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# Determination of Hansen solubility parameters for cellulose acrylate by inverse gas chromatography

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## Summary

The solubility parameters of cellulose acrylate (CEA) were examined by inverse gas chromatography (IGC). The test probes were pentane, hexane, heptane, octane, nonane, ether, acetone, tetrahydrofuran, toluene, chloroform, isopropanol, and hexanol. The minimal test probe was injected into chromatographic column in order to achieve the infinite dilution conditions. The retention times of the test probes were determined and Flory–Huggins interaction parameters ($\chi$) and solubility parameters ($\delta_2$) were calculated according to DiPaola-Baranyi and Guillet method from experimentally collected retention data for the series of carefully selected test probes. The Hansen's three-dimensional solubility parameters concept is applied to determine the components ($\delta_d$, $\delta_p$, $\delta_h$) of total solubility parameter ($\delta_T$). The solubility parameter ($\delta_T$) was increased with increasing temperature.

## Introduction

The solubility parameter is an important thermodynamic parameter for the polymers. The indirect method has to be used for measuring the solubility parameter, because of the molar evaporation heat of the polymer, which can not be evaporated can not be determined directly. The common indirect methods are static method, swelling method, viscometry and nephelometric end-point detection. But these methods usually get the thermodynamic parameter of the mixture of the polymer and the solvent. Then the IGC has been approved that it can be used to study the interaction between the polymer and the solvent.

Inverse gas chromatography is a method for the physicochemical characterization of any material which can be placed in a chromatographic column. In the IGC experiment, a non-volatile material to be examined is immobilized on a column. Then, this stationary phase is characterized by monitoring the passage of volatile probe molecules of known properties as they are transported through the column by carrier gas [1,2]. Retention data, collected during IGC experiments for the series of test probes, are further used in calculation of parameters characterising the examined material.

Inverse gas chromatography has been applied to determine solubility parameter [3-5]. The concept of the solubility parameter was proposed by Scatchard, Hildebrand and

Scott and initially applied to systems whose cohesion arises only from dispersion forces. This solubility parameter is the square root of cohesive energy density (*CED*) [6-8].

$$\delta = (CED)^{1/2} = \left[\frac{\Delta H_v - RT}{V_1}\right]^{1/2} = \left[\frac{\Delta E}{V_1}\right]^{1/2} \qquad \textbf{(1)}$$

where $\delta$ is the solubility parameter, $R$ the gas constant, $T$ the temperature, $\Delta H_\mathrm{v}$ the enthalpy of vaporization, $V_1$ the molar volume, and $\Delta E$ the energy of vaporization. The unit of solubility parameter used by authors is $(\mathrm{MPa})^{1/2}$.

The cohesive energy of a liquid is the energy of all the intermolecular interactions in a mole of the liquid, thus it is the energy necessary to break all interactions during vaporization of the liquid. The most widely used concept is that proposed by Hansen, called three dimensional solubility parameters or Hansen solubility parameters (HSP). According to the Hansen theory, the cohesive energy can be considered as a sum of contributions from dispersive ($E_\mathrm{d}$), polar ($E_\mathrm{p}$) and hydrogen bonding ($E_\mathrm{h}$) interactions:

$$E_\mathrm{coh} = E_\mathrm{d} + E_\mathrm{p} + E_\mathrm{h} \qquad \textbf{(2)}$$

And the total solubility parameter ($\delta_\mathrm{T}$) is expressed as [9]:

$$\delta_\mathrm{T}^2 = \delta_\mathrm{d}^2 + \delta_\mathrm{p}^2 + \delta_\mathrm{h}^2 \qquad \textbf{(3)}$$

where $\delta_\mathrm{d}$, $\delta_\mathrm{p}$, $\delta_\mathrm{h}$ denotes dispersive, polar and hydrogen bonding contribution, respectively.

Dispersion forces exist between all molecules, whether they are polar or nonpolar. These are the attractive forces arising as a result of temporary dipoles induced in atoms or molecules. Polar forces are due to permanent dipole or induced dipole interactions. Hydrogen bonding interactions occur when a hydrogen atom on one molecule is bound to an electronegative atom on another molecule.

The solubility parameter for the polymers can not be vaporized can not be calculated by Eq. (1), the solubility parameter of a polymer was able to be determined by linear regression by Eq. (4):

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{\delta_2^2}{RT} \qquad \textbf{(4)}$$

where $R$ is the gas constant, $T$ the temperature of column, and $V_1$ the molar volume of solvent. $\delta_1$ and $\delta_2$ are solubility parameters of probes and the polymer, respectively. Then, $\delta_2$, can be calculated by fitting $\chi_{12}^\infty$ and $\delta_1$ to the Eq. (4) [7,10]. The solubility parameter of the probe molecules, $\delta_1$ can be calculated according to the Eq. (1), where the enthalpy of vaporization, $\Delta H_v$, defined by the following relation [7,8,11]:

$$\Delta H_v = \Delta H_1^\infty - \Delta H_1^s = \left(R\frac{\partial \ln \Omega_1^\infty}{\partial 1/T}\right) - \left(-R\frac{\partial \ln V_g^0}{\partial 1/T}\right) \qquad \textbf{(5)}$$

where $\Delta H_1^s$ is the molar enthalpy [12]. The weight fraction activity coefficient, $\Omega_1^\infty$, the partial molar free energy, $\Delta G_1^\infty$ and the average partial molar enthalpy, $\Delta H_1^\infty$ at infinite dilution of the probes were calculated according to the following equations [7]:

$$\Omega_1^{\infty} = \frac{273.15R}{P_1^0 V_g^0 M_1} \exp\left( \frac{-P_1^0 \left( B_{11} - V_1 \right)}{RT} \right) \quad \textbf{(6)}$$

$$\Delta G_1^{\infty} = RT \ln \Omega_1^{\infty} \quad \textbf{(7)}$$

$$\Delta H_1^{\infty} = R \frac{\partial \ln \Omega_1^{\infty}}{\partial 1/T} \quad \textbf{(8)}$$

where $P_1^0$ is the vapor pressure of probe, $V_g^0$ the probe specific retention volume, $M_1$ the molecular weight of probe, and $B_{11}$ the second virial coefficient of probe in gaseous state.

The probe specific retention volume $V_g^0$ is [6,13]:

$$V_g^0 = 273.15 \times J \times F \frac{\Delta t}{w \times T} \quad \textbf{(9)}$$

where $\Delta t = t_R - t_M$ is the corrected retention time, $t_R$ is measured retention time and $t_M$ is the retention time of a marker probe, usually pentane. $F$ is the flow rate of carrier gas measured at room temperature $T_{room}$, $w$ is the mass of the polymer of stationary phase, and $J$ is a correction factor for gas compressibility defined by the following relation [11]:

$$J = \frac{3}{2} \frac{(P_i / P_o)^2 - 1}{(P_i / P_o)^3 - 1} \quad \textbf{(10)}$$

where $P_i$ and $P_o$ are the inlet and outlet pressures, respectively.$B_{11}$ were calculated by the following Eq. (11) [10,11,14]:

$$\frac{B_{11}}{V_c} = 0.430 - 0.886 \frac{T_c}{T} - 0.694 \left( \frac{T_c}{T} \right)^2 - 0.0375(n-1) \left( \frac{T_c}{T} \right)^{4.5} \quad \textbf{(11)}$$

where $T_c$ and $V_c$ are the critical temperature and molar volume of probe, respectively, and $n$ is the number of carbon atoms in probe molecule.

According to the Flory-Huggins theory, the parameter $\chi_{12}^{\infty}$ characterizes the interactions between the vapour-phase of the probe and the polymeric stationary phase. The values of $\chi_{12}^{\infty}$ were calculated according to the following equation [6,10]:

$$\chi_{12}^{\infty} = \ln \left( \frac{273.15\mathrm{R}}{P_1^0 V_g^0 M_1} \right) - \frac{P_1^0 \left( B_{11} - V_1 \right)}{RT} - 1 \quad \textbf{(12)}$$

where subscripts 1 and 2 denote the probes and examined material (polymer, filler), respectively.The vapor pressures $P_1^0$ were taken from reference book [15].

The purpose of determing the solubility parameter of CEA was to find out some solvents or mixed solvents, which solubility parameter was close to that of the CEA synthesized according to ours design. Then the CEA could be dissolved into homogeneous solution. So as to the property of solution of the CEA could be studied.

## Experimental

### *Materials*

The investigated material was cellulose acrylate (CEA) which was synthesized in our laboratory. CEA was obtained by adding a suitable amount of acryloyl chloride diluted in dimethylacetamide (DMAc) to a mother solution of cellulose in DMAc/(5% ~10%) LiCl at a polymer concentration $C_p$=2%(w/w). The experiment was performed at 50°C allowing the reaction to proceed for 2.5h. The sample, after precipitation by methanol and washing with distilled water for many times, was dried in vacuum oven at 60°C for 12h. And the sample was sieved to size 60~80 mesh. The degree of substitution (DS) of the sample was 2.36 obtained by the Euro Ea3000 Elementary Analyzer [16,17].

The Agilent Technologies 6850N Chromatograph with flame ionization detector (FID) was used. The test probes were pentane (C5), hexane (C6), heptane (C7), octane (C8), nonane (C9), ether, acetone, tetrahydrofuran (THF), toluene, chloroform, iso-propanol, and hexanol. They were analytical grade purity and purchased from Tianjin Kermel Chemical Reagents Development Center, China.

### *Methods*

The CEA was packed into the chromatographic column (350 mm long, 2.5 mm diameter). Columns were conditioned under nitrogen with a flow rate of 50 ml·min$^{-1}$ and 20°C above the maximum analysis temperature over night before use. The test condition were set as flow rates: hydrogen, 40 ml·min$^{-1}$; air, 450 ml·min$^{-1}$. Nitrogen was used as the carrier gas, with a flow rate of 50 ml·min$^{-1}$. Small volumes (0.02 μL) of probes were injected automatically to achieve the infinite dilution conditions. Retention data of the test probes were collected at 313.15, 318.15, 323.15, 328.15, 333.15 and 338.15 K. Solubility parameter of CEA, $\delta_2$ was calculated by using the Eq. (4). Plotting the left hand of this equation versus $\delta_1$ lead to $\delta_2$ of the examined material calculated from the slope of the straight line (Figure 1).

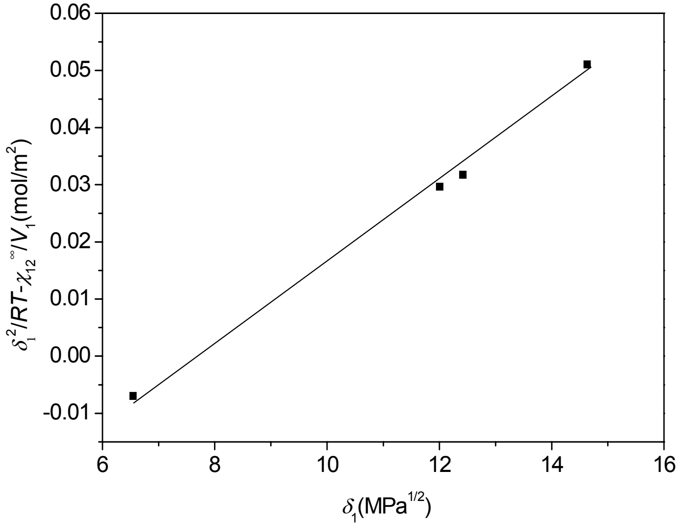

**Figure 1.** The example of $\delta_1^2/RT-\chi_{12}^\infty/V_1$ versus $\delta_1$ for n-alkanes on CEA at 40°C.

The components of total solubility parameter were calculated from the slope of straight line, plotted according to Eq. (4) for the respective group of probes representing different intermolecular interactions. These values were calculated by using the following relationships:

$$\delta_d = \frac{k_d \times RT}{2} \tag{13}$$

$$\delta_p = \frac{\left(k_p - k_d\right) \times RT}{2} \tag{14}$$

$$\delta_h = \frac{\left(k_h - k_d\right) \times RT}{2} \tag{15}$$

where $k_\mathrm{d}$ is the value of the slope for *n*-alkanes; $k_\mathrm{p}$ the value of the slope for ether, acetone, THF and toluene; $k_\mathrm{h}$ the value of the slope for chloroform, isopropanol and hexanol. The value of the total solubility parameter was obtained from Eq. (3)

## Results and Discussion

The solvent specific retention volume values were calculated according to Eq. (9) and listed in Table 1.

**Table 1.** Values of the solvent specific retention volume, $V_g^0$ at different temperatures

| probe | 313.15K | 318.15K | 323.15K | 328.15K | 333.15K | 338.15K |
|---|---|---|---|---|---|---|
| C6 | 1.43 | 1.29 | 1.27 | 1.14 | 1.08 | 1.01 |
| C7 | 4.76 | 3.75 | 3.12 | 2.95 | 2.42 | 2.08 |
| C8 | 14.52 | 10.31 | 7.96 | 6.93 | 5.22 | 4.16 |
| C9 | 46.31 | 32.34 | 23.88 | 17.84 | 13.11 | 9.82 |
| Ether | 15.95 | 11.72 | 10.84 | 7.84 | 6.57 | 5.37 |
| Acetone | 17.14 | 13.94 | 10.04 | 8.29 | 6.47 | 5.15 |
| THF | 288.09 | 260.60 | 227.26 | 209.60 | 187.67 | 169.89 |
| Toluene | 11.07 | 8.67 | 7.15 | 5.45 | 4.46 | 3.61 |
| Chloroform | 91.31 | 84.37 | 75.33 | 65.89 | 60.38 | 54.67 |
| Isopropanol | 1.31 | 1.29 | 1.04 | 1.02 | 0.92 | 0.84 |
| Hexanol | 12.74 | 11.02 | 9.46 | 7.95 | 6.94 | 6.01 |

Generally, $V_g^0$ decreases with an increase of temperature in all investigated systems as expected for an exothermic sorption process. Fig. 2 and Fig. 3 show the linear correlation between $\ln V_g^0$ and $1/T$, $\ln\Omega_1^\infty$ and $1/T$ for n-alkanes on CEA at six temperatures.

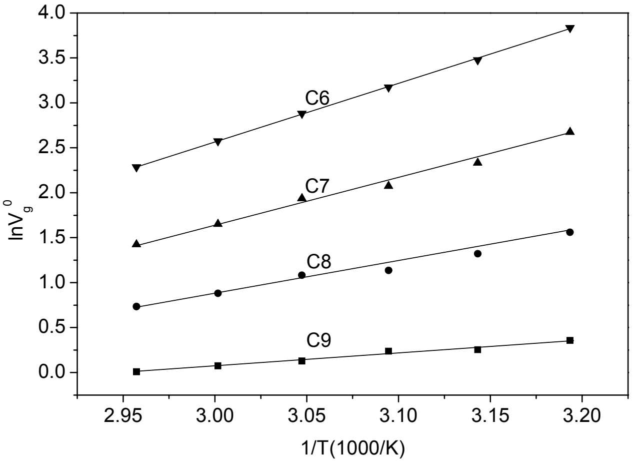

**Figure 2.** Plots of $\ln V_g^0$ versus $1/T$ for dispersive

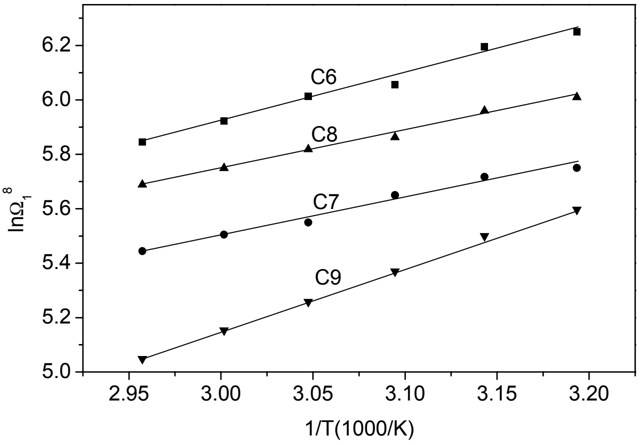

**Figure 3.** Plots of $\ln\Omega_1^\infty$ versus $1/T$ for dispersive

From the slope of the straight line in the Figure 2 and Figure 3, the values of $\Delta H_1^s$ and $\Delta H_1^\infty$ were calculated according to Eq. (5), the values of polar and hydrogen bonding can also be known by the same method, then the values of $\Delta H_v$ were listed in Table 2.

It is evident from the data that THF, isopropanol and hexanol exhibits higher values of $\Delta H_v$ than the others. The higher values of the $\Delta H_v$ the greater the interaction between the adsorbate and adsorbent.

Retention data of test probes are first converted into the values of Flory–Huggins interaction parameter $\chi$. Data found for the examined CEA are given in Table 3.

From the experiment, the maximum values of the Flory–Huggins interaction parameter were found for nonpolar test probes, *n*-alkanes, toluene, isopropanol and hexanol. These maximum values reflect the poor compatibility/miscibility of

**Table 2.** Values of the enthalpy of vaporization $\Delta H_v$

| probe | $\triangle H_v$ /kJ·mol$^{-1}$ |
|---|---|
| C6 | 26.67 |
| C7 | 34.74 |
| C8 | 28.24 |
| C9 | 10.39 |
| Ether | 25.63 |
| Acetone | 29.28 |
| THF | 49.65 |
| Toluene | 22.81 |
| Chloroform | 28.91 |
| Isopropanol | 42.85 |
| Hexanol | 47.30 |

**Table 3.** Values of the interaction parameter $\chi$, at different temperatures

| probe | 313.15K | 318.15K | 323.15K | 328.15K | 333.15K | 338.15K |
|---|---|---|---|---|---|---|
| C6 | 5.25 | 5.20 | 5.06 | 5.01 | 4.92 | 4.85 |
| C7 | 4.68 | 4.72 | 4.70 | 4.55 | 4.50 | 4.44 |
| C8 | 4.58 | 4.77 | 4.86 | 4.82 | 4.75 | 4.69 |
| C9 | 4.26 | 4.60 | 4.84 | 5.03 | 4.15 | 4.05 |
| Ether | 1.79 | 1.95 | 1.87 | 2.05 | 2.09 | 2.15 |
| Acetone | 2.66 | 2.69 | 2.85 | 2.87 | 2.96 | 3.03 |
| THF | 0.08 | 0.01 | -0.02 | -0.10 | -0.15 | -0.21 |
| Toluene | 4.96 | 4.96 | 4.89 | 4.90 | 4.87 | 4.84 |
| Chloroform | 0.46 | 0.36 | 0.30 | 0.27 | 0.20 | 0.15 |
| Isopropanol | 6.48 | 6.24 | 6.20 | 5.97 | 5.85 | 5.71 |
| Hexanol | 7.39 | 7.26 | 7.14 | 7.03 | 6.91 | 6.80 |

*n*-alkanes, toluene, isopropanol and hexanol with the examined polymers. For some polar test probes and chloroform, $\chi$ data are considerably lower than those for the test probes hereinbefore. In case of the polar test probes, THF exhibits negative values of $\chi$ at 323.15, 328.15, 333.15 and 338.15K, which reflects stronger interaction with examined CEA. Relatively strong interactions were also found for chloroform representing ability to hydrogen bonding interactions.

Values of dispersive ($\delta_d$), polar ($\delta_p$) and hydrogen bonding ($\delta_h$) component of solubility parameter for CEA were calculated according to Eq. (4) and Eq. (13-15). Then values of the total solubility parameter ($\delta_T$) were calculated according to Eq. (3) and listed in Table 4.

Values of $\delta_d$ parameter increase with increasing temperature, but values of polar ($\delta_p$) and hydrogen bonding ($\delta_h$) component of solubility parameter for CEA decrease with increasing of temperature. However the values of total solubility parameter,$\delta_T$ increase with the increasing of temperature owing to the $\delta_d$ term is biggest in components of the total solubility parameter. Value of the total solubility parameter of cellulose is 25.66 at 20°C. From the data of the total solubility parameter,$\delta_T$, it is obvious that the values of CEA are lower than that of cellulose. It is able to be understood that the intermolecular hydrogen bond of CEA were destroied by acryloyl leading-in and acidylating of cellulose. So the dissolving for CEA is easier than that for cellulose.

**Table 4.** Components of solubility parameter $\delta_d$, $\delta_p$ and $\delta_h$ and total solubility parameter $\delta_T$ at 313.15, 318.15, 323.15, 328.15, 333.15 and 338.15K for CEA

| T/K | $\delta_d$ /(MPa)$^{1/2}$ | $\delta_p$ /(MPa)$^{1/2}$ | $\delta_h$ /(MPa)$^{1/2}$ | $\delta_T$/(MPa)$^{1/2}$ |
|---|---|---|---|---|
| 313.15 | 17.44 | 8.85 | 7.03 | 20.79 |
| 318.15 | 19.44 | 7.27 | 5.56 | 21.49 |
| 323.15 | 20.69 | 7.12 | 5.51 | 22.56 |
| 328.15 | 21.55 | 6.00 | 5.50 | 23.06 |
| 333.15 | 22.00 | 5.79 | 5.39 | 23.38 |
| 338.15 | 22.65 | 5.31 | 5.17 | 23.83 |

## Conclusions

This work has shown that inverse gas chromatography can be applied for the estimation of solubility parameter for CEA. According to the Hansen's equation, total solubility parameters were calculated from dispersive, polar and hydrogen bonding components, which were get from the data of the IGC experiment. The degree of substitution (DS) of the CEA determined was 2.36. The values of components of solubility parameter $\delta_d$, $\delta_p$, $\delta_h$ were 17.44, 8.85 and 7.03, respectively; and the value of total solubility parameter, $\delta_T$ was 20.79 all at the temperature of 313.15K.

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