

PAPER • OPEN ACCESS

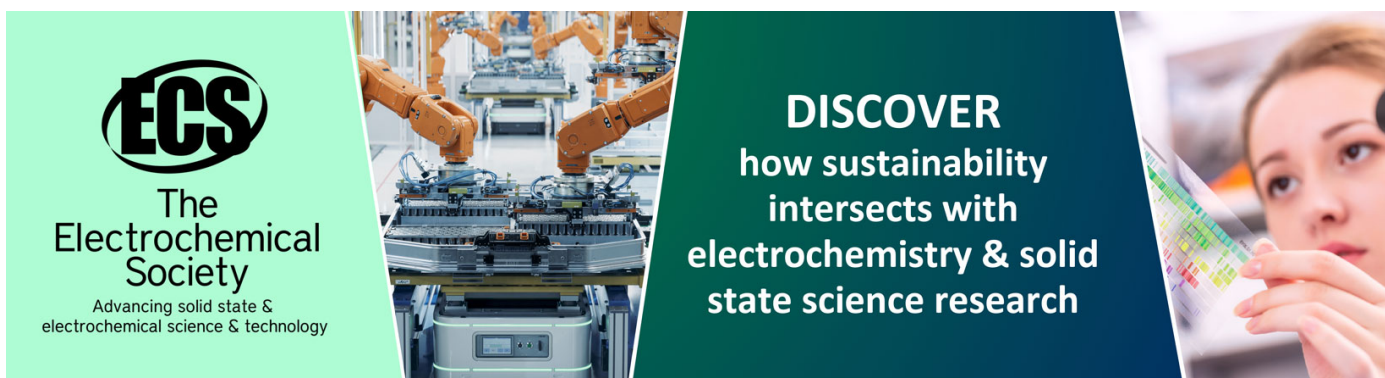
Estimation of Three-Dimensional Solubility Parameters of DM-700 Polyester Resin by Turbidity Titration

To cite this article: Qiang Liu *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **384** 012069

View the [article online](#) for updates and enhancements.

You may also like

- [Development of a head CT dose index \(CTDI\) phantom based on polyester resin and methyl ethyl ketone peroxide \(MEKP\): a preliminary study](#)
Rumaisya Hilmawati, Heri Sutanto, Choirul Anam et al.
- [Effect of fiber content on thermal and mechanical properties of euphorbia coagulum modified polyester and bamboo fiber composite](#)
Sanju Kumari, Ritesh Kumar, Bhuvneshwar Rai et al.
- [THE HALO MASS FUNCTION FROM EXCURSION SET THEORY. I. GAUSSIAN FLUCTUATIONS WITH NON-MARKOVIAN DEPENDENCE ON THE SMOOTHING SCALE](#)
Michele Maggiore and Antonio Riotto



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Estimation of Three-Dimensional Solubility Parameters of DM-700 Polyester Resin by Turbidity Titration

Qiang Liu¹, Xiaoqin Shi¹, Yanqiu Lu² and Liming Dong^{1, a, *}

¹School of Chemistry and Chemical Engineering, Xuzhou University of Technology, Xuzhou, China

²Jiangsu Delta Polyester Technology Co., Ltd., Xuzhou, China

^{a, *} Corresponding author e-mail: polymerdlm@163.com

Abstract. According to the method of turbidity titration and 63 cloud point data minimum volume closure ellipsoid fitting, the solubility parameter of polyester resin DM-700 was determined to be $22.84(\text{MPa})^{1/2}$, and the three-dimensional solubility parameter was $(\delta_d=17.15 (\text{MPa})^{1/2}; \delta_p=9.97(\text{MPa})^{1/2}; \delta_H=11.32(\text{MPa})^{1/2})$. This value is close to the result calculated by the group contribution method ($22.68(\text{MPa})^{1/2}$), which further proves that the method is accurate and reliable.

1. Introduction

With the continuous improvement of people's environmental requirements, the development of environmentally friendly coatings has become an inevitable trend. Powder coating is composed of solid resin and pigments, fillers and additives [1]. It has become the fastest growing coating product due to its resource saving, energy saving, pollution-free and high production efficiency. Polyester powder coatings are considered to be the most productive and versatile powder coatings. The polyester resin as the main film-forming substance mainly determines the properties of the coating [2-4]. In other words, the compatibility between the polyester resin and other components has a direct influence on the performance of the powder coating. Poor compatibility results in reduced film formation, mechanical and protective properties of the coating.

The solubility parameter is the square root of the cohesive energy density, which is an important indicator to measure the compatibility of materials. The closer the solubility parameters are, the better the compatibility between the substances is. There have been many scholars who have carried out related work on solubility parameters. Hildebrand [5] used a formal solution theory to determine the solubility parameters of a non-polar liquid mixture. Bagley [6] used the internal pressure of the liquid instead of the cohesive energy density to determine the solubility parameters of the polar system. Small [7] used the molar gravity constant of the group to determine the solubility parameter of the material. This method can also be used to estimate the solubility parameters of a polymer. As we all know, the polymer solubility parameter cannot be directly measured. Hansen [8-9] determined the three-dimensional solubility parameter of the polymer by using the dispersion parameter ($2\delta_d$) and the polarity parameter (δ_p) and the hydrogen bond parameter (δ_H) as a means of fitting the sphere into three-dimensional coordinates. This theory is considered to be the most accurate and applicable theory. However, there are still some shortcomings in Hansen theory. the workload is too large and it takes a long time for a lot of



solvent used. Positive spheres are artificially fitted with twice the value of the dispersion force, and so on.

In the previous work [10], the method of estimating the three-dimensional solubility parameter of the polymer by turbidity titration [11] was established, and was used to obtain the HSP value of the PPEN. In this paper, the three-dimensional solubility parameters of DM-700 polyester resin were determined by the above method, and the reliability of the previous method was further verified.

2. Experimental part

2.1. Experimental material

DM-700 polyester resin is from Jiangsu Delta Polyester Technology Co., Ltd., which is obtained by polymerization of terephthalic acid and neopentyl glycol as main raw materials. The good solvent of DM-700 pure polyester resin selected includes: N-methyl-2-pyrrolidone(NMP), Chloroform(CF), 1,1,2,2-tetrachloroethane(TCE), Acetone, Chlorobenzene(CB), Methyl isobutyl ketone(MIBK), N,N-Dimethylformamide(DMF), N,N-dimethylacetamide(DMAc), Ethyl acetate(EA); The poor solvent of DM-700 pure polyester resin selected includes: Methanol, Formamide(FA), Benzene, Xylene, Dimethyl sulfoxide(DMSO), Dodecane, Hexane, Perchloroethylene(PCE), Water. The three-dimensional solubility parameter values of the above reagents can be obtained from the literature[12]. In order to prevent the fitting data from being biased, some solvents with large differences in three-dimensional solubility parameter values were selected.

2.2. Experimental process

The DM-700 polyester 0.150g is uniformly dissolved in 100ml of good solvent. The volume of the poor solvent consumed was recorded by titration with a poor solvent until precipitation occurred and the precipitate no longer disappeared. The final result is the average of 5 titration experiments.

3. Results and discussion

The three-dimensional solubility parameter of the cloud point is calculated by the method of literature [10]. The calculation results are shown in Table 1. The calculation model is based on the theory that the internal energy of the system is unchanged before and after the system is mixed. However, the actual internal energy will change due to the solvent association and the exclusion of the repulsion, resulting in a certain systematic error in the fitting result. The fitting method is consistent with the method described in the literature [10]. The 63 sets of data were fitted as ellipsoid spherical coordinates by Matlab program, and the fitted ellipsoid is shown in Fig. 1. In the figure, "o" indicates a settling agent (non-good solvent); "+" indicates a good solvent; blue "*" indicates a cloud point (mixed solvent); and red "*" indicates an ellipsoid center point. The fitted ellipsoidal sphere can be considered as the three-dimensional solubility coordinate of the mixed solvent of several cloud points and the interface between the polymer soluble/insoluble. The fitting vector $\delta d=17.15$, $\delta p=9.97$, $\delta H=11.32$ is the spherical center of the ellipsoid, which is the three-dimensional solubility parameter of the DM-700 polyester resin.

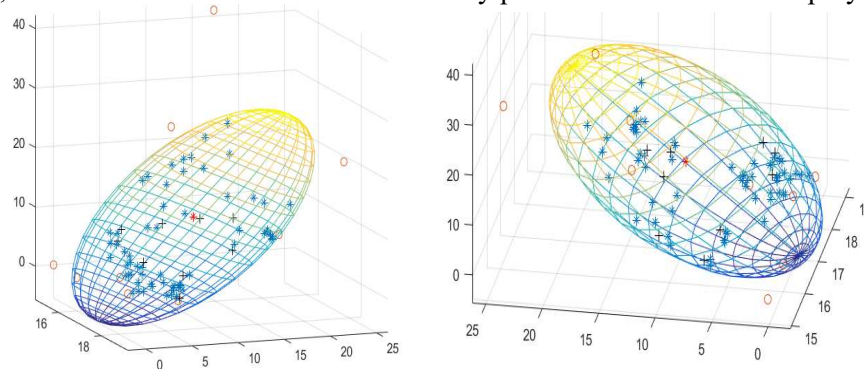


Figure 1. The ellipsoid fitting graph of cloud points

Table 1. The three-dimensional Solubility parameters of Cloud Point (MPa)^{1/2}

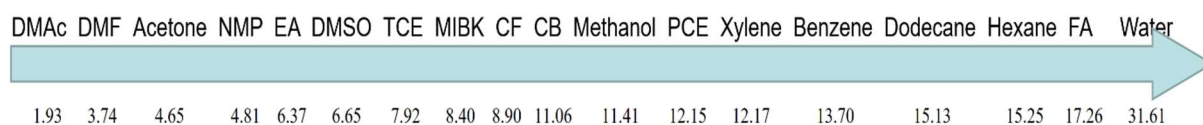
solvent	parameter	Methanol	FA	water	Benzene	Xylene	DMSO	Dodecane	Hexane	PCE
NMP	ϕ s/%	30.82	58.44	62.2	1.97	1.68	15.06	/	/	5.92
	d	16.05	17.67	17.10	18.39	17.61	18.34	/	/	18.28
	p	12.30	19.33	13.82	1.73	1.88	15.85	/	/	6.29
	h	18.97	13.43	26.62	2.22	3.21	9.81	/	/	1.75
CF	ϕ s/%	36.34	/	/	55.56	66.37	46.41	75.08	55.90	14.02
	d	16.13	/	/	18.07	17.73	18.12	17.37	16.58	18.23
	p	9.99	/	/	2.31	2.59	12.19	2.69	2.32	5.41
	h	18.12	/	/	4.45	4.98	8.42	4.94	4.26	2.13
TCE	ϕ s/%	/	/	/	45.45	54.54	11.24	/	/	34.30
	d	/	/	/	18.58	18.26	18.45	/	/	18.47
	p	/	/	/	3.44	3.83	15.55	/	/	5.50
	h	/	/	/	3.87	4.44	9.77	/	/	3.10
Acetone	ϕ s/%	89.67	91.49	92.4	9.15	14.08	36.95	86.07	77.38	7.00
	d	15.46	15.65	15.50	18.15	17.32	17.38	15.57	15.37	18.12
	p	10.61	12.54	10.93	3.15	4.01	14.48	9.65	9.15	6.15
	h	9.76	8.69	13.46	2.85	3.89	9.15	6.49	6.16	1.85
CB	ϕ s/%	35.42	/	/	61.55	45.81	11.26	95.18	91.05	16.54
	d	16.59	/	/	18.77	18.25	18.47	18.87	18.67	18.42
	p	10.21	/	/	3.37	3.00	15.52	4.20	4.10	5.49
	h	17.96	/	/	2.00	2.65	9.63	1.95	1.91	0.81
MIBK	ϕ s/%	63.41	/	/	71.74	71.54	7.11	87.20	79.89	9.14
	d	15.23	/	/	16.24	15.99	18.20	15.39	15.22	18.05
	p	8.89	/	/	5.17	5.19	15.89	5.70	5.45	5.74
	h	13.88	/	/	3.63	3.84	9.89	3.83	3.66	1.24
DMF	ϕ s/%	50.89	78.29	80.49	0.77	2.09	25.17	/	/	12.13
	d	16.31	17.36	17.05	18.39	17.60	18.15	/	/	18.19
	p	13.03	17.20	14.18	1.20	2.21	15.76	/	/	7.16
	h	17.58	13.35	21.26	2.22	3.48	10.49	/	/	3.94
DMAc	ϕ s/%	41.77	71.28	74.48	0.24	1.32	17.14	/	/	5.19
	d	15.83	16.92	16.48	18.40	17.59	18.14	/	/	18.23
	p	11.97	17.07	12.80	0.56	1.65	15.67	/	/	6.14
	h	18.25	13.34	23.11	2.06	3.29	10.20	/	/	2.32
EA	ϕ s/%	59.90	66.52	/	12.22	20.55	12.09	84.47	75.51	8.46
	d	15.52	16.28	/	18.10	17.25	18.11	15.83	15.58	18.10
	p	8.80	15.76	/	1.85	2.56	15.49	4.87	4.61	5.67
	h	15.18	12.46	/	3.14	4.28	9.89	6.62	6.26	2.09

"/"Solvent phase separation

Table 2. The mathematical expression of ellipsoid

Vector c	Positive definite matrix		
$\delta_d=17.15$	0.2199	-0.0023	0.0004
$\delta_p=9.97$	-0.0023	0.0137	-0.0068
$\delta_H=11.32$	0.0004	-0.0068	0.0068

The closer the solvent is to the center of the sphere, the stronger the ability to dissolve the polymer. The calculation results of the distance from the solvent to the center of the sphere are arranged from small to large as follows:



Among all the good solvents, DMAc was found to be closest to the center of the sphere. In the dissolution experiment, the DMAc was also found to have the fastest dissolution rate and the largest amount of dissolved per unit volume. CB is the solvent most distant from the center of the ball. Dissolution experiments have also found that polymers of the same quality require more solvent to dissolve, slower dissolution rates and even require proper temperature rise. The above experimental phenomena further verify the reliability of ellipsoid fitting.

According to the above HSP value, the solubility parameter can be calculated as:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} = \sqrt{17.15^2 + 9.97^2 + 11.32^2} = 22.84$$

In this experiment, the above total solubility parameters were verified by the group contribution method.

$$\delta = \sum F / V_m = \frac{\rho \sum F}{M_0} \quad (1)$$

ρ --- represents the relative density of the polymer;

M_0 ---represents the relative molecular mass of the structural unit.

According to the query data, the molar gravity constant of group were as follows: $-\text{CH}_2-$ =272.0, p-phenylene=1350, $-\text{COO}-$ =634 $[(\text{J}/\text{cm}^3)^{1/2}/\text{mol}]$. The relative density of DM-700 was 1.33 g/cm^3 , the relative molecular mass of the structural unit is 192 g/mol , then the solubility parameter is calculate ed according to formula (1) is:

$$\delta = \frac{\rho \sum F}{M_0} = \frac{1.33 \times (634 \times 2 + 1350 + 272 \times 2)}{192} = 21.90 (\text{J} / \text{cm}^3)^{1/2}$$

Their calculation results are very close, which proves the accuracy of the experimental data.

4. Conclusion

The three-dimensional solubility parameter value of the sample polyester resin was determined to be $\delta_d=17.15(\text{MPa})^{1/2}$; $\delta_p=9.97(\text{MPa})^{1/2}$; $\delta_H=11.32(\text{MPa})^{1/2}$ by fitting 63 sets of data obtained from turbidity titration experiments into ellipsoids. HSP value was successfully verified by group contribution method, which further proved the reliability of the fitting results. This method can be considered as a general method for the estimation of various polymer solubility parameters.

Acknowledgments

This work was financially supported by National Natural Science Foundation (51873232) and Xuzhou University of Technology (XKY2018123).

References

- [1] Tracton A A. Coatings technology handbook[M]. CRC press, 2005.W. Strunk Jr., E.B. White, The Elements of Style, third ed., Macmillan, New York, 1979.
- [2] Li Xiaomiao, Liu Dazhuang, Dong Xueru. Forty years for Hansen three-dimensional solubility parameter[J]. Adhesion, 2007, 28(6): 33-35.
- [3] Liu Dazhuang, Liu Yan, Liu Likao, Hou Lili. Optimum Methods of Three Dimensional Solubility

- Parameters[J].Chemical Industry Times, 2010, 24(2): 8-10.
- [4] Sun Zhijuan, Zhang Xinya, Huang Hong, Chen Huanqin. Application and development of the solubility parameters[J]. China Rubber industry,2007(01):54-58.
- [5] Hildebrand J.H., Scott R.L. The Solubility of Nonelectrolytes(3rd ed)[M]. New York: Reinhold, 1950.
- [6] Bagley, E. B., T. P. Nelson, and J. M. Scigliano. Three-dimensional solubility parameters and their relationship to internal pressure measurements in polar and hydrogen bonding solvents[J]. Journal of paint technology, 1971,43(555): 35-42.
- [7] Small P A. Some factors affecting the solubility of polymers[J]. Journal of Chemical Technology and Biotechnology, 1953, 3(2): 71-80.
- [8] Hansen C.M. The three-dimensional solubility parameter-key to paint component affinities: solvents, plasticizers, polymers, and resins. II. Dyes, emulsifiers, mutual solubility and compatibility, and pigments. III. Independent calculation of the parameter components[J]. Journal of paint technology, 1967, 39(511): 505-510.
- [9] Hansen C.M. 50 Years with solubility parameters—past and future[J]. Progress in organic coatings, 2004, 51(1): 77-84.
- [10] Dong Liming, Wang Renli, Chen Hao. Estimation of Three-Dimensional Solubility Parameters of Poly(phthalaziny) Poly(aryl ether nitrile) by Turbidity Titration[J]. Guangzhou Chemical Industry,2014,42(18):99-102.
- [11] Suh K.W. Corbett J.M., Solubility parameters of polymers from turbidimetric titrations[J]. Journal of Applied Polymer Science, 1968, 12(10): 2359-2370.
- [12] Hansen C.M. Hansen solubility parameters: a user's handbook Second Edition[M]. CRC press, 2007.