Dispersion and Flocculation Behavior of Fine Metal Oxide Particles in Various Solvents[†]

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Abstract

The objective of this study is to investigate the relation between the flocculation and dispersion of Al_2O_3, TiO_2 and Fe_2O_3 particles and the properties of solvents such as dielectric constant and solubility parameters. The median diameter of these metal oxide perticles was measured in many organic solvents. The effect of the kind of solvent on the flocculation/dispersion behavior of metal oxide particles was evaluated from these results.

Hansen's solubility parameters with three dimensions were applied to the evaluation of the flocculation/dispersion behavior for fine metal oxide particles in organic solvents. The numeral balance among the Hansen's solubility parameters of various solvents was plotted in a triangular chart, and then the points of solvents with similar median diameter of the particle were linked. In the triangular chart, these linked lines were not intersected each other and there was the specific point at which the best dispersibility of the particles was obtained.

1. Introduction

The dispersibility of fine particles in various solvents affects the quality of the products in the manufacturing process treating suspensions. It is important to control the dispersion/flocculation behavior of fine particles in various solvents in the field of paint, printer ink, magnetic material, electronic parts, etc. [1]. The DLVO theory, as is well known, explains the dispersion/flocculation behavior of fine particles in aqueous solution. However, this theory cannot be applied to the particles in organic solvents, because the factors on dispersibility in organic solvents are very complicated.

The dielectric constant of a substance is closely concerned with the dipole moment, and also the polarity of a substance with high dielectric constant is considered to be large. Generally, the affinity becomes higher between the solvent with large polarity and the metal oxide particle with large polarity. Therefore, dispersibility of fine particles in a solvent may be concerned with the dielectric constant of the solvent. On the other hand, Hildebrand [2] proposed the concept of regular solution theory and gave the experimental solubility parameter δ in order to expand it to real solutions. However, this concept is applicable only to nonionic solution with no dipole interaction. In order to extend this theory toward polymer solutions, the Hildebrand's solubility parameter δ was divided into London dispersion effect δ_d, polar effect δ_p and hydrogen bonding effect δ_h by Hansen, and then the applicability of these solubility parameters was investigated for the solubility of pigments and polymers [3, 4, 5, 6].

In this study, the relationship between dispersibility of fine particles and various properties of the solvent, such as dielectric constant and solubility parameters, was investigated in various solvents [7, 8]. The median diameters of fine particles of Al_2O_3, TiO_2 and Fe_2O_3 were measured in various solvents to evaluate the dispersibility of particles, and also Hansen's solubility parameters were used for the evaluation of dispersibility of fine particles in various solvents.

2. Hildebrand's solubility parameter and Hansen's solubility parameter

As the concept of ideal solution is not well applicable to real solutions, many useful approximations

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have been made to real solutions. Hildebrand proposed the concept of regular solution theory and he gave the following equation to evaluate the solubility of various materials [2],

$$\delta = \{(\Delta H - RT)/V\}^{1/2} \tag{1}$$

where R, T, ΔH and V are gas constant, temperature, enthalpy of vaporization and molar volume, respectively. The solubility parameter δ can be calculated by the following equation [2],

$$\delta = 3.75 \ (\gamma/V^{1/3})^{1/2} \tag{2}$$

where γ is surface tension of the solvent.

On the other hand, the concept of regular solution is applicable only to nonionic solutions in which association and dipole interaction do not take place between solvent and solute. However, hydrogen bonding and dipole interactive force should not be ignored in many solvents. It is important to extend the regular solution theory to real solutions. Hansen divided Hildebrand's solubility parameter δ into three terms as follows [3],

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2 \tag{3}$$

where δ_d, δ_p and δ_h are corresponding to London dispersion effect, polar effect and hydrogen bonding effect, respectively. In estimating the value of δ_h, Hansen noticed the fact that the hydrogen bonding energy of -OH group was about 5kcal and then he proposed the next equation taking account of the contribution of -OH group to aggregation [5],

$$\delta_h = \sqrt{5000 \ n/V} \tag{4}$$

where n is the number of -OH group in a unit molecule.

The value of δ_p is calculated by the following equation derived by Bottcher [9],

$$\delta_p{}^2 = 12.108/V^2 \ (\varepsilon - 1)/(2\varepsilon + n_D{}^2) \ (n_D{}^2 + 2)\mu^2 \tag{5}$$

where ε is dielectric constant, n_D is refractive index for Na-D ray and μ is dipole moment. The value of δ_d is estimated from the vaporization energy of the material in which the -OH and -CO groups do not exist.

As the dispersion phenomenon, similar to dissolution, is related to the diffusion phenomenon, it is possible to express the dispersion/flocculation behavior of fine particles using Hansen's solubility parameters. The fine particles of α-Al$_2$O$_3$, α-Fe$_2$O$_3$ and anatase type-TiO$_2$ were used as a model particle, and the median diameters of these particles in various solvents were measured. The dispersibility of the fine particles was considered from the obtained results.

3. Experimental

Fine particles of α-Al$_2$O$_3$ (Sumitomo Chemical Corp., 0.5μm median diameter), α-Fe$_2$O$_3$ (Toda Kogyo Corp., 0.7μm median diameter) and anatase type-TiO$_2$ (Ishihara Sangyo Kaisya Ltd., 0.2μm median diameter) were used as a model particle. These particles were dried in oven at 423K for 24hrs. Twenty seven types of solvents were selected as dispersion media. **Table 1** shows the list of used solvents with some physical properties. These solvents were dehydrated with molecular sieves for 24hrs before preparing suspensions. Each value of f_d, f_p and f_h shown in **Table 1** indicates the numerical balance among the Hansen's three solubility parameters, and these values are calculated by the following equations, respectively.

$$f_d = \delta_d/(\delta_d + \delta_p + \delta_h) \times 100 \tag{6}$$
$$f_p = \delta_p/(\delta_d + \delta_p + \delta_h) \times 100 \tag{7}$$
$$f_h = \delta_h/(\delta_d + \delta_p + \delta_h) \times 100 \tag{8}$$

The particles and solvents were mixed at 10g/dm^3 of slurry concentration, and then shaken at 300spm for 24hrs. The particle size distribution in each suspension was measured by using a laser scattering particle size analyzer (LA-910, Horiba Ltd.). The degree of dispersion and flocculation was evaluated from the value of the median diameter in each solvent.

4. Results and discussion

The median diameters of particles in various solvents are shown in **Fig. 1** as a function of dielectric
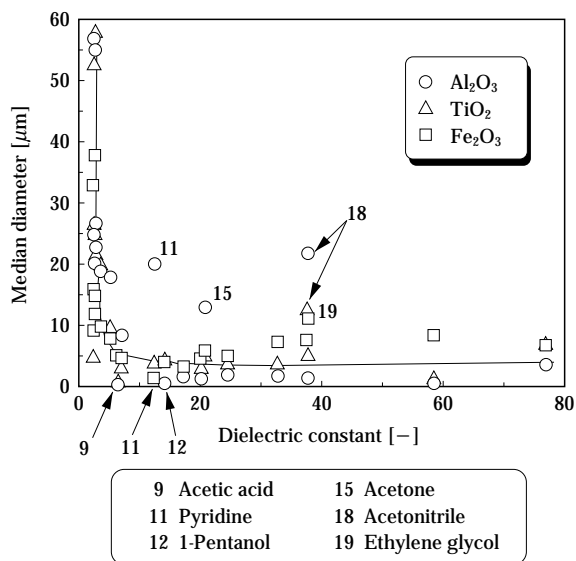

Fig. 1 Relationship between median diameter and dielectric constant of various solvents

constant of the solvent. Each number in **Fig. 1** means the kind of solvent listed in **Table 1**. The median diameter decreases with an increase in dielectric constant. In the range of dielectric constant over 5, the values of median diameter are under $10 \mu m$ for many particle-solvent systems and good dispersion can be obtained under this condition. However, some particle-solvent systems are confirmed to be against this tendency. For example, the values of median diameter are more than $10 \mu m$ in case of Al_2O_3-pyridine ($\varepsilon_r=12.3$), Al_2O_3-acetone ($\varepsilon_r=20.7$), Al_2O_3-acetonitrile ($\varepsilon_r=37.5$), Fe_2O_3-ethylene glycol ($\varepsilon_r=37.7$) and TiO_2-acetonitrile ($\varepsilon_r=37.5$) systems. The particles in these

suspensions indicate strong flocculation in spite of high dielectric constant of these solvents. On the other hand, the median diameter for Al_2O_3-acetic acid ($\varepsilon_r=6.15$), Al_2O_3-pentanol ($\varepsilon_r=13.9$) systems is less than $0.6 \mu m$, and good dispersion is confirmed in these systems though these solvents have low dielectric constant. In case of pyridine, Al_2O_3 particles have strong flocculation (median diameter $>20 \mu m$), while Fe_2O_3 particles indicate good dispersion (median diameter $<2 \mu m$). For almost all of metal oxide particles the dispersibility of particles tend to be related to the polarity of solvent, but there are some systems for which the dispersibility of particles does not obey the

Table 1 Physical properties of solvents used in this study

No.	Solvent	ε	δ	δ_d	δ_p	δ_h	f_d	f_p	f_h
1	Hexane	1.89	7.24	7.24	0.1	0.2	94	2	4
2	Cyclohexane	2.20	8.18	8.18	0.2	0.2	96	2	2
3	1,4-Dioxane	2.21	10.01	9.30	0.9	3.6	67	7	26
4	Benzene	2.28	9.02	8.95	0.5	1.0	85	5	10
5	Xylene	2.37	8.79	8.65	0.5	1.5	81	5	14
6	Toluene	2.38	8.90	8.82	0.7	1.0	84	7	9
7	Trichloroethylene	3.40	9.28	8.78	1.5	2.6	68	12	20
8	Chloroform	4.81	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	32.6	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	7.00	5.8	8.1	33	28	39
21	Water	78.3	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 parameter

above tendency. Furthermore, it is very interesting that water is not the best dispersion medium for metal oxide particles.

When the particles can be regarded as a complete spherical body with radius a, the van der Waals attractive energy V_A is expressed as follows,

$$V_A = -\frac{A_{131}}{12}\left[\frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2\ln\frac{x(x+2)}{(x+1)^2}\right] \qquad (9)$$

where x is the distance between particles (L) divided by the radius of particle (a), and A_{131} is Hamaker constant of particles in the solvent. Therefore, it is recognized from Eq.(9) that the van der Waals attractive energy between particles increases with an increase in the value of A_{131}. When A_{11} and A_{33} are individual Hamaker constants of particles and solvent, respectively, the Hamaker constant of the particles in the solvent A_{131} can be approximated by the following equation,

$$A_{131} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \qquad (10)$$

The relationship between the van der Waals attractive energy and the dispersibility of the particles was investigated. The relationship between Hamaker constant of particle A_{131} and dielectric constant of solvent is shown in **Fig. 2**. In case of Al_2O_3 and TiO_2 systems, some values of A_{131} are as high as 10×10^{-20} J in the range of dielectric constant around 5. Because the van der Waals attractive energy of them becomes large, the particles tend to flocculate under the condition. In case of Fe_2O_3 system, A_{131} values is less than 10×10^{-20} J through all range of dielectric constant. The results indicate that the van der Waals attractive
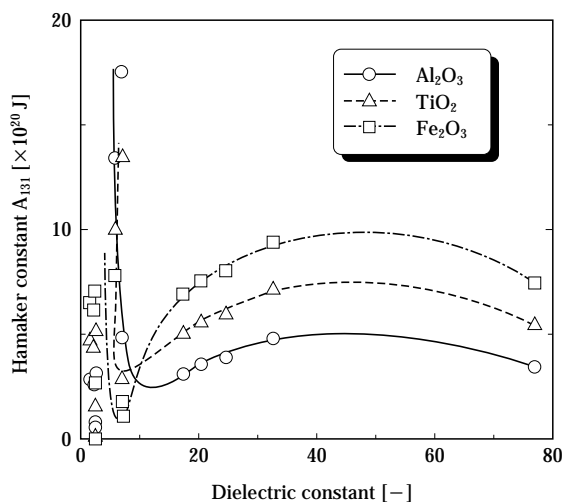

Fig. 2 Relationship between Hamaker constant and dielectric constant of various solvents

energy of Fe_2O_3 is small in the solvents used in this study and the particles have a tendency to disperse. Though high Hamaker constants are calculated in the range of dielectric constant more than 20, the electrostatic repulsive energy by charged particles affects strongly dispersion and flocculation. From the above results, it is difficult to evaluate the dispersibility of particles in a solvent by using only the Hamaker constant.

The Hansen's solubility parameters were used to investigate the dispersibility of particles without using dielectric constant and Hamaker constant. The numeral balance of Hansen's solubility parameters for each solvent was calculated from Eqs. (6)−(8), and then the value was plotted in the triangular chart. The points of solvents with a similar median diameter were linked to make the isometric particle lines.

Figure 3 shows the isometric particle lines for Al_2O_3. The intersected point of three broken lines in **Fig. 3** indicates the values of f_d, f_p and f_h of the hypothetical solvent in which the best dispersibility is obtained. The point is defined as the optimal dispersible point. The same examinations were carried out by using TiO_2 and Fe_2O_3 particles to evaluate the applicability of Hansen's solubility parameters to the dispersibility of several particles. In **Fig. 3**, the optimal dispersible point can be determined to be the center point of the largest inscribed circle for the closed isometric particle line comprising the solvents with the particle size of $1.0-4.0\mu m$. The values of the optimal dispersible point for Al_2O_3 are $f_d=44\%$, $f_p=19\%$ and $f_h=37\%$, respectively. As f_d, f_p and f_h values of a solvent approach to the optimal dispersible point, the dispersibility of the particles becomes better. The solvents causing high dispersion to Al_2O_3 particles are acetic acid, formic acid, 2-(2-butoxy ethoxy) ethanol, 2-ethoxy ethanol, diethylene glycol, ethanolamine and 1-pentanol, respectively.

The isometric particle lines of TiO_2 and Fe_2O_3 are shown in **Figs. 4** and **5**, respectively. The optimal dispersible point of TiO_2 system locates at $f_d=49\%$, $f_p=18\%$ and $f_h=33\%$, and the good solvents for TiO_2 are acetic acid, formic acid, 2-(2-butoxy ethoxy) ethanol and 2-ethoxy ethanol. In the case of Fe_2O_3 system, the optimal dispersible point exists at $f_d=55\%$, $f_p=22\%$ and $f_h=23\%$, and the good solvent for Fe_2O_3 is pyridine. From these results, the specific optimal dispersible point exists for each metal oxide particle.

Generally, the affinity between the two materials is considered to be high when the chemical and physical properties of two materials resemble each other. For example, nonpolar materials can be easily dis-
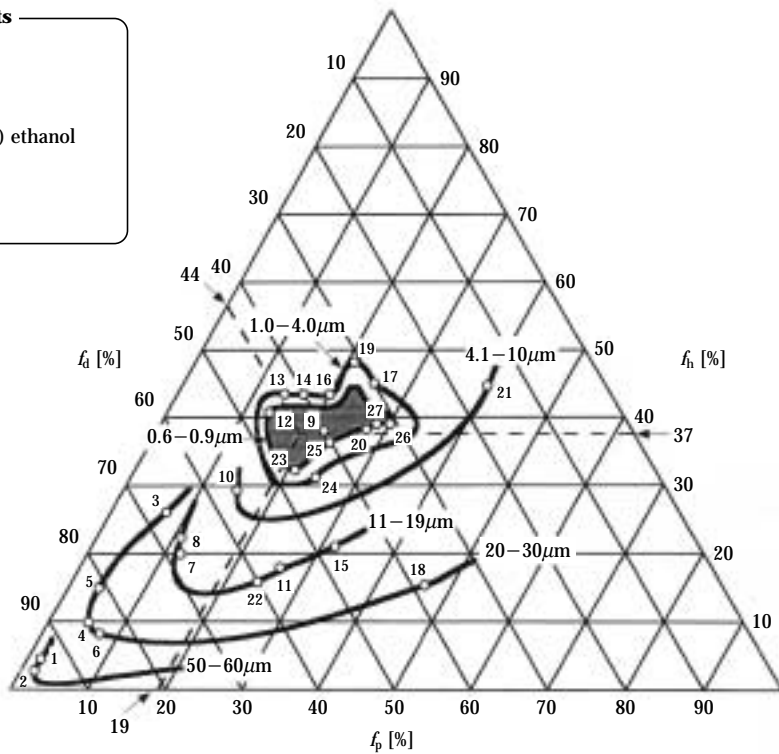
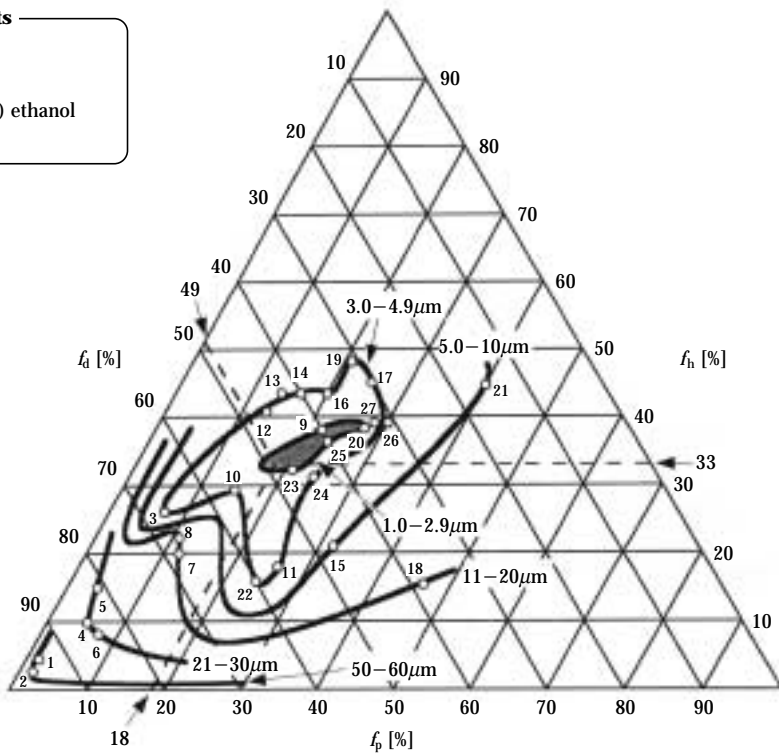**Fig. 3** Isometric particle lines on triangular chart for Al$_2$O$_3$ (Each number means a solvent listed in **Table 1**)

Fig. 4 Isometric particle lines on triangular chart for TiO$_2$ (Each number means a solvent listed in **Table 1**)
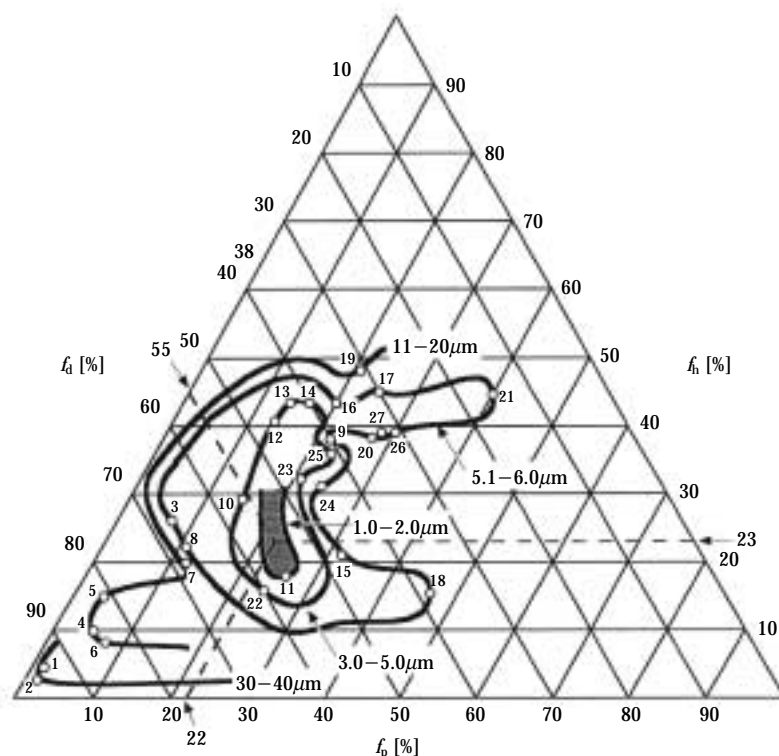
Fig. 5 Isometric particle lines on triangular chart for Fe_2O_3 (Each number means a solvent listed in **Table 1**)

solved in nonpolar solvents, but hardly dissolved in polar solvent. On the other hand, polar materials are easily dissolved in polar solvents, but hardly dissolved in nonpolar solvents. It can be also said that the dispersibility of fine particles is related with the affinity between a particle and a solvent. Therefore, the values of f_d, f_p and f_h of a hypothetical solvent for which the optimal dispersible point is obtained may correspond to the values of f_d, f_p and f_h of each particle itself. When the values of f_d, f_p and f_h of a solvent approach to the optimal dispersible point, the particle is well dispersed in the solvent.

5. Conclusion

In order to clarify the relationship between the flocculation/dispersion of fine metal oxide particles and the properties of solvents, the dispersibility of TiO_2, Al_2O_3 and Fe_2O_3 particles in various solvents was investigated in this study.

High polar solvents tend to disperse metal oxide particles. The Hamaker constant of particles becomes large in the solvent with low dielectric constant, and then the particles have tendency to flocculate. However, some particle-solvent systems do not obey this tendency. It is difficult, therefore, to evaluate the floc-

culation/dispersion behavior by using only polarity of solvent or the Hamaker constant of particle.

The dispersibility of particles in various solvents can be evaluated by using the numeral balance, f_d, f_p and f_h of Hansen's three solubility parameters. The values of f_d, f_p and f_h of the hypothetical solvent giving the optimal dispersion exist for each particle. As the values of f_d, f_p and f_h approach to the optimal dispersible point, the fine particles are well dispersed in a solvent. The f_d, f_p and f_h values for an optimal dispersible point seem to be the values of f_d, f_p and f_h of the particles themselves.

Nomenclature

A	= Hamaker constant	[J]
a	= Particle diameter	[m]
f_d, f_p, f_h	= Numeral balance of δ_d, δ_p, δ_h	[%]
H	= Enthalpy	[J mol^{-1}]
L	= Distance between particles	[m]
n	= Number of -OH group in a molecule	[−]
n_D	= Refractive index	[−]
R	= Gas constant	[J mol^{-1} K^{-1}]
T	= Temperature	[K]
V	= Molar volume	[m^3 mol^{-1}]
γ	= Surface tension	[N m^{-1}]

δ = Hildebrand's solubility parameter $[-]$
$\delta_f, \delta_p, \delta_h$ = Hansen's solubility parameters $[-]$
ϵ = Dielectric constant $[-]$
μ = Dipole moment $[C\ m]$

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