

## Determination of Alkali Lignin Solubility Parameters by Inverse Gas Chromatography and Hansen Solubility Parameters

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The physicochemical properties of alkali lignin are crucial to its potential applications and recyclability, as it is one of the most important natural polymer materials. In this study, the solubility parameter ( $\delta$ ) of alkali lignin was determined using Hansen solubility parameters (HSP) theory and inverse gas chromatography (IGC). The  $\delta$  of alkali lignin was determined by the IGC technique. Solute retention volumes ( $V_g^0$ ) of 6 solutes were determined using alkali lignin as the stationary phase. From 50 to 110 °C, the  $\delta$  of alkali lignin varied from 24.47 to 24.15 MPa<sup>1/2</sup>. Hansen solubility spheres were plotted using the data from the literature for the interactions of alkali lignin with 36 solutes to determine the three dimensional solubility parameter of alkali lignin at 25 to 100 °C. These determined  $\delta$  values were consistent with those calculated experimentally via IGC. Acetone was a moderate solvent for the alkali lignin.

*Keywords:* Inverse gas chromatography; Hansen solubility parameters; Alkali lignin; Solubility parameters

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### INTRODUCTION

Lignin is a main component of lignocellulosic biomass (Huber *et al.* 2006; Somerville *et al.* 2010; Zakzeski *et al.* 2010). More than 50 million tons of lignin residue are used in the paper industry each year (Zakzeski *et al.* 2010). Lignin is also a byproduct in ethanol fuel production from crop waste (Sannigrahi *et al.* 2010). Lignin accounts for 20 to 30 wt% of lignocellulosic biomass (Ragauskas *et al.* 2006), and it is a three-dimensional structured macromolecule in which a large number of aromatic rings are linked through C-O-C and C-C bonds. Alkali lignin is a structurally complex polymer consisting of phenylpropanoid units linked by alkyl-ether, aryl-ether, and carbon-carbon covalent bonds in a high-density cross-linked polymer network, with an average of 1 to 2 hydroxyl groups per C9-monomer (Boeriu *et al.* 2014). Therefore, it is an ideal feedstock for the production of renewable liquid fuels, biomaterials, and green chemicals. However, the (*p*-hydroxyphenyl)-propane units are linked with different chemical bonds in the structure of lignin (Kirk *et al.* 2011), which makes lignin very stable and difficult to decompose. Finding solvents that solubilize alkali lignin is important for further processing or recycling alkali lignin.

The solubility parameter ( $\delta$ ) is important for selecting stable solvents. It is also frequently used to predict the thermodynamic state of a polymer mixed with solvent or additive, swelled with liquid, blending with another polymer, or other applications where the interaction between the polymer and other components is important.

Essentially, solutes and solvents with similar solubility parameters result in better dissolution of the solute. However, the solubility parameter of many structurally complex compounds cannot be easily determined by direct measurements. The solubility parameters of these compounds are usually determined using functional group contribution methods (Ito and Guillet 1979), inverse gas chromatography (Verdier *et al.* 2005), micro-calorimetric measurements (Fang *et al.* 2005), and evaporative light scattering detection (Papadopoulou and Panayiotou 2012). Generally, these methods are time-consuming. Polymer materials, especially new synthetic polymers, require a simple and rapid method to theoretically calculate solubility parameters. Of the methods mentioned above, inverse gas chromatography may be regarded as the most effective tool.

Inverse gas chromatography (IGC) has been applied to organic materials such as powders (Mutelet *et al.* 2002), crude oils (Batko and Voelkel 2007), nanomaterials (Van Asten *et al.* 2000), fibers (Cordeiro *et al.* 2011), copolymers (Dritsas *et al.* 2009), polymer blends (Adamska and Voelkel 2005), hyperbranched polymers (Ahfat *et al.* 2000), and some non-food carbohydrates (Dimopoulou *et al.* 2000). Voelkel *et al.* (2009) used IGC to detect the physicochemical properties of polymers. This technique involves the preparation of a chromatographic column filled with the material under study. Furthermore, a series of test solute probes and temperatures are selected, and their  $V_g^0$  data is used to quantify the interaction of the solute probes with the stationary phase at the working temperature.

The IGC technique can be extended to determine Hansen three-dimensional solubility parameters. For these values, the total solubility parameter of a compound is dependent on the contribution of the dispersive, polar, and hydrogen bonding forces. The theory describes how it is possible for the characterization and selection of additives in polymer formulations to benefit from the “Hansen space” (Hansen 2007). In the “Hansen space”, all solvents and solutes can be located. The determined point in the center of the three dimensional space is the Hansen solubility parameter of the compound under study.

In this paper, two methods were applied to determine the solubility parameter of alkali lignin: the Hansen solubility parameter and inverse gas chromatography. For the Hansen solubility parameters approach, the group contribution method was used. For the inverse gas chromatography experiment, the solubility parameter was measured in a range of temperatures. The IGC technique was used to determine the solubility parameter of alkali lignin at a range of temperatures, and the solubility parameter values were verified using the Hansen three dimensional solubility parameter approach. Therefore, IGC provided a more accurate and efficient method for selecting appropriate solvents for a solute. Acetone was shown to be a moderate solvent for lignin.

## EXPERIMENTAL

### Materials

Commercial alkali lignin was supplied by Tralin Paper Co., Ltd. (Shandong, China). Alkali lignin was isolated by alkali-assisted extractions from wheat straw, resulting in a composition of 82.69% lignin, 8.35% carbohydrates, and 8.96% ash. Solute probes were obtained from Aladdin Industrial Co. Ltd. (Shanghai, China). All other chemicals and solvents were of analytical grade.

### Methods

#### *Preparation of the column*

For chromatographic column packing, the alkali lignin was initially coated on Chromosorb 6201 by concentrating the mixture in acetone. The alkali lignin coated mixture was then packed in a 100-cm, 1/8-in. O. D. solvent-rinsed stainless steel column using a mechanical vibrator and a vacuum pump. The end of the column was plugged with a small piece of glass wool and connected to the vacuum pump. Mechanical vibration and manual taps ensured better packing of the stationary phase in the column. The column was shaped in a coiled form so that it could be adjusted to the injector and detector ports. Prior to measurements, the column was conditioned overnight in the working conditions (temperature and helium flow rate) to remove any contaminants that could be eluted during measurements (Voelkel *et al.* 2009). The total lignin loadings were obtained by standard ashing procedures (Conder and Young 1979). The weight difference before and after pyrolysis was noted as the weight of the lignin coated on the inert diatomaceous earth.

#### *Inverse gas chromatography*

Experiments were performed with an Agilent 6890 gas chromatograph (Santa Clara, CA, USA) equipped with a flame ionization detector (FID) as previously described (Srinivas *et al.* 2009). The injector and detector were operated at 150 and 200 °C, respectively. The  $V_g^0$  values of the various solute probes chemicals were determined. High purity nitrogen was used as the carrier gas, and the flow rate was measured with a soap bubble flow meter at room temperature. The nitrogen flow rate maintained at 20 mL/min. The non-interacting marker used to determine the void volume of the column was n-pentane.

A stainless steel column was cleaned with water, NaOH (5%), and acetone prior to packing. After packing, the column was conditioned overnight in a stream of nitrogen at 130 °C. The column temperatures were maintained at 50, 60, 70, 80, 90, 100, and 110 °C. The following solute probes were selected: n-hexane, trichloromethane, ethyl acetate, tetrahydrofuran, acetone, and octane. Solute probes were injected manually with a 5- $\mu$ L Hamilton syringe. To achieve infinite dilution, the injection volume for each solute probes was 2  $\mu$ L. At least three injections were made for each solute probes, and the average retention time,  $t_R$ , was used for the calculations. The retention times of the solute probes were determined after the calculation of the first-order moment of the concentration distribution.

### Solubility test

The experimental determination of solubility parameters generally requires the choice of reference solvents whose solubility parameters are known and well distributed in the “Hansen space”. Swelling tests of the polymer have to be performed at well-defined temperature and concentration. The determination of the solubility volume (or solubility sphere) is derived from visual observations (Bordesa *et al.* 2010).

The solubility tests were initially carried out in 36 organic solvents. The Hansen solubility parameters of the 36 solutes were obtained from the literature. The “Hansen spheres” were plotted using the data processing software package HSP, developed by Hansen (2007). The center of mass of the sphere obtained from a computerized optimization method is assumed to be the Hansen three-dimensional solubility parameter of alkali lignin. To determine the solubility, 0.2 g of lignin was placed in a test tube containing 2 mL of the test solvent. The tube was sealed to prevent solvent evaporation and immersed in a bath at 25 °C for 24 h. The temperature was raised to 40, 60, 80, and 100, °C. The results were classified into five categories by visual observation: (a) soluble, (b) majority soluble, (c) partially soluble, (d) swelling, and (e) minority swelling. These classifications were then processed by a special HSP computer program (HSPiP 2nd edition) to calculate the HSP values of each polymer. The program was purchased from Dr. Charles M. Hansen in March 2009. The calculation mechanism of the program was introduced by Etxabarren *et al.* (2002).

## RESULTS AND DISCUSSION

### Inverse Gas Chromatography

#### Probe solvents retention volumes

IGC is used to study the thermodynamic properties of polymers (Yazici *et al.* 2008). The retention volume,  $V_g^0$ , was calculated from Eq. 1,

$$V_g^0 = 273.15JF \frac{\Delta t}{mT} \quad (1)$$

where  $\Delta t = t_r - t_m$ ,  $t_r$  is the retention time of the adsorbing solute probes,  $t_m$  is the mobile phase (n-pentane) hold-up time (dead time),  $F$  is the flow rate at ambient conditions,  $m$  is the mass of the solvent on the column packing, and  $T$  is the column temperature (K). The factor  $J$  corrected for the influence of the pressure drop along the column and is given by,

$$J = \frac{3(P_i / P_0)^2 - 1}{2(P_i / P_0)^3 - 1} \quad (2)$$

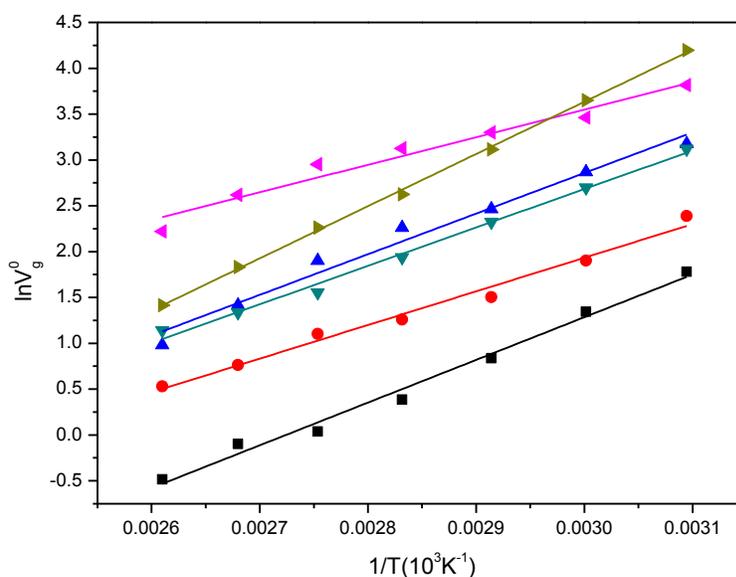
where  $P_i$  and  $P_0$  are the inlet and the outlet pressure, respectively.

The  $V_g^0$  is necessary to determine the physicochemical or thermodynamic properties of materials by IGC. The  $V_g^0$  of six solvents on lignin were obtained from IGC measurements between 323.15 K and 383.15 K (Table 1). The  $V_g^0$  of the solute probes on lignin varied with reciprocal temperatures for each solute probes and decreased with increasing temperatures (Fig. 1). The linear relationship between  $V_g^0$  and temperature

which indicated that an equilibrium between the solute probes and lignin had been established (Li *et al.* 2010).

**Table 1.** Specific Retention Volumes ( $V_g^0$ ) at Different Temperatures ( $\text{mL}\cdot\text{g}^{-1}$ )

Probe Solvent	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K	373.15 K	383.15 K
<i>n</i> -Hexane	5.93	3.83	2.31	1.47	1.04	0.91	0.62
Trichloromethane	10.89	6.69	4.5	3.52	3.01	2.14	1.7
Ethyl Acetate	23.94	17.63	11.77	9.59	6.69	4.12	2.66
Tetrahydrofuran	22.64	14.86	10.2	6.94	4.72	3.8	3.13
Acetone	45.36	31.9	27.07	22.8	19.11	13.69	9.2
Octane	66.51	38.53	22.52	13.79	9.6	6.23	4.12



**Fig. 1.** Plot of  $\ln V_g^0$  versus  $1/T$  for the solute probes: ■ *n*-hexane; ● trichloromethane; ▲ ethyl acetate; ▼ tetrahydrofuran; ◀ acetone; ▶ octane

**Table 2.** Weight Fraction Activity Coefficients at Infinite Dilution ( $\Omega_1^\infty$ ) at Different Temperatures

Probe Solvent	323.15K	333.15K	343.15K	353.15K	363.15K	373.15K	383.15K
<i>n</i> -Hexane	85.04	93.97	114.16	134.24	145.36	129.83	151.55
Trichloromethane	26.01	30.45	33.34	32.09	28.77	31.52	31.6
Ethyl Acetate	28.56	26.52	27.95	24.74	26.2	32.12	38.17
Tetrahydrofuran	23.98	25.47	26.57	28.67	31.6	30.05	28.48
Acetone	10.8	10.96	9.45	8.4	7.65	8.31	9.79
Octane	45.4	50.54	57.66	64.73	65.7	73.44	82.4

*Probe solvents thermodynamics parameters*

The weight fraction activity coefficient of solute probes solvents,  $\Omega_1^\infty$ , at infinite dilution was calculated from Eq. 3,

$$\ln \Omega_1^\infty = \ln \frac{273.15R}{P_1^0 V_g^0 M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (3)$$

where  $M_1$  is the molecular mass of solute probes solvents,  $R$  is the ideal gas constant, and  $B_{11}$ ,  $P_1^0$ , and  $V_1$  are the second virial coefficient, the saturated vapor pressure, and the molar volume of the solute probes, respectively. The values of  $B_{11}$ ,  $P_1^0$ , and  $V_1$  were calculated at column temperature. (Yazici *et al.* 2008)

An  $\Omega_1^\infty$  value higher than 10 indicates poor polymer-sorbate solubility, while values lower than 5 suggests good solubility. Values between 5 and 10 indicate a moderate solvent. While acetone was a moderate solvent for lignin, the others tested were not suitable in the temperature range of 323.15 to 383.15 K (Table 2).

The molar absorption enthalpy  $\Delta H_1^s$  was obtained from the slope of the plot of  $1/T$  versus  $\ln V_g^0$  according to Eq. 4:

$$\Delta H_1^s = -R \frac{\partial(\ln V_g^0)}{\partial(1/T)} \quad (4)$$

The partial molar heats of mixing  $\Delta H_1^\infty$  were obtained from the slope of the plot of  $1/T$  versus  $\ln \Omega_1^\infty$  according to Eq. 5:

$$\Delta H_1^\infty = R \frac{\partial(\ln \Omega_1^\infty)}{\partial(1/T)} \quad (5)$$

The molar evaporation enthalpies  $\Delta H_v$  of the solute probes adsorbed by the polymers are related to  $\Delta H_1^\infty$  and  $\Delta H_1^s$  as follows:

$$\Delta H_1^\infty = \Delta H_{v1} + \Delta H_{1s} \quad (6)$$

### Interaction parameters

According to the Flory-Huggins approach, the interaction parameter  $\chi_{12}^\infty$  of a given solute polymer pair is defined as (Yazici *et al.* 2008):

$$\chi_{12}^\infty = \ln \frac{273.15R}{P_1^0 V_g^0 M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) - 1 \quad (7)$$

**Table 3.**  $\chi_{12}^\infty$  Values at Different Temperatures

Probe Solvent	$\chi_{12}^\infty$ at Given Temperature (K)						
	323.15	333.15	343.15	353.15	363.15	373.15	383.15
n-Hexane	3.44	3.54	3.74	3.9	3.98	3.87	4.02
Trichloromethane	2.26	2.42	2.51	2.47	2.36	2.45	2.45
Ethyl acetate	2.35	2.28	2.33	2.21	2.27	2.47	2.64
Tetrahydrofuran	2.17	2.24	2.28	2.36	2.45	2.4	2.35
Acetone	1.38	1.39	1.25	1.13	1.03	1.12	1.28
Octane	2.81	2.92	3.05	3.17	3.19	3.3	3.41

The calculated interaction parameters at the seven different temperatures are presented in Table 3. When  $\chi_{12}^\infty$  is less than 0.5 (critical value), the solute probe is generally characterized as a good solvent, while a value higher than 1 designates a poor solvent that may lead to phase separation. The values of  $\chi_{12}^\infty$  confirmed the  $\Omega_1^\infty$  data showing that acetone was a moderate solvent for the lignin, and the other solvents were not suitable between 323.15 and 383.15 K (Sreekanth and Reddy 2008). All results were consistent with the  $\Omega_1^\infty$  values. Additionally, the interaction parameter values for all the solutes were positive numbers, showing an endothermic mixing with the solvent. As temperature was increased, the interaction parameter values increased, indicating a decrease in their miscibility with lignin at higher temperatures (Fig. 2). However, this was not the case for all solute-solvent interactions. Acetone showed a decrease in the interaction parameter with increasing temperature, indicating greater solute-solvent miscibility with increasing temperature.

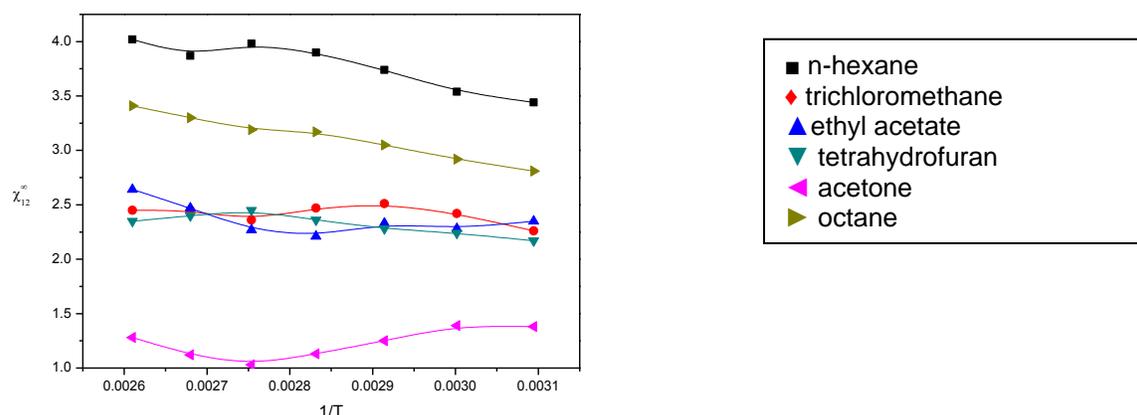


Fig. 2. Plot of  $\chi_{12}^{\infty}$  versus  $1/T$

### Solubility parameters

The solubility parameter of each of the solute probes,  $\delta_1$ , was calculated from Eq. 8,

$$\delta_1 = \left( \frac{\Delta E_v}{V_1} \right)^{1/2} = \left( \frac{\Delta H_v - RT}{V_1} \right)^{1/2} \quad (8)$$

where  $\Delta E_v$  is the energy of vaporization of the compound,  $V_1$  is the molar volume of the compound, and  $\Delta H_v$  is the molar heat of vaporization of the compound. The data are summarized in Table 4.

The  $\delta_1$  values decreased with increasing temperature due to two reasons: (i) the heat of vaporization decreases with temperature, and (ii) the molar volume increases with temperature. The solubility parameter of the polymer ( $\delta_2$ ) was calculated using Eq. 9.

$$\left( \frac{\delta_1^2}{RT} - \frac{\chi_{12}^{\infty}}{V_1} \right) = \left( \frac{2\delta_2}{RT} \right) \delta_1 - \frac{\delta_2^2}{RT} \quad (9)$$

The data of each group were evaluated individually, and the calculated  $\delta_2$  values are given in Table 5. Generally,  $\delta_2$  values decreased with increasing temperature. The average value of  $\delta_2$  was  $24.29 \text{ (J} \cdot \text{cm}^{-3})^{1/2}$ . These experiments were performed at higher temperatures, where the solubility parameters are expected to be smaller.

Table 4. Solubility Parameters  $\delta_1$  at Different Column Temperatures  $\text{MPa}^{1/2}$

Probe Solvent	323.15K	333.15K	343.15K	353.15K	363.15K	373.15K	383.15K
n-Hexane	13.8	13.68	13.55	13.42	13.29	13.16	13.02
Trichloromethane	17.63	17.7	17.44	17.18	17.02	16.86	16.69
Ethyl Acetate	17.15	17	16.85	16.69	16.53	16.36	16.18
Tetrahydrofuran	18.33	18.19	18.04	17.89	17.72	17.57	17.4
Acetone	18.53	18.37	18.18	18	17.8	17.61	17.41
Octane	14.28	14.18	14.07	13.96	13.85	13.74	13.63

**Table 5.** Solubility Parameters  $\delta_2$  at Different Column Temperatures ( $\text{J}\cdot\text{cm}^{-3}$ )<sup>1/2</sup>

Probe Solvent	323.15K	333.15K	343.15K	353.15K	363.15K	373.15K	383.15K
n-Hexane	22.04	22.1	22.36	22.37	22.39	22.17	22.25
Trichloromethane	26.16	26.72	26.64	26.31	26	26.07	25.95
Ethyl Acetate	25.03	24.81	24.8	24.49	24.46	24.69	24.83
Tetrahydrofuran	26.67	26.71	26.72	26.77	26.85	26.65	26.43
Acetone	25.48	25.4	24.87	24.41	23.97	24.05	24.32
Octane	20.98	21.06	21.17	21.25	21.21	21.28	21.34
Average	24.39	24.47	24.43	24.27	24.15	24.15	24.19

### Hansen Solubility Parameters

The Hansen three-dimensional solubility parameter is given by Eq. 10 (Hansen 2007),

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (10)$$

where  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  are the solubility parameters of the compound due to dispersion, polar, and hydrogen intermolecular forces contributions to the solubility parameter, respectively, and  $\delta_T$  is the total solubility parameter of the compound. To determine the Hansen solubility parameters of alkali lignin, its interactions with 36 organic solutes were used to plot Hansen spheres. The solubility parameters of alkali lignin at room temperature were as follows:  $\delta_D$ , 17.21  $\text{MPa}^{1/2}$ ;  $\delta_P$ , 12.35  $\text{MPa}^{1/2}$ ; and  $\delta_H$ , 12.33  $\text{MPa}^{1/2}$ . Thus, the total solubility parameter  $\delta_T$  was 24.51  $\text{MPa}^{1/2}$ .

The relative energy difference (RED) was used to determine the miscibility of alkali lignin with selected organic compounds (Eq. 11),

$$RED = \frac{R_a}{R_0} \quad (11)$$

where  $R_0$  is the radius of the Hansen sphere obtained by a computerized optimization method as described above.  $R_a$  is defined by Eq. 12,

$$R_a^2 = 4(\delta_{D1}^2 - \delta_{D2}^2)^2 + (\delta_{P1}^2 - \delta_{P2}^2)^2 + (\delta_{H1}^2 - \delta_{H2}^2)^2 \quad (12)$$

where the subscript “1” refers to the organic compound and “2” refers to lignin. Table 6 contains RED values obtained by the computerized optimization of lignin-solvent interactions. In principle, the lowest RED value indicates the solvent most compatible with lignin. Hansen spheres were plotted from values obtained at room temperature (25 °C); the three axes were the dispersion, polar, and hydrogen bonding solubility parameters (Fig. 2). Organic compounds with a RED value of 1.00 formed the boundary of the Hansen sphere. Those solutes (solvents) with RED values greater than 1.00 showed poor solute-solvent interactions; hence, alkali lignin would not be a suitable substitute for these solvents. These RED values are consistent with the  $\chi_{12}^\infty$  values shown in Table 3.

However, the Hansen three-dimensional solubility parameter method does not fully account for the entropy of mixing ( $\chi_{12}^{\infty}$ ) effect to the relatively large size disparity between alkali lignin and the solute probes.

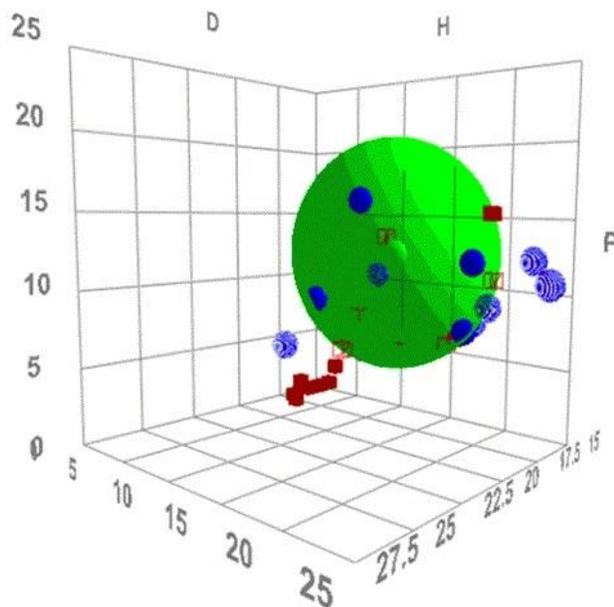


Fig. 3. Three-dimensional solubility sphere of lignin

Table 6. RED Values of Selected Solvents

Solvent	$\delta_D^*$	$\delta_P^*$	$\delta_H^*$	RED				
				25 °C	40 °C	60 °C	80 °C	100 °C
Heptane	15.3	0	0	2.24	1.06	1.04	0.98	1.01
Ethanol	15.8	8.8	19.4	1	0.99	0.49	0.25	0.21
Decane	15.7	0	0	2.2	1.06	1.03	0.99	1.01
Nonane	15.7	0	0	2.2	1.06	1.03	0.99	1.01
Hexane	14.9	0	0	2.27	1.07	1.06	0.98	1.01
Methyl alcohol	14.7	12.3	22.3	1.32	0.98	0.61	0.42	0.33
Acetone	15.5	10.4	7	1.01	0.67	0.91	0.71	0.71
Benzene	18.4	0	2	1.97	1.08	0.95	0.95	0.96
Methylbenzene	18	1.4	2	1.84	1.02	0.95	0.92	0.94
Pyridine	19	8.8	5.9	0.97	0.76	0.9	0.82	0.8
Dimethyl Sulfoxide	18.4	16.4	10.2	0.58	0.6	1	0.85	0.81
Thionyl chloride	16.9	6.4	6.1	1.11	0.82	0.83	0.71	0.73
Ethylene glycol	17	11	26	1.53	1.22	0.55	0.51	0.41
2-Propanol	15.8	6.1	16.4	1	1	0.5	0.22	0.27
Diethyl Ether	14.5	2.9	4.6	1.78	1.01	0.97	0.75	0.81
n-propanol	16	6.8	17.4	0.97	1	0.46	0.22	0.23

Butyl alcohol	16	5.7	15.8	1	1.01	0.47	0.25	0.29
2-Octyl alcohol	16.1	4.9	11	1.05	0.94	0.62	0.46	0.5
1,4-Butylene glycol	16.6	11	20.9	0.97	1	0.53	0.39	0.31
Di-ethylene glycol	16.6	11	20.9	0.75	0.94	0.62	0.46	0.4
N,N-Dimethylformamide	17.4	13.7	11.3	0.29	0.64	0.85	0.68	0.66
Carbon tetrachloride	17.8	0	0.6	2.1	1.07	1	0.99	1
Quinoline	20.5	5.6	5.7	1.38	1.02	0.95	0.9	0.91
n-Butyl acetate	15.8	3.7	6.3	1.43	0.92	0.8	0.67	0.7
Ethyl acetate	15.8	5.3	7.2	1.24	0.87	0.8	0.63	0.66
Aniline	20.1	5.8	11.2	0.99	1.03	0.73	0.67	0.68
Triethylamine	15.5	0.4	1	2.11	1.04	1	0.94	0.96
Water	15.5	16	42.3	3.43	1.7	1	1.22	1.03
Dichloromethane	17	7.3	7.1	1	0.78	0.82	0.67	0.68
Methylamine	14.4	7	16	1.27	1.25	1	0.28	0.43
Monoethanolamine	17	15.5	21	1.01	0.93	0.75	0.61	0.53
1-Octane	15.5	0	0	2.21	1.06	1.03	0.98	1.01
Trichloromethane	17.8	3.1	5.7	1.43	0.95	0.81	0.74	0.75
Dodecane	16	0	0	2.18	1.07	1.02	0.99	1.01
Tetradecane	16.2	0	0	2.16	1.07	1.02	0.99	1.01
Tetrahydrofura	16.8	5.7	8	1.06	0.86	0.75	0.61	0.63

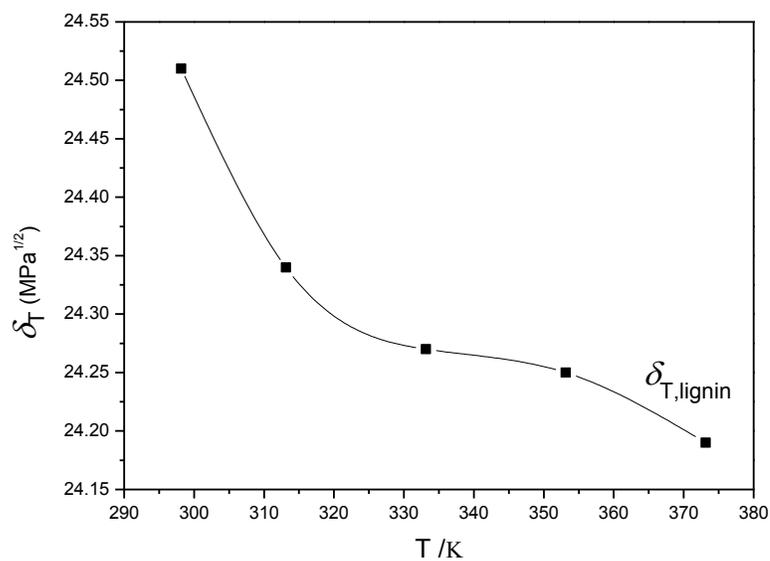
\*MPa<sup>1/2</sup>

The 3D plots that are outside the sphere of Fig. 3 show certain immiscible solutes. The lowest RED value was obtained for acetone; this solute probe also had a low  $\chi_{12}^{\infty}$  value, as discussed previously.

The  $\delta_2$  values decreased with increasing temperature (Table 7). There are many aromatic rings present in alkali lignin, which means that there is a lot of space between the molecules. With the increasing temperature, the distance between molecules became larger. So that intermolecular forces became smaller and the  $\delta_2$  values decreased. According to the Hansen solubility parameters, the average  $\delta_2$  value was 24.31 MPa<sup>1/2</sup>. Figure 4 showed a decrease of the solubility parameters with an increase in temperature, so the data in this work was obtained at higher temperatures, where the solubility parameters are expected to be smaller. The total  $\delta_T$  of alkali lignin obtained by this method was consistent with that obtained from the former IGC technique.

**Table 7.** Alkali Lignin Solubility as a Function of Temperature (MPa<sup>1/2</sup>)

T (°C)	25	40	60	80	100	Average
$\delta_T$	24.51	24.34	24.27	24.25	24.19	24.31



**Fig. 4.** Plot of  $\delta_T$  versus  $T$  for alkali lignin at ordinary pressure

Solubility test results are shown in Table 7. The solubility behavior of the test lignin was coded as soluble (1) (Table 8, classifications a, b, and c) or insoluble (0; Table 8, d and e). The experiments were conducted in 36 available analytical grade solvents; of these, 11 were good solvents for alkali lignin (0.2 g in 2 mL). The remaining 25 solvents were not suitable at 25 °C. At 100 °C, there were 31 good solvents and 5 non-solvents for alkali lignin.

**Table 8.** Swelling Test Results

CAS Number	Solvent	25 °C	40 °C	60 °C	80 °C	100 °C
142-82-5	Heptane	e	e	e	e	e
64-17-5	Ethanol	b	a	a	a	a
124-18-5	Decane	e	e	e	e	e
111-84-2	Nonane	e	e	e	e	e
110-54-3	Hexane	d	d	d	d	c
67-56-1	Methyl alcohol	b	a	a	a	a
67-64-1	Acetone	b	a	a	a	a
71-43-2	Benzene	d	d	c	c	c
108-88-3	Methylbenzene	e	e	e	d	d
110-86-1	Pyridine	b	a	a	a	a
67-68-5	Dimethyl Sulfoxide	b	a	a	a	a
7719/9/7	Thionyl chloride	b	b	a	a	a
107-21-1	Ethylene glycol	c	c	b	a	a
67-63-0	2-Propanol	d	d	c	c	c
60-29-7	Diethyl ether	e	e	e	e	e
71-23-8	n-Propanol	c	c	a	a	a
71-36-3	Butyl alcohol	d	c	c	a	a
123-96-6	2-Octyl alcohol	e	e	c	c	c
110-63-4	1,4-Butylene glycol	e	c	c	a	a
111-46-6	Di-ethylene glycol	c	c	a	a	a
1968/12/2	N,N-Dimethylformamide	e	d	c	a	a
56-23-5	Carbon tetrachloride	e	e	c	c	c
91-22-5	Quinoline	c	b	b	a	a
123-86-4	n-Butyl acetate	e	e	c	c	c
141-78-6	Ethyl acetate	d	c	c	c	c
62-53-3	Aniline	e	d	c	a	a
121-44-8	Triethylamine	e	e	c	c	c
7732-18-5	Water	e	e	d	c	c
1975/9/2	Dichloromethane	e	c	c	c	c
74-89-5	Methylamine	b	b	a	a	a
141-43-5	Monoethanolamine	d	c	b	a	a
111-65-9	1-Octane	d	d	c	c	c
67-66-3	Trichloromethane	d	c	b	b	b
112-40-3	Dodecane	d	d	d	c	b
629-59-4	Tetradecane	d	c	c	c	b
109-99-9	Tetrahydrofura	d	c	a	a	a

a, Soluble; b, Majority Soluble; c, Partially Soluble; d, Swelling; and e, Minority Swelling

## CONCLUSIONS

1. This study of alkali lignin focused on determining its solubility parameters and interactions with different test solvents. In the investigated temperature range, the solubility parameter of the alkali lignin decreased as the temperature increased.
2. The solubility parameters of alkali lignin were determined for the first time.
3. IGC and HSP methods were used to calculate the solubility parameters of alkali lignin, and the calculated values were consistent.
4. Acetone was found to be a moderate solvent for alkali lignin.

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