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Dispersion and Flocculation Behavior of Metal Oxide in Organic Solvent

Katsuya Fujii[1], Hideki Yamamoto[1] and Junji Shibata[1]
[1] Department of Chemical Engineering, Kansai University, Japan

The relation between the flocculation and dispersion of metal oxide powders and the properties of solvents, such as dielectric constant and solubility parameter, was investigated for TiO_2, Al_2O_3 and Fe_2O_3 particles. The particle size and median diameter of these metal oxides were measured in many organic solvents, from which the effect of solvents on the flocculation and dispersion of metal oxide powders was considered. The metal oxide powders of TiO_2, Al_2O_3 and Fe_2O_3 tend to disperse in a solvent of higher polarity, whereas they are apt to flocculate in a solvent of low dielectric constant, because the Hamaker constant between the particles becomes larger in such a solvent. There are, however, some solvents that do not obey these tendencies. It is possible to evaluate the flocculation and dispersion of these metal oxide powders in many solvents by using numeral balances of Hansen's three-dimensional solubility parameter (f_d, f_p and f_h). There exists a solvent giving the optimal dispersion for each metal oxide, and the optimal dispersion point of f_d, f_p and f_h is determined by the combination of various metal oxide powders and solvents.

Introduction

Many metal oxides are widely used as raw materials for optical material, catalysts, corrosion-resistant materials, paint, pigment and ceramics. Functions and quality of these products depend on not only raw materials of the products but also size and shape of particles in the products. The combination of particle and solvent determines the dispersibility of these particles. Dispersibility of particles in aqueous solution is explained by the D.L.V.O. theory. However, the factors of dispersibility for particles in many solvents are not cleared.

In this study, the solvents shown in Table 1 and Al_2O_3, TiO_2 and Fe_2O_3 particles were used. To evaluate median diameter of these particles in each solvent , the factors of dispersibility that depend on these combinations were investigated using Hansen's solubility parameter,.

Experiment

For model particles, α-Al_2O_3 (Sumitomo Chemical Corp., median diameter is 0.5 μm) , α-Fe_2O_3 (Toda Kogyo Corp., median diameter is 0.7 μm) and anatase type TiO_2 (Ishihara Sangyo Kaisya Ltd., median diameter is 0.2 μm) were used. For solvents, 27 types of solvents shown in Table 1 were used. These particles were dried in oven at 423 K for 24 hrs and these solvents were dehydrated with Molecular Sieves for 24 hrs before preparing suspensions. Each value of f_d, f_p and f_h in Table 1 is calculated by the following eqs.(1) - (3), respectively.

$$f_d = \{ \delta_d / (\delta_d + \delta_p + \delta_h) \} \times 100 \quad (1)$$

$$f_p = \{ \delta_p / (\delta_d + \delta_p + \delta_h) \} \times 100 \quad (2)$$

$$f_h = \{ \delta_h / (\delta_d + \delta_p + \delta_h) \} \times 100 \quad (3)$$

where δ_d, δ_p and δ_h are corresponding to dispersion effect [1], polar effect [1,2] and hydrogen binding effect [1] of the Hansen's solubility parameter, respectively. Suspension was prepared from the combination of these particles and solvents. Suspensions of 10g/dm^3 dry particles were prepared in various solvents. They were shaken at 300spm for 24 hrs. Particle size in these suspensions was measured by using a laser scattering particle size distribution analyzer (LA-910, Horiba Ltd.).

Table1 Solvents used in this study and their physical propert

No.	Solvent	ε	δ	δ_d	δ_p	δ_h	f_d	f_p	f_h
1	Hexane	1.890	7.24	7.24	0.1	0.2	94	2	4
2	Cyclohexane	2.203	8.18	8.18	0.2	0.2	96	2	2
3	1,4-Dioxane	2.209	10.01	9.30	0.9	3.6	67	7	26
4	Benzen	2.284	9.02	8.95	0.5	1.0	85	5	10
5	Xylene	2.374	8.79	8.65	0.5	1.5	81	5	14
6	Toluene	2.379	8.90	8.82	0.7	1.0	84	7	9
7	Trichloroethylen	3.400	9.28	8.78	1.5	2.6	68	12	20
8	Chloroform	4.806	9.21	8.65	1.5	2.8	67	11	22
9	Acetic acid	6.15	10.45	7.10	3.9	6.6	40	22	38
10	Aniline	6.89	11.05	9.53	2.5	5.0	56	15	29
11	Pyridine	12.3	10.60	9.25	4.3	2.9	56	26	18
12	n-Pentanol	13.9	10.59	7.81	2.2	6.8	46	13	41
13	1-Butyl alcohol	17.1	11.32	7.81	2.8	7.7	42	16	42
14	1-Propyl alcohol	20.1	11.97	7.75	3.3	8.5	40	17	43
15	Acetone	20.7	9.75	7.58	5.1	3.4	47	32	21
16	Ethyl alcohol	24.3	12.98	7.73	4.3	9.5	36	20	44
17	Methyl alcohol	32.63	14.49	7.42	6.0	10.9	30	25	45
18	Acetonitrile	37.5	11.95	7.50	8.8	3.0	39	46	15
19	Ethylene glycol	37.7	16.07	8.23	5.4	12.7	31	21	48
20	Formic acid	58.5	12.18	7.0	5.8	8.1	33	28	39
21	Water	77	23.43	6.00	15.3	16.7	16	40	44
22	Methyl isobutyl ketone	-	8.31	7.49	3.0	2.0	60	24	16
23	2-(2-butoxy ethoxy) ethanol	-	9.97	7.80	3.4	5.2	47	21	32
24	Diacetone alcohol	-	10.13	7.65	4.0	5.3	45	24	31
25	2-Ethoxy ethanol	-	11.44	7.85	4.5	7.0	41	23	36
26	Diethylene glycol	-	14.56	7.86	7.5	9.7	31	30	39
27	Ethanolamine	-	15.35	8.35	7.6	10.4	32	29	39

ε : Dielectric constant,δ : Hildebrand's solubility parameter,
δ_d,δ_p,δ_h : Hansen's solubility parameters

Results and Discussion

Fig. 1 shows the results of measuring median diameter of particles in many solvents as a function of dielectric constant. Each number in Fig. 1 means the solvent listed in Table 1. The median diameter is decreased with an increase in dielectric constant and the suspension shows better dispersibility. In the range of dielectric constant over 5, many systems show median diameter less than 10 μm. However, in that dielelctric constant, some systems including Al_2O_3 - pyridine (ε_r=12.3) and Al_2O_3 - acetonitrile (ε_r = 37.5) show median diameter more than 10 μm . It seems that not all the solvent of high dielectric constants makes Al_2O_3 particles disperse. Generally, highly polar materials show the high dielectric constant. Dispersibility of particles are affected not only by the polarity of solvent but also other factors.

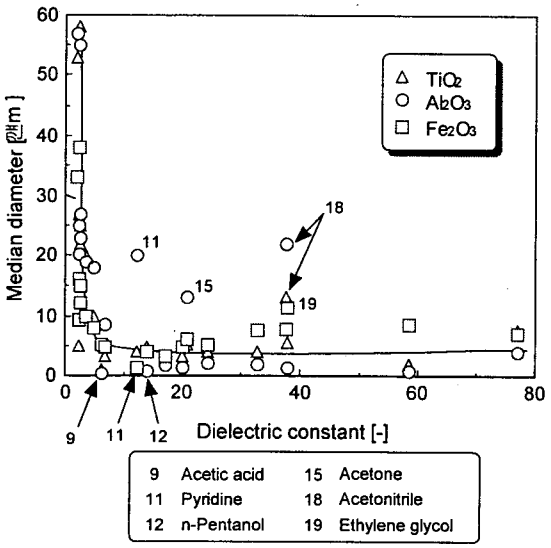

Fig.1 Relationship between median diameter and dielectric constant of various solvents

To investigate the relationship between the van der Waals attractive force and the dispersibility of particles, the Hamaker constant between solvents and particles was observed. The relationship between Hanaker constants (A_{131}) and dielectric constants is shown in Fig. 2. A_{131} means the Hanaker constant of the particle in solvents calculated from Eq. (4).

$$A_{131} = \{ (A_{11})^{1/2} - (A_{33})^{1/2} \}^2 \qquad (4)$$

In this equation, A_{11} and A_{33} are the Hamaker constant of solvents and particles, respectively. In the case of Al_2O_3 and Fe_2O_3 system, the values of A_{131} in the range about the dielectric constant of 5 is less than 10×10^{-20} J. In this range, van der Waals attractive energy is lower than others. Good dispersibility shown in this range is caused by a weak attractive force. In the range of dielectric constant more than 20, high Hamaker constants are calculated. In this range, however, an electrostatic repulsive force affects strongly. In the range of dielectric constant more than 20, it is difficult to evaluate the dispersibility only by the Hamaker constant.

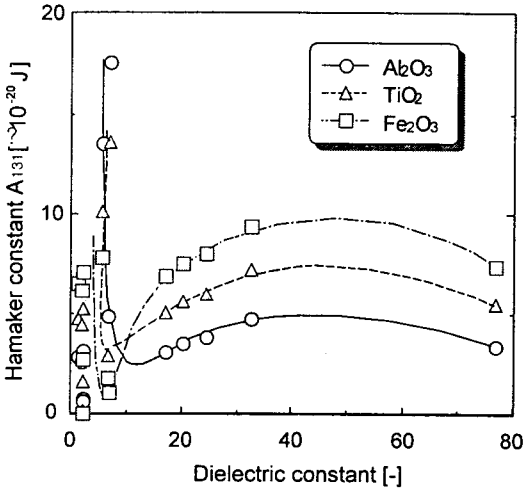

Fig.2 Relationship between Hamaker constant and dielectric constant of various solvents

Investigastion of dispersibilities without using dielectric constant and Hamaker constant was conducted. Fig.3 shows the isometric particle lines of Al_2O_3. This figure was made as follows. First, f_p, f_d and f_h of each solvent were plotted in triangular chart. Next, the median diameter of particles in each solvent was measured. Finally, the point of solvents showing resemble dispersibility is linked. Each number in Fig. 3 means the solvent listed in Table 1. All lines are not intersected and lies each other. Particularly, the lines of the median diameter from 0.6 to 0.9μm and from 1.0 to 4.0μm are described in closed area. There exists the point showing the optimal dispersibility for Al_2O_3 (optimal dispersive point) in the closed area from 0.6 to 0.9μm. If we use the closed line having many measured point (1.0 to 4.0μm), the center point of the inscribed circle in this area is supposed to be the optimal dispersive point of Al_2O_3 particle. The values of the optimal dispersive point are f_p = 44% , f_d =19% and f_h =37%. This point exists in the closed area from 0.6 to 0.9 μm. Generally, materials having similar property show good affinity. According to Hansen [1, 3, 4], when the solubility parameters of solvent and polymer are close, the polymer shows good solubility in the solvent. It seems that this optimal dipersive point means the f_d, f_p and f_h for the Al_2O_3 particles. When the solvent with the f_d, f_p and f_h closed to the optimal dispersive point is selected, Al_2O_3 particles show good dispersibility. To verify that many particles has each

has each optimal dispersive point, the similar examination was carried out using Fe_2O_3 and TiO_2 particles. Results of the examination were shown in Figs.3 and 4. In each figure, all lines are not intersected and lie each other. The optimal dispersive point of Fe_2O_3 and TiO_2 exist in the different point. These results resemble the dispersion of Al_2O_3. Many particles have the different optimal dispersive point in various solvent. The optimal dispersive point is represented by the value of the f_d, f_p and f_h of the solvents. These values can be estimated from isometric particle lines in the triangular chart.

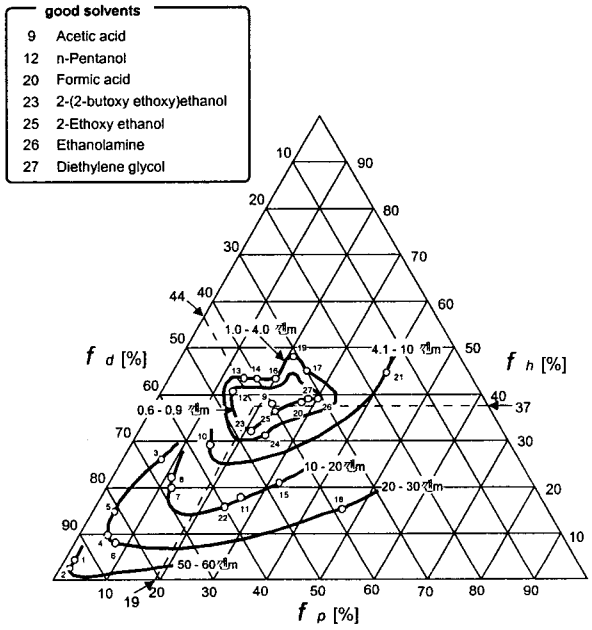

Fig.3 Isometric particle lines on triangular chart for Al_2O_3
(Each number means a solvent listed in Table1)

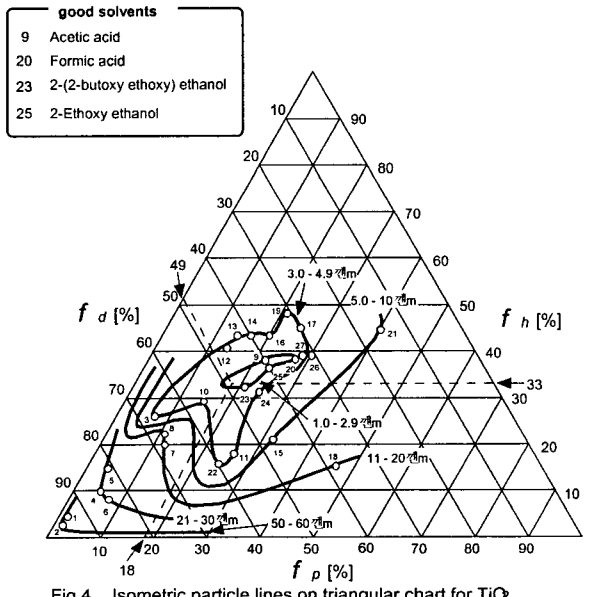

Fig.4 Isometric particle lines on triangular chart for TiO_2
(Each number means a solvent listed in Table1)

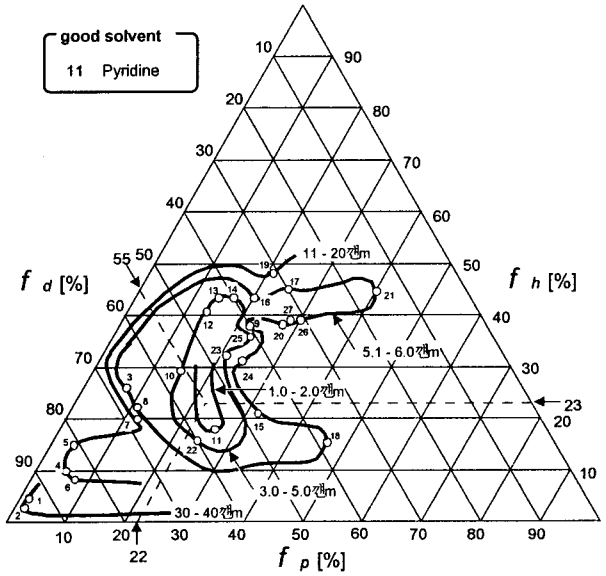

Fig.5 Isometric particle lines on triangular chart for Fe_2O_3
(Each number means a solvent listed in Table1)

Conclusion

The metal oxide powders such as TiO_2, Al_2O_3 and Fe_2O_3 tend to disperse in a solvent of higher polarity, whereas they are apt to flocculate in a solvent of low dielectric constant, because the Hamaker constant between the particles becomes larger in such a solvent. However, some solvents do not obey these tendencies. It is possible to evaluate the flocculation and dispersion of these metal oxide powders in many solvents by using Hansen's three-dimensional solubility parameters (f_d, f_p and f_h). From the results, the optimal dispersion point of f_d, f_p and f_h is determined by the combination of metal oxide powders and solvents. The value of f_d, f_p and f_h obtained as the optimal dispersive point may correspond to the values of f_d, f_p and f_h of the particle.

Nomenclature

f_d, f_p, f_h= numeral balance of δ_d, δ_p, δ_h [%]
δ= solubility parameter [-]
δ_d, δ_p, δ_h= element of dispersion power, polarity interaction, hydrogen bonding in the solubility parameter [-]
ε= dielectric constant

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