

## Solution Properties of Lignin. Thermodynamic Properties and Molecular Weight Determinations

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### Synopsis

Number-average molecular weights and the thermodynamic parameters  $\Delta\bar{F}_1$ ,  $\Delta\bar{H}_1$ , and  $\Delta\bar{S}_1$  have been obtained for lignin in the solvents dimethylsulfoxide, dimethylformamide, and dioxane. Widely different molecular weights were found in the different solvents and at the different temperatures as a consequence of molecular association. Analysis of the thermodynamic parameters revealed that these quantities are dominated by the change in solvent structure accompanying the solution process. A correlation between the "goodness" of a lignin solvent and the Hildebrand solubility parameter is consequently misleading in such systems.

### INTRODUCTION

Widely differing data are to be found in the literature on the molecular weights of lignins, leading to a measure of uncertainty in the interpretation of their structures as macromolecules. Recent work by Benko<sup>1</sup> and Gross et al.,<sup>2</sup> however, indicates that a prime cause of the variation lies in molecular association which, it is concluded, is to a large extent responsible for the actual molecular weight measured under any given set of conditions, for example, in different solvents. Consequently, if we are to form a more soundly based picture of lignin structure, the nature of the interactions of lignin with its solvents needs to be clarified.

To elucidate the degree to which lignin-solvent interactions can influence the apparent molecular weights, it was decided to use the technique of vapor pressure osmometry.<sup>4</sup> The latter provides for low molecular weight materials a measure of the thermodynamic interaction between solute and solvent in addition to the number-average molecular weight. Hitherto, vapor-pressure osmometry has been little used to obtain thermodynamic data and the results presented below illustrate the versatility of this comparatively new instrument.

Three solvents covering a range of polar character were chosen for the study (Table I). The vapor pressure measurements were made at two temperatures to allow estimates of the thermodynamic parameters  $\Delta\bar{F}_1$ ,

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TABLE I  
Physical Properties of Solvents

Solvent	Source	Molecular weight	Boiling point, °C.	Density $\rho_{25}$ , g./ml.	Viscosity, $\eta_{25}$ , cp.	Dielectric constant $\epsilon$	Dipole moment, $D$	Solubility parameter $\delta_s$ , (cal./cc.) <sup>1/2</sup>
Dimethylsulfoxide	Fisher	78.14	189	1.099	2.01	45.0	3.9	13.0
Dimethylformamide	Eastman	73.0	153	0.945	0.80	36.7	3.8	12.1
Dioxane	Fisher	88.11	101	1.034	1.70	2.2	0.0	10.0

$\Delta\bar{H}_1$ , and  $\Delta\bar{S}_1$  associated with the mixing process. The results are discussed in terms of current concepts of lignin and solvent structures.

## EXPERIMENTAL

### Solvents and Materials

The solvents used were: dimethylsulfoxide (DMSO), dimethylformamide (DMF), and dioxane. The DMF and dioxane were used as purchased, while the DMSO was further purified by vacuum distillation. Table I summarizes some of the physical characteristics of these liquids.

Lignin (softwood, kraft), REAX 20, was obtained from Polychemicals Division, West Virginia Pulp & Paper Company, Charleston, South Carolina. It was stored over  $P_2O_5$  prior to use. The lignin composition is given in Table II.

TABLE II  
Analyses for Lignin (Pine Kraft)

Component	Content, %
OCH <sub>3</sub>	14.35
C	66.5
H	5.9
O	25.9
S	1.6
Ash	0.2

Solutions were prepared on a weight-weight basis (g./100 g. solvent) and the concentrations corrected for moisture (2%) and ash content (0.2%).

### Measurements of Vapor Pressure Lowering

Measurements were made in a Mechrolab, Model 301, vapor pressure osmometer (F and M Scientific Division of Hewlett-Packard, Avondale, Pa.). For practical details of the use of the instrument the literature provided by the manufacturers should be consulted.

The instrument was calibrated with each solvent and at each temperature (65 and 39°C.); the apparatus constants are collected in Table III.

TABLE III  
Calibration Constants for Vapor-Pressure Osmometer

Solvent	39°C.		65°C.	
	<i>K</i> (molal)	<i>K</i> <sub>4</sub> (mole fraction)	<i>K</i> (molal)	<i>K</i> <sub>4</sub> (mole fraction)
Dimethylsulfoxide	21.3	273	21.3	273
Dimethylformamide	79.0	1080	56.0	740
Dioxane	292	3320	141	1680

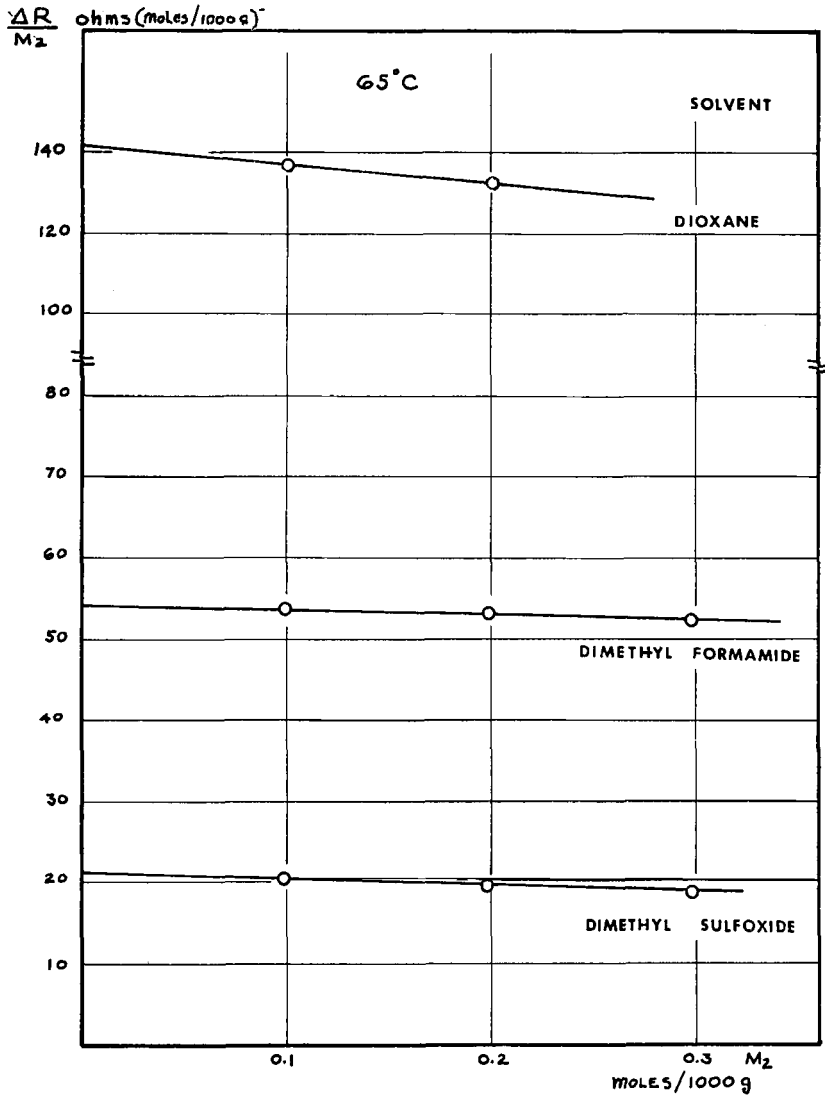


Fig. 1. Calibration data for vapor pressure osmometer with various solvents at 65°C.

Typical calibration curves,  $\Delta R/m_2$  versus  $m_2$  are depicted in Figure 1, where  $m_2$  is the concentration of the calibration solute expressed in moles per 1000g. solvent and  $\Delta R$  is the measured resistance change. Benzil (M.W. = 210.0) was used as the calibration substance. With the exception of DMSO, a 3 min. period was adequate to establish the steady-state temperature difference. DMSO solutions required 20 min.; there was, however, no "creep" of the galvanometer needle subsequent to this time interval.

Lignin solutions were measured in the concentration interval 10–30 g./100 g. solvent. Average values of triplicate determinations of  $\Delta R$  were taken

at each concentration and used to calculate the  $\Delta R/C$  values (see following section). As a further check on the calibration constants and to see if there were any unusual effects with lignin-like compounds, measurements were made on curcumin (M.W. = 368.4). Values of the molecular weight were obtained within 5% of this figure in the solvents used.

### Calculation of Activities and Thermodynamic Parameters

As conventionally employed, the prime purpose of the commercial form of the vapor pressure osmometer is the determination of number-average molecular weights,  $\bar{M}_n$ . The principle on which the instrument is based is the thermoelectric method first described by Hill<sup>3</sup> and involves the measurement of the small temperature difference resulting from different rates of solvent evaporation from drops of pure solvent and solution in an atmosphere of solvent vapor. If solvent activities are required, it is necessary to make the assumption which, however, appears to be well founded,<sup>4</sup> that the indirectly measured temperature difference is proportional to the difference in chemical potential between the pure solvent and the solvent in the solution; i.e.

$$\Delta T = K_1 \Delta \mu_1 \quad (1)$$

The steady-state temperature difference  $\Delta T$  is estimated by placing drops of solvent and solution on two matched thermistor beads; the change in resistance  $\Delta R$  is then measured by means of a Wheatstone bridge.

$$\Delta R = K_2 \Delta T \quad (2)$$

The chemical potential of the the solvent may be expressed:

$$\Delta \mu_1 = -RT \ln a_1 = gRTN_2 \quad (3)$$

where  $a_1$  is the solvent activity,  $g$  the rational activity coefficient,  $N_2$  the mole fraction of solute, and  $R$  and  $T$  the gas constant and absolute temperature, respectively. From eqs. (1), (2), and (3) we get

$$\Delta R = K_3 gRTN_2 = K_4 gN_2 = -K_4 \ln a_1 \quad (4)$$

The activity coefficient  $g$  approaches unity as  $N_2$  approaches zero, i.e.,

$$\lim_{N_2 \rightarrow 0} \Delta R/N_2 = K_4 \quad (5)$$

$K_4$  is a calibration constant (see Table III) for a particular solvent and temperature, obtained by measuring  $\Delta R$  at a series of concentrations for a solute of known molecular weight. Plotting  $\Delta R/N_2$  versus  $N_2$  yields  $K_4$  as the ordinate intercept. From the relationship:

$$\Delta R/K_4 = -\ln a_1 \quad (6)$$

one may evaluate the activity of the solvent  $a_1$  in solutions of the solute being studied. In terms of the usual molal calibration constant, as employed when calculating molecular weights, we should have

$$\Delta RM_1/(K \ 1000) = -\ln a_1 \quad (7)$$

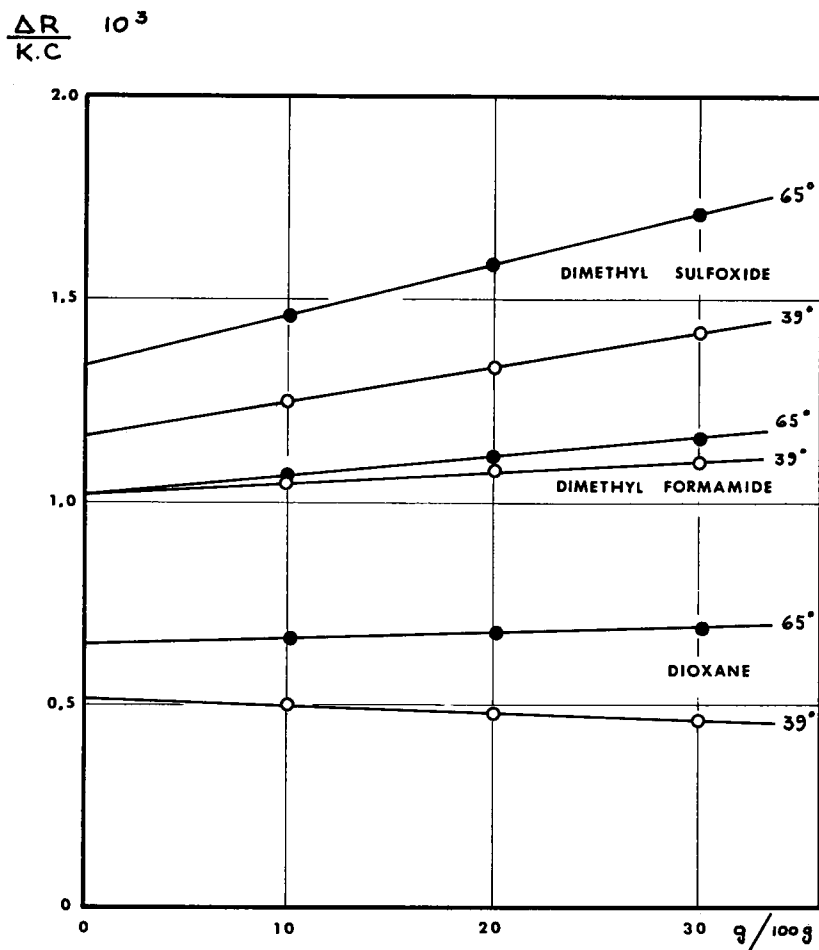


Fig. 2. Plots of  $\Delta R/KC$  at 39 and 65°C. for kraft lignin. The intercepts correspond to  $1/\bar{M}_n$  according to:  $(\Delta R/KC) = (1/\bar{M}_n) + bc + \dots$

$K$  is obtained as the ordinate intercept on plotting  $\Delta R/m_2$ , where  $m_2$  is the molal concentration of the calibration solute and  $M_1$  the solvent molecular weight. Number-average molecular weights are obtained by plotting  $\Delta R/C$  versus  $C$  ( $C$  expressed in grams per 1000 g. solvent) and dividing  $K$  by the ordinate intercept.

$$K/(\Delta R/C)_{c=0} = \bar{M}_n \quad (8)$$

The free energy of dilution is obtained from:

$$\Delta \bar{F}_1 = RT \ln a_1 \quad (9)$$

The thermodynamic parameters  $\Delta \bar{H}_1$  and  $\Delta \bar{S}_1$  may be derived if measure-

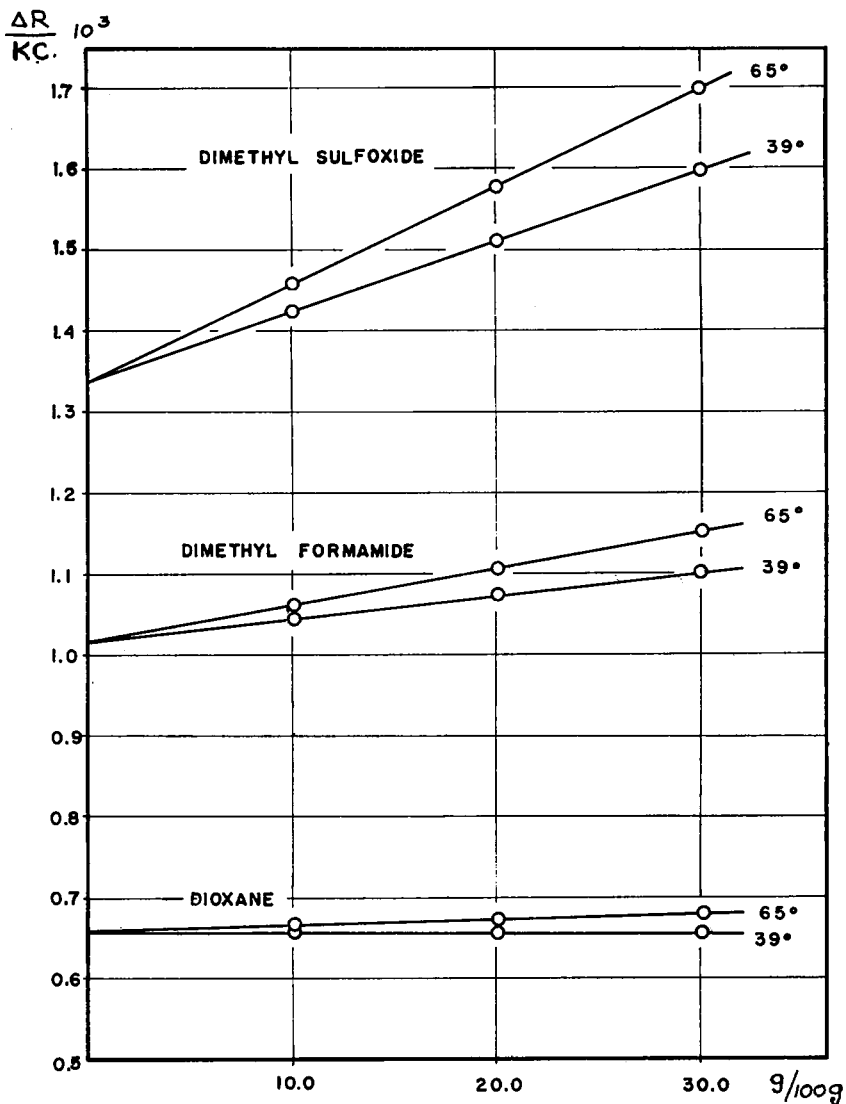


Fig. 3. Plots of  $\Delta R/KC$  vs.  $C$  for lignin at temperatures of 39 and 65°C. The slopes are proportional to the solute-solvent interactions.

ments of  $\Delta R$  are made at two or more temperatures. The following relationships are then applicable:

$$\Delta \bar{H}_1 = \delta(\Delta \bar{F}_1/T)/\delta(1/T) \quad (10)$$

and

$$-\Delta \bar{S}_1 = \delta \Delta \bar{F}_1/\delta T \quad (11)$$

## RESULTS

Plots of  $\Delta R/KC$  are shown in Figure 2 for lignin in the solvent series at both temperatures. The relationship (12) applies:

$$\Delta R/KC = (1/\bar{M}_n) + bc + \dots \quad (12)$$

If the concentration is expressed in grams per milliliter,  $c'$ , eq. (12) becomes:

$$(\Delta R/K'c') = (1/\bar{M}_n) + Bc' + \dots \quad (13)$$

where  $B$  is the second virial coefficient and is a measure of the solute-solvent interactions. Values of  $\bar{M}_n$  and  $B$  are collected in Table IV. Thermodynamic parameters were evaluated following the procedure outlined in the preceding section. For those solvents where significantly lower molecular weights were obtained at the two temperatures (DMSO and dioxane) the points at the lower temperature have been displaced vertically

TABLE IV  
Molecular Weight Data

Solvent	65°C.		39°C.	
	$\bar{M}_n$	$B \times 10^4$	$\bar{M}_n$	$B \times 10^4$
Dioxane	1520	0.7	1920	negative
Dimethylformamide	990	4.5	980	2.5
Dimethylsulfoxide	740	12.5	860	8.5

TABLE V  
Activities and Free Energies

Temperature, °C.	Solvent	$C$ , g. 100 g.	$\Delta R$ , ohms	$\Delta R \times 10^3/K_4$ ( $-\ln a_i$ )	$-\Delta \bar{F}_1$ ,
					cal./mole ( $-RT \ln a_i$ )
65	Dimethylsulfoxide	10	3.11	11.40	7.7
		20	6.74	24.70	16.6
		30	10.88	40.0	26.9
	Dimethylformamide	10	5.96	7.79	5.2
		20	12.40	16.20	10.9
		30	19.30	25.20	17.0
	Dioxane	10	9.38	5.86	3.9
		20	18.98	11.86	8.0
		30	28.80	18.0	12.1
39	Dimethylsulfoxide	10	3.04	11.1	6.9
		20	6.45	23.6	14.7
		30	10.23	37.5	23.3
	Dimethylformamide	10	8.26	7.65	4.7
		20	17.0	15.7	9.8
		30	26.1	24.2	15.0
	Dioxane	10	19.2	5.79	3.6
		20	38.3	11.52	7.2
		30	57.4	17.30	10.7



to bring the intercepts into coincidence (Fig. 3). This is necessary as the temperature coefficient of  $\Delta R/KC$  would otherwise be greater than if the molecular weight were unaltered and the thermodynamic parameters consequently larger than their true values. This procedure is justified because the change in molecular weight is an artefact resulting from the altered thermodynamic interactions. The slopes, however, are changed insignificantly by the small displacements. The thermodynamic parameters are listed in Tables V and VI.

TABLE VI  
Thermodynamic Parameters at 52°C.

Solvent	$C$ , g./100 g.	$\Delta\bar{F}_1$ , cal./ mole	$\Delta\bar{H}_1$ , cal./ mole	$T\Delta\bar{S}_1$ , cal./ mole	$T\Delta\bar{S}_1$ (ideal), cal./mole
Dimethylsulfoxide	10	-7.3	2.5	9.8	6.3
	20	-95.6	9.1	24.7	12.6
	30	-25.1	17.1	42.2	18.9
Dimethylformamide	10	-4.9	1.3	6.2	4.8
	20	-10.3	3.8	14.1	9.6
	30	-16.0	8.8	24.8	14.4
Dioxane	10	-3.8	0.6	4.4	3.3
	20	-7.6	2.9	10.5	6.6
	30	-11.5	5.8	17.3	9.9

TABLE VII  
Molecular Weights for Kraft Lignin

Solvent	Molecular weight <sup>a</sup>	Technique	Ref.
Tetrahydrofuran	1570	Vapor-pressure osmometry	13
Dioxane	1600	Vapor-pressure osmometry	13
Methyl cellosolve	1680	Vapor-pressure osmometry	13
Dioxane	1580	Cryoscopy	2
Ethylene carbonate	1020	Cryoscopy	2
Tetrahydrofuran	3500 <sup>b</sup>	Sedimentation Equilibrium	13

<sup>a</sup>  $\bar{M}_n$  unless otherwise noted.

<sup>b</sup>  $\bar{M}_w$ .

## DISCUSSION

The values of the molecular weights  $\bar{M}_n$  listed in Table IV vary considerably, the magnitude being dependent on the solvent and temperature. The values obtained in DMSO and DMF are significantly lower than those previously reported (Table VII); the latter are more in agreement with the values in dioxane.

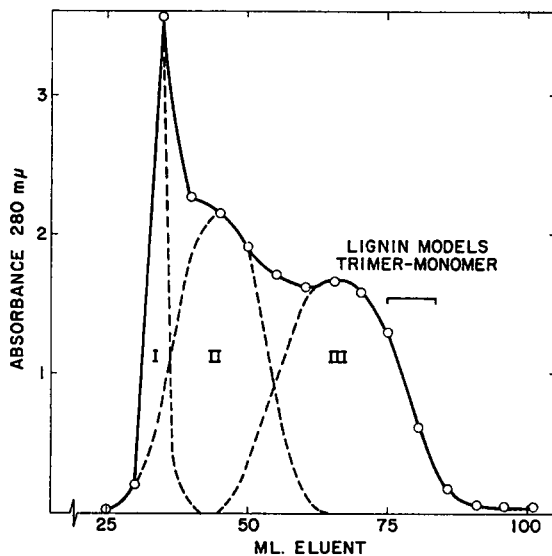


Fig. 4. Molecular size distribution obtained for kraft lignin on Sephadex (G50) with formamide as solvent. Zone I represents excluded material, zone II material of molecular weight 5,000–10,000 and zone III corresponds to molecular weight of approximately 1000.

The second virial coefficient  $B$  increases as the molecular weight decreases in the respective solvents. As  $B$  is a measure of the thermodynamic interaction between solute and solvent, this shows that the variation in molecular weight is a result of lignin association, which diminishes as the solvent becomes "better."

A variation in apparent molecular sizes in different solvents has recently been reported by Benko<sup>1</sup> by means of a technique involving diffusion through a porous glass disk. This author also concluded that association is responsible to a large extent for the molecular weights of lignins under any given set of conditions. It should be emphasized that the molecular weights reported by Benko are relative values (determined relative to potassium chloride and phenol) and cannot be compared with either  $\bar{M}_n$  or  $\bar{M}_w$  obtained for a polydisperse material such as lignin.

Lindberg<sup>5</sup> studied hydrogen bonding in a thiolignin by infrared spectroscopy and measured the molecular weight of the sample by cryoscopy. He concluded that these lignins exist in solution as three-dimensional aggregates held together by hydrogen bonding and in turn kept in solution by hydrogen bonds to solvent molecules.

As mentioned above, kraft lignin is a polydisperse material. Figure 4 shows a molecular size distribution obtained on Sephadex with formamide as solvent. The lowest molecular size zone (III) corresponds approximately to a trimeric phenyl propane unit. The center zone (II) corresponds to material with a molecular weight of 5,000–10,000. The excluded material (I) is, of course, of even higher molecular weight. The number-average

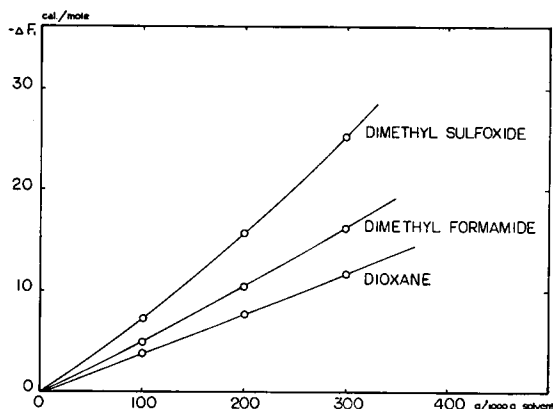


Fig. 5. Free energies of mixing as a function of concentration for lignin in various solvents; the larger  $-\Delta\bar{F}_1$ , the better the solvent.

molecular weight consequently supplies very limited information about the sample. An open question at present is whether the material of molecular weight greater than that of approximately 1,000 consists of molecularly associated lignin or if it is made up of covalent macromolecules. Further work is being carried out in an endeavor to settle this point.

It is known that kraft lignin consists of a complex mixture of structures based on the phenyl alkyl backbone and possessing a variety of functional groups. It is experimentally evident that these residues have a pronounced tendency to associate and form more complex structures to a degree dependent on the extent of interaction with the solvent. The lignin presently studied may have little in common, as regards molecular weight, with lignin present in wood, as it is known to be chemically changed by the kraft process. Nevertheless, from the data currently available on the molecular weights of lignin, it does not necessarily follow that lignin in the native state has an "infinite" molecular weight. Resolution of this question must await isolation techniques known to involve little degradation (or condensation) followed by unambiguous molecular weight determinations.

Tables V and VI summarize some thermodynamic properties of lignin in dimethyl sulfoxide, dimethylformamide, and dioxane. Figure 5 shows plots of  $\Delta\bar{F}_1$  versus concentration. The better the solvent the more negative is  $\Delta\bar{F}_1$ . The latter quantity sums the interactions between solvent and solute; for a more thorough understanding, it is necessary to break down  $\Delta\bar{F}_1$  into its enthalpy and entropy components according to the relationship.

$$\Delta\bar{F}_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1 \quad (14)$$

The relative magnitudes of the components are illustrated in Figure 6 for lignin in dimethylsulfoxide. When solute-solvent interactions greatly exceed solute-solute and solvent-solvent interactions, heat is evolved on solution, and  $\Delta\bar{H}_1$  will be negative. This behavior occurs in systems where

there is solvation and orientation of solvent molecules in the vicinity of the solute molecules. By solvation we mean that there are specific solute-solvent interactions, and some of the latter may be considered as bound to the solute. Systems exhibiting negative values of  $\Delta\bar{H}_1$  are, for example, cellulose trinitrate in acetone and cellulose triacetate in dioxane.<sup>6</sup> When  $\Delta\bar{H}_1$  values are negative, or small but positive, the entropy quantity  $T\Delta\bar{S}_1$  is also found to be small and close to the ideal value, indicating an extensive ordering of solvent.

Normally, however, solution is accompanied by an absorption of heat, i.e.,  $\Delta\bar{H}_1$  is positive, as the enthalpy contribution derives from the usual

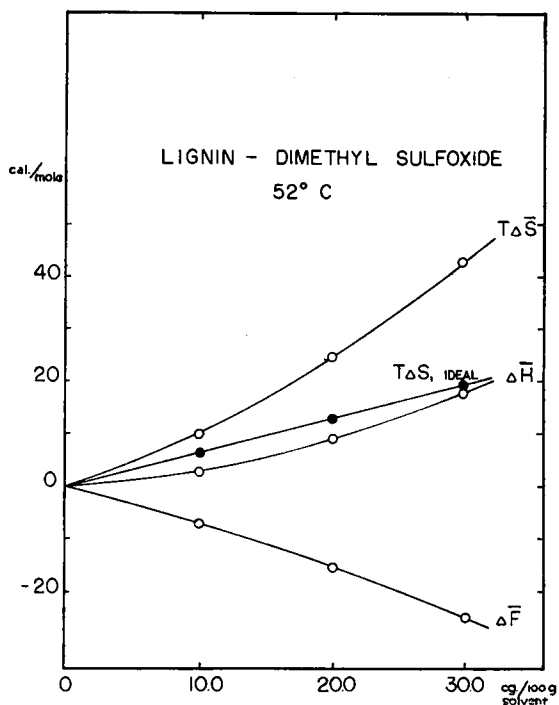


Fig. 6. Values of the thermodynamic interaction parameters for solutions of lignin in dimethylsulfoxide at 52°C. according to the equation:  $\Delta\bar{F}_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1$ .

endothermal dilution effects and the latter are normally greater than exothermal solvation effects. Mixing of solute and solvent also involves a considerable increase in entropy so that  $\Delta\bar{F}_1$  remains negative and the solution process is spontaneous.

Reference to Table VI shows that in all three solvents  $\Delta\bar{H}_1$  values are large and positive and increase with the polar nature of the solvent. It is probable that lignin forms hydrogen-bonded complexes with these highly polar solvents. This is because very strong solute-solvent interaction is necessary to overcome the attractive forces between lignin molecules which

are the cause of the observed association. One would consequently expect that the  $\Delta\bar{H}_1$  values would be negative or at least show small positive values. This is not the case here, however, because the above reasoning ignores an important feature of polar organic solvents which is their considerable degree of internal structure. Dimethylsulfoxide,<sup>7,8</sup> for example, is known to have three-dimensional network and chain structures at room temperature. The same phenomenon is presumably true for dimethylformamide, though to a smaller degree. Although dioxane is formally nonpolar (Table I), this is a result of internal compensation,<sup>9</sup> and the highly polar carbonyl groups are capable of considerable short-range interaction with each other and with polar groups on solute molecules; as a result dioxane is also an associated liquid. The degree of solvent association is related to the solvent viscosity; values of the latter are included in Table I. By this comparison, dimethylsulfoxide possesses the most internal structure and dioxane and dimethylformamide correspondingly less. Solvents which have an even more developed structure may, of course, be nonsolvents for lignin, the solvent-solvent bonds being stronger than solvent-lignin bonds. As a result, large  $\Delta\bar{H}_1$  values (and  $T\Delta\bar{S}_1$  terms) result from the reduction in order of the solvent structure on formation of the solution. These effects dominate the picture and overshadow the thermodynamic effects arising from the conventional interaction of the lignin with the solvent. The internal structure of the solvent leads to a restriction in the number of hydrogen bonds between lignin and solvent. This in turn means less heat evolved due to hydrogen bond formation than for the less polar solvents and the heat of mixing term will be greater. Lindberg<sup>10</sup> suggested that the hydrogen-bond accepting capability of lignins may be less than for carbohydrates owing to the appreciably lower oxygen content (30% compared to 50%). Owing to the radically different environments of the oxygen atoms in lignins and carbohydrates, however, this comparison is of dubious value.

Comparison of the estimated  $T\Delta\bar{S}_1$  factors with the values  $T\Delta\bar{S}_1$  (ideal) in Table VI, where  $T\Delta\bar{S}_1$  (ideal) =  $RN_2$ , illustrates their convergence towards low concentrations. This is because additional solvation is possible and there is further orientation of solvent with a corresponding reduction in  $T\Delta\bar{S}_1$ .

Schuerch<sup>11</sup> has pointed out a correlation between the "goodness" of a lignin solvent and the Hildebrand solubility parameter<sup>12</sup>  $\delta_s$  (Table I) and postulated that the solvent should have a  $\delta_s$  value of about 11; this would imply that the  $\delta_s$  value for lignin is close to this figure. If lignin could be regarded as effectively nonpolar, then  $\Delta\bar{H}_1$  should be related to the square of the difference between the  $\delta_s$  values of lignin and solvent. However, although such a correlation is indicated, it should be regarded as an artefact, as lignin itself is quite definitely polar and interacts strongly with the most polar organic solvents. In such cases, as observed above, entropy considerations are of dominant importance owing to the change in solvent order. This is substantiated by the further observation of Schuerch<sup>11</sup> that solvents having similar values of  $\delta_s$  may differ widely in their solvent power and that an additional parameter is required. It was suggested that lignin solubility

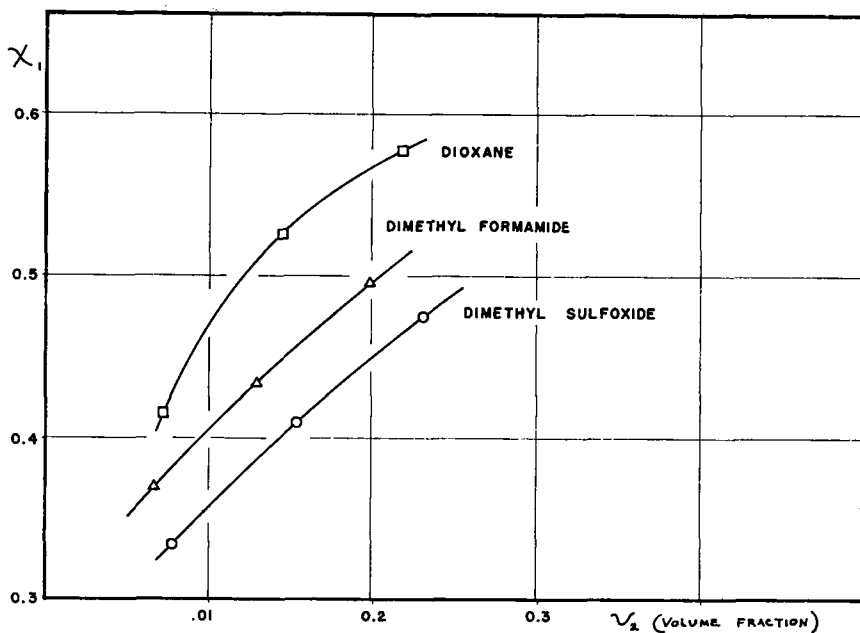


Fig. 7. Flory-Huggins interaction parameter  $\chi_1$  as a function of concentration for lignin in various solvents. The lower the value of  $\chi_1$ , the better (thermodynamically) the solvent.

was better described on the basis of the  $\delta_s$  of the solvent combined with a measure of the ability of the solvent to accept a hydrogen bond.

A widely used index of polymer-solvent interactions is the Flory-Huggins parameter  $\chi_1$ . Values of  $\chi_1$  have been calculated from the relationship

$$\ln a_1 = [\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2] \quad (15)$$

where  $v_2$  is the volume fraction of solute and  $x$  is the number of solute segments, having approximately the same size as a solvent molecule and is given by

$$x = \bar{v} \bar{M}_n / V_1 \quad (16)$$

Here  $\bar{v}$  is the partial specific volume,  $\bar{M}_n$  the molecular weight of the sample, and  $V_1$  the solvent molar volume;  $v_2 = c\bar{v}$ , where  $c$  is the concentration in grams per milliliter. The value  $\bar{v} = 0.70$  has been used<sup>13,14</sup> (there appears to be a negligible change in  $\bar{v}$  in different solvents). Values of  $\chi_1$  are given in Table VIII. In general, the lower the value  $\chi_1$ , the better the solvent.  $\chi_1$  decreases, as would be expected, as the concentration decreases and solubility is enhanced. The relationships between  $\chi_1$  and concentration are shown in Figure 7. The magnitude of  $\chi_1$  is similar to those for cellulosic derivatives and the concentration dependences are also similar. In the highly polar cellulose trinitrate system, however,  $\chi_1$  decreases to negative values as the concentration is increased. In the present work,  $\chi_1$  increases

to above the theoretical value of 0.5 in the solvent dioxane. This has been observed, for example, with cellulose triacetate<sup>6</sup> and presumably reflects the imminence of phase separation; note the slightly negative virial coefficient (Fig. 2) in dioxane at 39°C.

TABLE VIII  
Values of the Flory-Huggins Interaction Parameter  $\chi_1$   
and Enthalpy and Entropy Components at 52°C.

Solvent	$v_2$ , volume fraction	$\chi_1$	$\chi_H$	$\chi_S$	$\delta_s$ , (cal./cc.) <sup>1/2</sup>
Dimethylsulfoxide	0.077	0.34	0.64	-0.30	13.0
	0.154	0.41	0.60	-0.19	
	0.231	0.48	0.50	-0.02	
Dimethylformamide	0.066	0.37	0.35	+0.02	12.1
	0.132	0.44	0.25	+0.19	
	0.198	0.50	0.26	+0.24	
Dioxane	0.073	0.42	0.15	+0.27	10.0
	0.145	0.53	0.19	+0.34	
	0.218	0.58	0.17	+0.41	

$\chi_1$  can be expressed as the sum of heat and entropy contributions

$$\chi_1 = \chi_H + \chi_S$$

with  $\chi_H = \Delta\bar{H}_1/RTv_2^2$ . The lattice theories<sup>15</sup> predict that  $\chi_H$  should be independent of concentration. This is approximately true in dimethylformamide and dioxane and indicates that the lignin approaches limiting solvation in these solvents. The negative values of  $\chi_S$  in the case of dimethyl sulfoxide arise from the large heats of dilution.

We may finally summarize our main conclusions. Kraft lignin is a polydisperse material having a great, and underestimated, propensity for association. It exhibits overall acidic properties and dissolves most completely and with least association in bases and solvents with electron-donor characteristics, i.e., highly polar liquids. At least equally important, however, is the capability of the solvent to form hydrogen bonds with lignin. Good solvents for lignin (referring to those in which lignin is little associated) are highly polar and thus possess varying degrees of internal structure. Consequently, it is the change in solvent structure, rather than the nature of the lignin-solvent interactions, which govern the magnitudes of the estimated thermodynamic parameters.

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### Résumé

Les poids moléculaires moyens en nombre et les paramètres thermodynamiques  $\Delta \bar{F}_1$ ,  $\Delta \bar{H}_1$  et  $\Delta \bar{S}_1$  ont été obtenus pour la lignine dans le diméthyl sulfoxyde, le diméthylformamide, et le dioxane comme solvants. Des poids moléculaires fortement différents ont été trouvés dans les différents solvants et à différentes températures par suite d'associations moléculaires. L'analyse, des paramètres thermodynamiques révèle que ces valeurs sont déterminées par une modification dans les structures des solvants accompagnant le processus de dissolution. Une corrélation entre la qualité d'un solvant pour la lignine et le paramètre de solubilité de Hildebrand est par conséquent sujette à caution pour de tels systèmes.

### Zusammenfassung

Zahlenmittelwerte des Molekulargewichts sowie die thermodynamischen Parameter  $\Delta \bar{F}_1$ ,  $\Delta \bar{H}_1$  und  $\Delta \bar{S}_1$  wurden für Lignin in Dimethylsulfoxyd, Dimethylformamid und Dioxan als Lösungsmittel erhalten. In den verschiedenen Lösungsmitteln und bei den verschiedenen Temperaturen wurden als Folge der Molekülassociation stark unterschiedliche Molekulargewichte erhalten. Die Analyse der thermodynamischen Parameter zeigt, dass diese Größen durch die Änderung der Lösungsmittelstruktur beim Lösungsprozess bestimmt werden. Eine Korrelation zwischen der "Güte" eines Ligninlösungsmittels und dem Löslichkeitsparameter von Hildebrand ist daher in solchen Systemen irreführend.

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