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Solution Properties of Shellac, 4*

Solubility Parameter of Shellac

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SUMMARY:

The solubility parameter (δ) of shellac has been estimated from three dimensional approach and solubility map methods, and was found to be 11.3 $cal^{1/2}\ cm^{-3/2}$. The maximum ultimate strength σ_{max} of shellac has also been estimated.

ZUSAMMENFASSUNG:

Der Löslichkeitsparameter (δ) von Schellack wurde nach den Methoden der dreidimensionalen Näherung und in einem Löslichkeitsfeld bestimmt. Es ergab sich ein Wert von 11,3 $cal^{1/2}\ cm^{-3/2}$. Die Festigkeitsgrenze σ_{max} von Schellack wurde ebenfalls bestimmt.

Introduction

Solubility is the property which is easily accessible and depends on the structure of the polymer. In order to analyze it, the solubility parameter (δ) has proven to be a valuble concept in obtaining information on solubility behaviour of a polymer, specially in nonpolar solvents. Hildebrand and Scott[1] have proposed a solubility parameter concept. This theory related the energy of mixing to energy of vaporization of the polymer.

$$\delta = (\text{cohesive energy density})^{1/2} = (\Delta E_{vap}/V)^{1/2} \qquad (1)$$

where δ is the solubility parameter, ΔE_{vap} the energy of vaporization and V the molar volume.

Shellac is a natural resin of insect origin[2] and has extensive use in surface coatings. The determination of the solubility parameter of shellac is still a difficult and laborious undertaking. Khanna[3] has tentatively estimated solu-

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* Part 3, cf. lit.[11].

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bility parameter of shellac from anomalous solubility behaviour. In the present paper we have used the three dimensional solubility parameter approach as developed by Hansen[4] and solubility map method for estimation of solubility parameter of shellac. The present work is an extension of previous works on the solution properties of shellac[9-11]

Results and Discussion

With the purpose of analyzing the contribution of intermolecular forces to the solubility parameter of shellac, the three dimensional approach, as described by Hansen[4-6] has been used. If these interactions are due to dispersion (δ_d), dipole (δ_p), and hydrogen bonding (δ_h) forces, the original Hildebrand solubility parameter is related to these parameters by the following relationship

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

where $\delta_d = (E_d/V)^{1/2}$, $\delta_p = (E_p/V)^{1/2}$, and $\delta_h = (E_h/V)^{1/2}$, V being the molar volume and E the energy of vaporization.

All other terms have their usual meanings.

Solubility Parameter due to Dispersion Forces Contribution (δ_d)

The interaction energy manifested in this parameter is dependent on the polarizability (London dispersion forces). The polarizability can, on the other hand, be discussed by the Lorentz-Lorentz equation

$$\alpha = 3\,V\,(n_D^2 - 1)/(n_D^2 + 2)\,(4\pi N) \tag{3}$$

where the polarizability α is related to the index of refraction n_D and the molar volume V, N is the number of molecules per cm^3. It has been described by Koenhen and Smolders[7] that the dependence of δ_d on $V^{1/6}$, and so δ_d would be related to the ratio $n_D/V^{1/6}$. For shellac, we have found that the relation corresponds to

$$\delta_d = 11.41\, n_D\, V^{-1/6} \tag{4}$$

where $n_D = 1.5236$ and $V = 833\ cm^3$ for shellac[2]. From Eq. (4), the δ_d value was found to be 5.66 $cal^{1/2}\ cm^{-3/2}$.

Solubility Parameter due to Polar Contribution (δ_p)

The OH group, which is polar, is present in shellac. The polar contribution to the solubility parameter therefore must be taken into account for determination of δ of shellac. The contribution of permanent dipoles to cohesive energy density (CED) can be seen, at least qualitatively from the equations which relate the dipole moment to the polar component of the solubility parameter. Thus, Hansen[6] calculated this component from the following equation proposed by Böttcher[8]:

$$\delta_p^2 = \frac{12108}{V^2}\,\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\,(n_D^2 + 2)\,\mu^2 \tag{5}$$

where ε is the dielectric constant and μ the dipole moment. For shellac[2] $\varepsilon = 3.6$; $n_D = 1.5236$; $V = 833\ \mathrm{cm}^3$, and $\mu = 1.2024$ debye. The dipole moment of shellac cannot be determined directly because of well-known reasons[12]. Thus we have used the refractive index method (an indirect method)[13] to calculate the dipole moment using Eq. (6):

$$\frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{M}{p} = 1.05\,\frac{n_D^2 - 1}{n_D^2 + 2}\cdot\frac{M}{p} + \frac{4\pi N}{9\,kT}\cdot\mu^2 \tag{6}$$

Here all terms have their usual meanings. Thus, the calculated value of δ_p for shellac has been found to be 0.17 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$.

Solubility Parameter due to Hydrogen Bonding (δ_h)

Five-OH groups are present in shellac. δ_h can be estimated by using the following equation[7]:

$$\delta_h = \sqrt{E_h \cdot A/V} = \sqrt{5000\,A/V} \tag{7}$$

where A is the number of —OH groups in the molecule. The estimated value of δ_h for shellac has been found to be 5.47 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$.

Therefore, by equating the δ_d, δ_p, and δ_h, the δ of shellac has been found to be 11.3 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$.

Tab. 1 shows the observed solubility in 22 solvents listed in order of their solubility parameter. A detailed correlation for each solvent however is not to be expected since the range examined includes solvents having widely different polarity and hydrogen bonding character. Shellac is found to be

Tab. 1. Solubility of shellac; δ: solubility parameter, γ: hydrogen bonding index.

Solvent	$\frac{\delta^{a}}{(cal/cm^{3})^{1/2}}$	γ	Solubility[b]
n-Pentane	7.02	2.2	–
n-Hexane	7.27	2.2	–
Cyclohexane	8.19	2.2	–
Carbontetrachloride	8.55	2.2	–
Ethylacetate	8.91	5.2	–
Toluene	8.93	3.8	–
Chloroform	9.16	2.2	–
Benzene	9.16	2.2	–
Ethylmethyl ketone	9.45	5.0	–
Methyl acetate	9.46	5.2	–
Acetone	9.62	5.7	–
Chlorobenzene	9.67	2.7	–
Ethylene dichloride	9.86	2.7	–
Nitrobenzene	10.00	3.2	–
Acetic acid	10.1	—	+
Acetaldehyde	10.3	—	+
Cyclohexanone	10.42	6.4	±
Cyclopentanone	10.53	5.2	±
N-methyl-2-pyrrolidone	11.00	5.6	+
N,N′-Dimethyl formamide	11.79	6.4	+
Ethyl alcohol	12.7	—	+
Formyl morpholine	13.00	5.2	±

[a] In SI units: 1 $cal^{1/2} \cdot cm^{-3/2} = 2.045\ J^{1/2} \cdot cm^{-3/2}$.

[b] Solubility key: (–) insoluble; (±) partially soluble or swelling; (+) soluble.

soluble in highly polar solvents. This solubility may be explained by the effect[14–16] that the presence of large polar groups in a macromolecular chain increases the polymer solubilty.

A plot of δ against the hydrogen bonding index (γ) of the solvents used has been prepared. The δ value of shellac obtained from the midpoint of the solubility map (Fig. 1) has been found to be 11.3. This is in good agreement with the calculated value of i.e. 11.3 $cal^{1/2}\ cm^{-3/2}$ from three dimensional approach. The reported values[3,9] of δ of shellac are 12.2 $cal^{1/2}\ cm^{-3/2}$ (from anomalous solubility method[3]) and 10.01 $cal^{1/2}\ cm^{-3/2}$ (from van der Waals constant method[9]).

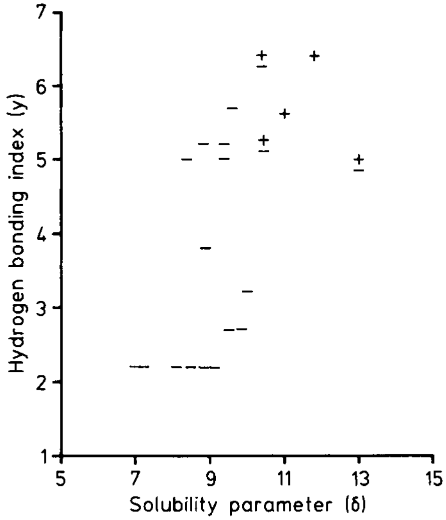

Fig. 1. Solubility map of shellac. For solubility key see Tab. 1.

However, the presented value of δ (11.3 $cal^{1/2}$ $cm^{-3/2}$) seems to be correct with respect to the solubility behaviour of shellac. It is concluded that the δ value so obtained, has to be the center of a solubility sphere which envelops the coordinates of the solvents in which shellac is soluble, and this excludes the coordinates of the nonsolvents. The δ value obtained for shellac satisfies this condition.

Further it is worth to mention that the solubility parameter is also related to the ultimate strength of a material[17]. Gorden[17] calculated σ_{max}, the maximum hypothetical uniaxial tensile strength a material can sustain in the absence of imperfections, shear stresses and viscous flow. We have used the Eq. (8)[17] for the estimation of σ_{max}:

$$\sigma_{max} = 1.025 \cdot 10^7 \cdot \delta^2 \tag{8}$$

The σ_{max} calculated from the above equation has been found to be $11.58 \cdot 10^7$ dyne · cm^{-2}, which is quite close to the experimental value[2] $12.94 \cdot 10^7$ dyne · cm^{-2}.

[1] J. H. Hildebrand, R. L. Scott, Theory of Non Electrolytes, 3rd ed., Dover, New York 1949

[2] P. K. Bose, Y. Sankaranarayan, S. C. Sengupta, Chemistry of Lac, Indian Lac Research Institute, Namkum, Ranchi, India 1963, p. 28, 30

[3] B. B. Khanna, Indian J. Technol. **87** (1970) 274

[4] C. M. Hansen, J. Paint Technol. **39** (1967) 104

[5] C. M. Hansen, K. Skaarup, J. Paint Technol. **39** (1967) 511

[6] C. M. Hansen, Ind. Eng. Chem., Prod. Res. Dev. **8** (1969) 2

[7] D. M. Koenhen, C. A. Smolders, J. Appl. Polym. Sci. **19** (1975) 1163

[8] C. F. Böttcher, The Theory of Electric Polarisation, Elsevier, Amsterdam 1952

[9] M. K. Mishra, J. Oil. Colour Chem. Assoc., in press

[10] M. K. Mishra, J. Oil. Colour Chem. Assoc., in press

[11] M. K. Mishra, J. Oil. Colour Chem. Assoc., in press

[12] G. N. Bhattacharya, Indian J. Phys. **14** (1940) 237

[13] P. C. Rakshit, Physical Chemistry, Science Book Agency, Calcutta, India 1970, p. 344

[14] S. V. Vinogradova, V. V. Korshak, Y. S. Vygodskii, Vysokomol. Soedin. **8** (1966) 809

[15] V. V. Korshak, S. V. Vinogradova, Y. S. Vygodskii, S. A. Pavlova, L. V. Bozhko, Izv. Akad. Nauk SSSR Ser. Khim. **50** (1967) 2267

[16] V. U. Korshak, S. V. Vinogradova, G. L. Slonimskii, S. N. Salazkin, A. A. Askadskii, Vysokomol. Soedin. **8** (1966) 548

[17] J. L. Gordon, in Encycl. Polym. Sci. Technol., H. F. Mark, N. G. Gaylord, N. M. Bikales (Eds.), Wiley-Interscience, New York 1968, Vol. 3, p. 843