Effects of Alkali Metal Cations on the $\zeta$-Potential of Carbon Black Particles*

Tetsuo MURATA**, Yoshiharu MATSUDA*** and the late Hiroshi IMAGAWA**

The influence of alkali metal cations on the $\zeta$-potential of carbon black particles was investigated in aqueous solutions of alkali metal chlorides in connection with the dispersion. One of the samples was an industrial black for printing ink and the others were samples the surface of which were treated. The $\zeta$-potential was measured by the electrophoretic migration method and its value was calculated by using the Hückel’s equation. The $\zeta$-potential obtained was negative, and its absolute value depended mainly on the selective adsorption of $\text{Cl}^-$ anions and dissociation reaction of acidic functional groups on the surface of carbon black particles. The higher absolute values of $\zeta$-potentials were observed on the surface with the more amount of acidic functional groups. Its absolute value decreased with an increase in the concentration of solutes in the dispersion medium, and increased with increasing crystal–ionic radii of cations in the medium. The specificity of Cs$^+$ cations on the $\zeta$-potential was clarified in connection with the apparent Stokes’ diameter.

1 Introduction

The dispersion of carbon (C) black particles is an important property in paint and pigment industries. The $\zeta$-potential of these particles is one of the factors determining the dispersion, and the mechanism of the origin on the $\zeta$-potential has not been clarified in detail. In the previous paper$^{19}$, the effects of halide anions on the $\zeta$-potential of industrial black for printing ink were measured in aqueous solutions of sodium halides, and the results obtained showed that the $\zeta$-potential was negative and the effect of the selective adsorption of $\text{Cl}^-$ anions on the surface of C black particles was stronger than that of the dissociation reaction of acidic functional groups on the surface of C black particles. Then the $\zeta$-potential decreased with an increase in the concentration of solutes in the dispersion medium, and the position of slipping plane in the electrical double layer at the C black particles/dispersion medium interface and lyotropic series of alkali metal cations were discussed in connection with the origin of the $\zeta$-potential. This paper treats the effects of alkali metal cations on the $\zeta$-potential of C black particles by measuring the influences of the concentration of cations in the dispersion medium, the position of slipping plane, the radii of cations and the amount of acidic functional groups on the surface of C black particles.

The theory on the $\zeta$-potential and its measurement were the same as those described in the previous papers$^{19}$–$^{31}$. The $\zeta$-potential was discussed in the absolute value in this paper, though it had negative sign.

2 Experimental

2.1 Samples and preparation

The samples used in this work were an industrial black for printing ink (No. 1) and surface-treated ones of it (No. 1-1, 1-2 and 1-5)$^{19}$. Sample 1-1 was prepared from the sample 1 by oxidation with $\text{H}_2\text{O}_2$ in sulfuric acid, sample 1-2 by heating in the air at 500°C for 1 hr and sample 1-5 through reaction with 4.5 mol dm$^{-3}$ $\text{HNO}_3$ at 100°C for 3 hrs. The properties of these samples are shown in Table 1. The testing methods of samples were the same as those in the previous papers$^{19}$. According to the observation by means of an electron microscope, all the samples consisted of particles of almost the same diameter. There-

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fore, the noticeable difference among the samples lie only in functional groups on the surface of particles.

The dispersion media used in measuring the $\zeta$-potential were 0.25, 0.5, 1 and 2 mmol dm$^{-3}$ aqueous solutions of LiCl, NaCl, KCl, RbCl and CsCl.

2.2 Equipment and methods

The apparatus and methods for measurement of the electrokinetic migration of C black particles were the same as those in the previous paper. The value of $\zeta$-potentials was calculated by using the Hückel’s equation. The measuring current for the migration was 0.1, 0.2, 0.4 and 0.8 mA in the case of 0.25, 0.5, 1, and 2 mmol dm$^{-3}$ aqueous solutions, respectively. The measurement was made at 27.1 ± 1.1°C.

3 Results and Discussion

3.1 The $\zeta$-potential of C black particles in aqueous solutions of alkali metal chlorides

The $\zeta$-potential of C black particles in aqueous solutions of alkali metal chlorides was measured and the results obtained are shown in Table 2. The $\zeta$-potential increased as acidic functional groups on the surface of samples increased for a given concentration of each dispersion medium. This phenomenon would be caused by the selective adsorption of Cl$^-$ anions in the dispersion medium, in the similar manner as the $\zeta$-potential in aqueous solutions of sodium halides and by the formation of negative charge through the dissociation reaction of acidic functional groups on the surface of C black particles.

The relation between the $\zeta$-potential and the

Table 1 Analytical results of carbon black samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mean particles diameter (nm)</th>
<th>Specific surface area (m$^2$/g)</th>
<th>pH</th>
<th>Carboxyl group (mg eq/g)</th>
<th>Phenolic group (mg eq/g)</th>
<th>Quinone group (mg eq/0.2 g)</th>
<th>Iodine adsorption number (mg/g)</th>
<th>Oil adsorption number (cm$^3$/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>General type</td>
<td>Lactone type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>254</td>
<td>4.9</td>
<td>0.030</td>
<td>0.052</td>
<td>0.145</td>
<td>0.785</td>
<td>208</td>
</tr>
<tr>
<td>1-1</td>
<td></td>
<td></td>
<td>3.1</td>
<td>0.201</td>
<td>0.114</td>
<td>0.178</td>
<td>0.795</td>
<td>178</td>
</tr>
<tr>
<td>1-2</td>
<td></td>
<td></td>
<td>3.0</td>
<td>0.462</td>
<td>0.257</td>
<td>0.406</td>
<td>1.715</td>
<td>270</td>
</tr>
<tr>
<td>1-5</td>
<td></td>
<td></td>
<td>2.4</td>
<td>1.109</td>
<td>0.417</td>
<td>0.629</td>
<td>0.926</td>
<td>93</td>
</tr>
</tbody>
</table>

Fig. 1 Correlation between $\zeta$-potential ($\zeta$) and amount of acidic groups ($Q$) on the surface

$\cdots$ : 2 mmol dm$^{-3}$ LiCl, $\bigcirc$ : 0.25 mmol dm$^{-3}$ RbCl

Table 2 $\zeta$-potential ($-mV$) of carbon black particles in aqueous solution of alkali metal chlorides

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>LiCl (mmol dm$^{-3}$)</th>
<th>NaCl (mmol dm$^{-3}$)</th>
<th>KCl (mmol dm$^{-3}$)</th>
<th>RbCl (mmol dm$^{-3}$)</th>
<th>CsCl (mmol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25 0.5 1 2 0.25 0.5 1</td>
<td>33.2 31.5 30.5 27.5 42.0 35.5 32.3 30.1 45.6 43.2 41.9 39.5 32.1 49.5 45.1 43.2 38.2 36.4 35.6 33.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-1</td>
<td>0.25 0.5 1 2 0.25 0.5 1</td>
<td>37.6 37.0 36.5 32.0 52.4 48.2 37.4 36.9 53.3 50.4 47.2 45.3 56.3 52.5 50.8 46.1 44.6 42.5 41.5 41.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>0.25 0.5 1 2 0.25 0.5 1</td>
<td>43.2 41.4 40.1 38.2 60.9 49.5 45.0 44.2 62.0 59.2 58.0 50.0 63.7 59.9 57.2 54.5 54.4 52.5 48.0 44.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-5</td>
<td>0.25 0.5 1 2 0.25 0.5 1</td>
<td>56.6 50.3 47.6 40.8 66.5 55.4 51.6 47.6 67.5 64.1 62.3 54.5 71.4 66.6 64.2 60.9 66.2 62.8 56.3 55.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
amount of acidic functional groups on the surface of samples is shown in Fig. 1. In this figure, the curves in 2 mmol dm$^{-3}$ LiCl and 0.25 mmol dm$^{-3}$ RbCl are shown. The former showed the minimal and the latter the maximal $\zeta$-potential. In the other solutions, the $\zeta$-potential observed had the same tendency against the amount of the acidic functional groups as in the above two solutions and their values lay in the region between the two curves in Fig. 1. The extrapolation of the curves to the ordinate axis would give the $\zeta$-potential which depends only on the selective adsorption of Cl$^-$ anions. Judging from the results on the case of 2 mmol dm$^{-3}$ LiCl, the rates of the selective adsorption Cl$^-$ anions and the dissociation of acidic functional groups on the surface of C black particles were almost of the same magnitude. However, the former influence was dominant over the latter in other dispersion media. In 0.25 mmol dm$^{-3}$ RbCl, the selective adsorption of Cl$^-$ anions was more predominant in the formation of negative charge on the $\zeta$-potential than the dissociation reaction of acidic functional groups.

It is found in Table 2 that the $\zeta$-potential of C black particles decreases with an increase in the concentration of solutes in the dispersion media. This would be caused by the influences of variation of the position of slipping plane and the surface charge density on C black particles. The surface charge density ($\sigma$) is calculated from the values of $\zeta$-potential measured by using eq.(1):

$$|\sigma| = -2DkTN_s\Gamma/(10^3)^{1/2}\sinh(e|\zeta|/2kT) (1)$$

Where $N_s$ is Avogadro’s number, $\Gamma$ ionic concentration of the solute, and the other symbols have usual meanings. In adaptation of eq.(1), it is assumed that the Stern’s potential is equal to the $\zeta$-potential. The relation between the concentration of RbCl and the surface charge density calculated by using eq.(1) from the measured $\zeta$-potential is shown in Fig. 2. The same correlations were obtained in other dispersion media.

It is clear from Fig. 2 that $|\sigma|$ on each C black sample increases with an increase in the concentration of solutes in the dispersion medium, though the $\zeta$-potential decreased. Therefore, both $\sigma$ and position of slipping plane are important factors determining the value of $\zeta$-potential.
dispersion medium increases, the influence of the position of slipping plane on the ζ-potential is important, because the thickness of the electrical double layer decreases with an increase in the concentration of solutes.

The influence of quinone groups on the ζ-potential of C black particles in aqueous solutions of alkali metal chlorides would be as small as that in alkaline and sodium halides solutions.

3.2 The relation between crystal-ionic radii of alkali metal cations and the ζ-potential

The ζ-potential was measured in 0.5 mmol dm⁻³ alkali metal halides in order to examine the influence of alkali metal cations on the ζ-potential. The ζ-potentials measured are plotted in Fig. 3 against crystal-ionic radii (rᵢ) of alkali metal cations. The similar tendency was obtained at other concentrations of solutes in the dispersion media. It is seen in Fig. 3 that the ζ-potentials increase with an increase in rᵢ from Li⁺ to Rb⁺ cations. It is assumed in the following discussion that the adsorbed amount of Cl⁻ anions on the surface of C black particles is constant at the given concentration (0.5 mmol dm⁻³) of alkali metal cations. In view of the size of hydrated alkali metal cations, the adsorbed amount of alkali metal cations was expected to increase with an increase in rᵢ from Li⁺ to Rb⁺ cations, if the above described assumption is applied, but the results obtained were reversed. These results would be connected to the degree of structure forming (or structure breaking) of hydration of alkali metal cations. The degree of structure forming of hydration of Li⁺ cations is the highest of all alkali metal cations and those of Na⁺ and K⁺ cations follow. On the contrary, the degree of structure forming of hydration of Rb⁺ and Cs⁺ cations are low and those of structure breaking of hydration are high. The degree of structure breaking of hydration of K⁺ cations is very low. If attention is paid only to the Stern’s layer, |σ| in aqueous solutions of alkali metal chlorides decreases in order of LiCl > NaCl > KCl > RbCl. The amount of Li⁺ cations in the electrical double layer would be the largest among alkali metal cations, next are those of Na⁺ and K⁺ cations, and that of Rb⁺ cations is the smallest. Moreover, the position of slipping plane would not be the same as that of the Stern’s layer on C black particles situated in the electrical double layer. Since the degree of structure forming of hydration of Li⁺ cations is the highest, the position of slipping plane would be apart from the surface of C black particles in aqueous solutions of LiCl, which would suppress σ and the ζ-potential. This influence probably becomes weak in the order of NaCl, KCl and RbCl, and would shift the position of slipping plane to the surface of C black particles. Then, the results as shown in Fig. 3 in which the ζ-potentials increased with an increase in rᵢ would be obtained.

Such an influence on the change of the position of slipping plane could be explained by considering hydration numbers of alkali metal cations. As the hydration number of cations becomes larger, the adsorbed amount of cations would decrease, and the larger value of |σ| would be obtained. The relation between the hydration number and rᵢ is shown by the dotted line in Fig. 3. If the assumption is made that the position of slipping plane is the same as that of Stern’s layer, these relationships would be related to the surface charge density of C black
particles. If the $\zeta$-potential depends directly on $\sigma$, the relation between these values should show the same tendency as that shown by the dotted line in Fig. 3. These results suggest that the position of slipping plane is not the same as that of Stern's layer on C black particles, but its position in the electrical double layer would be kept apart from the Stern's layer.

It is shown in Fig. 3 that the $\zeta$-potential is lower in CsCl than in RbCl. This phenomenon may be explained by the fact that $|\sigma|$ decreases with an increase in the amount of Cs$^+$ cations and on the basis of the consideration that Cs$^+$ cations would specifically adsorb on the C black particles. However, the detail is still unknown. Such a phenomenon may arise from stronger hydration of Cs$^+$ cations than Rb$^+$ cations, which is suggested from the ionic equivalent conductance of solutions. The specificity of Cs$^+$ cations will be further discussed in the following section (3.3).

3.3 The relation between the $\zeta$-potential and Stokes' radii

The dependences of the $\zeta$-potentials on C black particles and of the concentration of solutes in dispersion medium on $\sigma$ are shown by eq. (1). The adsorption of alkali metal cations is strongly controlled by the radii of hydrated cations. The apparent Stokes' radii ($r_s$) of C black particles were calculated, and the specificity of Cs$^+$ cations discussed under the assumption that $r_s$ would be a measure of kinetic volumes of C black particles. The relation between the $\zeta$-potential and $r_s$ for the sample 1 is shown in Fig. 4. Similar results were obtained for other samples.

Figure 4 indicates that $r_s$ decreases with an increase in the concentration of solutes in the dispersion medium. For a given concentration of alkali metal cations, the order of $r_s$ is Li$^+ >$ Na$^+ > $K$^+ > $Rb$^+$, and $r_s$ decreases with an increase in the value of $\zeta$-potential. The values of $r_s$ are presumed to correspond to the lyotropic series of alkali metal cations to the C black particles.

The apparent Stokes' radii for Cs$^+$ cations lie between $r_s$ for Li$^+$ and Na$^+$ cations at the concentration of 0.25 mmol dm$^{-3}$ and between $r_s$ for Na$^+$ and K$^+$ cations in the range of 0.5 – 2 mmol dm$^{-3}$. Therefore, the specificity of Cs$^+$ cations changes probably with the concentration. From these considerations, it can be expected that the behavior of Cs$^+$ cations adsorbed on C black particles is analogous to that of Na$^+$ cations.

4 Conclusion

The conclusions to be drawn from the experimental results are as follows.

1) The $\zeta$-potential on C black particles was negative in aqueous solutions of alkali metal chlorides, and its value depended mainly on the selective adsorption of Cl$^-$ anions and the dissociation reaction of acidic functional groups on the surface of C black particles.

2) The value of $\zeta$-potential on each sample for a given concentration of solutes increased with an increase in the amount of acidic functional groups.

3) The value of $\zeta$-potential decreased with an increase in the concentration of solutes for a given dispersion medium.

4) The $\zeta$-potential was controlled by the surface charge density on the C black particles and by the position of slipping plane in the electrical double layer.
5) For a given concentration of aqueous solutions of alkali metal chlorides, the value of ζ-potential was the largest in aqueous solution of RbCl, followed by KCl, CsCl and NaCl in this order, and LiCl, though the order of the magnitude of $r_s$ is $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+ > \text{K}^+ > \text{Rb}^+$. 

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