc., New York (1976).

3) T. Imamura and F. Tokiwa, *Nippon Kagaku Kaishi*, **1972**, 2177.

4) A. L. Loeb, P. H. Wiersema, and J. Th. G. Overbeek, "The Electrical Double Layer Around Spherical Colloid Particles," The MIT Press, Cambridge, MA (1961), p. 7.

5) A. Kitahara, *Kagaku No Ryoiki*, **24**, 402 (1970).

6) S. Usui, "Kaimen Denki Gensho," ed by A. Kitahara and A. Watanabe, Kyoritsu, Tokyo (1978), p. 81.

7) R. Hogg, T. W. Healy, and D. W. Fuerstenau, *Trans. Faraday Soc.*, **62**, 1638 (1966).

8) H. C. Hamaker, *Physica*, **4**, 1058 (1937).

9) J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier Publ. Co., Amsterdam (1948).

10) F. M. Fowkes, *Ind. Eng. Chem.*, **56**, 40 (1964).

11) A. W. Flegmann, J. W. Goodwin, and R. H. Ottewill, *Proc. Brit. Ceram.*, **13**, 31 (1969).

12) H. P. Boehm, *Angew. Chem.*, **78**, 617 (1966).

13) T. Murata and H. Imagawa, *Denki Kagaku*, **41**, 708 (1973).

14) T. Imamura and F. Tokiwa, *Nippon Kagaku Kaishi*, **1973**, 2051.