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Dispersion-Flocculation Behavior of Fine Lead Particles in an Organic Solvent

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Methyl ethyl ketone (MEK) is a good solvent for polyvinyl chloride (PVC) and it has been proposed for use in PVC recycling. In the recycling process, fine particles of $3PbO{\cdot}PbSO_4{\cdot}H_2O$, used as a thermal stabilizer in PVC products, are dispersed and not dissolved in the solvent. To establish methods for removing of $3PbO{\cdot}PbSO_4{\cdot}H_2O$ particles from the solvent, factors affecting the dispersion-flocculation behavior of the particles in MEK were investigated.

The zeta potential and particle distribution of $3PbO{\cdot}PbSO_4{\cdot}H_2O$ particles in MEK solutions containing known amounts of H_2O were measured. Above 5 vol%H_2O in MEK solutions, the zeta potential of $3PbO{\cdot}PbSO_4{\cdot}H_2O$ particles approached zero and the flocculation of particles was achieved. In addition, it was found that Pb^{2+} and Cl^- affect the zeta potential of the particles. These results indicate that the dispersion-flocculation behavior of lead particles can be influenced by the concentration of H_2O, Pb^{2+}, and Cl^- in MEK.
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1. Introduction

A variety of polyvinyl chloride (PVC) products contains lead in a thermal stabilizer.[1)] Recently, use of toxic substances such as lead is regulated strictly. According to RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment), lead concentration in electrical and electronic equipment is needed to be less than 1000 ppm. In other industrial products as well, the demand for PVC without lead is expected to increase. Subsequently, there is a need to develop methods to remove lead from waste PVC products in PVC recycling.

A conventional PVC recycling method can be summarized as follows:[2)] The PVC products are first dissolved in an organic solvent, and then the PVC solution is filtered to remove large particulate impurities. In the next step, PVC and soluble additives are recovered with a deposition method by steam injection. The used organic solvent is recovered by a salting-out method and reused. In this process, removal of lead is difficult because lead is contained in very fine compounds (average particle size, 1–2 µm) and the compounds are not caught by the filtration.

To develop a removal process for this kind of fine particles, an evaluation of the factors influencing the dispersion-flocculation behavior of the particles in organic solvents is important. This paper describes the effect of the H_2O content and some ion species on the zeta-potential of fine lead particles in an organic solvent.

2. Materials and Methods

2.1 Materials

STABINEX TC[3)] ($3PbO{\cdot}PbSO_4{\cdot}H_2O$, a thermal stabilizer of PVC products), Mizusawa Industrial Chemicals, Ltd., was used as the sample of lead particles. A scanning electron microscope image of this sample is shown in Fig. 1. The average particle size is about 2 µm, and the solubility in H_2O is 2.0×10^{-6} mol/dm^3. STABINEX TC has a hydrophobic nature because of surface preparation by stearic acid coating.

Methyl ethyl ketone (MEK), tetrahydrofuran, and cyclopentanone are known as good solvents for PVC. In this study, MEK (Daishin Chemical Corporation) was chosen as the solvent due to its low toxicity and cost. The viscosities and relative dielectric constants of MEK solutions with various concentration of H_2O are shown in Table 1. The viscosities were estimated based on the experimental data.[4)] Relative dielectric constants were calculated on a volume fraction basis. Lead particles were easily dispersed in MEK because of the hydrophobic surface.

The electrolytes in the MEK reported here were $PbCl_2$ (99.0%, Wako Chemical Co. Ltd., Japan), $Pb(NO_3)_2$ (99.5%, Koso Chemical Co. Ltd., Japan), K_2SO_4 (99.0%, Wako Chemical Co. Ltd., Japan), Na_2SO_4 (99.5%, Wako Chemical Co. Ltd., Japan), NaCl (99.5%, Wako Chemical Co. Ltd., Japan), and KNO_3 (99.5%, Koso Chemical Co. Ltd., Japan).

2.2 Preparation of suspension

First, MEK solutions containing known concentrations of H_2O and electrolytes were prepared by adding H_2O and aqueous electrolyte solution to MEK, respectively. The MEK solutions were homogeneous and depositions of electrolytes or phase separation were not observed.

Lead particles (0.01 g) were suspended in the MEK solutions (100 cm^3) and agitated by magnetic stirrer for 24 hours.

2.3 Zeta potential measurement

The suspension was treated ultrasonically for 10 s (VS-25, Velvo-Clear Ltd), and the zeta potential was measured by using Zeta-PALS (Brookhaven Instruments Co., USA) with Phase Analysis Light Scattering method.[5)] The Smoluchowski relationship[6)] shown in eq. (1) was used to calculate the zeta potential:

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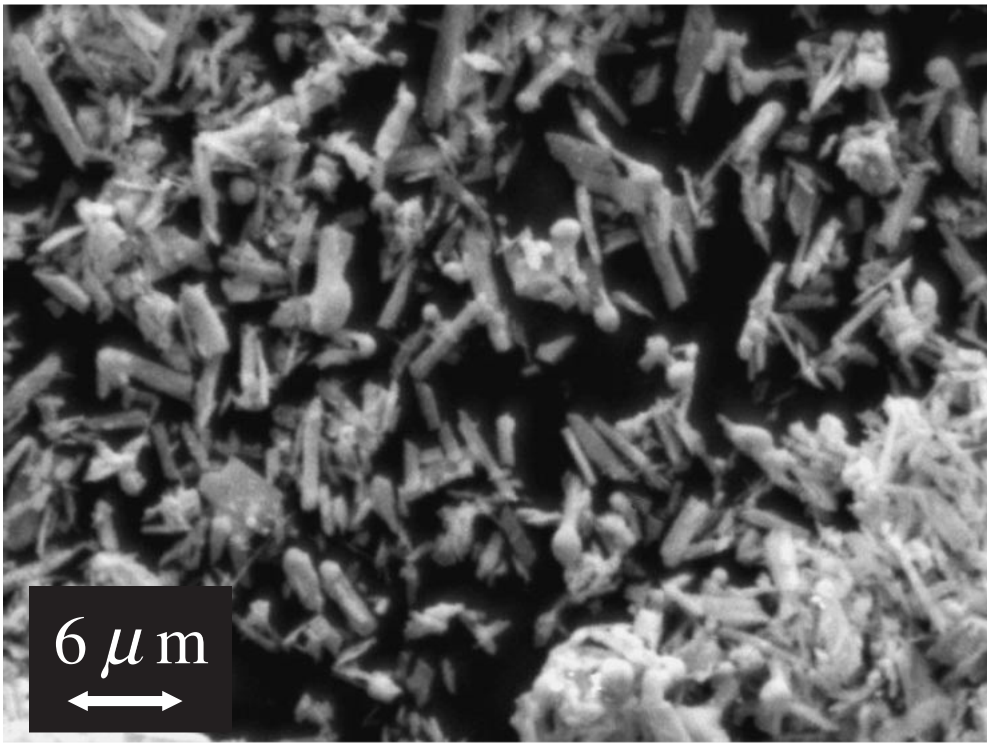

Fig. 1 SEM image of lead particles.

Table 1 Physical properties of MEK with various concentration of H_2O.

H_2O content (vol%)	Viscosity, η/mPa × s	Relative dielectric constant, ε_r
0	0.42	18.4
1	0.45	19.3
3	0.47	20.2
5	0.51	21.4
7	0.54	22.6

$$\zeta = \mu \cdot \frac{\eta}{\varepsilon_r \varepsilon_0} \quad (1)$$

Where, ζ: zeta potential, μ: electrophoretic mobility, η: viscosity of dispersion medium, ε_r: relative dielectric constant of dispersion medium, and ε_0: the absolute permittivity.

Measurements were repeated ten times and the average was calculated.

2.4 Electric conductivity measurement

Electric conductivity of the MEK solutions containing H_2O and electrolytes was measured by a conductance meter (CM-30G, TOA DKK Ltd.) and the conductivity of the filtrate of lead particles suspension, where lead particles are suspended in MEK containing various concentrations of H_2O, was measured after filtration with a membrane filter (pore size, 0.2 µm).

2.5 Particle size distribution measurement

The particle size distribution of lead particles in the MEK solutions was measured using a particle size analyzer (MT3300SX, Microtrac Inc.) with laser light scattering and diffraction method.

2.6 Microscope observation of the behavior of lead particles

The dispersion-flocculation of lead particles in the MEK solutions was observed under a digital microscope (VH-Z450, Keyence Co. Ltd.). In the dry condition, the dispersion-flocculation of lead particles was observed under the scanning electron microscope (SS-550, Shimadzu Co. Ltd.) after filtration with a membrane filter (0.2 µm, SEMpore, Jeol Datum Ltd.).

All experiments were carried out at room temperature.

3. Results and Discussion

3.1 Effect of H_2O addition on the zeta potential of lead particles in MEK

Figure 2 shows the zeta potential of lead particles in MEK solutions containing various concentrations of H_2O (without electrolytes). The absolute value of zeta potential of lead particles decreased with increasing H_2O content and reached about zero with H_2O content above about 5%.

Figure 3 shows the electric conductivity of filtrates of lead particles suspension where lead particles are suspended in MEK solutions containing H_2O. The conductivity increased with increasing H_2O content, where H_2O is dissolved in MEK up to 26.6 mass% and is dissociated. This may indicate that the ion concentration in MEK solution increased. The electric double layer thickness ($1/\kappa$) is compressed with the increase of ion concentration, according to eq. 2.[7]

$$1/\kappa = \left(\frac{\varepsilon_r \varepsilon_0 kT}{e^2 \sum n_i z_i^2} \right)^{1/2} \quad (2)$$

Where, k: the Boltzmann constant, T: temperature, e: charge

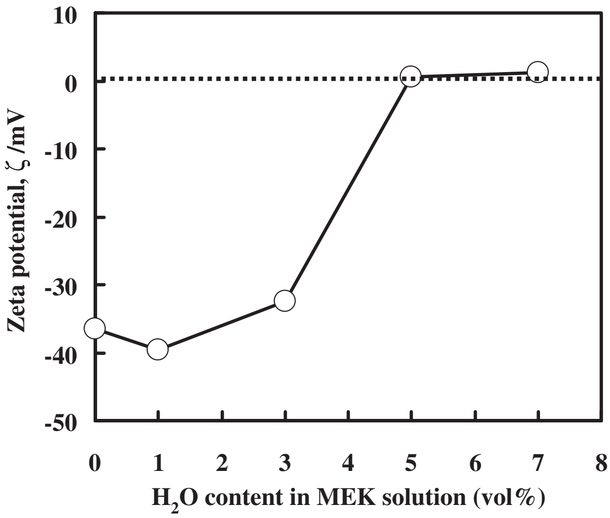

Fig. 2 Zeta potential of lead particles in MEK solutions containing various concentration of H_2O.

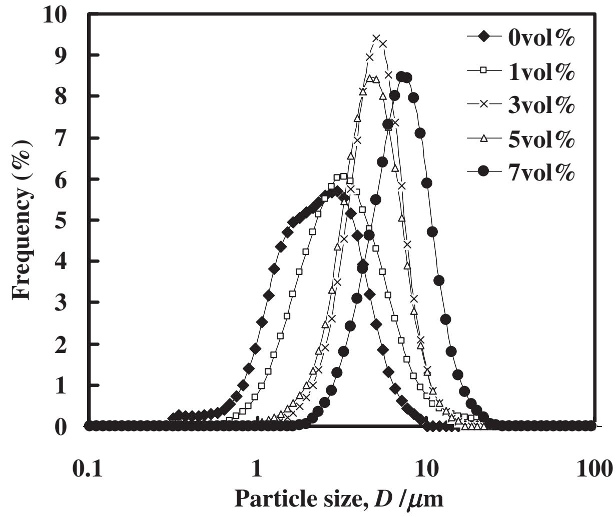

Fig. 4 Particle size distribution of lead particles in the MEK solutions containing various concentration of H_2O.

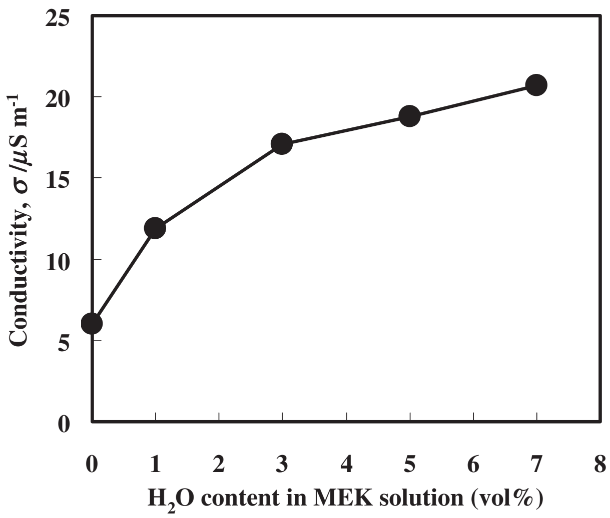

Fig. 3 Electric conductivity of filtrates of MEK solutions containing H_2O. Filtrates were prepared by filtration of lead particles suspension, where lead particles are suspended in MEK containing various concentrations of H_2O.

of electron, n: bulk ion concentration, and z: valence of ion.

In general, the absolute value of zeta potential decreases by a compression of the electric double layer thickness. So the decrease in the zeta potential of lead particles may have occurred due to the compression of the electric double layer thickness caused by H_2O addition and the increase in ion concentration.

With the decrease in absolute values of zeta potential, the flocculation of particles occurs according to DLVO theory. Figure 4 shows the particle size distribution of lead particles in the MEK solutions containing H_2O. With increasing the H_2O addition, the distribution shifted to large size. Figure 5 shows the photograph of lead particles in the MEK solutions with H_2O content of 0 and 7 vol%. In the case of H_2O content of 0 vol%, lead particles were dispersed. On the other hand, with H_2O content of 7 vol%, lead particles were flocculated.

3.2 Effect of ion species on the zeta potential of lead particles

Adsorption and desorption of potential determining ions also affects the zeta potential. Since lead particles are $3PbO{\cdot}PbSO_4{\cdot}H_2O$, it is expected that Pb^{2+}, $SO_4{}^{2-}$, OH^-, and H^+ may behave as potential determining ions of lead particles, and this section describes the influences of Pb^{2+} and $SO_4{}^{2-}$.

The zeta potential of particles may be affected by the concentration of potential determining ions and the compression of the electric double layer thickness. Therefore it is necessary to maintain the ionic strengths in the zeta potential measurements to investigate the effects of potential determining ions. Here, NaCl and KNO_3 were used as supporting electrolytes to maintain the ionic strength. Figure 6 shows the electric conductivity of MEK solutions containing 3 vol% H_2O and various concentrations of NaCl or KNO_3. The conductivity increased with increasing NaCl and KNO_3 concentration indicating that NaCl and KNO_3 can dissolve into the MEK solution and can be used as supporting electrolytes to maintain the ionic strength of the solution.

Figure 7 shows the zeta potential of lead particles in MEK solutions containing various concentrations of electrolytes, $PbCl_2$, $Pb(NO_3)_2$, Na_2SO_4, and K_2SO_4, and a specific amount of supporting electrolyte, NaCl or KNO_3 of 3.0×10^{-5} mol/dm^3. H_2O content of MEK solution was 3 vol%. The zeta potential of lead particles changed from negative to positive with increasing $Pb(NO_3)_2$ concentration, while the zeta potentials with $PbCl_2$, K_2SO_4, and Na_2SO_4 did not significantly change.

Figure 8 shows the electric conductivity of MEK solution containing various concentrations of electrolytes such as $PbCl_2$, $Pb(NO_3)_2$, Na_2SO_4 and K_2SO_4, in the absence of supporting electrolytes. The electric conductivity increased with increasing $Pb(NO_3)_2$ concentration and increased slightly with increasing concentration of $PbCl_2$, K_2SO_4, and Na_2SO_4. This suggests that $Pb(NO_3)_2$ may dissolve and dissociate in the solution, while $PbCl_2$, K_2SO_4, and Na_2SO_4 dissolve as neutral molecules. It is considered that the zeta

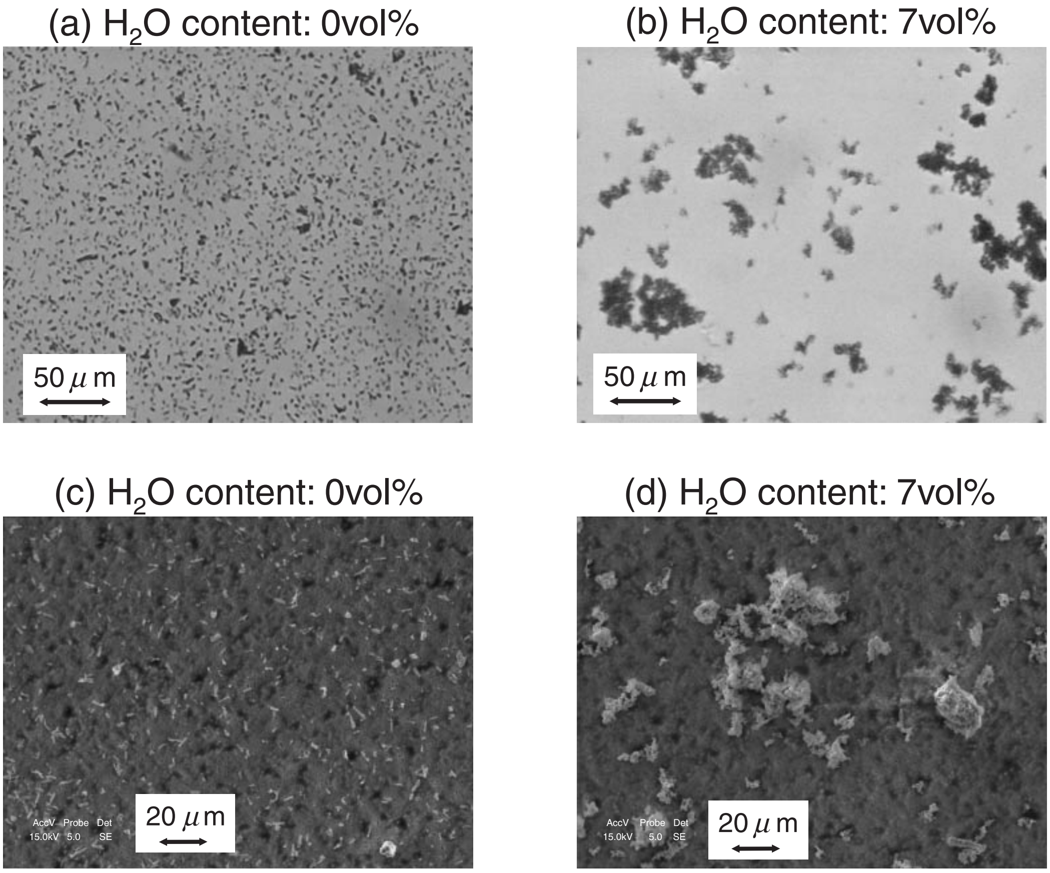

Fig. 5 Photograph of lead particles. (a), (b) Lead particles in the MEK solution with or without H_2O under the digital microscope. (c), (d) Lead particles after filtration of MEK solution with or without H_2O under SEM.

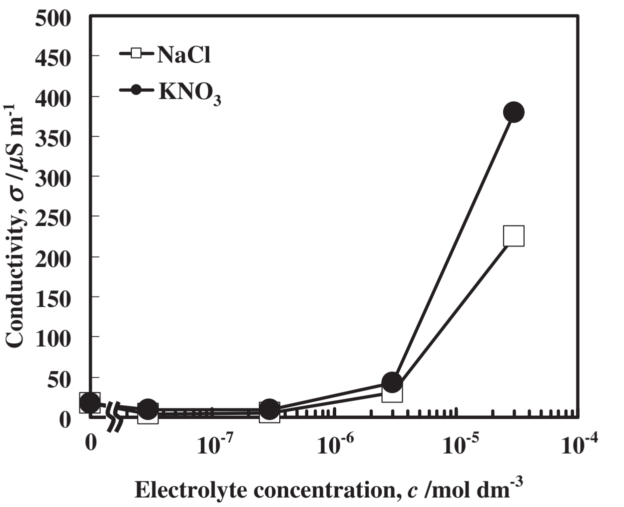

Fig. 6 Electric conductivity of MEK solutions containing various concentrations of electrolyte (H_2O content: 3 vol%).

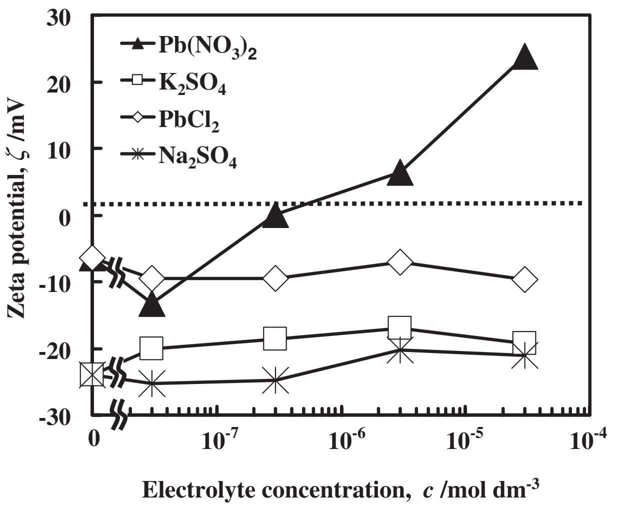

Fig. 7 Zeta potential of lead particles in MEK solutions with various concentrations of $PbCl_2$, $Pb(NO_3)_2$, Na_2SO_4, or K_2SO_4, under a supporting electrolyte concentration of 3.0×10^{-5} mol/dm^3 (H_2O content: 3 vol%). KNO_3 was used as supporting electrolyte for $Pb(NO_3)_2$ and K_2SO_4, and NaCl was used as supporting electrolyte for $PbCl_2$ and Na_2SO_4.

potential of lead particles changed from negative to positive as $Pb(NO_3)_2$ easily dissociated in solution and that the dissociated Pb^{2+} adsorbed on the lead particles surface as the adsorption amount increased with increasing $Pb(NO_3)_2$ concentration. Results in Fig. 8 show that $PbCl_2$, K_2SO_4, and Na_2SO_4 are present as neutral molecules in MEK. This may be a reason why these compounds do not affect the zeta potential of lead particles (Fig. 7).

3.3 Effect of chloride ion concentration on the zeta potential of lead particles

It was suggested that Pb^{2+} behaves as a potential determining ion of lead particles, and the effect of Pb^{2+} is influenced by co-existing anions like NO_3^- and Cl^- because

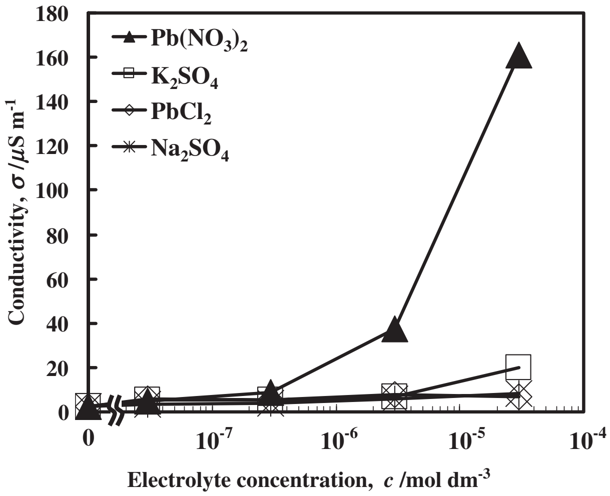

Fig. 8 Electric conductivity of MEK solutions containing various concentrations of $PbCl_2$, $Pb(NO_3)_2$, Na_2SO_4, and K_2SO_4 without supporting electrolyte (H_2O content: 3 vol%).

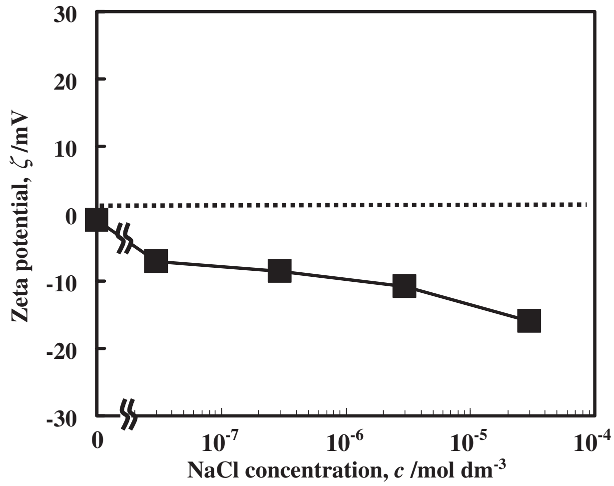

Fig. 9 Zeta potential of lead particles in MEK solutions containing various concentrations of NaCl under a supporting electrolyte concentration of 10^{-4} mol/dm^3 KNO_3 (H_2O content: 3 vol%).

the changes of the zeta potential in $Pb(NO_3)_2$ solutions were large and that in $PbCl_2$ solutions were small. Since the results in Fig. 8 show that $PbCl_2$ may exist as neutral molecules and dissociation is difficult, it is expected that Cl^- in solutions would adsorb onto the Pb^{2+} site of lead particles surface and the zeta potential of lead particles would be changed by Cl^-.

To verify this possibility, the zeta potential of lead particles in MEK solutions containing various concentrations of NaCl, with 10^{-4} mol/dm^3 KNO_3 as the supporting electrolyte, was measured and the results are shown in Fig. 9. The zeta potential of lead particles became more negative and it is confirmed that Cl^- affects the zeta potential of lead particles. It is assumed that the change in zeta potential is caused by the effect of (1) specific adsorption of Cl^- on lead particles surface, or (2) selective desorption of Pb^{2+} from lead particles due to the formation of neutral molecules like $PbCl_2$ in the solution.

4. Conclusions

The presence of small amounts of H_2O in MEK solutions affects the zeta potential of lead particles and leads to flocculation of lead particles. It is assumed that this is caused by the increase of solution conductivity.

The Pb^{2+} ion behaves as one of the potential determining ions of lead particles in MEK solutions containing $Pb(NO_3)_2$, and the effect of Pb^{2+} is influenced by co-existing anions like NO_3^- and Cl^-. The Cl^- ion also affects the zeta potential of lead particles in MEK solutions containing NaCl. Because the zeta potential affects the dispersion-flocculation behavior of fine particles, these results indicate that the dispersion-flocculation behavior of lead particles can be influenced by the concentration of H_2O, Pb^{2+}, and Cl^- in MEK.

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