Cohesive-energy density of shellac

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The solubility parameter ($\underline{\delta}$) of shellac has been ascertained by the methods of solubility, structural contributions and intrinsic viscosity $[\eta]$. From the solubility method, respective δ ranges for shellac have revealed that shellac is not soluble in poorly H-bonded solvents but dissolves in moderately and strongly H-bonded solvents. The δ value of shellac estimated by the structural contribution technique has been found to be slightly lower. The δ values of shellac computed from $[\eta]_{max}$ and related extrapolation are in close agreement with each other and with average value ascertained from the solubility spectra method. The molar volume of shellac from contribution technique has also been estimated. Shellac has been classified as a class III type of material for encapsulation having excessive polar groups.

Keywords Solubility; structure; density; cohesive-energy; shellac

INTRODUCTION

Cohesive-energy density is one of the fundamental properties of a polymeric material. It is numerically equal to the potential energy of one cc of material[1]. Knowledge of intermolecular forces in polymers is essential in interpreting their solution properties on a molecular basis. Cohesive-energy density is a very convenient measure or the intensity of intermolecular interactions in a pure solid or liquid; the strength of solvent–solvent molecule bonds of polymer–polymer segment bonds can be related to it.

The cohesive-energy density concept has been used mainly in the context of solubility properties and solution theory. Knowledge of this property is useful in assessing the compatability characteristics, either in solution or during evaporation of solvents in the course of drying of a polymeric coating[1–4]. It also helps in encapsulation in the choosing a solvent/core/polymer wall capsular combination[5].

The solubility parameter (δ) is defined as the square root of the cohesive-energy density[1,35]. Theoretical determination of solubility parameters of polymeric materials by the use of fundamental equations has not been possible because the data on various physical constants of polymers such as boiling point, heat of vaporization, Van der Wall's constant, compressibility factor, surface tension, etc. are not available[6–9].

However, Burrell[3] developed a method of ascertaining the solubility parameter of a polymer by solution in a series of solvents and then equating its solubility parameter to that of the solvent in which the polymer is soluble in all proportions. Gee[9] also made efforts to determine this parameter by measuring the degree of swelling of 'cross-linked' polymers in various solvents, but difficulties have been experienced in measuring the relative swelling accurately because of the poor sensitivity of the measuring device. The phenomenon of equilibrium swelling has been used by the Mangaraj[11] to estimate the cohesive-energy density of crosslinked polymers. However, it has been observed[36] that polymers, whose glass transition (T_g) are above the experimental temperatures, often shatter. Mangaraj *et al.*[36,37] estimated the cohesive-energy density of a series of polyacrylates and polymethacrylates from swelling measurements to study the effect of alcoholic chain length on intermolecular forces. Since a number of these polymers have glass transition temperature above the room temperature, the crosslinked samples used, often shatter during the process of swelling and hence accurate estimation of the equilibrium swelling coefficient were difficult. This, combined with the difficulty of achieving suitable crosslinking presents a serious handicap against wide application of the above method. Mangaraj *et al.*[12] brought forward a further method of estimation of cohesive-energy density by viscosity measurements. Wolf[13] also suggested an extrapolation method for the determination of δ of polymers and demonstrated it for polyethylene.

Small[14] gave a method of estimating the cohesive-energy density of polymers by group contribution technique based on Scatchard's[15] findings. Theoretical methods based on the principles of additivity of contributions due to the groups present in the polymer molecules have also been suggested[3,8,16–24]. Ahmad and Yaseen[25] have estimated the solubility parameter of low molecular weight compounds and a series of polymers by the contribution technique based on the summation of contributions due to groups, individual atoms and bonds.

Shellac is a natural resin of animal origin[26], and has an average molecular weight of about 1000. It consists of one free carboxyl, one aldehyde, three ester and five hydroxyl groups and one unsaturated linkage[27]. It is apparently a mixture of polyesters made up of various hydroxy aliphatics and sesquiterpenic acid[26]. This resin is of industrial importance and has extensive use in surface coatings.

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Table 1 Solubility data of shellac for moderately hydrogen bonded solvents

Sl. No.	Moderately H-bonded solvents	Solubility parameter δ (Cal/cc)$^{1/2}$	δ_s range (Cal/cc)$^{1/2}$	Mid-point of δ range (Cal/cc)$^{1/2}$	Half breadth of solubility parameter Δ_{max} (Cal/cc)$^{1/2}$
1	Acetaldehyde	10.3			
2	Diacetone alcohol	9.2			
3	1,4-Dioxan	9.9			
4	Diethylene glycol ethyl ether	10.2			
5	Ethyl lactate	10.0			
6	Ethyl glycol butyl ether	9.5	9.0–11.4	10.2	1.2
7	Ethylene glycol ethyl ether	10.5			
8	Ethylene glycol methyl ether	11.4			
9	Mesityl oxide	9.0			
10	Propylene glycol methyl ether	10.1			

Table 2 Solubility data of shellac for strongly hydrogen bonded solvents

Sl. No.	Strongly H-bonded solvents	Solubility parameter δ (Cal/cc)$^{1/2}$	δ_s range (Cal/cc)$^{1/2}$	Mid point of δ range (Cal/cc)$^{1/2}$	Half breadth of solubility parameter Δ_{max} (Cal/cc)$^{1/2}$
1	Acetic acid	10.1			
2	Amyl alcohol	10.9			
3	Aniline	10.3			
4	Butyric acid	10.5			
5	iso-Butyl alcohol	10.5			
6	n-Butyl alcohol	11.4			
7	s-Butyl alcohol	10.8			
8	ter-Butyl alcohol	10.6			
9	Diethylene glycol	12.1	9.9–14.5	12.2	2.3
10	*N-N*—Dimethyl formamide	12.1			
11	Ethyl alcohol	12.7			
12	Formic acid	12.1			
13	Methyl alcohol	14.5			
14	iso-Propyl alcohol	11.5			
15	Propionic acid	9.9			
16	Pyridine	10.7			
17	Propylene glycol	12.6			

Burrell and Immergut[35] have described the solubility spectrum of the shellac in the moderately and strongly hydrogen bonded groups of solvents. Khanna[28] has mentioned a tentative and approximate value of solubility parameter of shellac which is based on the observation on anomolous solubility of shellac in organic solvents. Therefore, this study has been taken up to get a clearer understanding regarding cohesive-energy density of shellac.

EXPERIMENTAL

Solubility method

The literature reveals that the solubility method of Burrell[3] is very suited for ascertaining the solubility parameter of a polymer. Therefore, this has been followed also for shellac. Data of solubility as ascertained earlier[27,29] have been utilised in establishing the solubility parameter of shellac.

Structural contribution technique

This is a theoretical estimation method[25] based on the values of individual structural contributions. The molecular formula $C_{16}H_{90}O_{15}$ has been used for the shellac. Krevelen values of F_i of atoms etc. have been taken from the literature[24] for the calculation of the solubility parameter. The molar volume of shellac has been found from its molecular formula[34] and also from molecular weight and density values[27].

Intrinsic viscosity method

Since the glass transition temperature (T_g) of shellac[32] is above the experimental temperature and viscosity of shellac in solvents can be easily determined, the method of Mangaraj *et al.*[12] for the determination of cohesive-energy density of shellac by estimating the intrinsic viscosity has been followed. Values of intrinsic viscosity $[\eta]$ of shellac in n-butyl alcohol, n-butyric acid, 1-4 dioxane, ethyl alcohol and iso-propyl alcohol estimated by the usual extrapolation method[33] have been used for the computation study.

RESULTS AND DISCUSSIONS

Results of solubility parameter determined and ascertained by the different methods are as below:

Solubility method

Solvents for shellac[27,29] have been alphabetically arranged in groups according to their hydrogen bonding values and their solubility parameter have been found from the literature[1,35]. The solubility parameter of shellac has been equated to that of poorly, moderately and strongly hydrogen bonded solvents and solubility parameter range (δ range), mid-point of δ range and breadth of δ, i.e. Δ_{max} for shellac for each group of solvents have been ascertained and are presented in *Tables 1* and *2*.

Table 3 Computation of $[\eta]_{max}$ from intrinsic viscosity $[\eta]$ and solubility parameter (δ)

Sl. No.	Solvent	Molar volume V (cc)	Solubility parameter δ (Cal/cc)$^{1/2}$	Intrinsic viscosity $[\eta]$	$[\eta]_{max}$ From *Figure 1*
1	n-Butyl alcohol	91	11.4	0.071	
2	n-Butyric acid	92	10.5	0.067	
3	1,4-Dioxan	86	9.9	0.055	0.073
4	Ethyl alcohol	57.5	12.7	0.066	
5	n-Propyl alcohol	76	11.9	0.070	

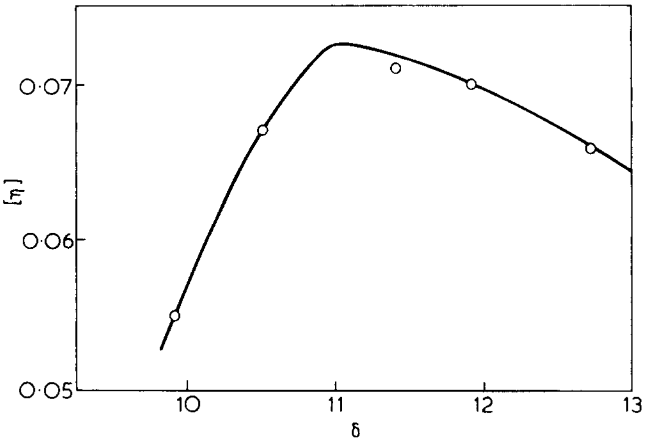

Figure 1 Computation of δ_p from $[\eta]_{max}$

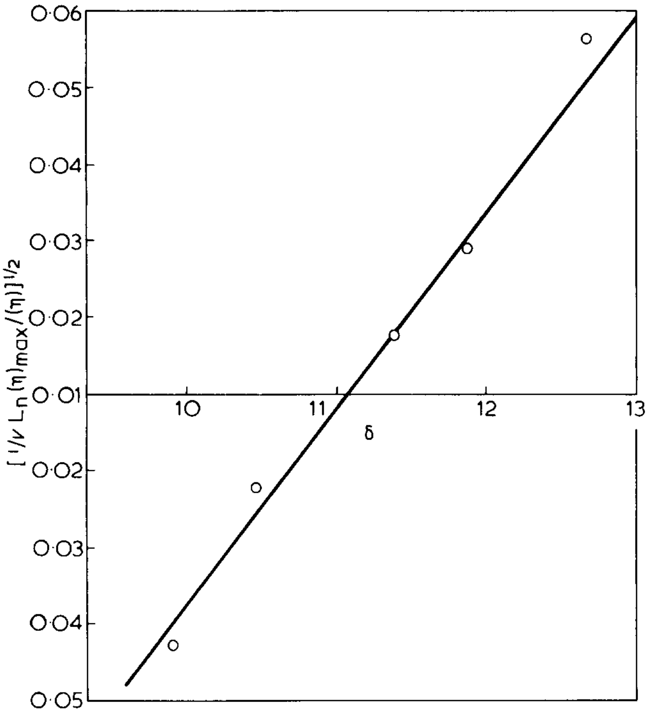

Figure 2 Computation of δ_p from intercept on axis

Contribution technique

The reported value of F_i due to atoms etc. have been used for the calculation of molar attraction constant (F) and solubility parameter (δ) by the following relationship[25]:

$$\delta=\frac{F}{V}=\frac{(EV)^{1/2}}{V}=\left(\frac{E}{V}\right)^{1/2} \qquad (1)$$

where δ is the solubility parameter (cal/cc)$^{1/2}$, E is the molar internal energy (cal mol^{-1}), V is the molar volume (cc) and F is the attraction constant.

Values of F for shellac are found from the sum of individual contributions (F_i) of chemical atoms etc. present in the molecule, i.e.

$$F=\sum F_i \qquad (2)$$

The molar volume of shellac has been calculated by adding the contributions due to atoms etc. to the molar volume[25] and further confirmed from the values of M wt. and density[27].

Molar volume of shellac

(a) *From molecular formula.* Proposed molecular formula of shellac: $C_{16}H_{90}O_{15}$. Atoms and bonds contributions to molar volume: 60(C) = 60 × 1.85 = 111.0; 90(H) = 90 × 6.59 = 593.1; 15(O) = 15 × 7.70 = 115.0; 1(=) = 1 × 8.94 = 8.94; total = 828.04. Molar volume of shellac = 828.04.

(b) *From molecular weight and density.* M wt. of shellac = 1 000; density of shellac = 1.2; molar volume of shellac = 1 000/1.2 = 833.3.

Solubility parameter of shellac

Molecular formula of shellac: $C_{16}H_{90}O_{15}$. Contributions due to atoms: 60 (C), Krevelen value[24] (F_i) 60 × 0.0 = 0.0; 90 (H), Krevelen value[24] (F_i) 90 × 68.5 = 6165; 15 (O), Krevelen value[24] (F_i) 15 × 125.0 = 1875; $F=\sum F_i=8040$; $\delta=\frac{F}{V}=8040/833=3.65$ (cal/cc)$^{1/2}$.

Intrinsic viscosity method

The intrinsic viscosity $[\eta]$ of shellac in solvents (*Table 3*) have been plotted against solubility parameter (δ) (*Figure 1*). The $[\eta]_{max}$ has been estimated from the curve and equated as δ_p, i.e. solubility parameter of shellac. These values have been used to calculate

$$\left[1/V\frac{L_n[\eta]_{max}}{[\eta]}\right]^{1/2}$$

values[12] and the latter have been plotted against δ (*Figure 2*). The value of δ_p for shellac has been obtained by the intercept on the axis.

The solubility spectra of shellac reveals that it is soluble only in moderately and strongly H-bonded solvents and not in poorly H-bonded solvents (*Tables 1* and *2*). The solubility parameter range (δ range) for shellac for moderately H-bonded is 9.0–11.4 (cal/cc)$^{1/2}$. The half breadth of solubility parameter ($2\Delta_{max}$) for these solvents is 1.2 (cal/cc)$^{1/2}$ [$\Delta_{max}=|\delta_p-\delta|_{max}$] and the mid-point of

Table 4 Solubility parameter (δ) of shellac

Material	Solubility spectra method				Intrinsic viscosity [η] measurement method			Structural contribution technique δ (from Krevelen Constants) (Cal/cc)1/2	Earlier reported values	
	Mid-point of δ range (Weakly H-bonded) (Cal/cc)1/2	Mid-point of δ range (Moderately H-bonded) (Cal/cc)1/2	Mid-point of δ range (Strongly H-bonded) (Cal/cc)1/2	Mid-point of δ range (from all solvents ranges) (Cal/cc)1/2	δ From $[\eta]_{max}$ (Cal/cc)1/2	δ From intercept (Cal/cc)1/2	Mean δ (Cal/cc)1/2		Solubility spectra method (Burrel and Immergut) Mid-point of δ range (From all solvent ranges) (Cal/cc)1/2	Solubility behaviour (Khanna) δ (Cal/cc)1/2
Shellac	0	10.2	12.2	11.2	11.0	11.1	11.05	9.66	12.2	12.5

solubility parameter of shellac for this range comes to 10.2 $(cal/cc)^{1/2}$. The solubility parameter range for shellac for strongly H-bonded solvents is 9.9–14.5 $(cal/cc)^{1/2}$. For this range Δ_{max} is 2.3 $(cal/cc)^{1/2}$ and the mid-point of the solubility parameter range for shellac is 12.2 $(cal/cc)^{1/2}$. Thus the mean of the mid-point of solubility parameter range for shellac for both the moderately and strongly H-bonded solvents is 11.2 $(cal/cc)^{1/2}$. Burrell and Immergut[35] reported that δ range for shellac for moderately and strongly H-bonded solvents is 9.9–10.8 $(cal/cc)^{1/2}$ and 9.5–14.5 $(cal/cc)^{1/2}$ respectively. Khanna[28] reported that the solubility parameter for shellac is 12.5 ±2 $(cal/cc)^{1/2}$ (*Table 4*).

The solubility parameter range of shellac (*Table 4*) ascertained here is based on exhaustive findings on the solubility of shellac in a wider range of solvents. Therefore here, the solubility parameter is more correct than the values reported earlier[28] and the compiled ranges[35].

The δ value for shellac by the contribution technique based on its molecular formula has been worked out to be 9.65 $(cal/cc)^{1/2}$. The molar volume of shellac calculated by the method of Sewel[34] is 328.04 cc, which is in good agreement with the calculated molar volume (833.3 cc). Therefore, the proposed molecular formulae has been logically used for the calculation of δ for shellac by using Krevelen constants[24]. The δ value 9.65 $(cal/cc)^{1/2}$ for shellac obtained by structural contribution is 'a little lower' than the δ value for shellac ascertained by the solubility spectra method. This may be due to the fact that the structure of the shellac molecule is not fully known[26] and, therefore, contributions due to other factors could not be included in the sum of contributions, which may further raise the δ value of shellac.

The method of Mangaraj *et al.*[12] for the estimation of cohesive-energy density by viscosity measurements has revealed that the δ value of shellac is 11.0 $(cal/cc)^{1/2}$ by the computation of $[\eta]_{max}$ obtained by drawing a δ plot of δ vs. $[\eta]$ (*Table 3*) and drawing a curve through most of the points. The nature of the curve thus obtained (*Figure 1*) for shellac is almost the same as obtained by Mangaraj *et al.*[12] for the estimation of δ_p for other polymers.

The value of $[\eta]_{max}$ estimated by the above computation is presented in *Table 3* and has been used for the calculation of $\left[1/V\,\frac{L_n[\eta]_{max}}{[\eta]}\right]^{1/2}$ values[12] which have been plotted against δ. As expected an almost straight line has been obtained (*Figure 2*) covering all the points. Mangaraj *et al.*[12] have made similar observations. The value of δ for shellac obtained by the intercept on the axis comes to be 11.1 $(cal/cc)^{1/2}$ and is presented in *Table 4* along with the corresponding δ value computed from the $[\eta]$ against δ curve (*Figure 1*). In view of the approximate nature of the straight line the δ values reported here are likely to have an error of ±0.1 which is in close agreement with the observations made by Mangaraj *et al.*[12]. Thus the mean value of δ for shellac by viscosity measurement comes to be 11.05 $(cal/cc)^{1/2}$, which is very close to the mean value 11.2 $(cal/cc)^{1/2}$ of δ for shellac by solubility measurements (*Table 4*).

Thus it may be seen (*Table 4*) that the δ value for shellac observed by viscosity measurements by computation through $[\eta]_{max}$ and the intercept are in good agreement with the δ value for shellac ascertained from the solubility spectra, whereas the δ value for shellac calculated by Krevelen constants, i.e. the structural contributions technique is somewhat lower. In encapsulation, generally a polymeric material at the opposite end of the solubility parameter scale from the core material offers the most efficient containment. These studies thus indicate that shellac, which possesses a high level of polar groups can be catagorised as the class III type of cell wall material for the purpose of encapsulation.

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