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An experimental study of the stability of TiO_2 particles in organic–water mixtures

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Abstract

The stability of TiO_2 (Anatase) particles in various organic-water mixtures is examined experimentally. The results obtained reveal that the addition of $AlCl_3$ to a methanol–water dispersion leads to charge reversal on particle surface. If the concentration of methanol is high, $CaCl_2$ also leads to charge reversal, but NaCl does not have this effect. This implies that if the concentration of methanol is low, the coagulation between TiO_2 particles is due to double-layer compression for Na^+ and Ca^{2+}, and due to charge adsorption and neutralization for Al^{3+}. A methanol dispersion is unstable without the addition of electrolyte, and the addition of both $CaCl_2$ and $AlCl_3$ has the effect of stabilizing the dispersion; the addition of NaCl does not have this effect. The qualitative behaviors of an acetone–water dispersion are similar to those of a methanol–water dispersion. It is interesting to observe, however, that the absolute mobility of a pure acetone dispersion has a maximum as the concentrations of both $CaCl_2$ and $AlCl_3$ vary, but charge reversal does not occur. Among the dispersions without the addition of electrolyte, a 50% organic–water mixture is most stable. Also, a methanol–water dispersion is more stable than an acetone–water dispersion, which can be explained based on the degree of dissociation of an electrolyte. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: TiO_2 (Anatase) particles; Organic–water mixture; Methanol; Acetone; Zeta potential; Mobility; Turbidity; Critical coagulation concentration

1. Introduction

Liquid suspensions formed by dispersing colloidal particles in an organic medium play a significant role in various applications in practice. Most of the available results in the literature, however, are mainly focused on aqueous suspensions, and relatively little attention is paid to organic dispersions. Lyklema [1] summarized the behavior of lyophobic colloids in non-aqueous media. Van Der Hoeven and Lyklema [2] examined the electrically stabilized phenomenon of a colloidal dispersion containing organic solvent. On the basis of the magnitude of the dielectric constant of the liquid media three stability categories were defined: semi-polar media, low-polar media, and apolar media where stabilizing a colloidal dispersion through electrostatic interaction is difficult. De Rooy et al. [3] investigated the

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stability of silver, silver iodide, α-goethite, and copper phthalocyanine colloids in methanol, ethanol, isopropanol, and acetone. A parameter Q_c was proposed to decide the controlling mechanism for coagulation. It was concluded that for monovalent ions, double-layer compression is the main mechanism, and for multivalent ions, charge neutralization plays the major role. Kithara [4] discussed the effect of an ionic surfactant, AOT, on the stability of both TiO_2 and α-Fe_2O_3 colloids in a water–dioxane mixture. They found that AOT behaves as a dispersing agent in a pure dioxane or a water-rich medium, but becomes a coagulating agent for a dioxane-rich medium, which has a relative permittivity in the range 10–50. Kosmulski and Matijevic [5] examined the elctrophoretic behavior of silica colloids in a medium containing 80–95% dioxane. It was found that the presence of KCl has the effect of decreasing the absolute mobility of silica in a 80% dioxane–water mixture. Also, charge reversal occurred in both 90% dioxane–water and 95% dioxane–water mixtures. Kosmulski [6] examined the behavior of oxide colloids in an organic-water medium containing 1:1 electrolytes. Kosmulski and Matijevic [7] studied the effects of pH and concentration of KCl on the elctrophoresis of silica in a methanol solvent. They found that the isoelectric point of silica shifts toward more basic pH, and the negative zeta potential decreases with the increase in both methanol content and KCl concentration. Ketelson et al. [8,9] discussed the stability of Stober silica in both pure acetone and water–acetone mixture. For pure acetone they found that, due to the occurrence of charge reversal, the addition of CaI_2 yields two critical coagulation concentrations (CCC). If NaI was used, charge reversal was not observed, and only one CCC was recorded. For an acetone–water mixture and NaI, the higher the concentration of acetone, the lower the CCC. However, if the dielectric constant of the mixture exceeds 33, CCC can not be observed. For CaI_2, the higher the concentration of acetone, the lower the CCC. Kosmulski and Matijevic [10] found that if the concentrations of methanol and alkali salts in a silica methanol–water dispersion are sufficiently high, the negative zeta potential of silica decreases. The phenomenon is explained by the adsorption of monovalent cations to silica surface, which was not observed in a methanol-absent dispersion. Raju and Yaseen [11] observed the behavior of TiO_2 particles in 62 organic solvents. It was concluded that a stable dispersion has the nature that the solvent tends to adsorb to particle surface. Heijman and Stein [12] investigated the effect of polyacrylic acid (PAC) on the stability of TiO_2 dispersion. They found that if the concentra-

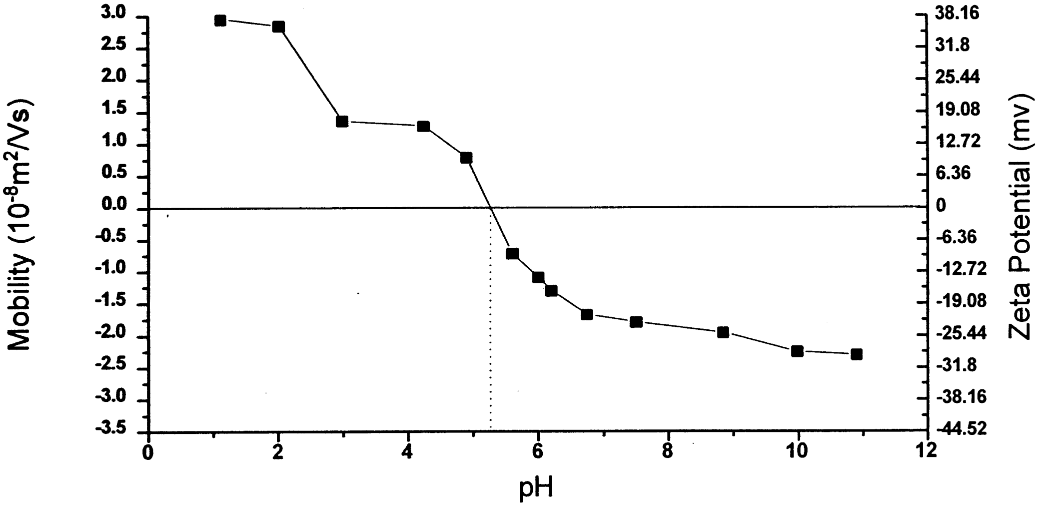

Fig. 1. Variations of electrophoretic mobility and zeta potential as a function of pH for an aqueous dispersion of TiO_2.

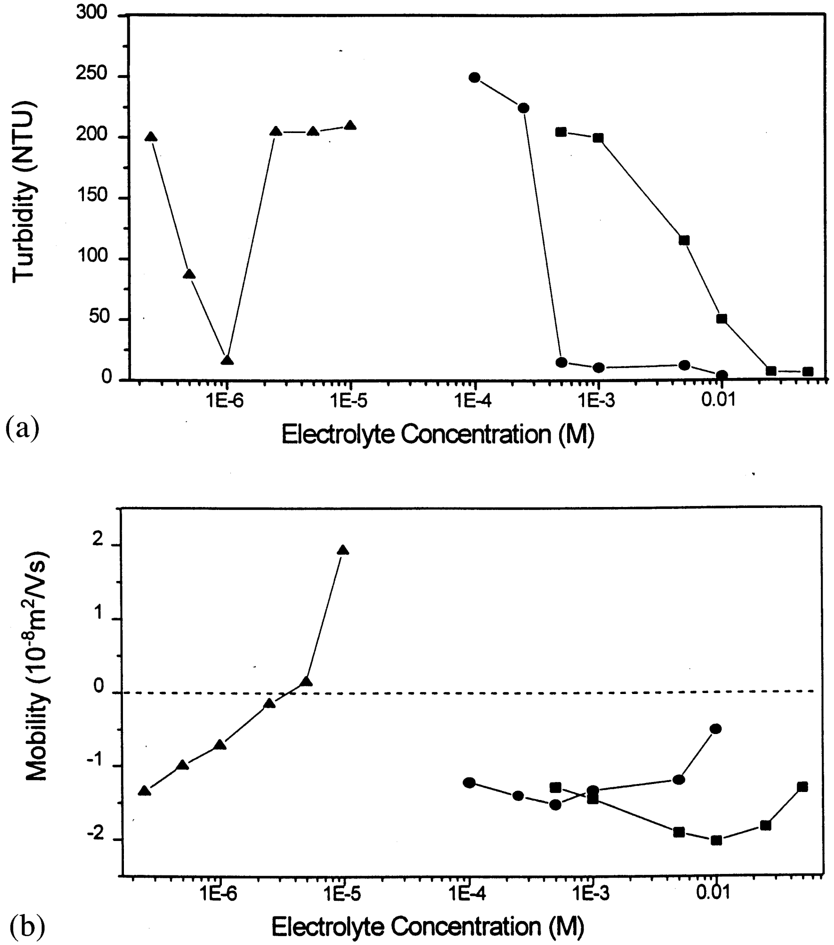

Fig. 2. Variation of turbidity, (a), and mobility, (b), as a function of the concentration of NaCl, ■; $CaCl_2$, ●; and $AlCl_3$, ▲, in pure water.

tion of PAC is low, it has the effect of destabilizing the dispersion; the reverse is true if the concentration of PAC is high.

Unlike the case of an aqueous dispersion, the degree of dissociation of electrolytes in an organic solvent is usually low, and estimating its value becomes essential. The effect of the concentration of electrolyte on the stability of a colloidal dispersion can be reflected by the Debye parameter κ defined by Ref. [13].

$$\kappa = \left(\frac{e^2 \Sigma n_i^0 Z_i^2}{\varepsilon_0 \varepsilon_r k_B T} \right)^{1/2} \tag{1}$$

Here e is the elementary charge, n_i^0 denotes the bulk concentration of ionic species i, ε_r and ε_0 are respectively the relative permittivity and the permittivity of a vacuum, k_B and T are respectively the Boltzmann constant and the absolute temperature. For fixed solvent, the higher the concentration of electrolytes, the thinner the double layer, and two colloids can get more close to each other, and a higher the probability they coagulate. In an organic dispersion, since the dissociation of electrolyte is incomplete, the relatively low concentrations of ionic species yields a thicker double layer, and therefore a more stable dispersion.

In the present study the stability of TiO_2 particles in both methanol–water and acetone–water mixtures are examined. Experimental data for CCC are gathered and the qualitative behavior of the system under consideration elaborated on the basis of turbidity and electrokinetic measurements.

2. Experimental

The chemicals used in the experiments included the followings: NaCl (extra pure, Nacalai Tesque), KCl (extra pure, Yakuri Pure), $CaCl_2$ (anhydrous, extra pure, Junsei), $AlCl_3$ (anhydrous, extra pure, Wako Pure), NaOH (extra pure, Shimakyu's Pure), HCl (extra pure, Shimakyu's Pure), methanol (LC grade, Alps), acetone (LC grade, Alps), and deionized water (NANO pure, Barnstead). TiO_2 (Anatase, Sigma) particles with a mean diameter of 260 nm were used. The SEM and TEM pictures reveal that these particles are roughly spherical. The electrolytes used to destabilize a TiO_2 dispersion include NaCl, $CaCl_2$, and $AlCl_3$, and the dispersion medium used included pure water, 25% methanol (or acetone)–water, 50% methanol (or acetone)–water, pure methanol, and pure acetone. TiO_2

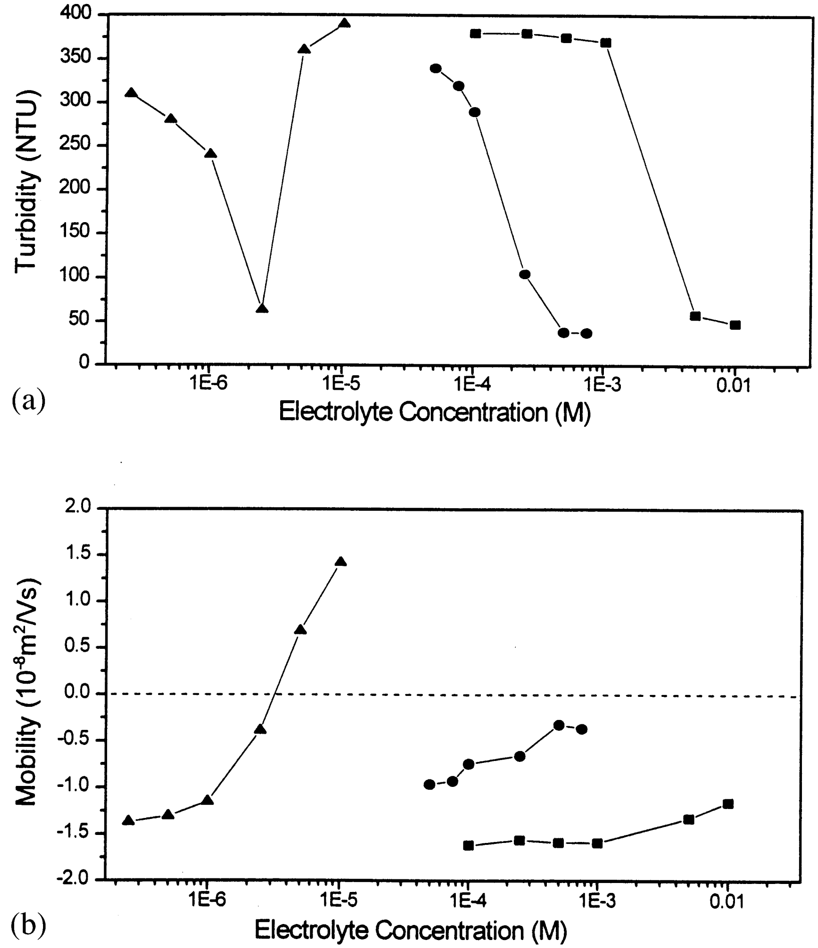

Fig. 3. Variation of turbidity; (a) and mobility; (b) as a function of the concentration of NaCl, ■; $CaCl_2$, ●; and $AlCl_3$, ▲, in 25% methanol–water mixture.

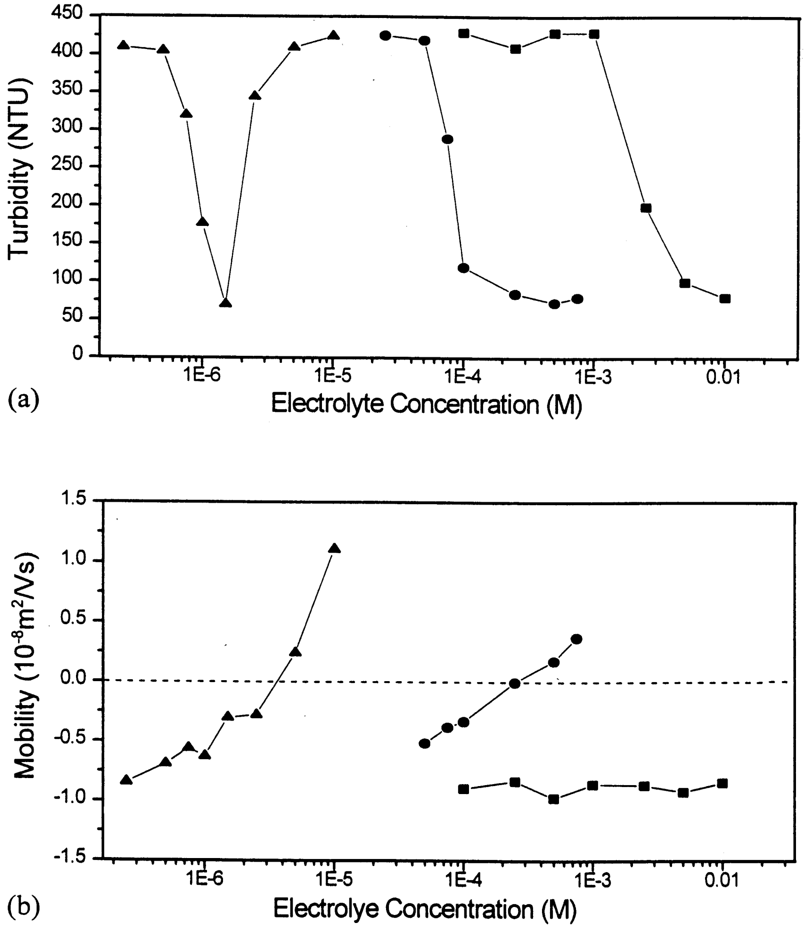

Fig. 4. Variation of turbidity, (a) and mobility; (b) as a function of the concentration of NaCl, ■; $CaCl_2$, ●; and $AlCl_3$, ▲, in 50% methanol–water mixture.

dispersion is prepared by introducing 0.0125 g of TiO_2 powder in 250 cm^3 medium. The dispersion was agitated by an ultrasonic device (Ultrasonic Cleaners, Branson Model 5210) for an hour, followed by magnetic stirring for 10 min. The TiO_2 dispersion thus obtained was used in the subsequent preparation for samples under various conditions.

The turbidity (Nephelometric Tubidity Unit, NTU) was measured by a turbidity meter (Hach Turbidimeter Model 2100A), and the electrophoretic mobility was measured by a zeta potential meter (Malvern Zeta Master). The measurements of each sample were made 24 h after it was prepared. Each measurement was repeated three times, and the averaged value was used. The degree of dissociation of an electrolyte in a medium was estimated by measuring the conductivity of the medium (Suntex Digital Conductivity Meter, Model SC-17A). The instrument was calibrated by a 0.01 mol dm^{-3} KCl solution. Several methods are available in the literature [2,14] for the estimation of the degree of dissociation of an electrolyte in an organic medium based on conductivity measurements. Often, the Arrhenius–Ostward equation is first adopted to obtain an approximate limiting equivalent conductivity, the Shedlovsky equation is then used to obtain a more accurate result. The numerical procedure for the estimation of the degree of dissociation of an electrolyte is summarized briefly in Appendix A.

3. Results and discussion

For metal oxide the following surface reactions occur in an aqueous solution [12,15]:

$$SOH + H^{+} \rightarrow SOH_2^{+} \tag{2}$$

$$SOH + OH^{-} \rightarrow SO^{-} + H_2O \tag{3}$$

where S denotes metal atom. The surface of the TiO_2 particles used in the present study is also of amphoteric nature, as can be justified by the mobility-pH curve illustrated in Fig. 1. At a low pH, H^+ adsorbs to particle surface and the mobility of a particle is positive. On the other hand, if pH is high, H^+ is released from particle surface, and the mobility becomes negative. The estimated isoelectric point is about 5.3, which is slightly lower than that reported in the literature [12].

The variation of the turbidity of a TiO_2 dispersion as a function of electrolyte concentration in an aqueous dispersion is shown in Fig. 2(a). The turbidity is about 230 NTU for a dispersion without the addition of electrolyte. Fig. 2(a) reveals that for both NaCl and $CaCl_2$, the turbidity decreases with the increase in electrolyte concentration. For $AlCl_3$, the turbidity decreases with electrolyte concentration first, passes through a minimum, and then increases with a further increase in electrolyte concentration. The critical coagulation concentration (of counterions) (CCC) is estimated by the electrolyte concentration at

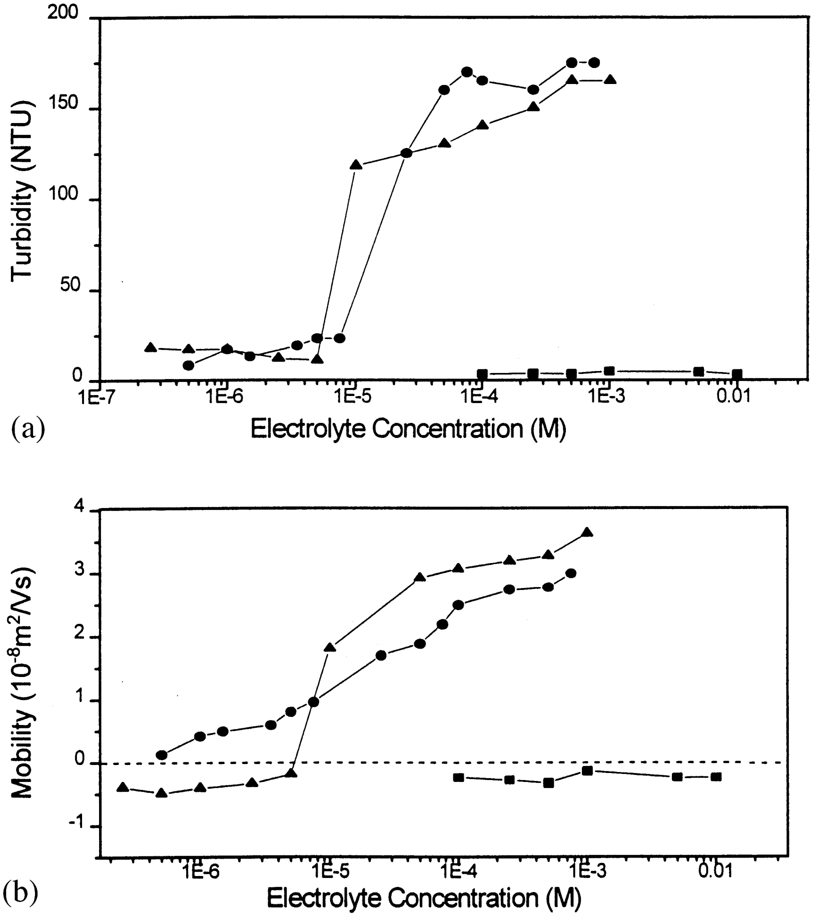

Fig. 5. Variation of turbidity, (a) and mobility; (b) as a function of the concentration of NaCl, ■; $CaCl_2$, ●; and $AlCl_3$, ▲, in pure methanol.

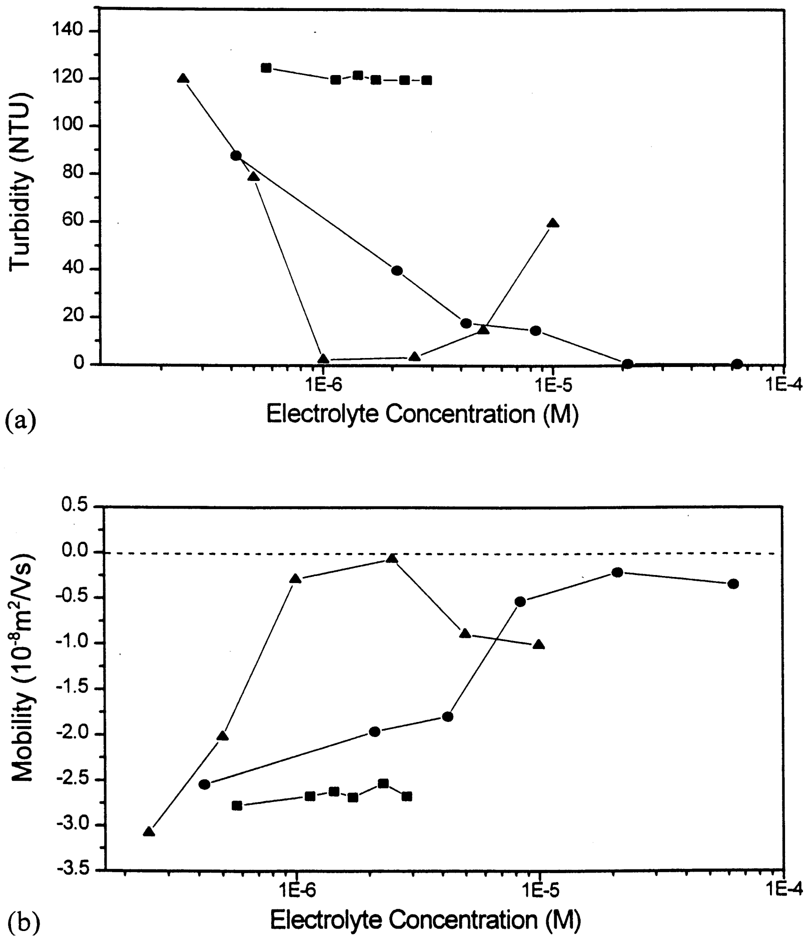

Fig. 6. Variation of turbidity, (a), and mobility, (b), as a function of the concentration of NaCl, ■; $CaCl_2$, ●; and $AlCl_3$, ▲, in pure acetone.

which the variation of the turbidity against electrolyte concentration curve has a drastic decrease. According to Fig. 2(a), the estimated CCCs of NaCl, $CaCl_2$, and $AlCl_3$ are respectively 7.24×10^{-3} M, 4.05×10^{-4} M, and 5.33×10^{-7} M. Note that in an aqueous dispersion Al^{3+}may yield hydroxo complexes such as $Al(H_2O)_5(OH)^{2+}$, hydroxo polymer such as $Al(H_2O)_n(OH)_\ell^{\pm m}$, and hydroxo precipitate such as $Al(OH)_3$ [16]. Among these, hydroxo polymer is capable of adsorbing to the surfaces of colloidal particles. This has the effect of lowering the CCC of $AlCl_3$. The results of mobility measurements for the case of an aqueous dispersion are presented in Fig. 2(b). The mobility of a dispersion without the addition of electrolyte is about -1.77×10^{-8} m^2 V^1 s^{-1}. As can be seen form Fig. 2(b), for both NaCl and $CaCl_2$, the absolute mobility increases slightly with the increase in electrolyte concentration, after passing a maximum, it decreases with a further increase in electrolyte concentration. However, the surface of TiO_2 particle remains negatively charged. For $AlCl_3$, the absolute mobility decreases with the increase in electrolyte concentration, vanishes at a certain critical electrolyte concentration, and then increases with a further increase in electrolyte concentration. Apparently, charge reversal occurs.

The variations of the turbidity of a dispersion as a function of electrolyte concentration for the cases of 25% methanol–water, 50% methanol–water, and pure methanol are presented in Fig. 3(a), Fig. 4(a), and Fig. 5(a), respectively. The turbidities for 25% methanol–water and 50% methanol–water dispersions without the addition of electrolyte are 365 and 430 NTU respectively; these turbidities are greater than the turbidity of an aqueous dispersion without the addition of electrolyte. The general trends of the curves shown in Figs. 3 (a) and 4 (a) are similar to those illustrated in Fig. 2(a) for the case of an aqueous dispersion. The estimated CCCs for NaCl, $CaCl_2$, and $AlCl_3$ for the case a 25% methanol–water dispersion are 4.46×10^{-3}, 3.25×10^{-4}, and 2.29×10^{-6} M, respectively, and 9.96×10^{-3}, 3.34×10^{-4}, and 1.44×10^{-6} M, respectively for the case of a 50% methanol–water dispersion. As can be seen from Fig. 5(a), the turbidity of a pure methanol dispersion without the addition of electrolyte is only about 8 NTU, that is, the dispersion is unstable without the addition of electrolyte. In this case, the addition of NaCl has a negligible effect on the turbidity of the dispersion. However, the dispersion tends to become stable when either $CaCl_2$ or $AlCl_3$ is added. The variations of the electrophoretic mobility for the cases of 25% methanol–water, 50% methanol–water, and pure methanol dispersions as a function of electrolyte concentration are shown in Figs. 3 (b), 4 (b), and 5 (b). The corresponding mobilities of the dispersions without the addition of electrolyte are respectively -1.56×10^{-8}, -0.89×10^{-8} and -0.52×10^{-8} m^2 V^1 s^{-1}. This implies that the higher the methanol concentration, the smaller the absolute mobility, which is consistent with the result reported in the literature [6,7], and was explained based on the activity of ions and the competitive adsorption between the molecules of organic solvent and water to particle surface. The higher the concentration of organic solvent, the easier for ions to adsorb to particle surface. Since the surface charge is reduced due to charge neutralization, the absolute mobility decreases. According to Kosmulski [17], methanol adsorbs on silica surface. If it also adsorbs to TiO_2 surface, then the amount of surface charge will be reduced. This has the effect of lowering the stability of a dispersion. As can be seen from Figs. 3 (b) and 4 (b), for both 25% methanol–water and 50% methanol–water dispersions, the absolute mobility remains roughly the same as the concentration of NaCl varies. The qualitative behavior of the variation of the absolute mobility as a function of the concentration of $AlCl_3$ is similar to that for an aqueous dispersion shown in Fig. 2(b). Fig. 3(b) reveals that for $CaCl_2$ charge rever-

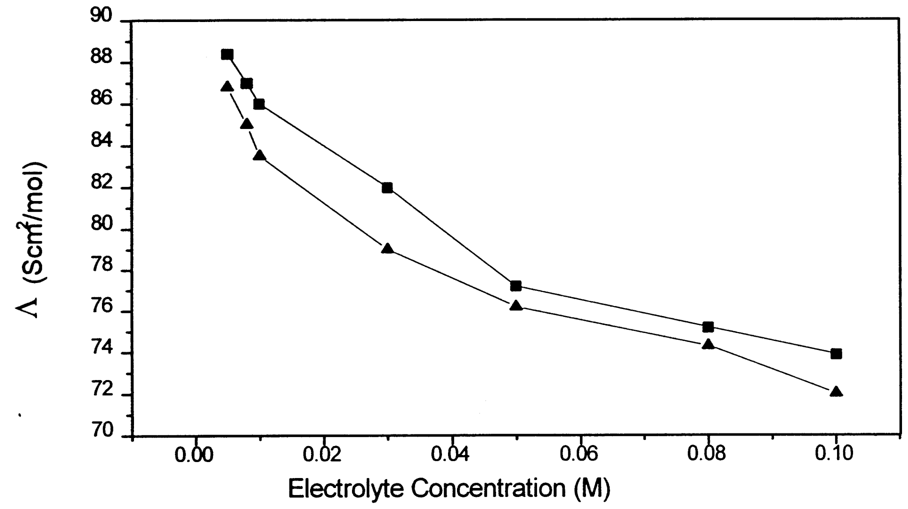

Fig. 7. Variation of equivalent conductance Λ as a function of NaCl concentration for a 25% methanol–water mixture, ■, and 25% acetone–water mixture, ▲.

Table 1
The conductivity k, equivalent conductivity Λ, degree of dissociation of electrolyte α, and Debye length $1/\kappa$ of a dispersion containing NaCl and methanol–water mixture[a]

Concentration/M	k/μS cm	Λ/Scm^2 mol^{-1}	α	$(1/\kappa)$/m[b]	$(1/\kappa)$/m[c]
(a)					
1.00E-01	7390	73.9	0.83	9.02E-10	9.90E-10
5.00E-02	3860	77.2	0.87	1.28E-09	1.37E-09
3.00E-02	2460	82	0.92	1.65E-09	1.72E-09
1.00E-02	860	86	0.97	2.85E-09	2.90E-09
5.00E-03	442	88.4	0.99	4.04E-09	4.06E-09
(b)					
1.00E-02	620	62.00	0.59	2.61E-09	3.39E-09
5.00E-03	320	64.00	0.64	3.69E-09	4.62E-09
1.00E-03	64.2	64.20	0.75	8.26E-09	9.53E-09
5.00E-04	35.1	70.20	0.82	1.17E-08	1.29E-08
2.50E-04	19.53	78.12	0.91	1.65E-08	1.73E-08
1.50E-04	12.00	80.00	0.93	2.13E-08	2.21E-08
1.00E-04	8.25	82.50	0.96	2.61E-08	2.66E-08
(c)					
1.00E-02	701	70.10		2.0E-09	
8.00E-03	610	76.25	0.794	2.2E-09	2.47E-09
5.00E-03	406	81.20	0.861	2.8E-09	2.99E-09
3.00E-03	256	85.33	0.904	3.6E-09	3.77E-09
1.00E-03	89.4	89.40	0.946	6.2E-09	6.39E-09
8.00E-04	73.0	91.25	0.965	6.9E-09	7.07E-09
5.00E-04	45.8	91.60	0.969	8.8E-09	8.93E-09
3.00E-04	28.3	94.33	0.997	1.1E-08	1.14E-08
1.00E-04	10.22	102.20	1.000	2.0E-08	1.96E-08

[a] (a):25% methanol–water mixture, $\Lambda_0 = 89.65$ Scm^2 mol^{-1}, $r_{\text{ion}} = 2$E-8 cm; (b): 50% methanol–water mixture, $\Lambda_0 = 85.79$ Scm^2 mol^{-1}, $r_{\text{ion}} = 3$E-8 cm; (c):pure methanol, $\Lambda_0 = 94.7$ Scm^2 mol^{-1}, $r_{\text{ion}} = 4$E-8 cm.

[b] Without considering α.

[c] α considered.

sal does not occur in a 25% methanol–water mixture, but occurs in a 50% methanol–water mixture, as shown in Fig. 4(b). Fig. 5(b) indicates that for a pure methanol dispersion the absolute mobility remains about the same as the concentration of NaCl varies, and charge reversal occurs for both $CaCl_2$ and $AlCl_3$. The phenomenon that the higher the concentration of organic solvent the easier for charge reversal to occur is also observed by Kosmulski et al. [5] for the case silica is dispersed in a water–dioxane medium, and KCl used as electrolyte. Fig. 5 (a) and (b) suggest that in a pure methanol dispersion, the increase in turbidity at a high concentration of $CaCl_2$ or $AlCl_3$ is due to both charge adsorption and neutralization.

The variations of the turbidity and the mobility of a 25% acetone–water and a 50% acetone–water dispersions as a function of electrolyte concentration are similar to those of a 25% methanol–water and 50% methanol–water dispersions, respectively. The turbidities of 25% acetone–water and 50% acetone–water dispersions without the addition of electrolyte are respectively 301 and 337 NTU, both are greater than the corresponding turbidity of an aqueous dispersion. The variations of the turbidity and the electrophoretic mobility of a pure acetone dispersion as a function of electrolyte concentration are shown in Fig. 6. Note that, although NaCl and $CaCl_2$ can be dissolved completely in both 25% acetone–water and 50% acetone–water mixtures, the solubility of NaCl in pure acetone is only

3.33×10^{-5} g per 100 ml, and is 1.18×10^{-2} g per 100 ml for $CaCl_2$ [18]. This is why the addition of NaCl has a negligible effect on the turbidity of a dispersion, as can be seen from Fig. 6(a). On the other hand, it was observed that $AlCl_3$ forms a yellow fog-like precipitate in pure acetone. The CCCs of NaCl, $CaCl_2$, and $AlCl_3$ for a 25% acetone–water dispersion are 4.16×10^{-3}, 2.23×10^{-4}, and 9.00×10^{-7} M, respectively, and 3.81×10^{-3}, 4.82×10^{-5}, and 8.87×10^{-7}

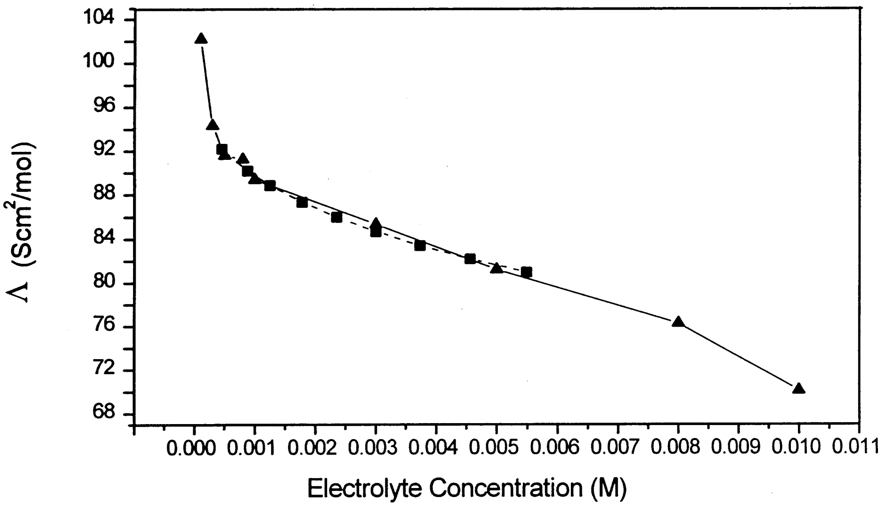

Fig. 8. Variation of equivalent conductance Λ as a function of NaCl concentration in pure methanol. ■: Barthel and Neunder [19]; ▲: present study.

Table 2
The conductivity k, equivalent conductivity Λ, degree of dissociation of electrolyte α, and Debye length $1/\kappa$ of a dispersion containing NaCl and acetone–water mixture[a]

Concentration/M	k/μS cm^{-1}	Λ/Scm^2 mol^{-1}	α	$(1/\kappa)$/m[b]	$(1/\kappa)$/m[c]
(a)					
1.00E-01	7200	72	0.83	8.69E-10	9.54E-10
5.00E-02	3810	76.2	0.87	1.23E-09	1.32E-09
3.00E-02	2370	79	0.91	1.59E-09	1.66E-09
1.00E-02	835	83.5	0.96	2.75E-09	2.81E-09
5.00E-03	434	86.8	0.99	3.89E-09	3.91E-09
(b)					
1.00E-02	619	61.90	0.58	2.40E-09	3.14E-09
5.00E-03	311	62.20	0.62	3.39E-09	4.29E-09
1.00E-03	65.3	65.30	0.73	7.58E-09	8.88E-09
5.00E-04	34.4	68.80	0.79	1.07E-08	1.21E-08
2.50E-04	18.50	74.00	0.84	1.52E-08	1.65E-08
1.50E-04	11.20	74.67	0.85	1.96E-08	2.12E-08
1.00E-04	7.80	78.00	0.89	2.40E-08	2.54E-08
5.00E-05	4.68	93.60	1	3.39E-08	3.39E-08

[a] (a):25% acetone–water mixture, $\Lambda_0 = 87.6$ Scm^2 mol^{-1}, $r_{ion} = 2E\text{-}8$ cm; (b): 50% acetone–water mixture, $\Lambda_0 = 87.57$ Scm^2 mol^{-1}, $r_{ion} = 3E\text{-}8$ cm.

[b] Without considering α.

[c] α considered.

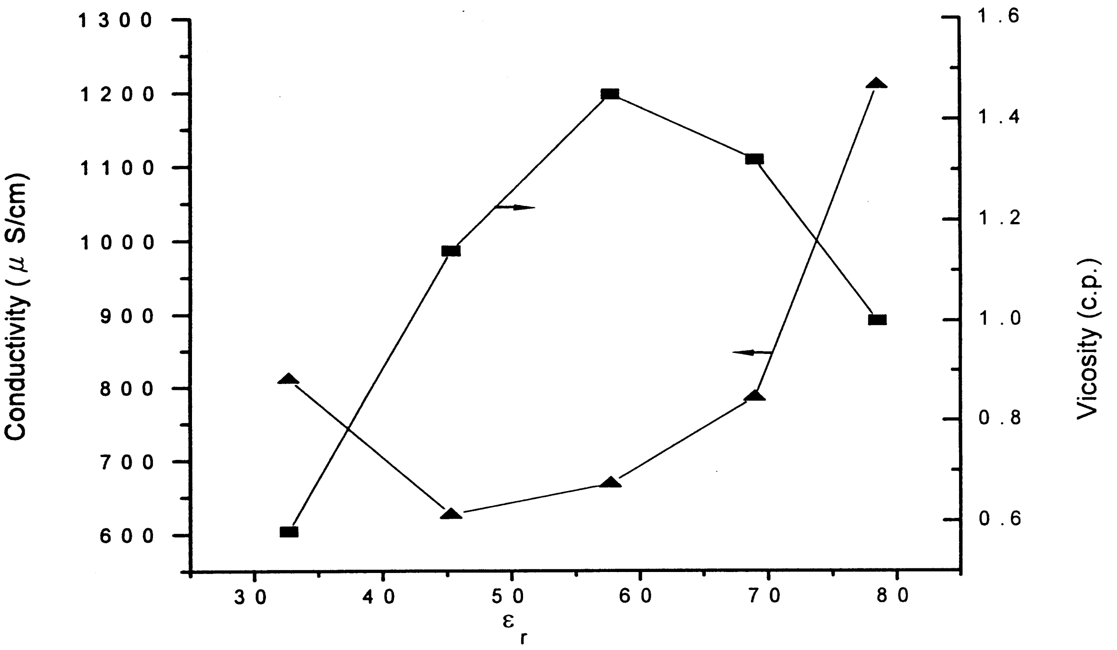

Fig. 9. Variation of the conductivity, ▲, and the viscosity, ■, as a function of the relative permittivity of methanol–water mixtures ε_r at 25°C. The electrolyte concentration is fixed at 0.01 M. Pure water, 25% methanol–water, 50% methanol–water, 75% methanol–water, and pure methanol are used.

M, respectively for a 50% acetone–water dispersion. In the case of a pure acetone dispersion, the CCCs of $CaCl_2$ and $AlCl_3$ are 5.46×10^{-7} and 4.8×10^{-7} M, respectively, and the CCC of NaCl is inestimable. The electrophoretic mobilities of 25% acetone–water, 50% acetone–water, and pure acetone dispersions without the addition of electrolyte are -1.08×10^{-8}, -0.89×10^{-8}, and -2.63×10^{-8} m^2 Vs^{-1}, respectively. That is, a pure acetone dispersion has the highest absolute mobility. This may be due to the fact that acetone has a low viscosity, and it is nonpolar. A comparison between Figs. 5(b) and 6(b) shows that, similar to the case of a pure methanol dispersion, the absolute mobility of a pure acetone dispersion remains about the same as the concentration of NaCl varies. However, it is interesting to note that the absolute mobility of a pure acetone dispersion has a maximum as the concentrations of both $CaCl_2$ and $AlCl_3$ vary. Also, charge reversal does not occur in these cases. A comparison between Figs. 6(a) and (b) suggests that the results of turbidity measurements are in good agreement with those of mobility measurements.

Among the dispersions without the addition of electrolyte, the one with 50% organic–water mixture has the greatest turbidity, or is most stable. For the same concentration in organic component, the turbidity of a methanol–water dispersion is greater than that of an acetone–water mixture. This can be explained based on the degree of dissociation of an electrolyte, α. Fig. 7 illustrates the variations of equivalent conductivity Λ as a function of the concentration of NaCl for a 25% organic–water dispersion. This figure shows that the relation between Λ and electrolyte concentration is nonlinear. The same conclusion can be drawn from a 50% organic–water dispersion. As can be seen from Tables 1 and 2, for the same electrolyte concentration, Λ for a methanol–water dispersion is greater than that for an acetone–water dispersion. It is known that the solvation ability of ions with solvent molecules has a significant effect on Λ. For example, the fact that hydration of Na^+ occurs in an aqueous solution is advantageous to the dissociation of electrolytes such as NaCl. The functional group of methanol molecule is similar to that of water molecule, and therefore hydration of ions is possible to occur. On the other hand, this is not the case for acetone molecule. Therefore the Λ of a methanol–water dispersion is higher than that of an acetone–water dispersion.

The variation of Λ as a function of electrolyte concentration for the case of pure methanol is shown in Fig. 8; the data reported by Barthel and Neueder [19] are also shown for comparison. As can be seen from this figure, the agreement be-

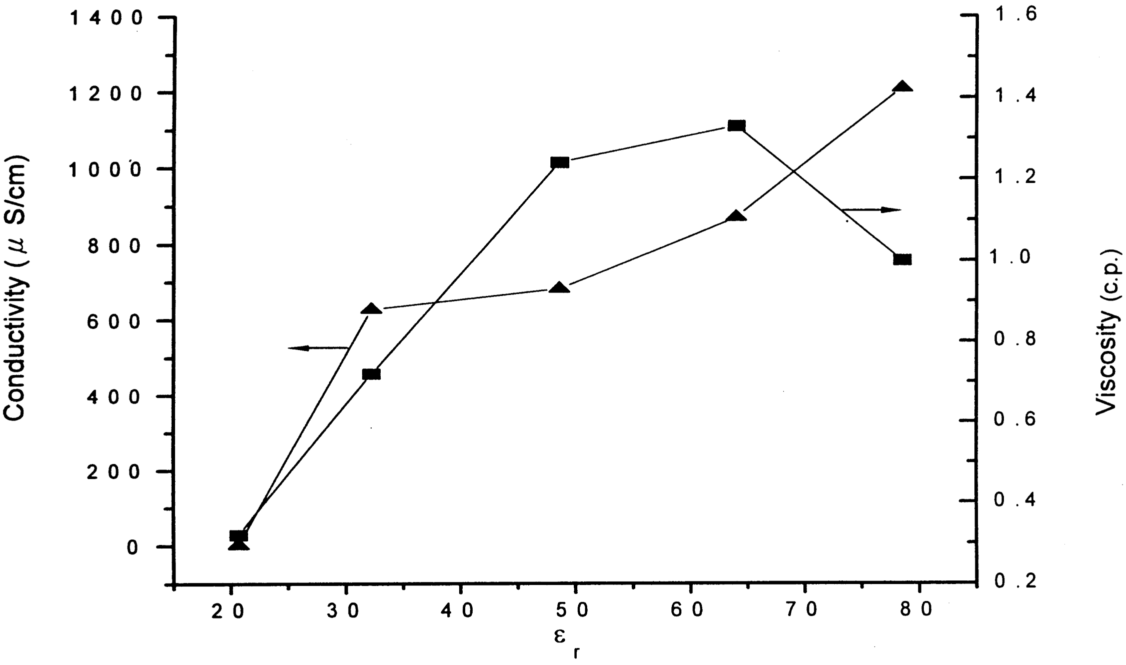

Fig. 10. Variation of the conductivity, ▲, and the viscosity, ■, as a function of the relative permittivity of acetone–water mixtures ε_r at 25°C. Theelectrolyte concentration is fixed at 0.01 M. Pure water, 25% acetone–water, 50% acetone–water, and 75% acetone–water, and pure acetone are used.

Table 3

Relative permittivity ε_r, critical coagulation concentration (CCC), CCC ratio of counterions, and paramter Q_c defined in Eq. (4) for various methanol-water dispersions

	Pure water	25% Methanol–water	50% Methanol–water	Pure methanol	
ε		78.54	68.96	57.71	32.70
Q_c	Na^+	1	0.91	3.47	–
	Ca^{2+}	1	1.18	2.08	–
	Al^{3+}	1	6.35	6.81	–
CCC	Na^+	7.24E-3	4.46E-3	9.96E-3	–
	Ca^{2+}	4.05E-4	3.25E-4	3.34E-4	–
	Al^{3+}	5.33E-7	2.29E-6	1.44E-6	–
CCCratio	100:5.59:0.01		100:7.29:0.05	100:3.35:0.01	–

Table 4
Relative permittivity ε_r, critical coagulation concentration (CCC), CCC ratio of counterions, and paramter Q_c defined in Eq. (4) for various acetone-water dispersions

	Pure water	25% Acetone–water	50% Acetone–water	Pure acetone	
ε		78.54	64.00	48.60	20.70
Q_c	Na^+	1	1.06	2.22	–
	Ca^{2+}	1	1.02	0.50	0.07
	Al^{3+}	1	3.12	7.02	49.19
CCC	Na^+	7.24E-3	4.16E-3	3.81E-3	–
	Ca^{2+}	4.05E-4	2.23E-4	4.82E-5	5.46E-7
	Al^{3+}	5.33E-7	9.00E-7	8.87E-7	4.80E-7
CCC ratio	100:5.59:0.01		100:5.36:0.02	100:1.27:0.02	–

tween the two is satisfactory. The solubility of NaCl in pure acetone is too small for conductivity to be measured accurately. For the cases of $CaCl_2$ and $AlCl_3$, since both the dissociation mechanism and the concentrations of intermediates formed during the dissociation reactions are unknown, estimating the degree of dissociation of these electrolytes in an organic–water mixture is unfeasible, and therefore the variation of Λ as a function of electrolyte concentration for these electrolytes is not examined. The estimated degree of dissociation of NaCl and the corresponding double layer thickness $1/\kappa$ for various organic-water mixtures are summarized in Tables 1 and 2. These tables reveal that, for methanol–water dispersions, if the concentration of added electrolyte is fixed, a 50% methanol–water dispersion has the smallest α, which leads to the thickest double layer, the largest electrical repulsive force between two particles, and therefore is most stable.

Figs. 9 and 10 show respectively the variations of the viscosity and the conductivity of a dispersion as a function of its composition, measured by the relative permittivity, ε_r, for both methanol–water and acetone–water mixtures at a fixed electrolyte concentration. Fig. 9 suggests that, for the case of a methanol-water mixture, the viscosity and the conductivity are closely related with each other, the larger the former, the smaller the latter. Also, the conductivity against ε_r curve has a minimum, and the viscosity against ε_r curve has a maximum. These behaviors are also observed by Ketelson et al. [9] for the case of NaI and an acetone–water mixture. Similar behaviors as those observed in Fig. 9 are found in Fig. 10 for the case of an acetone–water mixture, except that the maximum of the conductivity against ε_r curve occurs at 0% acetone (pure water).

The CCC ratio of counterions for the case of an aqueous dispersion is often described by the Schulze–Hardy rule, which states that the ratio is inversely proportional to the sixth power of counterion valence [13]; for mono-, di-, and trivalent counterions the ratio is about 100: 1.6: 0.14. The Schulze–Hardy rule can be elaborated by the DLVO theory, which assumes that the coagulation between particles is due to double-layer compression. According to the previous discussions, charge reversal is the main coagulation mechanism for Al^{3+}, and therefore, applying Schulz–Hardy is inadequate in this case. This is justified by Tables 3 and 4. For an organic solvent–water dispersion, De Rooy et al. [3] proposed the parameter Q_c below to decide if a coagulation phenomenon is due to double-layer compression:

$$Q_c = \frac{\mathrm{CCC_{org}}}{\mathrm{CCC_{aq}}} \times \left[\frac{\varepsilon_{aq}}{\varepsilon_{org}}\right]^3 \tag{4}$$

where $\mathrm{CCC_{org}}$ and $\mathrm{CCC_{aq}}$ denote respectively the CCC for the case of an organic dispersion and that for the case of an aqueous dispersion, and ε_{org} and ε_{aq} are respectively the dielectric constants of the organic and aqueous dispersions. If Q_c is close to unity, coagulation of particles is due to double-layer compression. Tables 3 and 4 summarize the experimental results for CCC and Q_c. According to these tables, the deviation of Q_c from unity for Na^+ and Ca^{2+} in a 25% methanol–water or a 25% acetone–water dispersion is inappreciable, but becomes significant in a 50% methanol–water or a 50% acetone–water dispersion, which implies that double-layer compression is the main coagulation mechanism for Na^+ and Ca^{2+} if the concentration of organic component is low, but it may not be the case if it is high. For Al^{3+}, since the deviation of Q_c from unity is appreciable for both methanol–water and acetone–water dispersions, the coagulation is more possible to be caused by charge adsorption and neutralization. This is consistent with the results obtained from both turbidity and electrophoretic mobility measurements.

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Appendix A

The equivalent molar concentration of electrolyte, C, and the equivalent conductivity, Λ, are related by [2,14]

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda K_D}{\Lambda_0^2} \tag{A1}$$

where K_D denotes the equilibrium dissociation constant, and Λ_0 is the limiting equivalent conductivity, the value of Λ at infinite dilution. Also, $\Lambda = 1000k/C$, k being the conductivity. In practice, C, k, and Λ can either be found in the literature, or measured experimentally, and K_D and Λ_0 need to be estimated experimentally. According to Eq. (A1), if $1/\Lambda$ is plotted against $C\Lambda$, a straight line should result, and Λ_0 and K_D can be estimated based on its intercept and slope. It should be pointed out that since ideal solution is assumed in its derivation, the result based on Eq. (A1) may lead to an appreciable deviation. Nevertheless, it can be used as an initial guess for subsequent calculations. The Shedlovsky equation can be expressed as

$$\frac{1}{\Lambda S(Z)} = \frac{\Lambda S(Z) f_{\pm}^2 C}{\Lambda_0^2 K_D} + \frac{1}{\Lambda_0} \tag{A2}$$

where $S(Z)$ is the Shedlovsky factor defined by

$$S(Z) = \left[\frac{Z}{2} + \left(1 + \left(\frac{Z}{2}\right)^2\right)^{1/2}\right]^2 \tag{A3}$$

with $Z = (a\Lambda_0 + b)(C\Lambda)^{1/2}\Lambda_0^{-3/2}$, $a = 8.204 \times 10^5/(\varepsilon T)^{3/2}$, and $b = 82.49/\mu(\varepsilon T)^{1/2}$, T, μ, and ε being respectively the absolute temperature, the viscosity, and the dielectric constant of the liquid phase. The degree of dissociation of an electrolyte, α, can be evaluated by $\alpha = S(Z)(\Lambda/\Lambda_0)$, where $f_{\pm}$ represents the mean ionic activity coefficient. According to the Debye–Huckel theory

$$-\log f_{\pm} = \frac{1.824 \times 10^6 (\varepsilon T)^{-3/2} C_i^{1/2}}{1 + 5.029 \times 10^{11} r_{\mathrm{ion}} (\varepsilon T)^{-1/2} C_i^{1/2}} \tag{A4}$$

where C_i is the actual concentration of ion species i, and r_{ion} is the sum of the radii of cations and anions in the liquid phase.

The Λ_0 evaluated from Eq. (A1) is used as the initial guess, and substituted into Eq. (A3) to evaluate $S(Z)$. Eq. (A2) is then used to update Λ_0 by plotting $1/\Lambda S(Z)$ against $\Lambda S(Z) f_{\pm}^2 C$, and estimating the intercept of the line obtained. The procedure is repeated until a convergent Λ_0 is obtained, and α is then calculated.

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