Evaluation of the Dispersion Behavior of Nanopowder in Organic Liquids

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Abstract: The relation between total colloid potential energy and the surface energy of nanopowder in organic solvent was given by the DLVO theory and EDLVO theory, which mainly considered that total colloid potential energy consisted of Vander Waals energy, electrostatic energy and interfacial polarity interaction energy. Three kinds of nanopowder (TiO_2, SiO_2 and ZnO) and seven organic solvents (glycol, dimethyl sulfoxide, formamide, methanol, n-hexane, cyclohexane, and acetone) were used in our experiments. Their surface energies in seven organic solvents were measured respectively. Total colloid potential energy of each nanopowder was obtained by computer program. The dispersion behavior of nanopowder in organic liquids was checked up by two experiments: one of experiments was the sedimentation of TiO_2, SiO_2 and ZnO in glycol, dimethyl sulfoxide, formamide, methanol, n-hexane, cyclohexane, and acetone; another of experiments was the ultraviolet absorbency of TiO_2 powders treated by plasma in different conditions in glycol. Experimental results showed that there was high correlation between the maximum colloid potential energy and the dispersion behavior of the nanopowder in organic solvent. So the dispersion behavior of the nanopowder in organic solvent can be evaluated by the maximum colloid potential energy.

Keywords: nanopowder; surface energy; DLVO theory; dispersion behavior; evaluation

1. Introduction

In recent years, the stability of colloid has received increasing attention due to its wide usage in the nano composites [1]. Nanopowder with improved properties should be well dispersed by putting into organic liquids, which becomes a form of colloid. It is very important to keep it well dispersed during the industrial process. Actually, with different powders and solvents, the dispersions are not the same. Obviously, some of the dispersions are diluted after some time, which will take greatly effect in the manufacture of nano composites. Therefore, the dispersion behavior is a key problem in the composite techniques. In order to predict the dispersion effect, a measurement based on DLVO theory[2] and EDLVO theory[3] is build up to evaluate it. As nanopowder is greatly divided into pieces, its surface energy raised up quickly. So the surface energy is considered as the unstable factor in the dispersion. Then, the relation between total colloid potential energy and the surface energy of nanopowder in organic solvent is found out by DLVO and EDLVO theory which mainly consider that total colloid potential energy consists of Vander Waals energy, electrostatic energy and interfacial polarity interaction energy.

2. Evaluation theory

As the character of nanopowder is between the macroscopy and microcosm, the gravity factor of particle is too low to be considered in the liquid. Generally speaking, the interactions among the particles take greatest effect on the behavior of the powders. In the research of the colloid stability, DLVO theory is widely used now, which is set up by Darjaguin and Landan from Russia in 1941 and Verwey and Overbeek from Holland in 1948 respectively. It is said that there are two main kinds of forces in colloid: one is the attraction from long Vander Waals; another is the repulsion from electrical double layer interactions. The two forces make the decision of the stability. When the repulsion is bigger enough, the particles collision can be mostly avoided and the dispersion will be stable. When the attraction is larger, the particles will easily gather into big groups and sedimentation appears quickly. Furthermore, during the recent research of the colloid stability, interfacial polarity interaction energy is found to take great effect in the polar liquid, so it is invited in EDLVO theory. So we consider these three forces as the main factor of the total colloid potential energy.

2.1. Vander Waals energy

Attraction energy exists among the particles like atoms and molecules in the colloid. London-Vander Waals interaction U_A, is always present and always attractive between particles and is an important parameter in colloidal suspensions. The potential energy can be expressed as follow [4],

$$U_A = -\frac{A}{12}\frac{R}{H_0} \tag{1}$$

where R is the radius of a particle, H_0 is the minimum distance between the surfaces of two particles, and A is the effective Hamaker constant for two particles of material 1 through a medium of material 2. A can be expressed as follow,

$$A = \left(\sqrt{A_{11}} - \sqrt{A_{00}}\right)^2 \tag{2}$$

where A_{11} is the Hamaker constant of two particles in vacuum, and A_{00} is the Hamaker constant of the dispersion medium.

Because of the complex situation in the dispersion, it is difficult to get A_{11} and A_{00} directly. Here we use the experiential formula approximately. The relationship between surface energy and Hamaker constant is

$$A = \frac{4\pi}{1.2}\gamma^f a^2 \tag{3}$$

where γ^f is the non-polar part of the surface energy, a is the dispersing distance between two particles. Then A_{11} and A_{00} can be estimated by using particle and solvent surface energy respectively. Generally, A is at 10^{-20} order of magnitude.

2.2. Electrostatic energy

Electrified particle will attract the surrounding dispersed medium to form diffused double electrostatic layer. When the diffused layers do not touch each other, the two particles will not make any repulsion. But if the two layers are overlapped, the particles will have to move to decrease the overlapped concentration. So the higher concentration it is, the stronger the force is. This relationship also depends on the shape of particles, which is regarded as spheroid in this study. So we get the electrostatic energy U_R [2], that is

$$U_R = \frac{\varepsilon R \psi_0^2}{2}\exp(-kH_0) \tag{4}$$

where ψ_0 is the surface electronic energy, R is the average radius of the particles, ε is the liquid dielectric constant, k is the Boltzmann constant, H_0 is the minimum distance between the surfaces of two particles.

2.3. Interfacial polarity interaction energy

DLVO theory traditionally deals with apolar vander Waals attraction and electrical double layer repulsion, as a function of distance. However, when the liquid in question is polar and especially when the liquid is water which is very polar, another category of non-covalent interactions is quantitatively more dominant, i.e. the interfacial polarity interaction, by EDLVO theory. Interfacial polarity interaction energy U_H is expressed as follow [3],

$$U_H = \pi R \cdot \lambda \cdot \Delta G_{l0}^{AB} \cdot \exp\left[\left(l_0 - H_0\right)/\lambda\right] \tag{5-1}$$

$$\Delta G_{l0}^{AB} = -4\left(\sqrt{\gamma_L^+\gamma_L^-} + \sqrt{\gamma_S^+\gamma_S^-} - \sqrt{\gamma_S^+\gamma_L^-} - \sqrt{\gamma_L^+\gamma_S^-}\right) \tag{5-2}$$

where l_0 is the average minimum distance between two particles' surfaces. At 20 °C, $l_0 = 0.157 \pm 0.01$nm. In the hydrophilic system, $\lambda = 1.0$ nm, and in the hydrophobic system, $\lambda = 2.0$ nm. And γ_L^+, γ_L^-, γ_S^+, γ_S^- are the polar surface energies of liquid and solid. Thus, the total colloid potential energy is expressed like

$$U = U_A + U_R + U_H \tag{6}$$

2.4. Measure of surface energy

As mentioned above, the relation between total colloid potential energy and the surface energy is set up. If the value of the potential energy is wanted, the surface energy should be firstly given. Not only the liquid surface energy, but also the solid surface energy is needed in evaluation.

Generally, surface energy γ can be divided into three parts: one is the apolar energy γ^f; the other two, electron accepter energy γ^+ and electron deliver energy γ^-, belong to the polar energy γ^{AB}. Their relationship can be expressed like [4] [5] [6]

$$\gamma_s = \gamma_s^f + \gamma_s^{AB}, \quad \gamma_s^{AB} = 2\sqrt{\gamma_s^+ \cdot \gamma_s^-} \tag{7}$$

Both of the solid surface energy and liquid surface energy are made up of these energies. As many commonly used organic liquid's surface energy can be easily found in books [7], we only need to measure the powder's surface energy.

The surface energies of the 7 organic liquids used in our experiment are firstly listed out to do the further works.

Table 1 Liquid Physical Characters

Liquid	γ (mJ/m^2)	γ^f (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)
water	72.6	21.6	25.5	25.5
methanol	22.5	22.5	0.0	0.0
glycol	48.3	29.3	1.9	47.0
Dimethyl sulfoxide	44.0	36.0	0.5	32.0
formamide	58.0	39.0	2.3	39.6
n-hexane	18.4	18.4	0.0	0.0
cyclohexane	25.3	25.3	0.0	0.0
acetone	23.7	23.7	0.0	0.0

A relation is set up between solid surface energy and liquid surface energy when the solid contacts with the liquid, which is like[8]

$$(1+\cos\theta)\gamma_L = 2(\sqrt{\gamma_S^f\cdot\gamma_L^f}+\sqrt{\gamma_S^+\cdot\gamma_L^-}+\sqrt{\gamma_S^-\cdot\gamma_L^+}) \tag{8}$$

where θ is the contact angle of the liquid on the solid surface, and γ, γ_L^f, γ_L^+, γ_L^- are the liquid surface energy, which can be found in table 1. Therefore we can use it to measure the solid surface energy respectively. But the question left is how to get the contact angle θ. Generally, contact angle can be observed by special photography instrument. Because of the high penetrability, we cannot measure the contact angle between the powder and organic liquid directly. So a wetting ability experiment is involved. A glass pipe filled with powders is put upon the liquid surface. One side of the pipe touches the liquid, and another side is hung up. We try to note the weight change of the pipe with the time. With experience, it always becomes a linear increase. So we can get the slope C. To compare the difference, Methanol is used to be regarded as the totally wetted liquid. So we can find contact angle from this,

$$\cos\theta = \frac{\eta\rho_m^2\gamma_m}{\eta_m\rho^2\gamma}\cdot\frac{C}{C_m} = A\cdot\frac{C}{C_m}\,,\quad （A = \frac{\eta\rho_m^2\gamma_m}{\eta_m\rho^2\gamma}） \tag{9}$$

where subscript m means the methanol, ρ is the liquid density, γ is the liquid surface energy, η is the liquid stickiness. These figures also can be easily found. Thus, the solid surface energy can be got by using 4 kinds of liquid. One of them is considered as totally wetted liquid, and the others are the referring liquid. But it should be reminded that the liquid won't dissolve the powder and not to be too sticky and volatile. Water, which is a kind of polar liquid, is helpful to get the polar part of surface energy of the powder. So we use methanol, water, glycol, and Dimethyl sulfoxide to do this measurement.

3. Experiments and Results

3.1. Sedimentation

Firstly, in order to know the dispersion behavior of nanopowder in organic liquids, we select the sedimentation experiment. Powders like TiO_2, SiO_2 and ZnO are put into 7 organic solvents, like glycol, dimethyl sulfoxide, formamide, methanol, n-hexane, cyclohexane, and acetone, respectively. The former 3 solvents are the polar liquids, and the later 4 are the apolar liquids. And the 3 powders are nano-sized with high pure ratio. Therefore, 21 test tubes are made. Each one mixes 0.1g powder and 10ml organic solvent. After ultrasonication for 15 min, white colloid appears in each tube. We believe that they are well dispersed, then take these 21 tubes out of the instrument, and put them aside to wait for their changes.

Table 2 Sedimentation results and maximum potential energy (KT)

	Glycol	Dimethyl sulfoxide	formamide	methanol	n-hexane	Cyclohexane	acetone
TiO_2	☆☆☆☆☆	☆☆	☆☆	☆☆☆☆	☆	☆	☆☆☆
	3.20	-15.17	-3.35	-0.31	-2.58	-0.63	-4.30
SiO_2	☆☆☆☆☆	☆☆	☆☆	☆☆☆	☆	☆	☆☆☆
	1.36	1.33	0.97	-0.09	-0.12	-0.14	-0.13
ZnO	☆☆☆☆☆	☆☆☆	☆☆☆	☆☆☆	☆	☆	☆☆
	5.29	6.18	-1.89	-4.70	-6.55	-7.84	-7.08

The more ☆ means the better dispersion it is in the sedimentation experiment. And the figure listed is the colloid potential energy evaluated from surface energy.

3.2. Ultraviolet absorbency

In order to tell the further relation between surface energy and dispersion behavior, nano powder TiO_2 is treated by PECVD (Plasma Enhanced Chemical Vapor Deposition) [9] at different power, time and pulse ratio in the work gas of crylic acid. These treated powders are dispersed in glycol by ultrasonication. After that, the colloid will immediately do the ultraviolet absorbency test to scale the dispersion behavior. And the powders' surface energy is also measured to evaluate the potential energy.

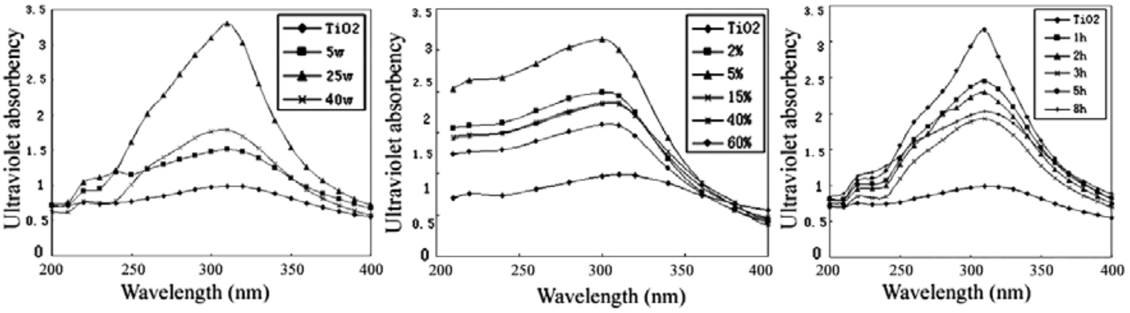

Figure 1 powder TiO_2 treated at different power, pulse ratio and time cause ultraviolet absorbency change

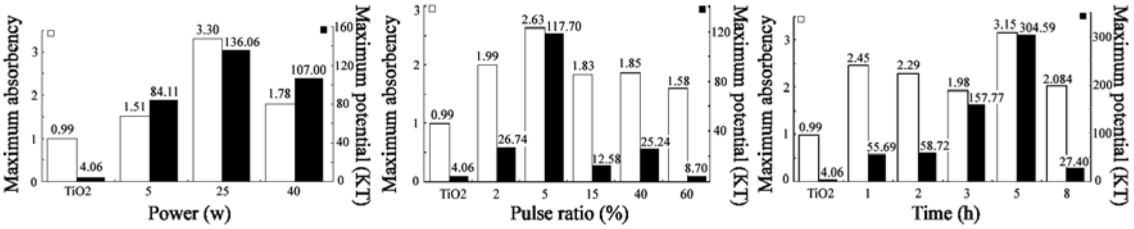

Figure 2 Compare with the maximum ultraviolet absorbency and maximum potential energy

4. Discussion and Conclusion

In the sedimentation experiment, powders TiO_2, SiO_2 and ZnO are better dispersed in the polar organic liquids like glycol, dimethyl sulfoxide and formamide than in the apolar organic liquids like methanol, n-hexane, cyclohexane, and acetone. In the ultraviolet absorbency experiment, the dispersion behaviors of treated powders TiO_2 are obviously improved.

From the recording tables and figures, it is found that evaluations of those two experiments are successful. The maximum potential energy based on surface energy can generally predict the dispersion behavior. The higher potential has, the better dispersion will be. It can qualitatively estimate the colloid stability. The tendency of the dispersion behavior is met very well by the evaluation in these two experiments. However, it should be emphasized that mistakes often happen in the solid surface energy measurement. So the evaluations may contain some errors. And further more, it should be reminded that the effective factors in the dispersion behavior are too complex to find them all in nature. Surface energy is just one of the factors to do this research. Fortunately, we got a valuable relationship to evaluate the nature phenomena.

References

[1] Zhang LD, Mou JM. Nano material and nano structure. Beijing science publisher, 2001

[2] Wang GT, Colloid stability. Beijing science publisher, 1990

[3] Carel Jan van Oss. Long-range and short-range mechanisms of hydrophobic attraction and hydrophilic repulsion in specific and aspecific interactions. Journal of molecular recognition, J.Mol.Recognit. 2003, **16**, 177

[4] Manish seth, Savvas G. Hatzikiriakos and Thomas M. Clere. Gross Melt Fracture Elimination: The Role of Surface Energy of Boron Nitride Powders. Polymer engineering and science, 2002, **l**, 4

[5] Cheng CX. Surface physics and chemistry. Beijing science technology literature publisher, 1995

[6] Hu JH. Colloid and interface chemistry. South china south and technology publisher, 1996

[7] Yuanzhi Chen, The dispersion behavior of Si-C-N nanopowder in organic liquids. Ceramics international, 2001

[8] Jun Ren, Shouci Lu, Jian Shen, Chunhong Yu. Research on the composite dispersion of ultra fine powder in the air. Materials chemistry and physics, 2001, **69**, 204

[9] Wang X, Zu Y, Li XE. Nano TiO_2 surface modification. Chemistry and technology development, 2000, **19**, 67