Alcell® Lignin Solubility in Ethanol–Water Mixtures

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SYNOPSIS

The lignin solubility in aqueous solutions of different ethanol concentrations was studied. The concept of the solubility parameter was applied to account for the effect of ethanol concentration on the lignin solubility. Experimental results showed that the lignin solubility increased strongly as the ethanol concentration increased from 9.5 to 47.5%; then, it increased much more slowly until a maximum was reached at an ethanol concentration of about 70%. Further increase in the ethanol concentration resulted in a slight decrease in the lignin solubility. Based on the lignin molecular formula, the solubility parameter (δ-value) of the ALCELL® lignin was 13.7 $(cal/cm^3)^{1/2}$. The δ-value of aqueous ethanol solutions of increased ethanol concentration was calculated and was found to decrease continuously from 22.31 $(cal/cm^3)^{1/2}$ for pure water to 12.08 $(cal/cm^3)^{1/2}$ for pure ethanol. The effect of ethanol concentration on the solubility of the ALCELL lignin was then explained based on the theory that lignin exhibited the maximum solubility when the δ-value of the solvent was close to that of the ALCELL lignin and the H-bonding capacity of the solutions with different ethanol concentrations was similar. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Lignin and carbohydrates are the main constituents in wood, and the former acts as a "glue" to bind the fibers together. The pulping process is to remove lignin from wood so that fibers can be separated from each other. The ALCELL® process is an ethanol-based organosolv pulping process, which is currently being developed by Repap Enterprises. Unlike the kraft process, no alkali is added to the cooking liquor and there is no requirement for a complex and expensive recovery boiler and lime kiln. The lignin- and hemicellulose-derived products are valuable products. In addition, the ALCELL pulping process offers significant environmental advantages when compared with conventional pulping processes. Therefore, it has been concluded[1] that the ALCELL process will become an increasingly important alternative pulping process in the near future.

Since, the ALCELL process utilizes the good solubility of lignin in a solvent system consisting of ethanol and water, characterization of lignin solubility in aqueous ethanol solutions is of direct importance for the ALCELL process. However, the solubility of lignin in the ethanol–water mixture as a function of the ethanol concentration has never been studied. The objectives of this article were, therefore, to determine the lignin solubility in ethanol–water mixtures and to explain the effect of ethanol concentration on the lignin solubility.

EXPERIMENTAL

The sample used in this study was the ALCELL lignin which was received from ALCELL Developments Inc. located in Newcastle, NB, Canada. Its chemical composition and other related properties are listed in Table I. Reagent ethanol, 95.0%, was used throughout this study. Solutions of different ethanol concentrations were made by adding the required amount of purified water into 95.0% ethanol.

The following steps were performed in the experimental procedure:

1. Dissolve lignin in the ethanol solution.

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Journal of Applied Polymer Science, Vol. 57, 1441–1446 (1995)
 CCC 0021-8995/95/121441-06

Table I Chemical Composition and Other Related Properties of the ALCELL Lignin

Carbon (%)	65.13
Hydrogen (%)	5.72
Methoxyl (%)	19.0
H/C_9	7.26
O/C_9	2.17
OCH_3/C_9	1.15
Mol wt (C_9)	185.4
T_g (C)	93.0
Moisture (%)	0.3
Ash (%)	0.8
Wood sugar (%)	< 0.5
Specific gravity	1.27

2. Separate the undissolved lignin by filtration.
3. Determine the dissolved lignin concentration by UV.
4. Determine the undissolved lignin gravimetrically.

A 30 mL vial was used to contain the weighted amount of lignin. The ethanol solution was slowly added to the vial. Mixing was provided by an ultrasonic bath for about 3 h to ensure that the maximum solubility was achieved.

The filtration was performed in a fritted glass crucible. The lignin concentration in the filtrate was analyzed in a UV spectrophotometer (Spectronic 1001 plus spectrophotometer) at 280 nm. The undissolved lignin in the vial and crucible was determined by the weight difference with and without the residual lignin.

RESULTS AND DISCUSSION

Lignin Mass Balance

To ensure the accuracy of the experimental procedure and analytical methods, the lignin mass balance during the solubilization was determined by comparing the input lignin with the sum of dissolved and undissolved lignin, i.e., the lignin mass balance is expressed as

$$W_{in} = [C \times V_t/1{,}000{,}000] + W_r$$

with W_{in} the initial lignin added (g), C the lignin concentration (mg/L), V_t the total volume (mL), and W_r the residual lignin (g).

Two experiments were performed, using ethanol concentrations of 28.5 and 47.5%. The results in Table II show that the lignin mass balance is 97.37 and 95.69%, respectively. In addition, we found that the repeatability of the experiments was within 4%. Therefore, one can conclude that the experimental procedure and analytical methods are reliable.

Effect of Ethanol Concentration

The effect of ethanol concentration on the lignin solubility was first investigated at an assumed lignin concentration of 20,000 mg/L, i.e., 0.2000 g of the ALCELL lignin was dissolved in a 10.0 mL solution. The ethanol concentrations were 9.5, 28.5, 38.0, 47.5, 57.0, 68.5, 71.3, 85.0, and 95.0%. The determined lignin concentrations in the filtrate are shown in Table III. Listed in the last column is the solubility factor, which is defined as the ratio of the determined lignin concentration to the assumed lignin concentration. One can observe that the lignin solubility increases strongly as the ethanol concentration increases. For example, at 9.5% ethanol concentration, the lignin concentration in the filtrate is only 1140.3 mg/L, i.e., only 5.7% lignin is dissolved in solution. However, at 47.5% ethanol concentration, the lignin concentration in the filtrate is 13824.0 mg/L, indicating that 69.1% of lignin is dissolved. This is about 12 times higher in comparison to that in the 9.5% ethanol concentration solution. Table III also shows that the ALCELL lignin solubility increases much more slowly when the ethanol concentration is more than 57.0%, until a maximum is reached at an ethanol concentration of about 70%; further in-

Table II Lignin Mass Balance

Ethanol Concentration (%)	Lignin Input (g)	Lignin Concentration (mg/L)	Residual Lignin (g)	Lignin Mass Balance (%)
28.5	0.4008	4533.4	0.2996	97.37
47.5	0.4023	13247.2	0.1200	95.69

Total volume: 20 mL, 23°C.

Table III Effect of Ethanol Concentration on Lignin Solubility at 23°C and an Assumed Lignin Concentration of 20,000 mg/L

Ethanol Concentration (%)	Actual Lignin Concentration (mg/L)	Solubility Factor
9.5	1,140.3	0.057
28.5	4,582.0	0.229
38.0	8,959.0	0.448
47.5	13,824.0	0.691
57.0	16,798.9	0.840
68.5	18,020.2	0.901
71.3	18,673.4	0.934
85.0	17,780.4	0.889
95.0	16,656.4	0.833

Total volume: 10.0 mL.

crease in the ethanol concentration leads to a slight decrease in the solubility factor.

Additional experiments of an assumed lignin concentration of 40,000 mg/L were performed to confirm the above observation. The results are shown in Figure 1. Included are also the results from the assumed lignin concentration of 20,000 mg/L. It shows that the two sets of data support each other and that the lignin solubility is strongly dependent on the ethanol concentration.

How can one explain this experimental finding? It has been suggested[2] that the ability of solvents to dissolve lignin can be characterized by the solubility parameters (δ-values) of the solvents and their hydrogen-bonding capacities. Generally, polymers, such as lignin, exhibit a maximum solubility in solvents with δ-value close to their own. Also, the lignin-dissolving property increases as the hydrogen-bonding capacity of the solvent increases when it is in an optimal δ-value.

The solubility parameter or δ-value was first identified by Hildebrand and Scott[3] as the square root of a substance's cohesive energy density. It is defined by the equation

$$\delta = (E/V)^{1/2}$$

where (E) is the energy of vaporization at zero pressure, and V, the molar volume. Therefore, to apply these concepts, the δ-value of the ALCELL lignin and those of the ethanol–water mixtures were determined.

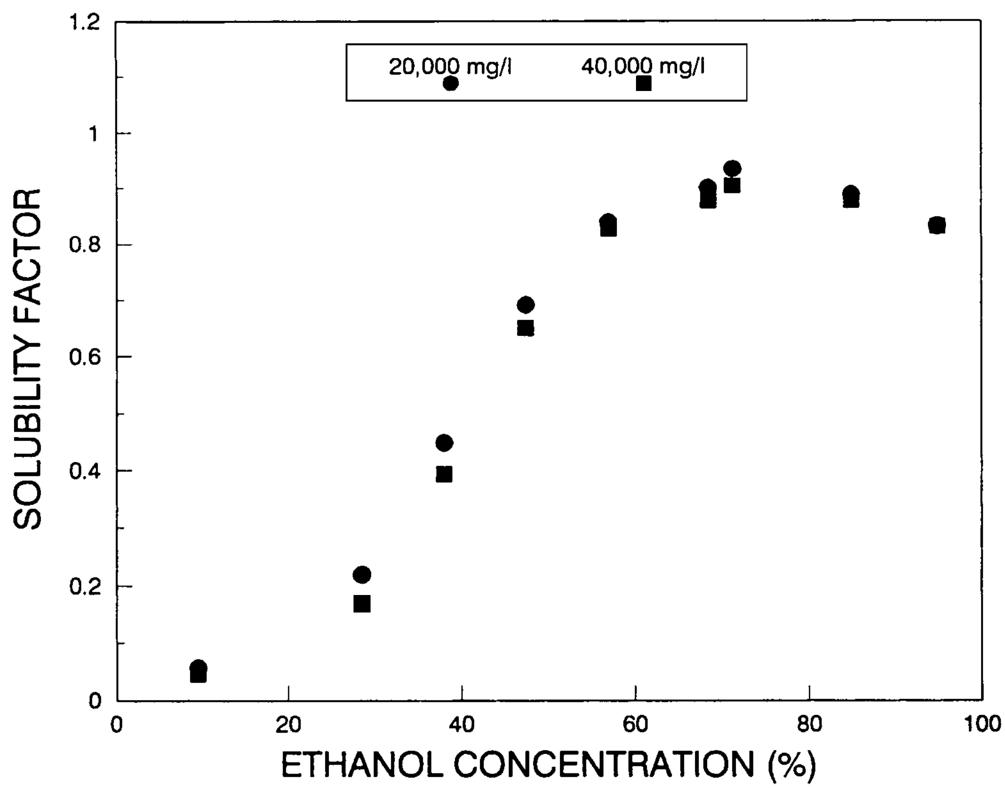

Figure 1 Effect of ethanol concentration on lignin solubility at the assumed lignin concentrations of 20,000 and 40,000 mg/L.

Table IV Calculation of δ-Value of Constructed Lignin

Atom or Group	Δe_i (cal/mol)	Δv_i (cm^3/mol)
	(a)	
OH	7,120	10.0
CH_2	1,180	16.1
C═	1,030	−5.5
CH	820	(−1.0)
Phenyl (trisubstituted)	7,630	33.4
CH_3	1,125	33.5
2 × O	2 × 800	2 × 3.8
Δv_i	$\Delta v_i = 2 \times n = 2 \times 9 = 18$	
Total	20,505	112.1
	(b)	
2 × OH	2 × 7,120	2 × 10.0
CH_2	1,180	16.1
2 × CH	2 × 820	2 × (−1.0)
Phenyl (tetra-substituted)	7,630	14.4
2 × CH_3	2 × 1,125	2 × 33.5
3 × O	3 × 800	3 × 3.8
Δv_i	$\Delta v_i = 2 \times n = 2 \times 9 = 18$	
Total	29,340	144.9
	(c)	
OH	7,120	10.0
CH_2	1,180	16.1
CH	820	−1.0
C═	1,030	−5.5
Phenylene (*p*)	7,630	52.4
2 × O	2 × 800	2 × 3.6
Δv_i	$\Delta v_i = 2 \times n = 2 \times 9 = 18$	
Total	19,380	97.2

The δ-Value of ALCELL Lignin

There are a few methods proposed in the literature[4] to estimate the δ-value of a polymer:

1. The equilibrium swelling of a polymer is determined in variety of solvents which have a wide range of δ-values. The extent of swelling will be a maximum when the δ-value of the solvent matches that of the polymer.
2. The intrinsic viscosity of a polymer is measured in a series of solvents. The δ-value for the polymer is taken to be the same as that of the solvent in which the polymer has the greatest viscosity.
3. The δ-value of a polymer can also be calculated based on the atomic and functional group contribution if the structure of the repeating unit of the polymer is known. Data of the atomic and functional group contribution to the heat of vaporization and the molar volume is available.[4]

In this study, the third method was used. It is based on the assumption that

$$E = \sum \Delta e_i$$

and

$$V = \sum \Delta v_i$$

where the Δe_i and Δv_i are the additive atomic and functional group contribution for the energy of vaporization and molar volume, respectively.

Table V Calculation of δ-Value for Ethanol–Water Mixture

	Ethanol Concn. (%)										
	0	9.5	28.5	38.0	47.5	57.0	68.5	71.3	85	95.0	100
ΔH (cal/g)	540.0	338.8	298.5	288.1	278.5	268.5	254.1	252.3	230.0	219.2	200.0
T (K)	373.0	363.7	356.6	355.1	353.9	352.9	352.0	351.5	351	350.7	350.8
Density (g/cm^3)	0.9982	0.9819	0.9538	0.9352	0.9138	0.8911	0.8626	0.8556	0.8241	0.8012	0.7893
MW (g/g mol)	18.00	19.10	21.78	23.42	25.32	27.56	30.87	31.80	37.34	42.68	46.00
ΔH (cal/mol)	9720	6472	6500	6746.8	7051	7399	7844	8024	8581	9357	9200
δ (cal/cm^3)$^{1/2}$	22.41	17.19	15.93	15.53	15.14	14.72	14.12	14.04	13.19	12.75	12.08

To calculate the δ-value of the ALCELL lignin, the structural elements and functional groups of the ALCELL lignin need to be known. The empirical molecular formula for the ALCELL lignin is $C_9H_{7.26}O_{2.17}(OCH_3)_{1.15}$ based on the chemical analysis shown in Table I. Since the functional-group contribution to the energy of vaporization and molar volume is not simply the sum of the atomic contribution,[4] it is necessary to include as many of the functional groups as possible. Therefore, the ALCELL lignin is approximated to be made of three repeating units Structures **I, II,** and **III** (Fig. 2) representing the guaiacyl (G) type of lignin, the syringyl (S) type of lignin, and the *p*-hydroxyphenyl (H) type of lignin, respectively.

The ratio of G : S : H of 76 : 20 : 4 is chosen to represent the ALCELL lignin in consideration of (1) the determined molecular formula of the ALCELL lignin, (2) the H-type lignin of 4% in the example given for hardwood,[5] and (3) the syringyl content of a typical hardwood lignin of 20%.[5] The constructed lignin monomer Structures **I, II,** and **III,** have the molecular formulas of $C_9H_7O_2(OCH_3)_1$, $C_9H_8O_3(OCH_3)_2$, and $C_9H_8O_3(OCH_3)_0$, respectively. By taking into account their respective molar ratios, we can obtain the overall constructed lignin formula of $C_9H_{7.24}O_{2.24}(OCH_3)_{1.16}$, which is very close to the determined molecular formula of the ALCELL lignin.

The δ-values are then calculated, as shown in a, b, and c of Table IV for Structures **I, II,** and **III,** respectively. Δv_i is a correction factor for the higher glass transition temperature (T_g) of the ALCELL lignin of 93°C, as shown in Table I. It was proposed[4] that for high molecular weight polymers, such as lignins which have a T_g of greater than 25°C, the divergence in the V values can be taken into account by the introduction of small correction factors, namely:

$$\Delta v_i = 4n, \; n < 3$$

$$\Delta v_i = 2n, \; n \geq 3$$

n is the number of main-chain skeletal atoms in the smallest repeating unit of the polymer. Since lignin consists of phenyl propane units, nine skeletal atoms are considered at the present time.

The δ-values for Structures **I, II,** and **III** thus obtained are 13.5, 14.2, and 14.1 (cal/cm^3)$^{1/2}$, respectively. The average solubility parameter for the ALCELL lignin is therefore 13.7 (cal/cm^3)$^{1/2}$, in consideration of their molar ratios.

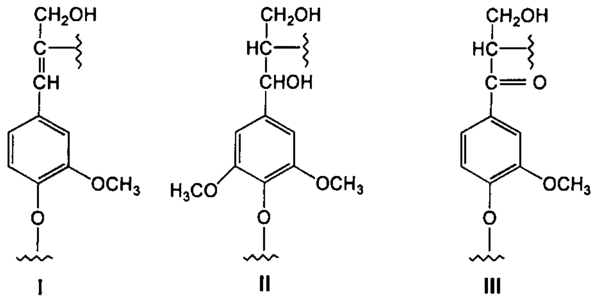

Figure 2 The repeating units of ALCELL lignin.

δ-Value for the Ethanol–Water Mixture

It was suggested[2] that the solubility parameter for a low molecular weight liquid can be calculated as follows:

$$\delta\text{-value} = [(\Delta H - RT) \times \text{s.g./MW}]^{1/2}$$

where ΔH is the heat of vaporization in cal/mol; T, the bp, K; s.g., the specific gravity; and MW, the molecular weight.

All the required data, i.e., heat of vaporization, boiling point, and specific gravity, were obtained from Ref. 6. The results are summarized in Table V. It shows that the δ-value of the ethanol–water mixture decreases continuously as the ethanol concentration increases. For example, the δ-values for pure water, 47.5% ethanol solution, and pure ethanol are 22.3, 15.14, and 12.08 $(\text{cal/cm}^3)^{1/2}$, respectively.

The hydrogen-bonding capacity of the ethanol–water mixture was studied throughout the entire range of composition by Coccia et al.[7] They found that the hydrogen-bonding capacity hardly changes as an increasing amount of ethanol is added to water. This is supported by the theoretical study carried out by Laiken and Nemethy[8] that the water–water and water–ethanol hydrogen-bond energies have approximately the same value of 3.57 kcal/mol.

GENERAL DISCUSSION AND SUMMARY

The experimental results show that the solubility of the ALCELL lignin in ethanol–water mixtures increases strongly as the ethanol concentration increases from 9.5 to 47.5%, then it increases much more slowly until a maximum is reached at an ethanol concentration of about 70%. The practical implication of this finding is that during the ALCELL pulping operation, such as cooking and washing, the optimum ethanol concentration for lignin removal is in the range of 55–70%.

The effect of ethanol concentration on the solubility of the ALCELL lignin can be explained by the δ-value theory, i.e., the ALCELL lignin has the maximum solubility when the δ-value of the solvent is close to its own and when the H-bonding capacity of the solvent is similar. The δ-value of the ALCELL lignin was calculated as 13.7 $(\text{cal/cm}^3)^{1/2}$. Therefore, one would expect that the ALCELL lignin would have the maximum solubility when the δ-value of an ethanol–water mixture is around 13.7 $(\text{cal/cm}^3)^{1/2}$. The δ-value for increasing ethanol concentration solutions decreases from 22.3 $(\text{cal/cm}^3)^{1/2}$ for pure water to 12.08 $(\text{cal/cm}^3)^{1/2}$ for pure ethanol. The maximum solubility of the ALCELL lignin observed in this study is at an ethanol concentration of about 70%; its δ-value is, indeed, very close to that of the ALCELL lignin. Further increase in the ethanol concentration leads to a slight decrease in the solubility of the ALCELL lignin.

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Received October 25, 1994
Accepted March 10, 1995