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Solubility parameter of chitin and chitosan[1]

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Abstract

The solubility parameter of chitin and chitosan was determined by group contribution methods (GCM) and the values were compared with the values determined from maximum intrinsic viscosity, surface tension, the Flory–Huggins interaction parameter and dielectric constant values. The values, thus, obtained were confirmed by values obtained from GCM. The solubility parameters of chitosan determined by these methods are more or less equal and the average is approximately 41 $J^{1/2}/cm^{3/2}$. A method for estimating the overall solubility parameter of chitosan having any degree of deacetylation is proposed. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Chitosan; Solubility parameter; Chitin

1. Introduction

The solubility parameter (δ) is an important property of polymers which is defined as the square root of cohesive energy density. In low molecular weight compounds it is an indication of the heats of vaporization. There are several methods to estimate δ by group contribution methods, proposed by various investigators (Hoftyzer and Van Krevelen, 1976; Van Krevelen, 1965; Hoy, 1970; Small, 1953; Hansen, 1967; Hildebrande, 1916). Owing to some specific properties, deviations were found in δ values determined by group contribution method when compared with experimental or physical methods. The main advantage of group contribution methods is that it is easy to estimate individual contributions such as dispersive (δ_d), polar (δ_p),and hydrogen bonding (δ_h) of polymers/low molecular weight compounds, through which the overall solubility parameter (δ_t) can be estimated by using Eq. (1)

$$\delta_t = \sqrt{(\delta_d^2 + \delta_p^2 + \delta_h^2)} \quad (1)$$

In many instances, the physical properties of polymers are found to correlate strongly with interconnections between the atoms of a molecule. The values of heats of vaporization, molar refraction, molar volume, refractive index, boiling point, specific gravity and viscoelasticity are mainly governed by the molecular topology of that particular compound (Rouvray and Pandey, 1986; Bonchev, 1983; Kier and Hall, 1976). Hence, an attempt was made to determine the δ_t of polymer δ_{pt} by the maximum intrinsic viscosity number (MIV) (Garden, 1965), surface tension measurement (Thomos, 1975), refractive index (Mandel et al., 1982), dielectric constant (Darbye et al., 1967), and Flory–Huggins interaction parameter (Shultz and Glory, 1955).

Chitosan, a transformed oligosaccharide, is obtained by deacetylation of chitin, the latter being a bio-polymer obtained from crab and shrimp shells. Chitin is a pure polymerized form of *N*-acetyl glucosamine, as shown by the structure in Fig. 1. It has drawn more attention than other bio-polymers because of its ability to form specific complexes with number of ions or dyes as well as specific complexes with organic molecules (Muzzarelli, 1973a Muzzarelli, 1973b; Roberts, 1992). A fraction of the repeating units in the chitosan backbone contains -NH_2 pendant groups while the rest contains acetamide group (-NHCO-) in its place. The degree of deacetylation can be controlled by time, temperature and concentration of alkaline treatment of chitin (Struszczyk, 1987). Chitin and chitosan are practically insoluble in many of the organic or inorganic compounds, but soluble in salt organic mixtures of LiCl-*N*,*N*-DMAc (Striegel and Timpa, 1995), and dilute acids (water–acid mixtures). It is worth mentioning that no information is available in literature regarding δ_t of chitosan. Hence, the objective of this study is to determine δ_t of chitosan by using well known and simple physical methods. Thus, the values of surface tension, and dielectric constant, of the polymer were determined by instrumental as well as

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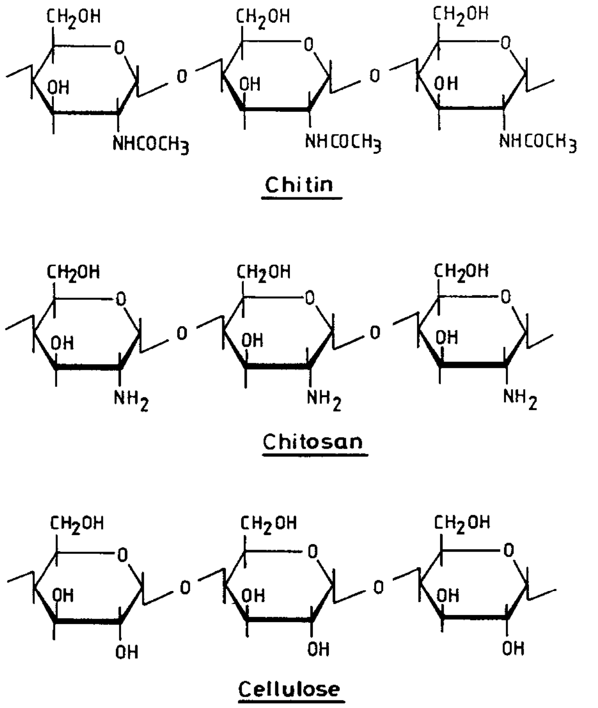

Fig. 1. Chemical structures of polysaccharides.

group contribution methods. Since it is also well known that no pure solvent can dissolve chitin or chitosan, polymer solutions were prepared by using mixtures of solvents. In the present context, 'solvent' refers to the solvent mixture of hydrochloric acid (HCl) and water, with varying compositions, and the value of δ_{pt} is expressed in $J^{1/2}/cm^{3/2}$.

2. Experimental

2.1. Materials

Chitosan was purchased locally in India. It's viscosity average molecular weight M_v (Lee, 1974), was found to be $\approx 500\,000$ and the degree of deacetylation determined as 64% by the IR method (Sannon et al., 1978). Acetic acid was purchased from Merck (India) limited. Double distilled water was used throughout the experimental work.

2.2. Purification of polymer

Chitosan was purified by dissolving in 2% aqueous acetic acid solution and precipitating in 10 wt% NaOH solution. The precipitate was first washed with distilled water to neutrality and then rinsed with acetone. It was then vacuum dried at 70°C for about 8 h. Its degree of deacetylation, determined by IR method (Sannon et al., 1978), was found to be 64%.

2.3. Membrane preparation

A known amount of purified chitosan was dissolved in 100 ml of 2 wt% aqueous acetic acid solution by continuous stirring to get a clear homogeneous polymer solution. The solution was cast on a clean glass plate to a desired thickness and the solvent was allowed to evaporate initially at room temperature and then the residual solvent was removed by vacuum drying. The membrane was peeled off from the glass plate and vacuum dried at ambient temperature.

2.4. Methods of estimation of δ by group contribution

Extensive work has been published on δ since Small (1953) put forward his now famous method based on the contributions owing to individual groups, atoms and bonds constituting the molecules. Similar methodologies were advanced by other researchers. Among those, of special significance are Van Krevelen (1965), Hoftyzer and Van Krevelen (1976), and Hoy (1970). Another method of estimation of δ is by the cohesive energy densities of groups. However, this method is not so suitable for strong hydrogen bonding materials as in the present case and, hence, it is not discussed here. All the above stated methods are applicable to both low and high molecular weight compounds, but some corrections need to be applied.

Table 1
Values of molar volumes (at room temperature, in cm^3/mol) proposed by Fedors

Group	V_i		V_t	
	Chitin	Chitosan	Chitin	Chitosan
-O-	3.8	3.8	7.6	7.6
-OH (primary)	10	10	10	10
-OH[a]	13	13	13	13
$-CH_2$	16.1	16.1	16.1	16.1
-CH	− 1	− 5	− 1	− 5
$-NH_2$	—	19.2	—	19.2
-NHCO	9.5	—	9.5	—
$-CH_3$	33.5	—	33.5	—
Ring structure	16.0	16.0	16.0	16.0

[a]Secondary or adjacent carbon atom.
ΣV_f for pure chitin = 100.7.
ΣV_t for pure chitosan = 76.9.

Table 2
Values of molar attraction constant of various groups proposed by Van Krevelen and Hoy

Group	Van Krevelen				Hoy			
	F_i		F_t		F_i		F_t	
-O-	256	256	512	512	235.5	235.5	470.6	470.6
-OH	754	754	1508	1508	462.0	462.0	924.0	924.0
$-CH_2$	280	280	280	280	269.0	269.0	269.0	269.0
-CH	140	140	700	700	176	176	880	880
$-CH_3$	420	—	420	—	303.4	—	303.4	—
-CONH	1228	—	1228	—	906.4	—	906.4	—
$-NH_2$	—	683	—	683	—	595	—	595

2.5. The molar volumes of chitin and chitosan

Molar volume (V) is the product of specific volume (ν) and molecular weight (M) of the repeating unit as given below.

$$V = (M)(\nu) = \frac{M}{\rho} \tag{2}$$

where ρ is the density.

Molar volume is the basic value needed for estimating the δ values of chitin and chitosan by applying various methods. V value contributions of specific groups in their molecular structures are given by Fedors (1974). Based on the structures of chitin and completely deacetylated chitosan, one can estimate the V value again by Fedor's group contribution method. Chitin consists of -CH, -OH, $-CH_2$, -NHCO-, $-CH_3$, whereas chitosan in completely deacetylated state (CDA) contains only -NH, and no -NHCO- groups. These are schematically shown in Fig. 1. The estimated values are compared with published values of cellulose and ethyl cellulose which are similar in structure. Table 1 gives V values of various groups of chitin/chitosan proposed by Fedors. Total V value, i.e. V_t, of chitin and chitosan was estimated to be 100.7 and 76.9 in cm^3/mol.

2.6. Estimation of δ from molar attraction constants: Hoy and Van Krevelen's method

The contribution values to the molar attraction constant (F), or individual (F_i) and total (F_t) for groups contained in chitin and chitosan are presented from the values published by Hoy and Van Krevelen in Table 2. The total molar attraction constant (ΣF_t) of a group in a molecules is obtained from

$$F_t = (\sum F_i)(N_i) \tag{3}$$

where N_i is the number of groups i present in the molecule. F_t for pure chitin is found to be 4648 by Van Krevelen's and 3753.4 by Hoy's contribution methods. Similarly, the values for pure chitosan are obtained as 3683 using Van Krevelen and 3138.6 by Hoy values. The solubility parameter is defined by

$$\delta_t = \frac{F_t}{V} \tag{4}$$

and from Table 1, δ_{pt} of CDA chitosan equals to 47.89 by Van Krevelen's method and it is 40.814 by Hoy's method. Similarly, δ_{pt} for pure chitin is 46.157 by Van Krevelens method and is 36.57 by Hoy's method.

The methods of Hoy and Van Krevelen can give only the overall solubility parameter value. To determine the individual δ_p, δ_d and δ_h values, the methods of Hoftyzer and Van Krevelen (1970), and Hoy's system (Hoy, 1985) are particularly useful. The dispersion component of the molar attraction constant (F_{pi}) and contribution of the hydrogen bonding forces to the cohesive energy (E_{hi}) and E_{ht} (total) for the groups from the Hoftyzer–Van Krevelen method are given in Table 3. The calculated values of δ_p, δ_d, and δ_h along with the δ_t are given in Table 4 and compared with

Table 3
Values of F_d, F_p (in $J^{1/2}/cm^{3/2}$/mol) and E_{hi} (in J/mol) proposed by Hoftyzer–Van Krevelen

Group	F_{di}		F_{dt}		F_{pi}		F_{pt}		E_{hi}		E_{ht}	
	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan
-O	100	100	200	200	400	400	800	800	3000	3000	6000	6000
-OH	210	210	420	420	500	500	1000	1000	20 000	20 000	40 000	40 000
$-CH_2$	270	270	270	270	0	0	0	0	0	0	0	0
-CH	80	80	400	400	0	0	0	0	0	0	0	0
$-NH_2$	—	280	—	280	—	310	—	310	—	8400	—	8400
-NH	160	—	160	—	210	—	210	—	3100	—	3100	—
-C = O	290	—	290	—	770	—	770	—	2000	—	2000	—
CH_3	420	—	420	—	0	—	0	—	0	—	0	—
Ring structure	190	190	190	190	0	—	0	—	0	—	0	—

Table 4
Values δ_d, δ_p, and δ_h ($J^{1/2}/cm^{3/2}$) obtained from Hoftyzer–Van Krevelen method and Hoy's system

Polymer	δ_d		δ		δ	
	Hoftyzer–Van Krevelen method	Hoy's system	Hoftyzer–Van Krevelen method	Hoy's system	Hoftyzer–Van Krevelen method	Hoy's system
Chitin	23.887	23.323	17.985	23.28	22.257	26.49
Chitosan	22.807	29.22	17.134	26.492	26.597	24.156

the values obtained by the Hoy's system. These are estimated according to the following equations

$$\delta_d = \frac{\sum Fd_i}{V} \tag{5}$$

$$\delta_p = \frac{\sqrt{(\sum F_{pi})^2)}}{V} \text{ and} \tag{6}$$

$$\delta_h = \sqrt{\frac{\sum F_{hi}}{V}} \tag{7}$$

δ_t is given by Eq. (1).

2.7. Estimation of δ from molar attraction constants by Hoy's system

As mentioned above, this is an alternative method to determine individual values of δ_d, δ_p and δ_h which is somewhat different from that of Hoftyzer–Van Krevelen. Table 5 lists constants for three additive molar functions: molar attraction constant (F_t), polar components (P_p) and Cyderson correction ($\Delta_t^{(p)}$) for polymer. These values are to be used in auxiliary equations and the expression for δ_t. The values of various groups are given in Table 5. The molecular aggregation number for the polymer is given by

$$\alpha^{(p)} = \frac{777\sum \Delta_t^{(p)}}{V} \tag{8}$$

where 777 is a constant and V is molar volume. Substituting the values from Table 5 we obtain $\alpha^{(p)}$ as 2.188 and 2.1335 for chitosan and chitin, respectively.

The number of repeating units per effective chain segment of the polymer is given by

$$n = \frac{0.5}{\Delta_T^{(p)}} \tag{9}$$

and is obtained as 2.3095 and 1.808 for chitosan and chitin, respectively. The contributions of δ_d, δ_p and δ_h are obtained from

$$\delta_t = \frac{F_t + \left(\frac{B}{n}\right)}{V} \tag{10}$$

$$\delta_p = \delta_t\left[\left(\frac{1}{\alpha^{(p)}}\right)\left(\frac{F_p}{F_t + \frac{B}{n}}\right)\right]^{\frac{1}{2}} \tag{11}$$

$$\delta_h = \delta_t\left(\frac{\alpha^{(p)} - 1}{\alpha^{(p)}}\right)^{\frac{1}{2}} \tag{12}$$

$$\delta_d = (\delta_t^2 + \delta_p^2 + \delta_h^2)^{\frac{1}{2}} \tag{13}$$

Based on the above average δ_{pt} values of pure chitin and chitosan, one can estimate the overall solubility of chitosan having any other degree of deacetylation. For example, the δ_{pt} of chitosan having $X\%$ of degree of acetylation can be

Table 5
Values of F_t^a, F_p^a and $\Delta_T^{(p)}$ proposed by Hoy's system

Group	F_{ti}		F_{tt}		F_{pi}		F_{pt}		$\Delta_t^{(p)}$		Δ_t corrected for both	$\Delta_t^{(p)}$	
	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan	Chitin	Chitosan		Chitin	Chitosan
-O-	235	235	470	470	216	216	432	432	0.018	0.018	(x)2/3	0.024	0.024
-OH (primary)	675	675	675	675	675	675	675	675	0.049	0.049	—	0.049	0.049
-OH (secondary)	591	591	591	591	591	591	591	591	0.049	0.049	—	0.049	0.049
$-CH_3$	269	269	269	269	0	0	0	0	0.020	0.020	—	0.020	0.020
-CH	176	176	880	880	0	0	0	0	0.013	0.013	(x)2/3	0.043	0.043
-CONH	1131	—	1131	—	895	—	895	—	0.073	—	—	0.073	—
$-CH_3$	303.5	—	303.5	—	0	—	0	—	0.022		—	0.022	—
$-NH_2$	—	464	—	464	—	464	—	464	—	0.035	—	—	0.035
Ring structure	− 48	− 48	− 48	− 48	61	61	61	61	− 0.0035	− 0.0035		− 0.0035	− 0.0035

For bi, tri, and tetra valent group in saturated ring the $\Delta_t^{(p)}$ values should be multiplied (×) by a value 2/3.
[a]The values are given in $(J/cm^3)^{1/2}/mol$.

Table 6
Overall solubility parameter (δ_t) obtained by various methods in $J^{1/2}/cm^{3/2}$

Polymer	Hoy	Van Krevelen	Hoftyzer–Van Krevelen	Hoy's system	Average δ_t
Chitin	37.27	46.16	37.28	43.9	41.15
Chitosan	40.81	47.89	39.05	44.49	43.06

obtained as

$$= [\delta_t \text{ of } 100\% \text{ chitosan}\left(\frac{X}{100}\right)] + [\delta_t \text{ of chitin } 1-\left(\frac{X}{100}\right)] \text{ (for chitosan)} \quad (14)$$

The ratio (X/100) represents the molar consent of 100% chitosan present as a fraction in the chitosan of interest. Likewise, (1 − X/100) represents the fraction of chitin units present in the molecule.

It appears from Table 6 that Hoy's and Hoftyzer–Van Krevelen methods give similar δ_t values in this particular case, whereas the values by Van Krevelen method and Hoy's system are closer. These predictions will be compared with the experimentally obtained values for further evaluation of the various group contribution methods.

2.8. Maximum intrinsic viscosity value (MIV)

Generally, polymers dissolve in various solvents and their δ_t value can be estimated by knowing the maximum swelling index value. Compatibility of any polymer with the solvent(s) is estimated by its intrinsic viscosity $[\eta]$ value which is equal to

$$[\eta]_{c\to 0} = \lim_{c\to 0}(\eta_{sp/c}) = \lim\eta_{inh} \quad (15)$$

where $\eta_{sp/c}$ is specific viscosity at concentration 'c' and η_{inh} is inherent viscosity. In either case, the value is obtained as the zero concentration intercept of the extrapolated curve of $\eta_{sp/c}$ or η_{inh} versus concentration. Viscosity is determined by using Ubbelohde viscometer. The estimation of MIV is complicated in the case of chitosan, since the polymer does not dissolve in any pure solvent, but dissolves in mixture of solvents like aqueous acid solutions at room temperatures or solvent and salt mixtures like DMAc-LiCl at higher temperatures. In the former case, the solubility parameter of the mixture or solvents can be determined by using the formula

$$\delta_{sol} = \nu_1\delta_1 + \nu_2\delta_2 \quad (16)$$

where ν and δ are volume fraction and solubility parameters of component 1 (water) and 2 (HCl) in the mixture of solvents. In the present study, the concentration of HCl in water–HCl solution is varied from 2–50 vol%.

2.9. Surface tension measurements

The surface tension (γ) is a manifestation of intermolecular forces. It is related to other properties derived from intermolecular forces, such as internal pressure, compressibility and cohesion energy density. γ is an important tool for measuring the interaction capacity of the solvent(s) with the polymer. This value is minimum when the polymer and solvent are highly compatible. Known concentrations of polymer solutions were prepared by dissolving in different water–HCl solvent solutions, whose δ_{sol} can be calculated from Eq. (16). γ values of the resulting polymer solutions were determined by using torsion balance (White Elec. Inst. Co.). Experiments were repeated three times for each polymer solution, and the average value was taken into consideration.

2.10. Calculation of surface tension from an additive function, the parachor

The molar parachor is a useful means of estimating surface tensions. It is expressed as

$$\sum P_S = \gamma^{1/4} V \quad (17)$$

where P_S is the parachor value which was introduced by Sudgen (1924), who gave a list of atomic constants from which the values of atoms that constitute chitin/chitosan is shown in Table 7, and V is the molar volume which is equal to 100.7 for chitin and 76.9 for chitosan. After calculating the γ of the polymer, its solubility parameter could be calculated by using Eq. (18)

$$\delta = \gamma^{3/4} \quad (18)$$

2.11. Correlation between dielectric constant and δ

Darbye et al. (1967) suggested a correlation between δ

Table 7
Prachor surface tension values proposed by Sugden

Group	CH_2	C	O	H	N	Six-membered ring
P_{si}	39.0	4.8	20	17.1	12.5	6.1
P_{st}	39	33.6	100	188.1	12.5	6.1

Table 8
Molar polarization values proposed by Vogel

Group	-CONH	O	$-CH_3$	$-CH_2$	OH primary	OH other	CH
P_{vi}	125	30	17.66	20.64	30	100	23.5
P_{vt}	125	60	17.66	20.64	30	100	117.5

and the electric forces resulting from polarizability and polar moment that determine the cohesive energy, with which δ can be directly determined using Eq. (19).

$$\delta \approx 7.0\varepsilon \quad (19)$$

where ε is the dielectric constant of polymer. The ε value was determined experimentally by using HP-4192A LF impedance analyzer by applying biased voltage equal to one. The frequency was varied from 1 to 450 KHz. ε can also be calculated from molar polarization (P_V). The P_V of a dielectric can be defined as follows.

$$\sum P_V = \varepsilon^{1/2} M$$

where M is molar mass per structural unit. The value of P_V can be calculated by using a group contribution method proposed by Vogel. Some of individual P_V values of different atoms and molecules are cited in the text of Van Krevelen (1990), and are given in Table 8.

2.12. Flory–Huggins interaction parameter (χ)

Sorption equilibrium between a swollen macromolecular coil and a component solvent considerably affects the thermodynamic, transport, rheological and optical properties of the polymer. A thermodynamic interpretation of data on preferential and total sorption is usually based on Flory–Huggins interaction parameter (χ). The δ of polymer can be estimated by inserting the value of χ in the following equation Shultz and Glory (1955);

$$\chi = (\delta_1 - \delta_{pt})^2 \left(\frac{V_1}{RT}\right) \quad (20)$$

where V_1 is molar volume of polymer, T is temperature in Kelvin at which the experiment is conducted, R is the universal gas constant, δ_1 and δ_{pt} are solubility parameters of the solvent and polymer, respectively. δ_{pt} can be estimated by known value of χ which can be determined by the formula written as (Shultz and Glory, 1955);

$$\chi = -\frac{[\ln(1 - \nu_p) + \nu_p]}{\nu_p^2} \quad (21)$$

where ν_p is the volume fraction of the polymer.

3. Results and discussions

Fig. 2 is a pictorial representation of $[\eta]$ versus δ_{sol} (solubility parameter of mixture of solvents). The maximum value of $[\eta]$, where the compatibility of solvent with polymer is maximum, is almost equal to the δ_t of polymer. For the present study, the maximum value for $[\eta]$ is obtained at 30 vol% of HCl–water solution and, hence, the δ_{pt} is equal to 41.48.

The average γ value of the polymer dissolved in the solution of solvents having different δ_{sol} is shown in Fig. 3. Initially, the γ value constantly decreases with increase in δ_{sol} and then it increases steeply. Two separate lines are drawn joining the points where γ decreases and then from where it starts to increase. The corresponding δ_{sol} value on the X-axis where the two lines coincide is considered as δ_{pt} and is equal to 39.8. The calculated γ value of the polymer was originally derived from parachor values by group contribution method. Here, it is found to be 144.77. The solubility parameter was determined by inserting γ in Eq.

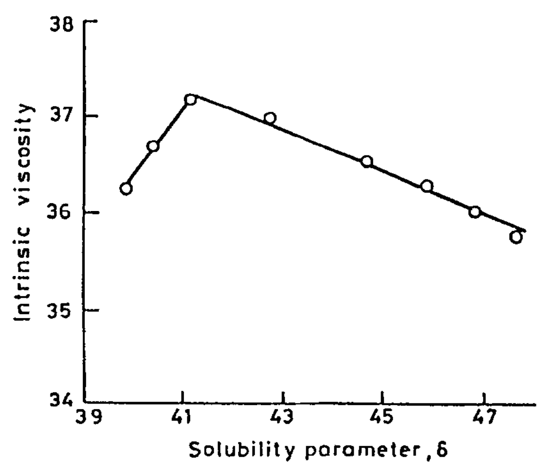

Fig. 2. Relationship between intrinsic viscosity and δ.

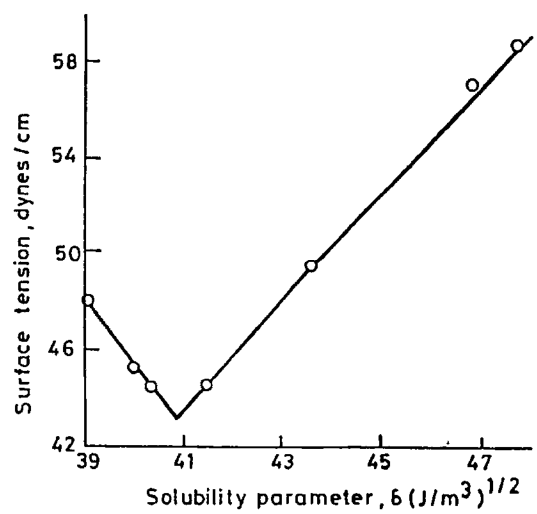

Fig. 3. Relationship between surface tension and δ.

Table 9
Overall solubility parameter of chitosan

Method	MIV	γ	ε	χ	
				Water	Hydrazine
δ_{pt}	41.48	39.8	37.02	43.45	41.73

(18), then δ_p of polymer was calculated and is found to be equal to 42.38.

The experimentally determined ε values are similar in the frequency range of 10–450 KHz, and the average value was 5.29. Inserting this ε value in Eq. (19), the δ of polymer was found be 37.02. From Table 8, P_V of chitosan is calculated which is equal to 5.37 and corresponding δ_{pt} is 37.65.

In the present case, the ν_p values of chitosan with water, and hydrazine are estimated. The values of χ were found to be 0.5917 and 0.951 for water and hydrazine, respectively. Inserting the value in Eq. (20) one can get the δ_{pt} of chitosan as 43.45 (from water) and 41.73 (from hydrazine).

4. Conclusions

In this first systematic attempt, the overall solubility parameter values of chitosan and chitin are estimated by Hoy, Van Krevelen, Hoftyzer–Van Krevelen, and Hoy systems. Results are tabulated in Table 6. The first two methods can yield δ_{pt} values only, whereas the latter two can also provide individual contributions of δ_d, δ_p and δ_h to the δ_{pt} values. The overall solubility parameter of chitosan polymer was also determined by maximum intrinsic viscosity, surface tension, dielectric constant, and Flory–Huggins interaction parameter values and the values are presented in Table 9. The average δ_t of 64% deacetylated chitosan was found to be 40.7. This value is in excellent agreement with the value of 42.366 obtained by applying group contribution method. Based on the δ_{pt} values of pure chitin and CDA chitosan, one can estimate δ_t for chitosan/chitin having any degree of deacetylation from Eq. (14).

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References

Bonchev, D. (1983). *Information theoretic indices for characterization of chemical structure*. New York: Research Studies Press.

Darbye, J.R., Touchette, N.W., & Sears, K. (1967). Dielectric constants of plasticizers as predictors of compatibility with poly(vinyl chloride). *Polym. Engng Sci.*, *7*, 295–300.

Fedors, R.F. (1974). Methods for estimating both the solubility parameters and molar volumes of liquids. *Polym. Engng Sci.*, *14*, 147–154.

Garden, J. (1965). *Encyclopedia of polymer science and technology* (Vol. 3, p. 833). New York: Wiley.

Hansen, C.M. (1967). The three-dimensional solubility parameter-key to paint-component affinities I. Solvents, plasticizers, polymers and resins. *J. Paint Technol.*, *39*, 104–117.

Hildebrande, J.H. (1916). Demonstration of the rational character of the new solubility formula. *J. Am. Chem. Soc.*, *38*, 1452–1473.

Hoftyzer, P.J., & Van Krevelen, D.W. (1970). Paper (Nr.IIIa-15). In *International Symposium on Macromolecules (IUPAC)*, Leylder.

Hoftyzer, P.J., & Van Krevelen, D.W. (1976). *Properties of polymers* (2nd ed., ch. 7, pp. 152–155). New York: Elsevier.

Hoy, K.L. (1970). New values of the solubility parameters from vapor pressure data. *J. Paint. Technol.*, *42*, 76–78 and 115–118.

Hoy, K.L. (1985). *Tables of solubility parameters: solvent and coatings materials research and development department*. Union Carbide Corporation.

Kier, L.B., & Hall, L.H. (1976). *Molecular connectivity in chemistry and drug research*. New York: Academic Press.

Lee, V. (1974). *Solution and shear properties of chitin and chitosan* (p. 446). University Microfilms, Ann Arbor, MI 74/29.

Mandel, M., Varkevisser, F.A., & Van Treslong, C.J.B. (1982). The measurement of the specific refractive index increment of polyelectrolytes in aqueous salt solutions with the chromatix KMX-16. *Macromolecules*, *15*, 675–676.

Muzzarelli, R.A.A. (1973). *Chitin*. New York: Pergamon Press.

Muzzarelli, R.A.A. (1973). *Natural chelating polymer*. Oxford: Pergamon Press.

Roberts, G.A.F. (1992). *Chitin chemistry*. London: MacMillion.

Rouvray, D.H., & Pandey, R.B. (1986). The fractional nature, graph invairants, and physicochemical properties of normal alkanes. *J. Chem. Phys.*, *84*, 2286–2290.

Sannon, T., Kurita, K., Ogura, K., & Iwakura, Y. (1978). Studies on chitin 7. Infared spectroscopic determination of degree of deacetylation. *Polymer*, *19*, 458–459.

Shultz, A.R., & Glory, P.J. (1955). Polymer chain dimensions in mixed-solvent media. *J. Polym. Sci.*, *15*, 231–242.

Small, P.A. (1953). Factors affecting the solubility of polymers. *J. Appl. Chem.*, *3*, 71–80.

Striegel, A.M., & Timpa, J.D. (1995). Molecular characterization of polysaccharides dissolved in Me_2NAc-LiCl by gel permeation chromatography. *Carbohydr. Res.*, *267*, 271–290.

Struszczyk, H. (1987). Microcrystalline chitosan I. preparation and properties of microcrystalline chitosan. *J. Appl. Polym. Sci.*, *33*, 177–189.

Sudgen, S. (1924). The variation of surface tension with temperature and some related functions. *J. Chem. Soc.*, *125*, 27–31.

Thomos, I. (1975). B.Sc. Applied Chemisty Dissertation, Torento Polytechnque.

Van Krevelen, D.W. (1965). Chemical structure and properties of coal XXVII—coal constitution and solvent extraction. *Fuel*, *44*, 229–242.

Van Krevelen, D.W. (1990). *Properties of polymers* (p. 322). Amsterdam: Elsevier.