

AN ABSTRACT OF THE THESIS OF

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Title: The Cloud Point Composition and Flory - Huggins
Interaction Parameters of Polyethylene Glycol and Sodium
Lignin Sulfonate in Water - Ethanol Mixtures

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In designing a solubility based separation process for solvent recovery of an organosolv pulping process, the phase behavior of polymeric lignin molecules in alcohol - water mixed solvent should be known. In this study, sodium lignin sulfonates (NaLS) samples were fractionated into three different molecular weight fractions using a partial dissolution method. The cloud point compositions of each of the three fractions were determined by a cloud point titration method. The experimental data were correlated using the three component Flory - Huggins equation of the Gibbs free energy change of mixing. The binary interaction parameter between water and that between ethanol and NaLS were found to be a weak function of the NaLS volume fraction, while that between water and ethanol was strongly depend on the solvent composition.

The Cloud Point Composition and Flory - Huggins
Interaction Parameters of Polyethylene
Glycol and Sodium Lignin Sulfonate
in Water - Ethanol Mixtures

by

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NOMENCLATURES

a	Activity coefficient
B_ϕ, B_x, B_x^0	Slope coefficient of cloud point equation
D_x	Constant in the slope coefficient equation
E, E_i	Energy of vaporization, of component i
$\Delta G, \Delta G_m$	Gibbs free energy change, of mixing
H, ΔH_m	Enthalpy, enthalpy change of mixing
k	Boltzmann constant
M_{av}, M_w, M_n	Average molecular weight of polymer, weight average, number average
N_0	Avogadro's number
N_i	Number of molecules of component i
n_i	Number of moles of component i
n_2	Number of segments in a polymer chain
R	Universal gas constant
S, ΔS_m	Entropy, entropy change of mixing
T, T_2^0	Temperature, temperature of fusion of polymer
V_i	Molar volume of component i
v_i	Specific volume of component i
x, x_2	Number of segments of the polymeric solute in solution
Z	Number of neighboring units of a lattice site
δ	Solubility parameter
ϵ_{ij}	Interaction energy between molecules i and j
$\phi_i, \phi_i^i, \phi_i^\theta$	Volume fraction of component i, at incipient of phase separation, composition

X_H, X_S	The enthalpic, entropic component of X
Ω	Number of possible arrangements when putting N_1 solvent molecules and N_2 polymer chains into $N_1 + xN_2$ lattice sites

Superscripts

i	Incipient of phase separation
o	Infinite dilution
θ	θ composition

Subscripts

1	Solvent
2	Polymeric solute
3	Precipitant
i	Component i
n	Number average, for M_n
m	Mixing
t	Total
w	Weight average, for M_w
ϕ	Volume fraction
X	Interaction parameter

THE CLOUD POINT COMPOSITION AND FLORY-HUGGINS INTERACTION
PARAMETERS OF POLYETHYLENE GLYCOL AND SODIUM LIGNIN
SULFONATE IN WATER - ETHANOL MIXTURE

INTRODUCTION

The phase behavior of synthetic polymers in solvents plays an important role in the polymer industry, in areas such as suspension polymerization, and paint and pigment dissolution. To predict the solubility of synthetic polymers in a solvent, the Flory - Huggins equation gives a good quantitative result. Unlike the synthetic polymers, natural polymers such as protein, polypeptides, nucleic acid, rubber, gutta percha, polysaccharides, and lignins always have non-homogeneous but similar base units, and their molecular weight distributions are broader than those of synthetic polymers. There is no readily available theory to predict the solubilities of these natural polymers in solvents. However, it is necessary to quantify their phase behaviors in solutions when the following applications are considered.

1. Isolation and purification of protein, nucleic acid, etc., using fractional precipitation method⁽¹⁾.

2. Erodible controlled-release of pesticides, antifertility agent, or other human medicines which are encapsulated in a polymeric cover. The latter will gradually dissolve in the body after its application⁽²⁾.

3. Isolation and purification of polysaccharides or lignins as biomass feedstock for other useful chemicals syntheses⁽³⁻⁷⁾.

The present study attempts to apply the Flory - Huggins theory to a model system, i.e., the sodium lignin sulfonate - water - ethanol system, to interpret the phase behavior of a natural polymer in a mixed solvent. The sodium lignin sulfonate, a polydisperse polymer, which comes from the sulfite pulping process is first fractionated into three fractions of high, medium, and low molecular weight. By using the cloud point titration technique⁽⁸⁾, the cloud point compositions of each of the three fractions in mixed solvents of different ethanol to water ratio can be determined. The cloud point compositions, i.e., the volume fraction of each component when in equilibrium, can then be used with the Flory - Huggins equation to obtain the binary interaction parameters.

Lignin sulfonates are polydisperse and complex and each base unit has similar but not the same chemical structure⁽⁹⁾. This might result in a poor agreement between the experimental data and the Flory - Huggins theory. Therefore, as a preliminary study, three samples of polyethylene glycol, each having a Mw to Mn ratio of less than 1.1, were used to test the experimental procedures and the data treatment method.

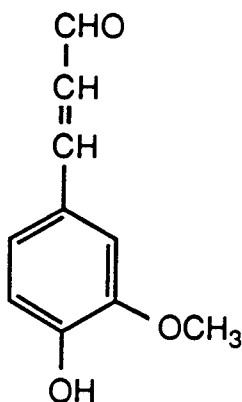
LITERATURE REVIEW

In previous work, experimental data on the solubility of lignins in various solvents were largely interpreted by the solubility parameter concept⁽¹⁰⁾, and only a few of them^(11,12) were correlated using Flory - Huggins polymer solution theory. The latter were published in Finnish. This makes it difficult to compare results from the present study to the earlier research in the field. In the only reference available⁽¹³⁾, the Flory - Huggins interaction parameters were calculated from measurement of the chemical potential difference between solvent and solution, which is totally different from solubility measurements made by cloud point titration as used in the present study. However, the earlier published studies in the related field do provide guidance in experimental methods in sample preparation, cloud point titrations, and data interpretation. Some of them will be reviewed in this chapter. Some basic concepts of polymer solution theories related to the present study will also be reviewed. The Flory - Huggins theory will be discussed in detail in the next chapter as the theoretical background of this study.

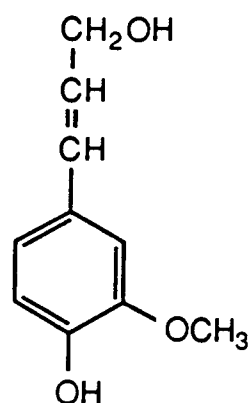
1. On the Characterization of Lignin Sulfonates

A. Lignin Sulfonates

Lignin sulfonates come from sulfonation of lignin. The precursor of lignin sulfonates, i.e., the lignin molecules, are complex, cross-linked polymers of phenyl propanoid units joined largely by benzylic and phenolic ether linkages and carbon-carbon linkages. The degree of polymerization is on the order of several hundreds. The base units are coniferyl aldehyde and coniferyl alcohol. Softwood and hardwood lignins are different. In the former, only one methoxyl group attaches to the benzene ring at the third carbon atom of the benzene ring; in the latter, one more methoxyl group attach to the fifth carbon atom^(3,9). The following chemical structures show the two base units of a softwood lignin.

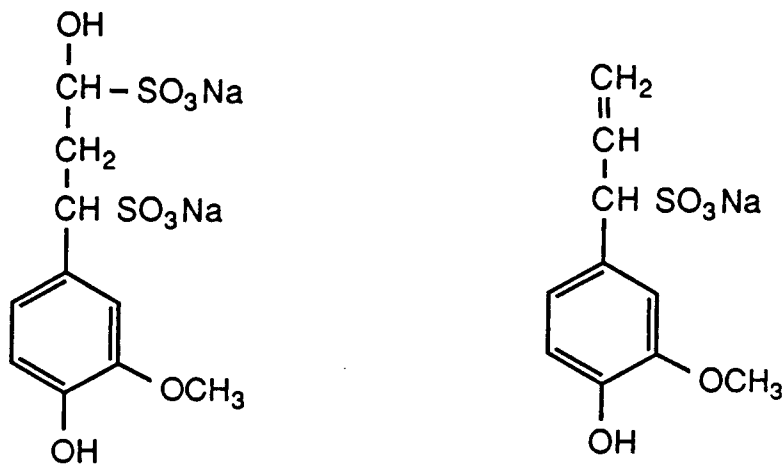


Coniferyl Aldehyde



Coniferyl Alcohol

In nearly neutral sulfite pulping of wood, bisulfite ions, SO_3H^- , attach to the α and γ carbon atoms of the coniferyl aldehyde unit while the coniferyl alcohol unit remains unchanged. In the acidic condition, the carbon atom of the coniferyl alcohol is also attached by a sulfite ion. The above sulfonation reactions result in lignin sulfonic acids. If the sulfite used in the pulping reaction is sodium based, the sulfonation product is sodium lignin sulfonate. The following chemical structures show the two base units of softwood lignin sulfonate⁽¹⁴⁾.



Sodium Lignin Sulfonate

Due to the difficulties in separating the hydrolyzed hemicelluloses and lignins in the lignin sulfonates

production process, the commercially available lignin sulfonates always contain various polysaccharides.

B. Fractionation and Molecular Weight Distribution of Lignin Sulfonates

In 1956, Felicetta et al.⁽¹⁵⁾ studied the molecular weight distribution of lignin sulfonates, which nearly cover all of the lignins from gymnosperm woods. The lignin sulfonates were prepared by pulping saw dust wood meal, and were purified by concentrating the spent liquor under reduced pressure, deashing using cation exchange resin, extraction with ether, and neutralization to pH 5.5 with 1 N NaOH solution, and then vacuum evaporation to a volume appropriate for fractionation. Fractionations were carried out using the above obtained solution. Sufficient sodium chloride was added to it to make a 0.1 N NaCl solution then sufficient amount of absolute ethanol was dropwisely added to the solution to make a solution of 90 % ethanol by volume. The solution was stirred vigorously and centrifuged. The clear supernatant solution was concentrated and dried to get the low molecular weight fraction, while the settled solids were redissolved in water/ethanol to prepare a solution of the higher molecular weight fraction. The average molecular weight of each fraction is obtained by measuring the

diffusivity and applying the following empirical correlation.

$$M = a D^{-b}$$

Where M is the average molecular weight, D is the diffusivity, a and b are constants. The amount of lignin sulfonates present in each fraction was determined by measuring the UV absorbance at 280 nm. In their study, eight fractions with average molecular weight in the range of around 500 to 70,000 were prepared. Their results show that over 40 % of the lignin sulfonates have molecular weights in the range of 10,000 to 20,000.

In 1962 and 1964, Forss and coworkers in Finland^(16,17) used the gel filtration technique to separate lignosulfonic acids of a spent sulfite liquor from other aromatics and low molecular weight ligninlike sulfonic acids. The molecular weight distribution of the original sample can be realized from the elution curve. Their work made two significant contributions to the field. For different molecular weight fractions the phenolic OH⁻ group content (expressed as number of OH⁻ groups per mass lignin) remains almost constant, which in turn indicates that by using UV to detect the phenolic ether bond, the absorbance is dependent on the mass concentration and not on the molecular weight of the sample. The idea of using the gel filtration to

fractionate a polydisperse macromolecular sample was first introduced to the field. Since then, it has been widely used in lignin fractionations.

In 1968, Gupta and McCarthy⁽¹⁸⁾ studied the molecular weight distribution of lignin sulfonates. A two meter long gel filtration column packed with Sephadex G-50 gel was used to fractionate the sodium lignin sulfonates. Several runs were carried out using different concentrations of NaCl solutions as eluent, and the molecular weight of each fraction was determined by equilibrium sedimentation in an ultracentrifuge. The results show that the molecular weights of the initial sample fall in the range of 400 to 75,000. Their molecular weight distribution is very similar to the results of Felicetta⁽¹⁵⁾.

2. On the Solubility of Lignin

In 1952, Schuerch⁽¹⁹⁾ qualitatively studied the possibilities of dissolving different kinds of lignins in various solvents. The solvents used had solubility parameters (δ) ranging from 7.4 (for hexane) to 23.4 (for water). Their results showed that solvents having δ values around 11 are the best solvents. The lignin sulfonic acid, however, were regarded as not comparable to the other lignins because of the introduction of the hydrophilic sulfonic acid groups, which will dramatically change its solubility behavior. In this study, although a

wide range of solvents and lignins were covered, no quantitative solubility data were given.

In 1967, Brown⁽¹³⁾ studied the solution properties of the unfractionated softwood kraft lignin in DMSO, DMF, and dioxane individually. By measuring the vapor pressure of the solution at different temperatures, the changes of the partial molar properties $\Delta\bar{F}_1$, $\Delta\bar{H}_1$, and $\Delta\bar{S}_1$ for the solvent can be calculated. To calculate the solvent-solute interaction parameter, X, the following Flory - Huggins equation was used.

$$\Delta\bar{G}_1 = RT \ln a_1 = \frac{1}{RT} (\ln(1-\phi_2) + (1-1/x_2)\phi_2 + X\phi_2) \dots\dots\dots (1)$$

Where R, T, and a_1 have their conventional meanings, ϕ_2 and x_2 are the volume fraction and the number of segments of lignin respectively given by the following equations.

$$\phi_1 = \frac{n_1 V_1}{\sum_i n_i V_i} \dots\dots\dots (2)$$

$$x_2 = \frac{Mav v_2}{V_1} \dots\dots\dots (3)$$

Where n_i is number of moles, V_i is the molar volume, and v_i is the specific volume of species i.

The concentration range of the lignin, ϕ_2 , in their study was from 0.07 to 0.23. The calculated value of the interaction parameter X is in the range of 0.34 to 0.58. It was further divided into its enthalpic and entropic contributions, X_H and X_S , by applying the following equations.

$$X = X_H + X_S \quad \dots\dots\dots(4)$$

$$X_H = \Delta H_1 / R T \phi_2^2 \quad \dots\dots\dots(5)$$

The results showed that, for DMSO, the X_S is negative due to large heat of dilution, while for the other two solvents, the X_H and X_S are both positive.

For more information about the interaction parameters between lignins and different solvents, the work done by Lindberg^(11,12) should be reviewed carefully, though unfortunately it was not published in English.

3. On the Method of Obtaining Phase Equilibrium Data -- the Cloud Point Titration

The phase separation of a homogeneous polymer solution can be induced by either adding a non-solvent (precipitant) or by changing the temperature. The new polymer-rich phase is often called a gel phase. When the size of the small gel particles reach the order of the wavelength of the incident light, light will be scattered and can be observed as visual turbidity. The first

detectable turbidity is called the cloud point. If the cloud point is induced by the addition of a precipitant, the method is called cloud point titration. Measurements of the cloud point and the titration curve can be used to determine interaction parameters, theta compositions, cohesive energies, and solubility parameters⁽⁸⁾.

Elias⁽⁸⁾ summarized the theories and experimental procedures for the cloud point titration for dilute solutions having ϕ_2 less than 0.01. For easy determination of the cloud point, the solvent and precipitant should be so chosen that at the cloud point, the volume fraction of precipitant, ϕ_3 , is in the range of around 0.15 to 0.5. The starting concentration of the polymeric solute is around 0.01. Addition of the precipitant to the solution should be at the rate of 0.5 to 1 ml/min-100 ml solution. The cloud point can be determined either by the naked eye or by the instrumental measurement of light transmittance or scattering⁽⁸⁾.

From the thermodynamic derivations⁽⁸⁾, the following relationship exists between the volume fraction of precipitant and that of polymer.

$$\phi_3^i = \phi_3^\theta - B_\phi \ln \phi_2^i \quad \dots\dots\dots(6)$$

Where B_ϕ is the slope coefficient, superscript i means incipient phase separation, and θ means the θ state composition.

For simplification purposes, the interaction parameters of a ternary system can be grouped together by "single liquid" approximation of Scott⁽²⁰⁾.

$$X = X_{12} + (X_{23} - X_{12} - X_{13}) \phi_3 + X_{13} \phi_3^2 \quad \dots\dots(7)$$

Where X_{ij} is the interaction parameter between component i and j .

For a system composed of a high molecular weight polymer, a thermodynamically bad solvent, and a strong precipitant, the last term in equation (7) is negligible, and equation (7) can be reduced to a form similar to equation (4).

$$X = X^0 - B_x \ln \phi_2^i \quad \dots\dots\dots(8)$$

Where X^0 is the extrapolated value of X when ϕ_2 is close to 1, and is theoretically equal to 0.5; B_x is the slope coefficient, and usually has a negative value.

As concern to the present study, the slope coefficient B_x is dependent on the molecular weight, or more precisely, the number of segments of the polymer. It is approximated by the following emperical equation.

$$B_x = B_x^0 + D_x \text{Mav}^{-0.61} \quad \dots\dots\dots(9)$$

Where Mav is the average molecular weight of the polymer. Accordingly, the smaller the polymer molecules, the steeper is the X versus $\ln \phi_2$ plot, and the larger is X at

the same ϕ_2 . The same trend also exists in the ϕ_3 versus $\ln \phi_2$ plot.

4. On Studies of the Phase Behavior of Polymer Solutions

There are three methods of treating the phase equilibrium of a polymer solution, and each has its own theory. These three theories will be reviewed in this section.

A. Solubility Parameter Theory

The solubility parameter concept was developed by Hildebrand⁽¹⁰⁾ in 1950. When considering the mixing of two liquids, the heat of mixing H_m is given by the following equation.

$$\Delta H_m = V_m \left(\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right)^2 \phi_1 \phi_2 \quad \dots(10)$$

Where V_m is the volume of the liquid mixture, ΔE_i is the energy of vaporation of the liquid, and V_i is the molar volume of the liquid i . The $\Delta E_i/V_i$ term indicates the amount of energy required to vaporize a unit volume of liquid i , and thus was designated as the "cohesive energy density". Its square root was later termed by Hildebrand and Scott⁽¹⁰⁾ as the "solubility parameter" δ . Thus

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} \quad \dots\dots\dots(11)$$

Then, equation (8) can be rewritten as

$$\Delta H_m = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \dots\dots\dots(12)$$

It can be realized from equation (12) that in order to decrease the enthalpic barrier of a mixing process, a solvent having a solubility parameter close to that of solute should be chosen so as to minimize $(\delta_1 - \delta_2)$. Though the original idea was developed for the non-electrolyte systems, some work has been done to extend its application to ionic systems as mentioned in Barton's review article⁽²¹⁾. For mixed solvents 1 and 3, the combined solubility parameter which can be put into equation (12) is calculated by the following equation.

$$\delta_{1-3} = \phi_1^* \delta_1 + \phi_3^* \delta_3 \dots\dots\dots(13)$$

Where the "effective volume fraction" ϕ_i^* is defined as

$$\frac{\phi_1^*}{\phi_3^*} = \frac{\phi_1 (\delta_2 - \delta_3)^2}{\phi_2 (\delta_2 - \phi_1)^2} \dots\dots\dots(14)$$

The value of the solubility parameter can either be calculated from thermodynamic quantities or measured by experiment⁽²²⁾. Solubility parameter for different solvents and most of the commercially available polymers are collected in Burrell's compilation⁽²³⁾. The theory

finds application in industry as a guide for selecting solvents for polymers⁽²³⁾.

B. Flory - Huggins Polymer Solution Theory

The Flory - Huggins polymer solution theory, since its development, has been used widely to treat experimental polymer solubility data. In 1978, Oishi and Prausnitz⁽²⁴⁾ applied a modified group contribution method, UNIFAC, to extend its usage, which can predict the activities and/or the interaction parameter without using any experimental data.

Flory⁽²⁵⁾ and Casassa⁽²⁶⁾ both gave a good review on the theory. The details of the theory will be discussed in the THEORETICAL BACKGROUND chapter.

C. Prigogine - Flory Corresponding State Theory

Instead of considering only the configurational entropic contribution ($N_1 \ln \phi_1 + N_2 \ln \phi_2$) and the intermolecular interaction contribution ($X_{12} \phi_1 \phi_2 / V_1$) by the Flory - Huggins theory, the Prigogine - Flory theory also considers the effect of different free volumes between solvent and polymer. The theory states that the free volume of a solvent molecule is larger than that of polymer molecule. Upon mixing, the solvent molecule contracts more than polymer molecule does, so that the solution has a free volume closer to the polymer than to

the solvent. The net effect is to bring the molecules of the system closer together and hence results in negative values of both ΔH_m and ΔS_m . However, the effects on ΔH_m and ΔS_m are not proportional in magnitude, and the final effect is an increase in ΔG_m , which in turn is unfavorable to mixing. The Prigogine - Flory theory merges the free volume effect into the X_{12} parameter, thus X_{12} contains not only the intermolecular interaction term but also a positive free volume contribution. Because the free volume changes with temperature and pressure, the theory gives a better prediction of solvent activity and/or interaction parameter if the changes in temperature and/or pressure are significant.

The equation for calculation of X_{12} / V_1 can be found elsewhere^(27,28). The theory finds its application in both polymer-solvent systems and polymer compatibility studies.

THEORETICAL BACKGROUND

As reviewed in the previous chapter, there are several theories available to treat the phase equilibrium data of a polymer solution. The present study tries to correlate the experimental cloud point composition data by using the Flory - Huggins equation of free energy of mixing. This chapter will lay the theoretical background for the research, starting from phenomenological description of the polymer dissolution process, continuing with a brief introduction to the Flory - Huggins lattice model, and finally focusing on the three component Flory - Huggins equation of free energy of mixing which is used in the present study.

1. Basic Thermodynamics of a Dissolution Process and the Polymeric Solute Dissolution Phenomena

The process of dissolution is just like other changes of state, in that whether the process will happen or not is governed by the entropy gain and the internal energy change of the system. Every system tends to reduce its internal energy or the enthalpy H and to increase its entropy S . The larger the increase in entropy (positive ΔS) and the lesser in enthalpy gain (negative ΔH), the larger is the driving force of the change, and the change of state will occur spontaneously. Conversely, a positive

enthalpy change and a negative entropy change means that no change of state will occur. The concept can be better described by the following fundamental thermodynamic equation.

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad \dots\dots\dots(15)$$

Briefly, a change of state can happen only when it is accompanied by a negative free energy change, ΔG .

During the dissolution process, the entropy is increased due to the increasing mobility of the solute molecules. Thus dissolution occurs spontaneously either when the enthalpy change is negative or when there is no enthalpy change at all. For an endothermic dissolution process, the driving force for the dissolution comes from entropy increase only. For a constant temperature dissolution process, the entropy gain will be the largest at the beginning, because the concentration of the solute in the solution is then the smallest which in turn results in the largest concentration difference. As the dissolution progresses, the concentration of the solute in the solution gradually increases, and ΔS becomes smaller, until finally $T \Delta S$ equal to ΔH so that ΔG equal to zero, the solution is said to be saturated and is thermodynamically in equilibrium, i.e., some of the dissolved solute molecules attach to the undissolved solute surface while an equal amount of solute molecules

come out of the undissolved solute surface to the solution.

For the case of a macromolecular solute in a good solvent, the dissolution is an exothermic process, and the polymer and solvent are miscible with each other in all proportions. The solvent molecule first penetrates into the interstices between the polymer chains at the surface. The secondary valence forces between the solvent molecules and those forces between the polymer chains are then replaced by the solvation between the solvent molecules and the polymer chains, and the polymer starts to swell. If whole units of a polymer chain have been solvated, the fully solvated polymer chain surrounded by the solvating solvent molecules may then move away from the solute surface into solution. The dissolution progresses as more solvent molecules diffuse into the depth of the polymeric solute, until all the polymer chains are solvated with solvent molecules and can move freely in the solution.

For the case of a macromolecular solute in a poor solvent, the dissolution is an endothermic process, i.e., the solvation energy is lower than the secondary valence bond energy between the solvent molecules and between the polymer chains. The diffusion of solvent molecules into the polymer chains progresses as long as the effect of enthalpy increase is lower than the effect of entropy increase to keep a negative free energy change. Once the

concentration of the solvated segments is high enough so that the entropy increase of the solvation process is just balanced by the enthalpy increase, the solvated and the unsolvated segments are said to be in equilibrium. In this case, there is no fully solvated chain that goes into solution. Before the last segment of a polymer chain is solvated, some of the previously solvated segments again attach to the segments of the unsolvated polymer chains to form secondary valence bonds. Thus, the polymer is swollen to some extent in a poor solvent but never dissolved.

If a solvent behaves intermediately between good solvent and poor solvent, then, before equilibrium is reached, some of the polymer chains which are fully solvated can move freely in solution. Once equilibrium is reached, both dynamic equilibria between the solvated segments and the unsolvated segments and between the dissolved polymer chains and the undissolved chains will happen simultaneously. The polymer is said to be partially soluble in the solvent.

If a polydisperse instead of a monodisperse polymeric solute is used, a point may be reached that below a certain molecular weight limit the polymer chains are fully solvated, can move freely in solution and are called the sol phase. The polymer chains longer than that limit can not fully solvate and are still bound in the

aggregate; this phase is called the gel phase. The partial precipitation or partial dissolution process for the fractionation of macromolecules is based on this phenomenon.

2. The Flory - Huggins Polymer Solution Theory

In treating the polymer solution phase equilibrium phenomena, the solubility parameter theory considers only the interaction energy between the adjacent molecules and is based on quantum mechanics, while the Flory - Huggins theory considers an additional term, the entropy of mixing, which in turn is deduced by applying statistical thermodynamics to a hypothetical lattice model⁽³⁰⁾. The detailed derivation of the theory can be seen elsewhere^(29,30). This section will explain the important concepts of each of the following equations which are related to the present study.

A. Configurational Entropy of a Macromolecular Solution

-- The Lattice Model

When putting N_2 polymer chains, each with n monomer segments, in a solvent containing N_1 molecules, the number of different arrangements of polymer chains and solvent molecules in the $nN_2 + N_1$ hypothetical lattice sites, Ω , is equal to $(N_1 + N_2)! / (N_1! N_2!)$ ⁽³⁰⁾, which leads to the following entropic contribution of mixing, ΔS config.

$$\Delta S \text{ config.} = k \ln \Omega = k \ln \frac{(N_1 + N_2)!}{N_1! N_2!} \dots\dots\dots(16)$$

Where k is the Boltzman constant. With the help of Stirling approximation, $\ln N! = N \ln N - N$, the following equation can be obtained.

$$\Delta S \text{ config.} = -k (N_1 \ln \phi_1 + N_2 \ln \phi_2) \dots\dots\dots(17)$$

Where volume fraction, ϕ_i , is defined by equation (2).

B. Enthalpy of Mixing

The enthalpy of mixing ΔH is given by the difference between the enthalpy of solution H_{12} and the enthalpy of the pure solvent and solute, H_{11} and H_{22} . Each of the above enthalpies is calculated by the interaction energy between the two adjacent units in the lattice sites, and is given by the following equations.

$$H_{11} = N_1 Z (0.5 \epsilon_{11}) = N_t \phi_1 Z (0.5 \epsilon_{11})$$

$$H_{22} = N_2 x_2 Z (0.5 \epsilon_{22}) = N_t \phi_2 Z (0.5 \epsilon_{22})$$

$$H_{12} = N_1 Z (0.5 \epsilon_{11} \phi_1 + 0.5 \epsilon_{12} \phi_2) + N_2 x_2 Z (0.5 \epsilon_{22} \phi_2 + 0.5 \epsilon_{12} \phi_1)$$

Where Z is number of neighboring units surround the specified unit, on which the interaction energy ϵ_{ij} is calculated, N_t is total number of lattice sites, x_2 is number of segments in a polymer chain as defined by equation (3), which takes into account the effect of the

volume difference between the solvent molecules and the monomers. The enthalpy change of mixing is given by the following equation.

$$\begin{aligned}\Delta H &= H_{12} - (H_{11} + H_{22}) = ZN_t \phi_1 \phi_2 (\epsilon_{12} - 0.5\epsilon_{11} - 0.5\epsilon_{22}) \\ &= ZN_1 \phi_2 \Delta\epsilon \quad \dots\dots\dots(18)\end{aligned}$$

C. The Flory - Huggins Interaction Parameter

The Flory - Huggins interaction parameter X is defined as

$$X = \frac{Z \Delta\epsilon}{k T} \quad \dots\dots\dots(19)$$

Where $\Delta\epsilon$ is given by equation (18) as the energy gain per solvent-solute contact. Then, the interaction parameter defined by equation (19) can be realized as the total energy gain of one solvent-solute contact, $Z \Delta\epsilon$, divided by the thermal energy per molecule, kT . Owing to the interaction energy $\Delta\epsilon$ is actually a measurement of the free energy and not of only enthalpy. Consequently, X can be divided into its entropic contribution X_s and its enthalpic contribution X_H .

$$X = X_s + X_H \quad \dots\dots\dots(4)$$

D. Gibbs Free Energy of Mixing

By combining equation (15), (17), (18), and (19), the following free energy equation of a polymer solution can be obtained.

$$\Delta G = kT (XN_1 \phi_2 + N_1 \ln \phi_1 + N_2 \ln \phi_2) \quad \dots\dots\dots(20)$$

E. Chemical Potential and Enthalpy of Fusion of the Polymeric Solute

Taking the partial derivative of equation (20) with respect to N_2 while keeping N_1 constant, the equation for the chemical potential of the polymeric solute can be obtained.

$$\frac{\mu_2 - \mu_2^{\circ}}{RT} = \ln \phi_2 - (x_2 - 1)(1 - \phi_2) + Xx_2 (1 - \phi_2)^2 \quad \dots\dots(21)$$

Where μ_2 is the chemical potential of polymeric solute, superscript $^{\circ}$ stands for solid (undissolved) state, x_2 is the number of segments of polymeric solute as defined by equation (3). The details of its derivation is described in Appendix A-1.

By applying the Gibbs - Helmholtz relation of the temperature dependence of free energy change

$$\left(\frac{\partial (\Delta G/T)}{\partial T} \right)_P = - \frac{\Delta H}{T^2} \quad \dots\dots\dots(22)$$

to equation (21), the equation relating the equilibrium phase composition and enthalpy of fusion of the polymeric solute can be obtained.

$$\begin{aligned} \frac{1}{x_2} \ln \phi_2 - (1 - 1/x_2)(1 - \phi_2) + X(1 - \phi_2)^2 \\ = \frac{\Delta H}{R x_2} \left(\frac{1}{T_2} - \frac{1}{T_2^0} \right) \end{aligned} \quad \dots\dots\dots(23)$$

Where T_2^0 is the solute fusion temperature. The details of its derivation is shown in Appendix A-2.

F. The Ternary System, Solvent(1) - Polymeric Solute(2) - Precipitant(3)

The Flory - Huggins equation for a ternary system can be derived in the same way as for a binary system. The following three component Flory - Huggins equation will be used to correlate the experimental phase equilibrium data of the present study.

$$\begin{aligned} \ln \phi_2 + (x_2 - 1)(1 - \phi_2) + x_2(X_{12}\phi_1 + X_{23}\phi_3)(1 - \phi_2) + x_2 X_{13}\phi_1\phi_3 \\ = \frac{\Delta H}{R x_2} \left(\frac{1}{T_2} - \frac{1}{T_2^0} \right) \end{aligned} \quad \dots\dots\dots(24)$$

Where X_{ij} is the interaction parameter between component i and j , and is based on per mole of i .

EXPERIMENTAL

The objective of the experimental work was to generate phase equilibrium data by using the cloud point titration method. To test the experiment procedures and the data treatment method, preliminary experiments were carried out using commercially available, nearly monodisperse polyethylene glycols as the solutes. After that, similar procedures were applied to study the more complicated polydisperse lignin sulfonates.

The overall approach logic of the research is better described by the block diagrams as shown in Figures 1 and 2.

The experiment is actually composed of two independent sections, and they will be described separately.

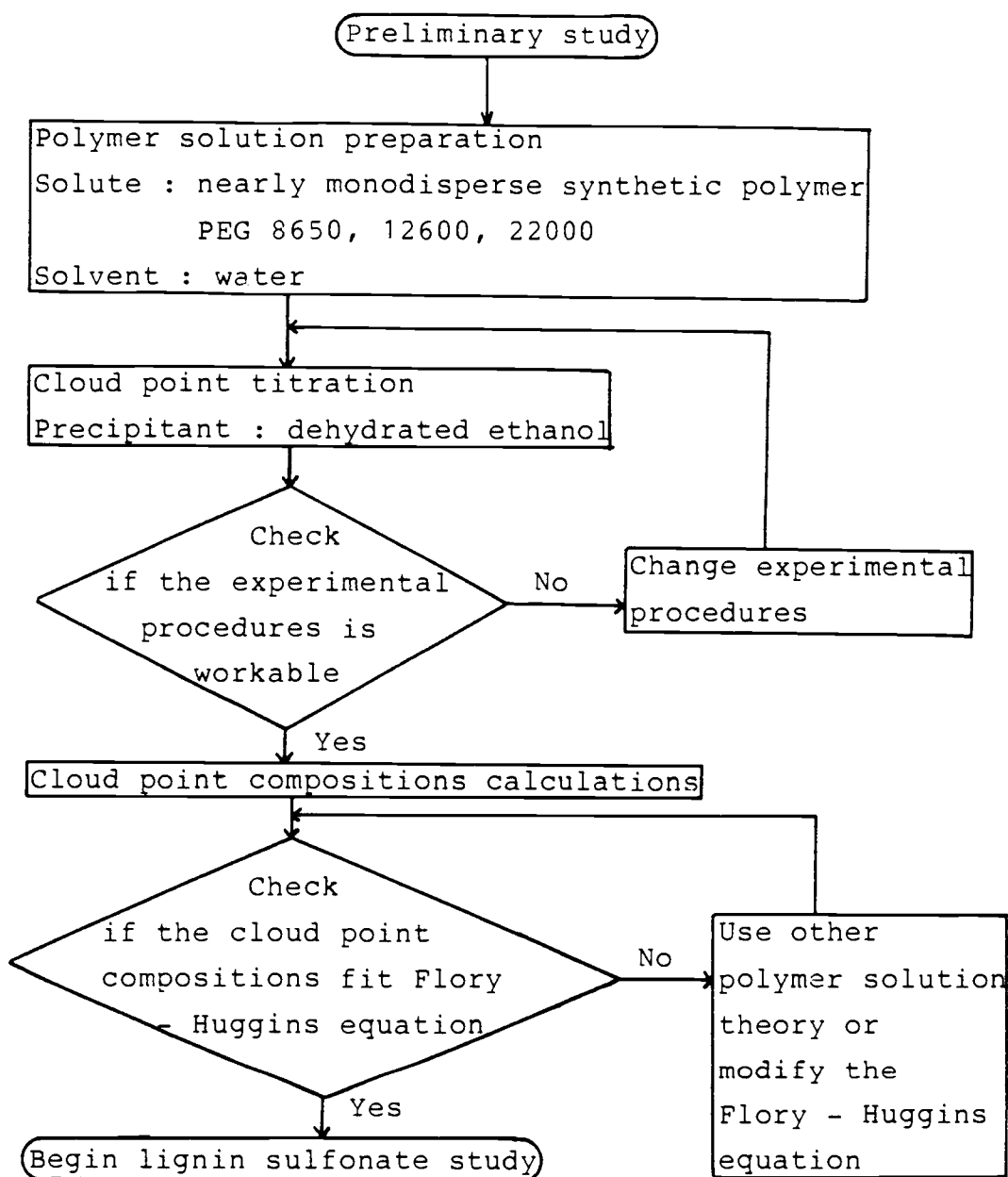


Figure 1. Block diagram of the study on the Water - PEG - Ethanol system

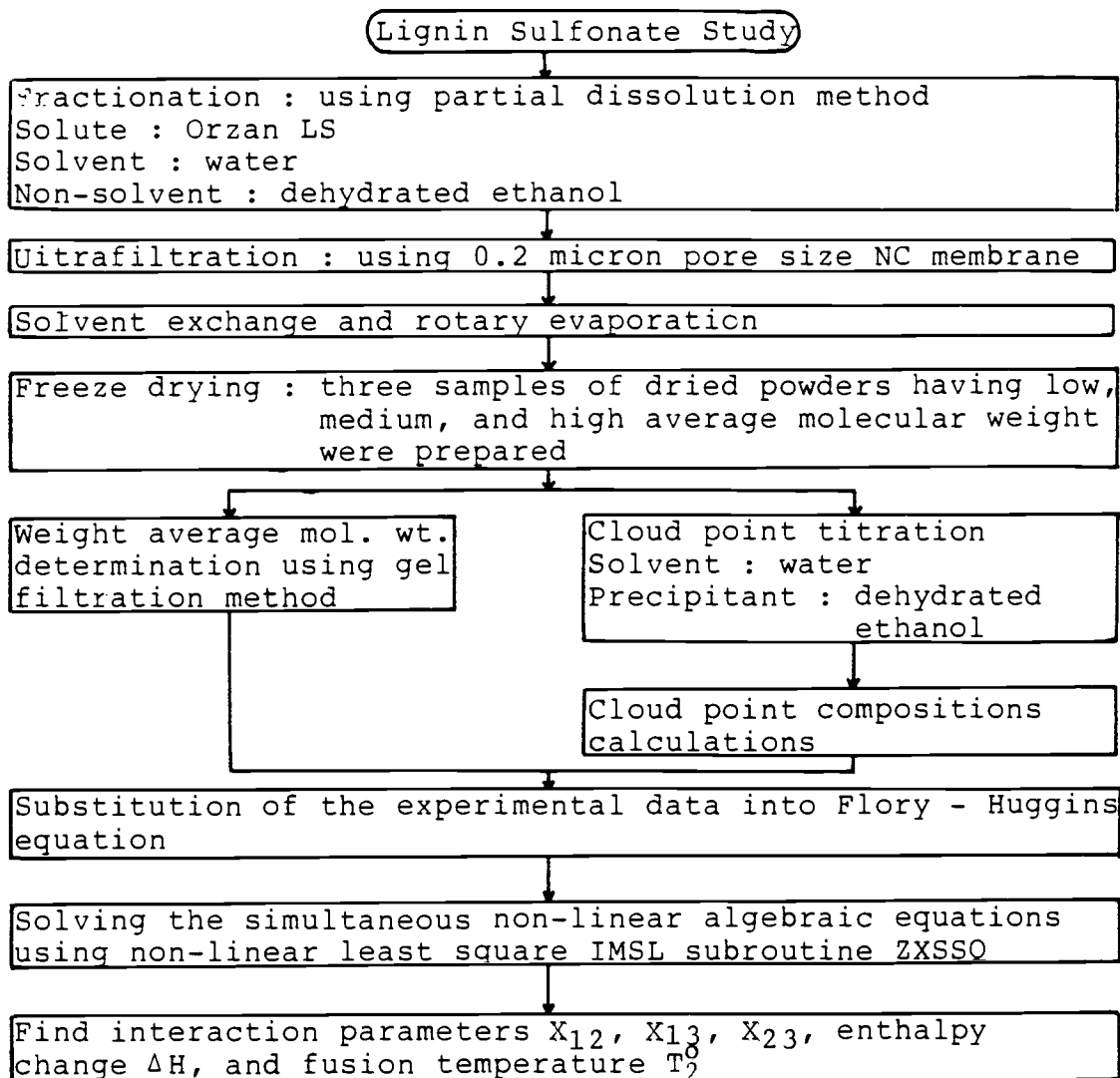


Figure 2. Block diagram of the study on the Water - NaLS - Ethanol system.

1. Water(1) - Polyethylene Glycol(2) - Ethanol(3) System

A. Materials

Polyethylene Glycol (PEG). Three samples of PEG having average molecular weight of 8650, 12600, and 22000 with Mw to Mn ratio of 1.03, 1.04, and 1.06 were obtained from Polymer Laboratories Inc..

Ethanol. Dehydrated ethanol with purity of nearly 100 % was obtained from National Distiller & Chemical Corporation and was used as precipitant.

Water. Distilled, demineralized, and Mini-Pore Filter filtered water was used as the solvent.

B. Experimental Procedures

Some preliminary experiments of cloud point determination were done by titrating the PEG - water solutions with ethanol. They showed that no matter how much precipitant was added to the solution, no visually detectable turbidity appeared. However, if the solution, in which some precipitant have been added, is allowed to stay overnight in a 25 °C water bath, under certain composition a heavy turbidity was revealed. The delay in the appearance of the cloud point led to a slight modification of the general cloud point method.

One gram of PEG is weighed in a 10 ml volumetric flask using a balance with readability to 0.0001 gm , 1.5 ml of water is then added to the flask to dissolve PEG . If the solution is too viscous, 1 to 2 ml of ethanol can be added to the solution to dilute it. After all the PEG solids are dissolved, the solution is diluted with ethanol to 10 ml. From the volume of the water and ethanol used, V_1 and V_3 respectively, the specific volume of the PEG can be calculated.

$$v_{\text{PEG}} = \frac{10 \text{ ml} - V_1 - V_3}{\text{wt. of PEG}} \dots\dots\dots(25)$$

Where v_{PEG} is the specific volume of PEG expressed in ml/gm. The so obtained specific volumes for PEG 8650, 12600, and 22000 are 0.828, 0.796, and 0.768 ml/gm respectively for the solution composition used in this study. Then, 1 ml of the above solution is pipetted into another 10 ml flask, certain volume of ethanol is added into the flask to prepared a sample for cloud point determination. Another sample with different ethanol content is prepared in the same way. The two samples are allowed to sit in a 25 °C water bath for over ten hours to see if turbidity appeared in any of the samples. The bisection technique is used to narrow down the range of turbid compositions, until the two consecutive turbid

samples having the PEG volume fraction difference less than 10 % under the same ethanol to water volume ratio.

The volume fraction of each component at the cloud point can be calculated using the following equation

$$\begin{aligned}\phi_1 &= \frac{V_1}{V_1 + w_2 v_2 + V_3} \\ \phi_2 &= \frac{w_2 v_2}{V_1 + w_2 v_2 + V_3} \dots\dots\dots(26) \\ \phi_3 &= \frac{V_3}{V_1 + w_2 v_2 + V_3}\end{aligned}$$

Where V_i is the partial volume of component i in the solution, $w_2 v_2$ is the partial volume of PEG in the solution.

2. Water(1) - Sodium Lignin Sulfonates (NaLS)(2) - Ethanol (3) System

A. Materials

NaLS. Orzan Lignin Sulfonate Sodium Salt (Orzan LS) was obtained from Crown Zellerbach Corporation (Camas, Wa.). It is generally used as binder, dispersant, or emulsifier. No further information about its chemical analysis is available.

Ethanol and Water. The dehydrated ethanol and water used in this system are the same as those used in the PEG system.

B. Orzan LS Fractionation and NaLS Dry Powders Preparation

Fractionation. In order to reduce the polysaccharide content in the low molecular weight fraction, a partial dissolution method was used to prepare three fractions of lignin sulfonates with low, medium, and high average molecular weight. The procedures are similar to those of Felicetta⁽¹⁵⁾ et al.

Ten grams of Orzan LS is weighed into a 1 liter beaker, 400 ml of dehydrated ethanol is added into the beaker. The suspension is stirred, so that Orzan LS is evenly dispersed in ethanol. 100 ml of water are added slowly while stirring to make a final 80 vol. % ethanol solution. The solution is filtered using Whatman No. 42 filter paper. The yellowish brown filtrate, which contains the lower molecular weight lignin sulfonate, is thus designated as low molecular weight fraction. The viscous mud from the above filtration is then washed into another 1 liter beaker with 300 ml of ethanol, and 130 ml of water is added to the suspension while stirring to make a final 70 vol. % ethanol solution. The solution is filtered as the above, and the filtrate is designated as medium molecular weight fraction. The viscous mud from

the last filtration is then subjected to the same operation, except the ethanol content of the solution is now changed to 65 vol. %. The filtrate is designated as high molecular weight fraction. The remaining undissolved slurry are polysaccharides, this was confirmed by running a thin-layer chromatography on the slurry.

Ultrafiltration. In order to remove the carry-over of the undissolved larger lignin sulfonates and/or the polysaccharides by the filtrate, which might results in a broader molecular weight distribution, and/or the difficulty in cloud point titration, it is advisable to remove these undissolved particles by filtering through a membrane filter. 25 ml of each fraction are filtered using nitrocellulose membrane (Chemonics Scientific) having pore size of 0.2 micron. The originally cloudy solution becomes clear after the filtration.

Solvent Exchange and Rotary Evaporation. To raise the freezing temperature of the solution so that the sample can be frozen in a refrigerator, most of the ethanol in the solution must be removed. 50 ml of water is added to each of the above 25 ml of ultrafiltered sample, each sample is then subjected to ethanol removal by using rotary evaporator, the evaporation continued until the volume of each fraction is about 10 ml.

Freeze Drying. Each of the above 10 ml sample is transferred into a round bottle and laid in refrigerator to freeze the solution. After the solution is totally frozen, the round bottle is connected to a freeze dryer. Lignin sulfonates dry powder is retained in a loose structure at the bottle bottom after all the ice is sublimed.

C. Weight Average Molecular Weight (Mw) determination
Using Gel Filtration Column.

The weight average molecular weight, M_w , of each fraction is determined by using a gel filtration column. The schematic diagram of the gel filtration equipment is shown in Figure 3.

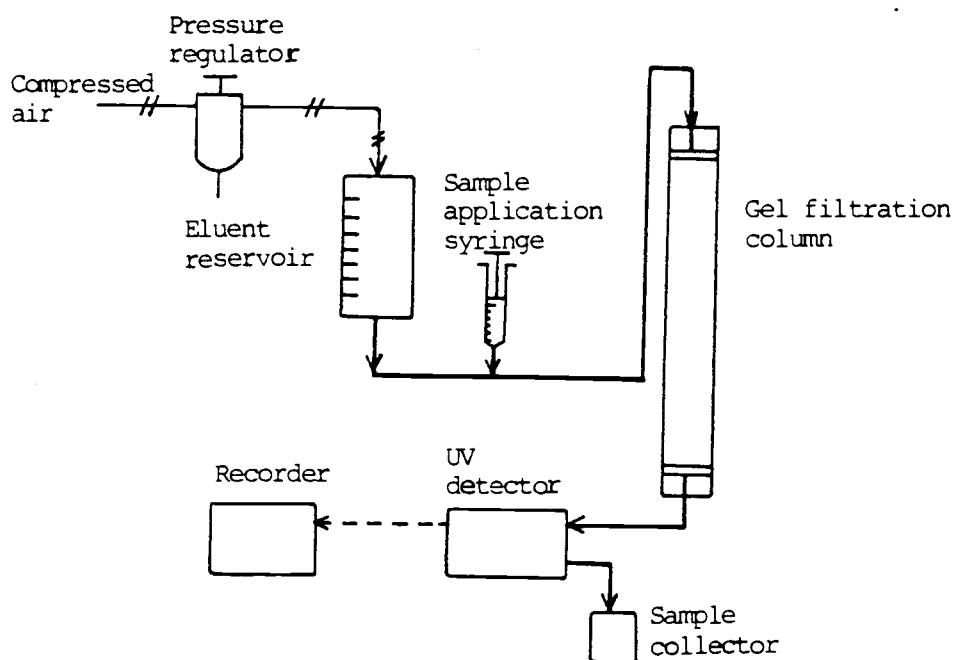


Figure 3. Schematic diagram of the gel filtration equipment for M_w determination.

For the low molecular weight fraction, an analytical column SR 10/50 (Pharmacia) packed with Sephadex G-50 Superfine gel (Pharmacia) is used. The length of gel in the column is 43 cm. For medium and high molecular weight fractions, a preparative column K 50/60 (Pharmacia) packed with Sephadex G-100 gel (Pharmacia) is used. The length of the gel is 41 cm. For each case, water is used as eluent. The UV absorbance was measured at the wavelength of 280 nm.

To get a better resolution, the sample size should be carefully chosen. In the present study, the sample size for the SR 10/50 column is 0.2 ml of the solvent exchanged and rotary evaporator concentrated solution, while that for K 50/60 column is 1 ml of the above solution and diluted to 5 ml. The eluent flow rate for the SR 10/50 column is from 0.16 ml/min. at the beginning of a run to 0.14 ml/min. at the end of a run, while that for the K 50/60 column is from 3.5 to 3.2 ml/min. The flow rate can be regulated by adjusting the air pressure in the eluent reservoir.

Calibration of the column is done by using sodium polystyrene sulfonate (NaPSS) standards (Polymer Laboratories, Inc.), which has a similar base unit chemical structure to NaLS, and paranitrophenol (PNP). The elution volume of each standards is divided by that of PNP to get a relative retention volume, V_R . The elution

volume of each NaLS fraction is also converted to V_R to determine the corresponding molecular weight. The molecular weight so obtained is not an absolute molecular weight but is relative to NaPSS.

D. Cloud Point Titration and Cloud Point Composition

Calculation

0.05 grams of the dry powder of a NaLS fraction from Section B is weighed into a 10 ml glass sample vial by using a balance with readability to 0.0001 gm. Then 0.1 ml of water is added into the sample vial via a precision buret with readability to 0.01 ml. The sample vial is shaken gently to dissolve the NaLS powders. The solution so obtained should be clear and have a color of brownish to reddish. The solution is then titrated with dehydrated ethanol via another precision buret until a visually detectable turbidity appears. The volume of ethanol used is recorded. The cloudy solution is made clear again by adding 0.03 ml of water into it. The same titration procedures are followed to titrate the now clear solution into cloudy again. The dissolution and titration process are repeated until more than ten data points are collected.

All the above titrations were carried out in the temperature range of 25 ± 3 °C.

The specific volume of NaLS, according to the published data^(13,18,32), ranges from 0.61 to 0.7 ml/gm.

In the present study we used the value of 0.7 ml/gm.

The cloud point composition at each cloud point can be calculated using the following equations.

$$\begin{aligned}\phi_1 &= \frac{V_1}{V_1 + (0.05)(0.7) + V_3} \\ \phi_2 &= \frac{(0.05)(0.7)}{V_1 + (0.05)(0.7) + V_3} \dots\dots\dots(27) \\ \phi_3 &= \frac{V_3}{V_1 + (0.05)(0.7) + V_3}\end{aligned}$$

Where 0.05 is the number of grams of NaLS, 0.7 is the specific volume of NaLS, and V_i is the partial volume of component i in the cloudy solution.

RESULTS AND DISCUSSION

1. On the Water(1) - PEG(2) - Ethanol(3) SystemA. The Cloud Point Compositions

The cloud point compositions calculated from the experimental data by using equation (26) are listed in the Appendix A-3.

Figure 4 shows the phase diagram of the system in triangular coordinates. The shaded area in the small triangle shows the range of the present study. Phase separation occurs when the composition of the solution is below the curve. Though the three curves are close to each other, the data shows that a polymer solution having higher molecular weight polymeric solute needs less precipitant to cause phase separation.

B. Flory - Huggins Equation Parameters

For a specified PEG, six cloud point compositions (ϕ_1, ϕ_2, ϕ_3) are substituted into equation (24). This results in six simultaneous non-linear algebraic equations, with each equation contains five unknown parameters. These simultaneous equations are solved by using the IMSL subroutine ZXSSQ, which minimized the sum of square of M functions in N variables using a finite

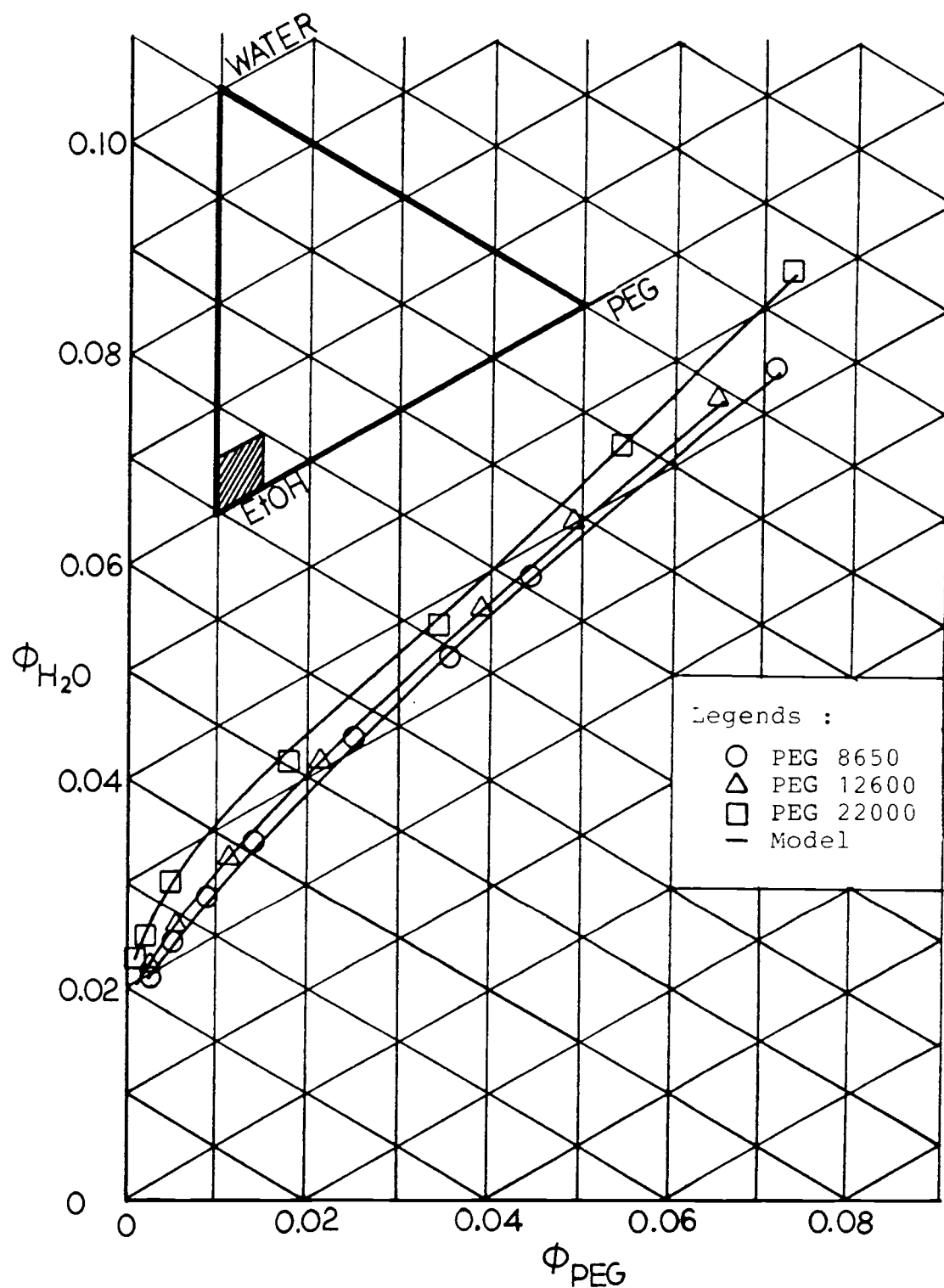


Figure 4. Cloud point composition of the Water - PEG - Ethanol system

difference Levenberg - Marquardt algorithm⁽³³⁾. The calling program is shown in Appendix A-4.

The calculated values of the parameters are shown in Table 1.

Table 1. The Flory - Huggins equation parameters of Water(1) - PEG(2) - EtOH(3) system

Polymer	PEG 8650	PEG 12600	PEG 22000
X_{12}	1.0001	0.6318	0.4741
X_{13}	-4.4412	-4.2339	-3.0060
X_{23}	-0.6862	-0.7451	-0.6600
ΔH (J/mol.)	189900	263800	514900
ΔH (J/mol. monomer)	966	921	1030
T_2^0 (K)	455	402	493

The interaction parameter between water and PEG 22000, X_{12} , is close to the literature value of 0.45⁽³⁴⁾, while the values for PEG 8650 and PEG 12600 are higher. This is probably due to a weak precipitant, which results in an over-titration, which in turn results in a higher experimental value of X_{12} . However, the trend of increasing of X_{12} as molecular weight of polymer is decreased is consistent with what equation (9) will predict. Since no published data is available, no further attempts were made to analyze the other parameters.

2. On the Water(1) - NaLS(2) - Ethanol(3) System

A. NaLS Fractions Characterizations

The gel filtration elution curves for the unfractionated Orzan LS and the low, medium, and high molecular weight fractions of NaLS are shown in Figures 5 through 8. In calculating the average molecular weight of each fraction, the V_R value was first converted to the corresponding molecular weight with the help of Figure 9, which is a calibration curve developed using nearly monodisperse polystyrene sulfonate sodium salt (NaPSS) samples as calibration standards. The elution curves for the NaPSS standards and PNP for both gel filtration columns are shown in Figure 10, in which the heavier dashed line is the elution curve of the mixed higher molecular weight calibration standards, the lighter dashed lines are the elution curves of each NaPSS standard when they are individually applied to the column, and the solid line is the elution curve of the mixed low molecular weight calibration standards.

Because the absorptivity of NaLS, expressed in $l/gm-cm$, remains nearly constant⁽¹⁶⁾ for different molecular weight molecules, the absorbance can be treated as the weight concentration multiplied by a constant. The weight average molecular weight, M_w , can be calculated by dividing the whole elution curve into sections and using

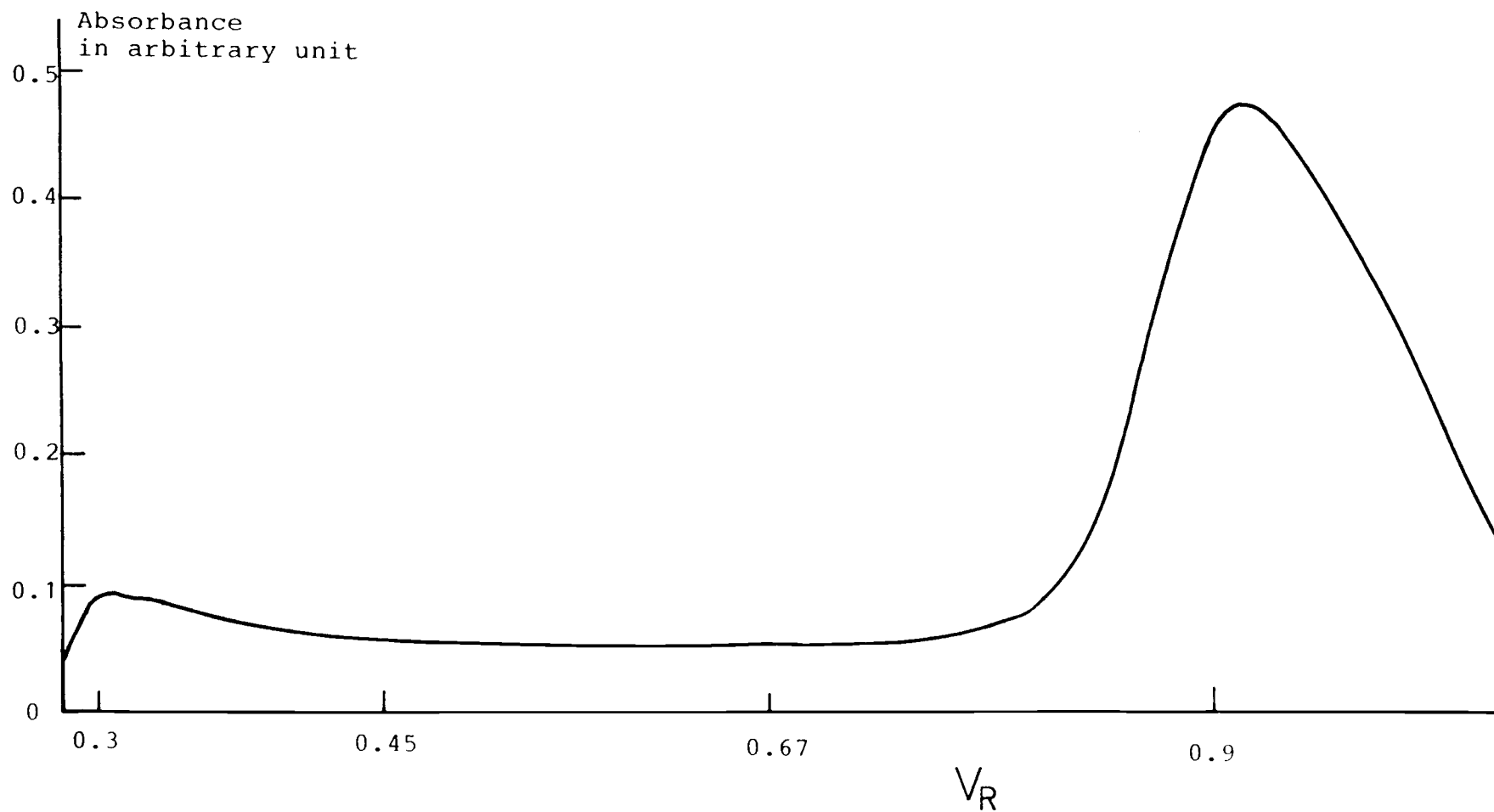


Figure 5. Elution curve of Orzan Lignin Sulfonate

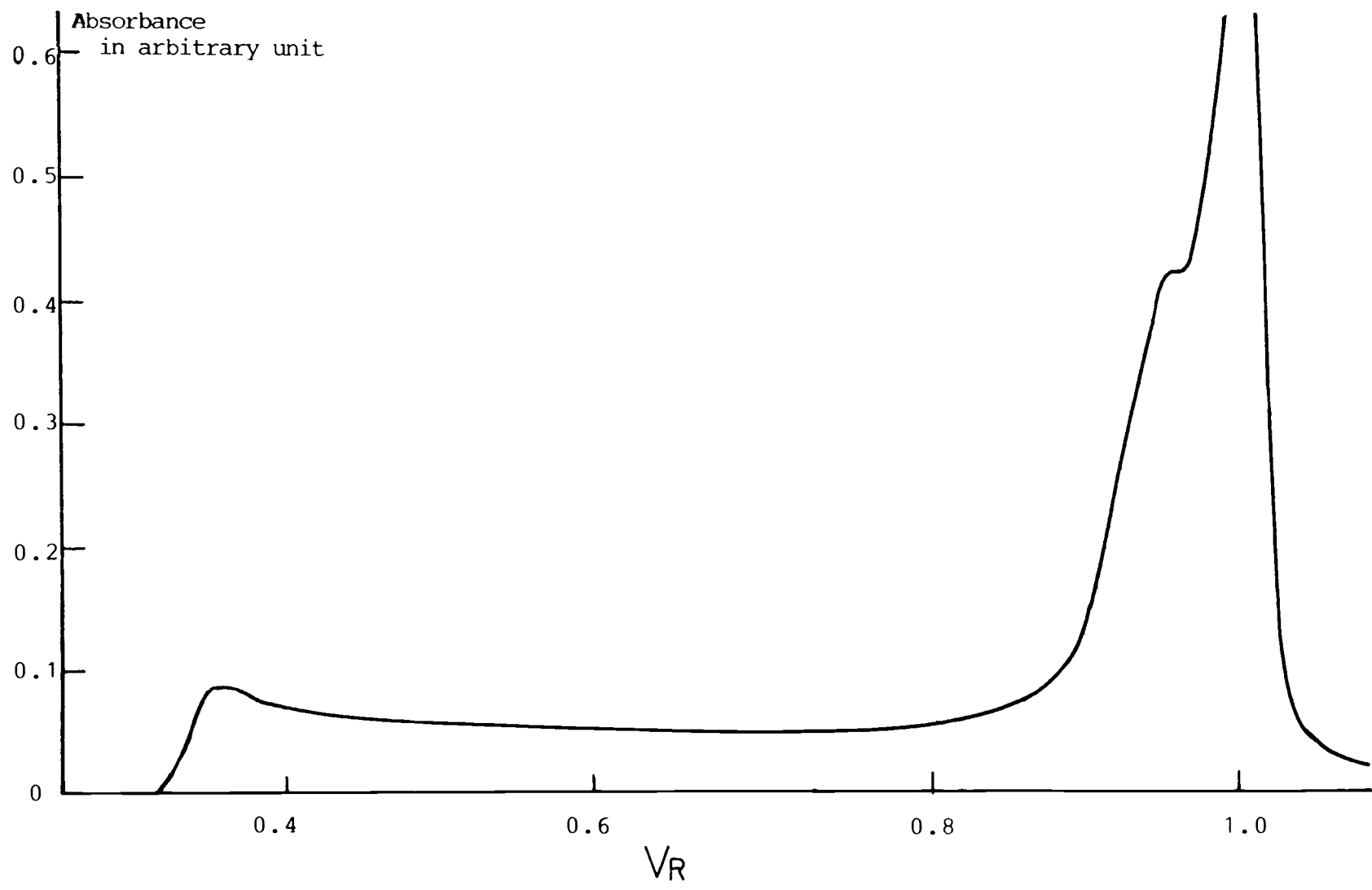


Figure 6. Elution curve of the low molecular weight NaLS

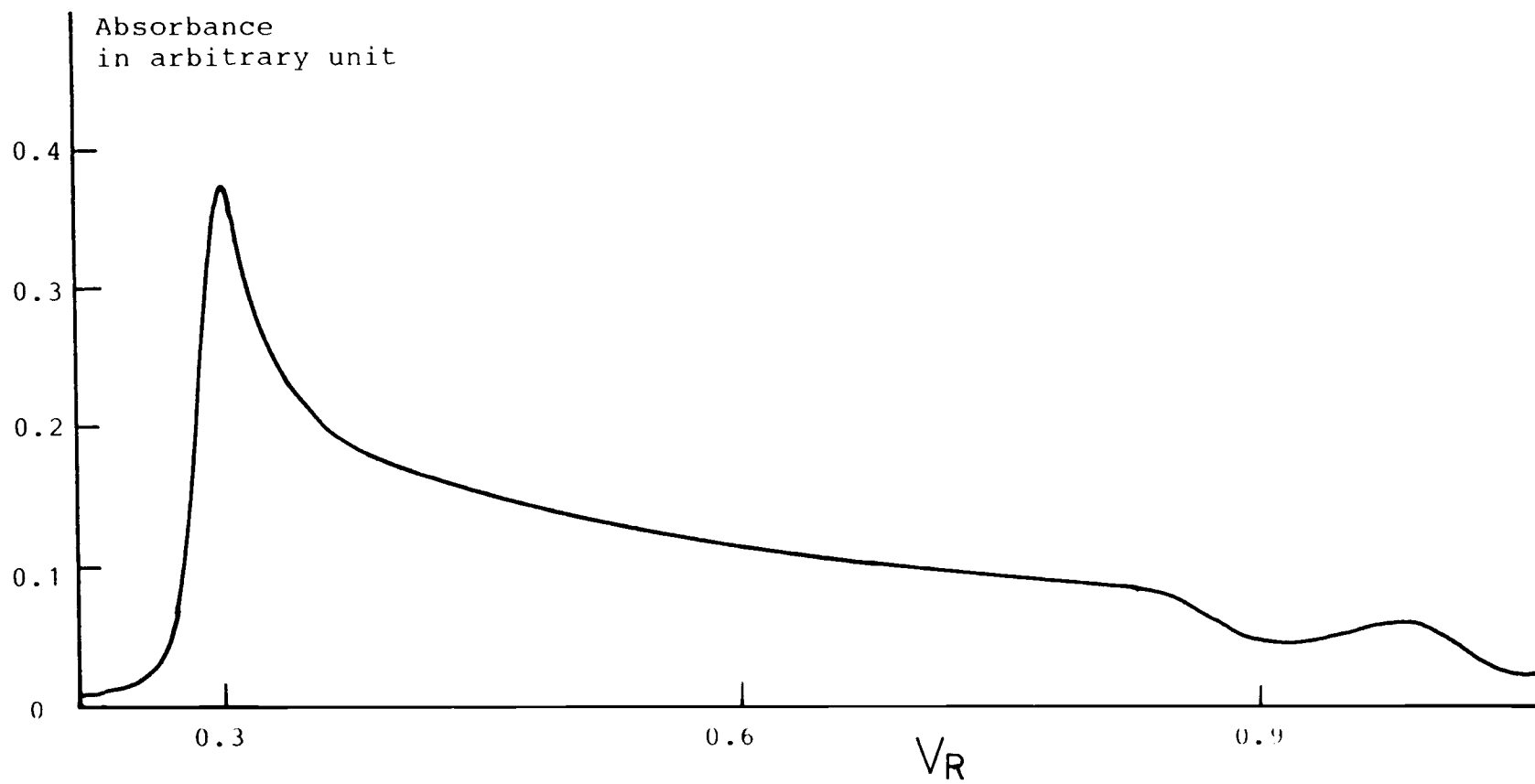


Figure 7. Elution curve of the medium molecular weight NaLS

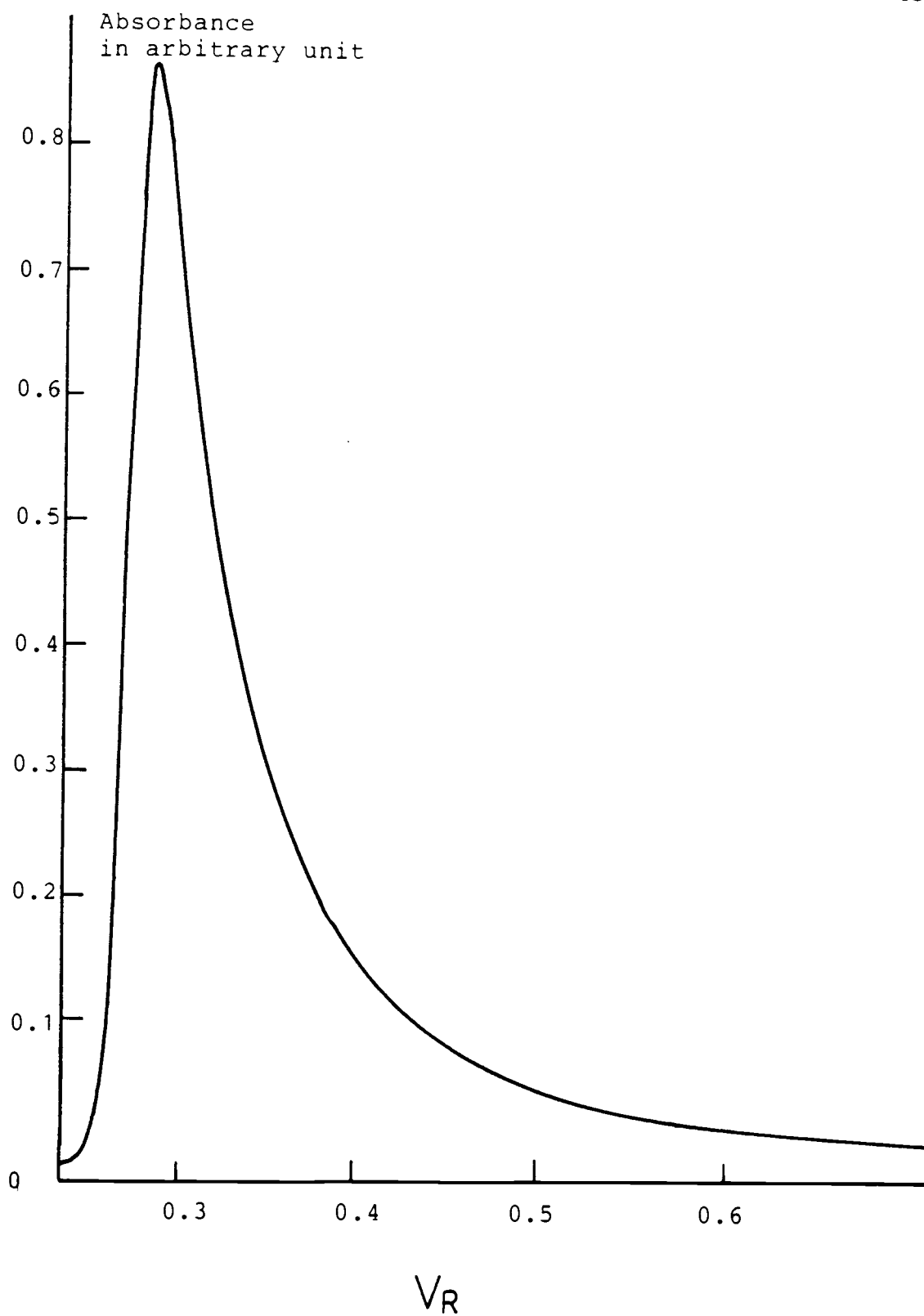


Figure 8. Elution curve of the high molecular weight NaPS

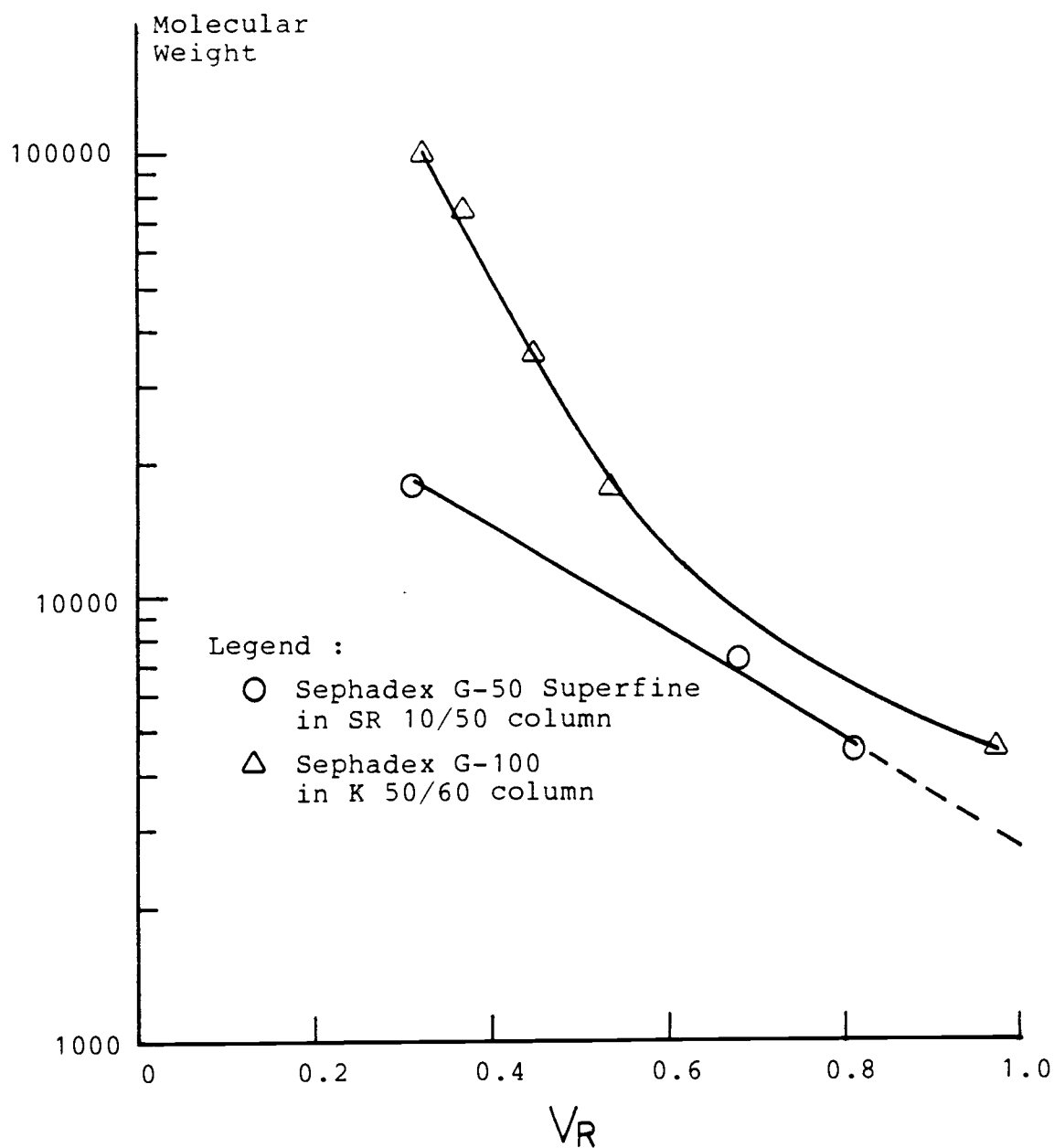


Figure 9. Calibration curves of the SR 10/50 and K 50/60 columns

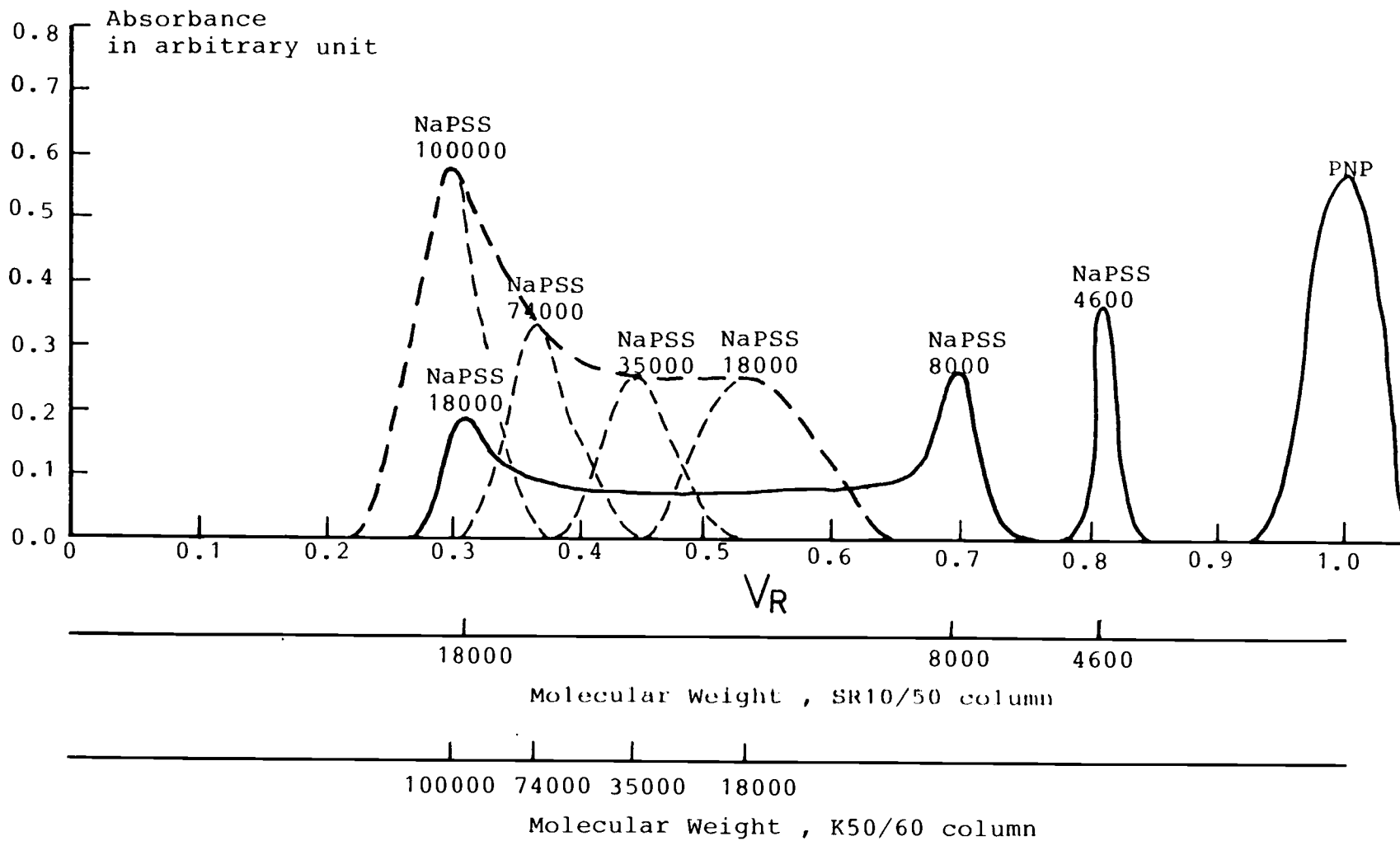


Figure 10. Calibration elution of the columns using Sodium Polystyrene Sulfonate Standards

graphical integration. The Mw for low, medium, and high molecular weight fractions, calculated by this method, are 4700, 40700, and 82500 respectively.

The molecular weight distribution for each fraction is shown in Figure 11. Combining Figure 11 and the elution curve for the unfractionated Orzan LS, Figure 5, it can be concluded that Orzan LS has a similar molecular weight distribution compared to the published work as shown in Figure 12⁽¹⁸⁾, i.e., an almost flat molecular weight distribution on an absorbance versus logarithmic of molecular weight plot from 500 to about 100000, the molecules whose size fall within this range contribute about 90 percent of the total weight of Orzan LS.

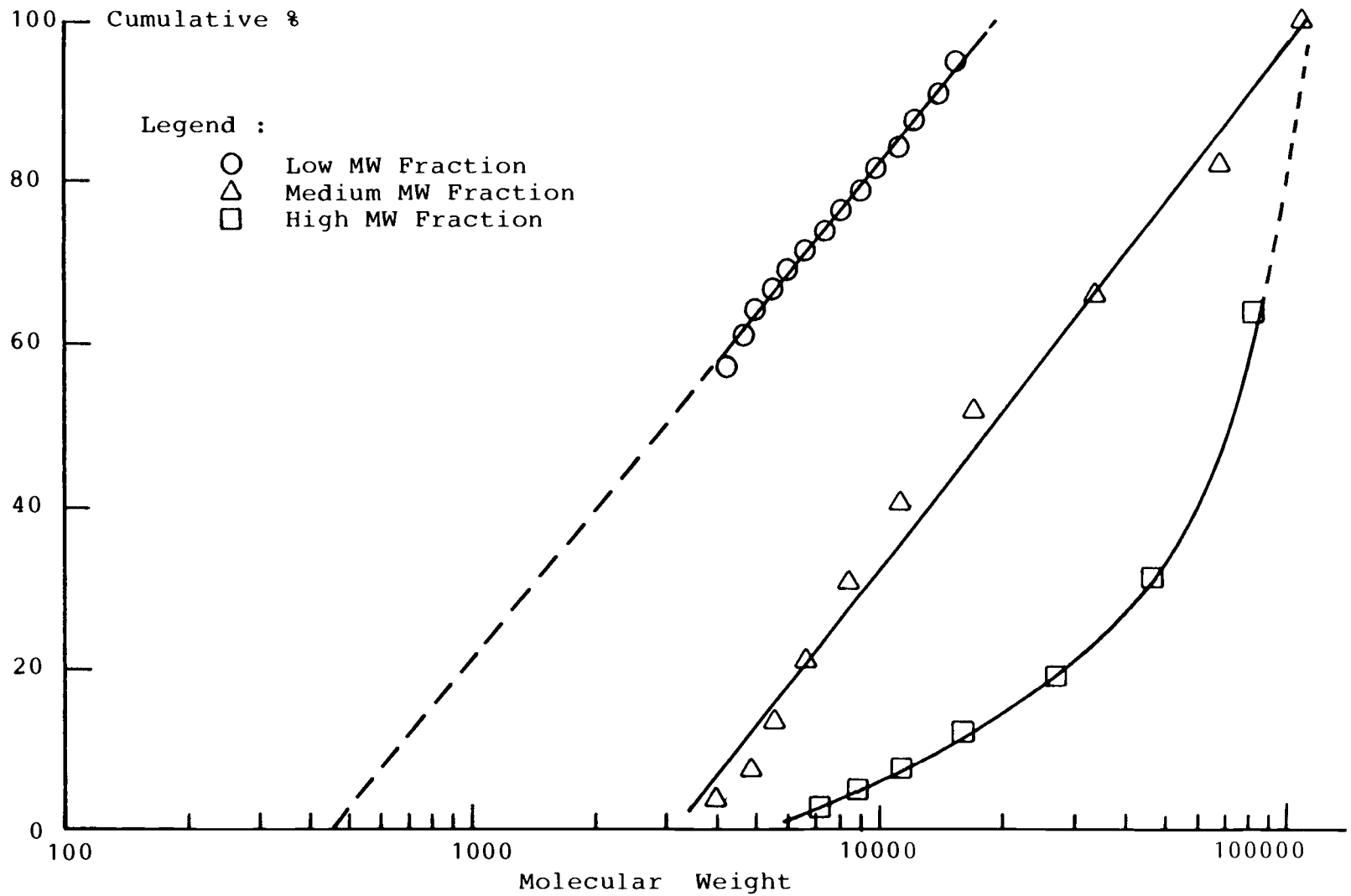


Figure 11. Molecular weight distribution of the three different fractions

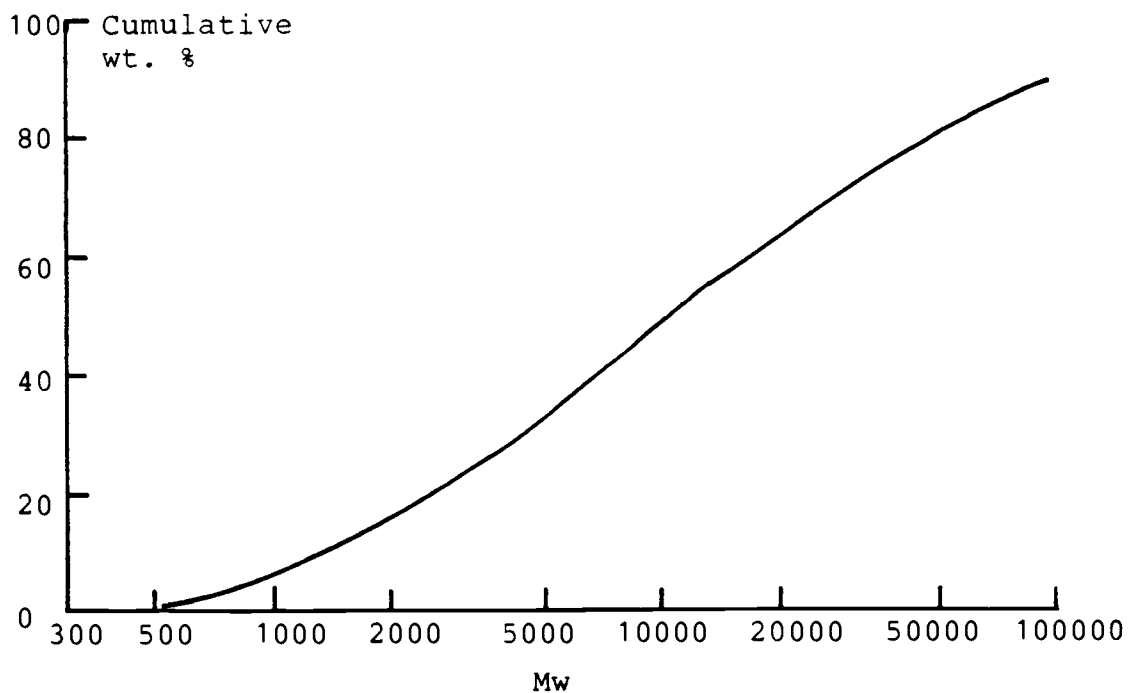


Figure 12. The molecular weight distribution of lignin sulfonates in Gupta's work⁽¹⁸⁾.

B. Cloud Point Compositions

The cloud point compositions calculated from the experimental data with the help of equation (27) are shown in the Appendix A-5.

Figure 13 shows the phase diagram of the three fractions of NaLS in the water-ethanol mixed solvent in triangular coordinates. The shaded area in the small triangle shows the range of the present study. For a given NaLS having an average molecular weight of M_w dissolved in water-ethanol mixed solvent, if the solution has a water volume fraction higher than that of the cloud point curve, all the NaLS molecules are in the dissolved state. If some NaLS or/and ethanol is added into the solution, the volume fraction of water will drop down with the accompanied increasing in volume fraction of the other two components. Once the cloud point curve is reached, phase separation will occur and further decreases in the water volume fraction will result in a NaLS rich gel phase and a NaLS deficient sol phase.

C. Flory - Huggins Equation Parameters

Thirteen cloud point compositions data of each NaLS fraction are substituted into equation (24). The substitutions result in thirteen simultaneous non-linear algebraic equations for each fraction. The IMSL subroutine ZXSSQ is then used to solve for the Flory - Huggins equation parameters. The calling program is shown in Appendix A-6.

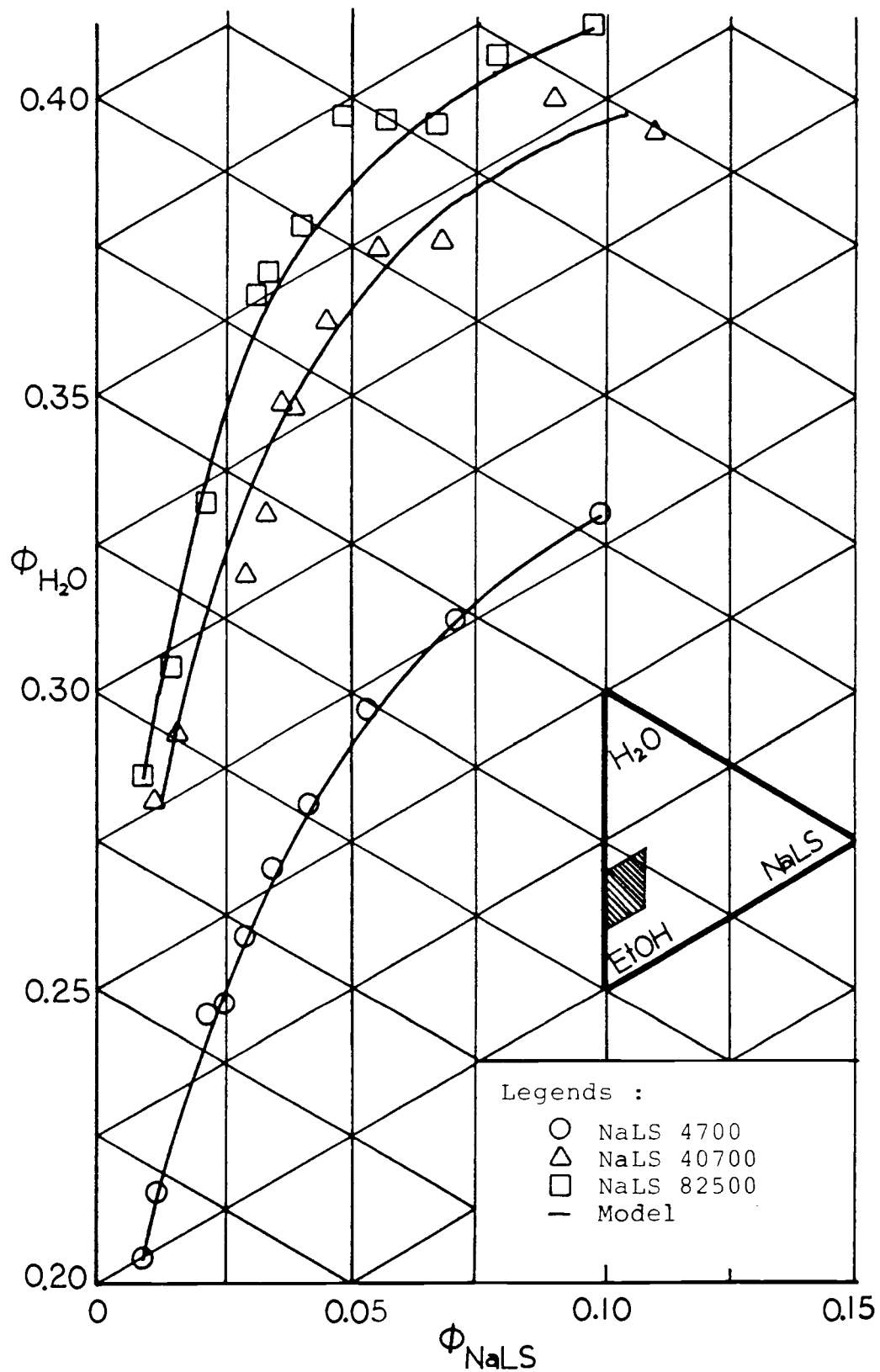


Figure 13. Cloud point composition of the Water - NaLS - Ethanol system

Table 2 shows the results of calculations. The experimental data fit the model well as can be seen through the small sum of square of residuals and the small individual residual of each data point (not shown in the table). However, the model has the weakness that all the parameters are independent of the solution composition, which is the most controversial point of the Flory - Huggins equation.

In order to include the composition dependence of the parameters, the following relationship is applied to substitute for the interaction parameters.

$$\begin{aligned}
 X_{12} &= A \frac{\phi_3}{\phi_1} + B \\
 X_{13} &= C \frac{\phi_3}{\phi_1} + D \quad \dots\dots\dots(28) \\
 X_{23} &= E \frac{\phi_3}{\phi_1} + F
 \end{aligned}$$

It is further assumed that the enthalpy of fusion ΔH and fusion temperature T_2^0 are independent of the solution composition in the range of the experimental study.

Table 2. Flory - Huggins equation parameters
(calculated under the assumption that
the parameters are independent of solution
composition).

NaLS Fraction	NaLS 4700	NaLS 40700	NaLS 82500
X_{12}	-0.3157	-0.9783	-0.9105
X_{13}	-1.1542	0.2953	0.2120
X_{23}	-0.1598	-0.3825	-0.3621
ΔH (J/mol.)	148300	1031000	2064000
ΔH (J/mol. monomer) *	7697	6182	6140
T_2^0 (K)	737	1156	1374
SSQ **	0.0118	0.1129	0.0980

* Based on the monomer having the chemical structure
as 1-(3-methoxyl-4-hydroxy phenyl)-2-propene-1-
sulfonate, which has molecular weight of 244⁽¹⁴⁾.

** Sum of square of residuals.

Equation (24) and (28) may be combined to give an
equation which has a linear dependence of the Flory -
Huggins interaction parameter X_{ij} on the solvent
composition ϕ_3/ϕ_1 . The cloud point compositions data are
then substituted into the above obtained equation with ΔH
and T_2^0 having values as listed in Table 2. The

Table 3. The Flory-Huggins interaction parameters and its solvent composition dependence. χ_{ij} values listed below are calculated from the coefficients A-F which were obtained by linear regression of the cloud point composition data.

Sodium lignin sulfonate	Composition		Interaction parameters								
	ϕ_3/ϕ_1	ϕ_2	A	B	$\chi_{12} = A\phi_3/\phi_1 + B$	C	D	$\chi_{13} = C\phi_3/\phi_1 + D$	E	F	$\chi_{23} = E\phi_3/\phi_1 + F$
NaLS 82500	1.300	0.132			-0.898			-2.983			1.017
	1.462	0.099			-0.891			-3.218			1.018
	1.500	0.081			-0.889			-3.274			1.018
	1.579	0.067			-0.886			-3.388			1.018
	1.565	0.056			-0.887			-3.368			1.018
	1.556	0.048			-0.887			-3.355			1.018
	1.678	0.041	0.041	-0.951	-0.882	-1.456	-1.090	-3.533	0.007	1.008	1.019
	1.730	0.034			-0.880			-3.608			1.020
	1.929	0.025			-0.872			-3.898			1.021
	2.166	0.018			-0.862			-4.244			1.023
	2.318	0.014			-0.856			-4.464			1.024
	2.461	0.012			-0.850			-4.673			1.025
	2.501	0.009			-0.848			-4.730			1.025
	NaLS 40700	1.560	0.119			-0.834			-3.615		
1.572		0.089			-0.837			-3.572			1.032
1.723		0.067			-0.819			-3.808			1.032
1.727		0.055			-0.819			-3.815			1.032
1.800		0.046			-0.809			-3.942			1.033
1.933		0.038			-0.794			-4.139			1.034
2.089		0.032	0.121	-1.028	-0.775	-1.569	-1.106	-4.383	0.006	1.022	1.035
2.185		0.028			-0.763			-4.533			1.035
2.278		0.018			-0.752			-4.680			1.036
2.450		0.015			-0.731			-4.950			1.037
2.569		0.013			-0.717			-5.136			1.037
2.667		0.012			-0.705			-5.289			1.038
2.692		0.011			-0.702			-5.329			1.038
NaLS 4700		2.200	0.099			-1.582			-3.353		
	2.358	0.069			-1.586			-3.603			1.109
	2.500	0.053			-1.590			-3.828			1.115
	2.681	0.041			-1.594			-4.116			1.122
	2.807	0.034			-1.597			-4.315			1.128
	2.967	0.029			-1.602			-4.568			1.134
	3.118	0.024	-0.025	-1.526	-1.605	-1.584	0.132	-4.808	0.043	1.008	1.141
	3.153	0.021			-1.606			-4.863			1.142
	3.249	0.017			-1.609			-5.014			1.147
	3.470	0.014			-1.614			-5.365			1.156
	3.698	0.011			-1.620			-5.767			1.166
	3.875	0.009			-1.625			-6.007			1.173
	4.152	0.007			-1.632			-6.446			1.185

substitutions will result in thirteen simultaneous equations for each NaLS fraction, with each equation having six unknowns. The simultaneous equations are then solved by the IMSL subroutine ZXSSQ. The calling program is shown in Appendix A-7. The results of the calculations are shown in Table 3.

By further analysis of the interaction parameter according to its two contributions, i.e., the $K_1 \phi_3/\phi_1$ term and the K_2 term, where K_1 are constants, the dominant term in the expression can be isolated as shown in Table 4.

Table 4. The dominant term of X_{1j} in equation (28)

NaLS Fraction	NaLS 4700	NaLS 40700	NaLS 82500
X_{12}	B	B	B
X_{13}	$C \frac{\phi_3}{\phi_1}$	$C \frac{\phi_3}{\phi_1}$	$C \frac{\phi_3}{\phi_1}$
X_{23}	F	F	F

For example, the data in the first row of Table 3 show that $A \phi_3/\phi_1$ contributes about -6 percent of X_{12} , while B contributes +106 percent of X_{12} , and B is said to be the dominant term of X_{12} .

The above analysis shows that the interaction parameters between NaLS and water (X_{12}) and between NaLS and ethanol (X_{23}) are influenced mainly by the constant term rather than by the solvent composition term, while the interaction parameter between water and ethanol (X_{13}) is influenced mainly by the solvent composition term rather than by the constant term.

In the light of equation (8) and its lesser dependence on the ϕ_3/ϕ_1 ratio, the interaction parameters X_{12} and X_{23} were modeled instead as having a linear relationship to the logarithm of ϕ_2 , while keeping X_{13} the same as in equation (28). However, after substituting the new relationship into equation (24), the calculations did not result in physically significant interaction parameters. Therefore, such relations were not considered further.

The interaction parameters listed in the Table 3 may be interpreted as follows. X_{12} has a negative value, which means a strong interaction energy exists between the NaLS molecules and the water molecules. The strong interaction thus results in an exothermic dissolution. The negative enthalpy change is consistent with the fact that water is a good solvent for NaLS. Strong interactions are expected to exist between the ionized sulfite groups of the NaLS monomers and the polar water molecules. The data indicates that the interaction

between the smaller NaLS molecules and water is stronger than that between the larger NaLS molecules and water. The explanation for this phenomenon is that the larger NaLS molecules have more unsolvated segments during their dissolution in the mixed solvent, while the smaller NaLS molecules have shorter chain length and smaller number of segments. The smaller NaLS molecules thus can expose more of their segments to the solvent molecules, which in turn results in a larger interaction per mole of solvent. The trend of increasing interaction with decreasing in molecule size can also be seen from the enthalpy value in Table 2, where ΔH increases from 6140 to 7679 J/mol.-monomer as the Mw changes from 82500 to 4700. However, the X_{12} values for NaLS 40700 and NaLS 82500 do not follow to the above arguments (see Figure 14). There are several possible explanations for this. One is that an over titration of NaLS 82500 resulted, because it has more larger molecules (see Figure 14), thus the volume of precipitant used will higher than a sample having the same Mw but a nearly normal distribution of molecular weight. Another explanation is that under titration of NaLS 40700 resulted, because of that the number of smaller molecules are enough (see Figure 7) to form visually detectable turbidity before enough precipitant is applied to a hypothetical nearly monodisperse NaLS with Mw equal to 40700 to cause a turbid solution.

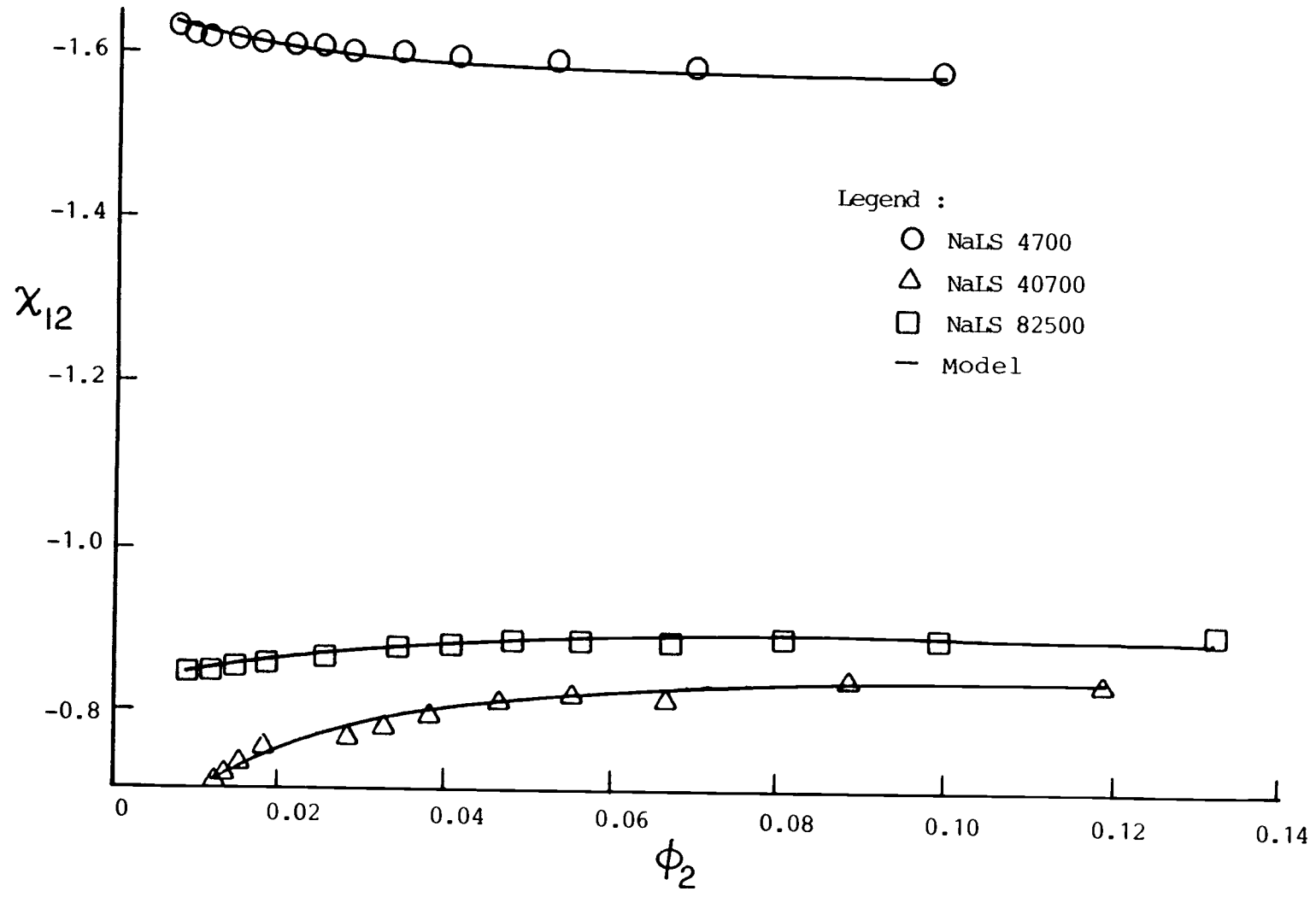


Figure 14. Interaction parameter χ_{12} as a function of ϕ_2 at the cloud point ϕ_3/ϕ_2 ratio ⁵⁹

Figure 15 shows the interaction parameter between water and ethanol, X_{13} , as a function of solvent composition, ϕ_3/ϕ_1 . The negative values of X_{13} are again consistent with the fact that ethanol and water can be mixed in any ratio with an exothermic effect. The magnitude of X_{13} in water - NaLS - ethanol system is quite similar to that in water - PEG - ethanol system in Table 1, which is a good cross check on the analysis. The slight differences between X_{13} for different molecular weight fractions might result from the different strength of interaction between NaLS, water, and ethanol molecules. When the smaller NaLS molecules dissolve in the mixed solvent, all the segments in a polymer chain are more readily contacted with the solvent molecules, and the induction of the dipole of water molecules toward the sulfonate group will thus decrease the interaction between water and ethanol. However, such effects should not be over emphasized, as the binary interaction parameter should be determined mainly by the nature of the two adjacent molecules.

Figure 16 shows the interaction parameter X_{23} as a function of NaLS volume fraction, ϕ_2 . For low molecular weight fraction, X_{23} decreases monotonically as ϕ_2 increases, while for the other two fractions, X_{23} remains almost constant. The positive values of the interaction

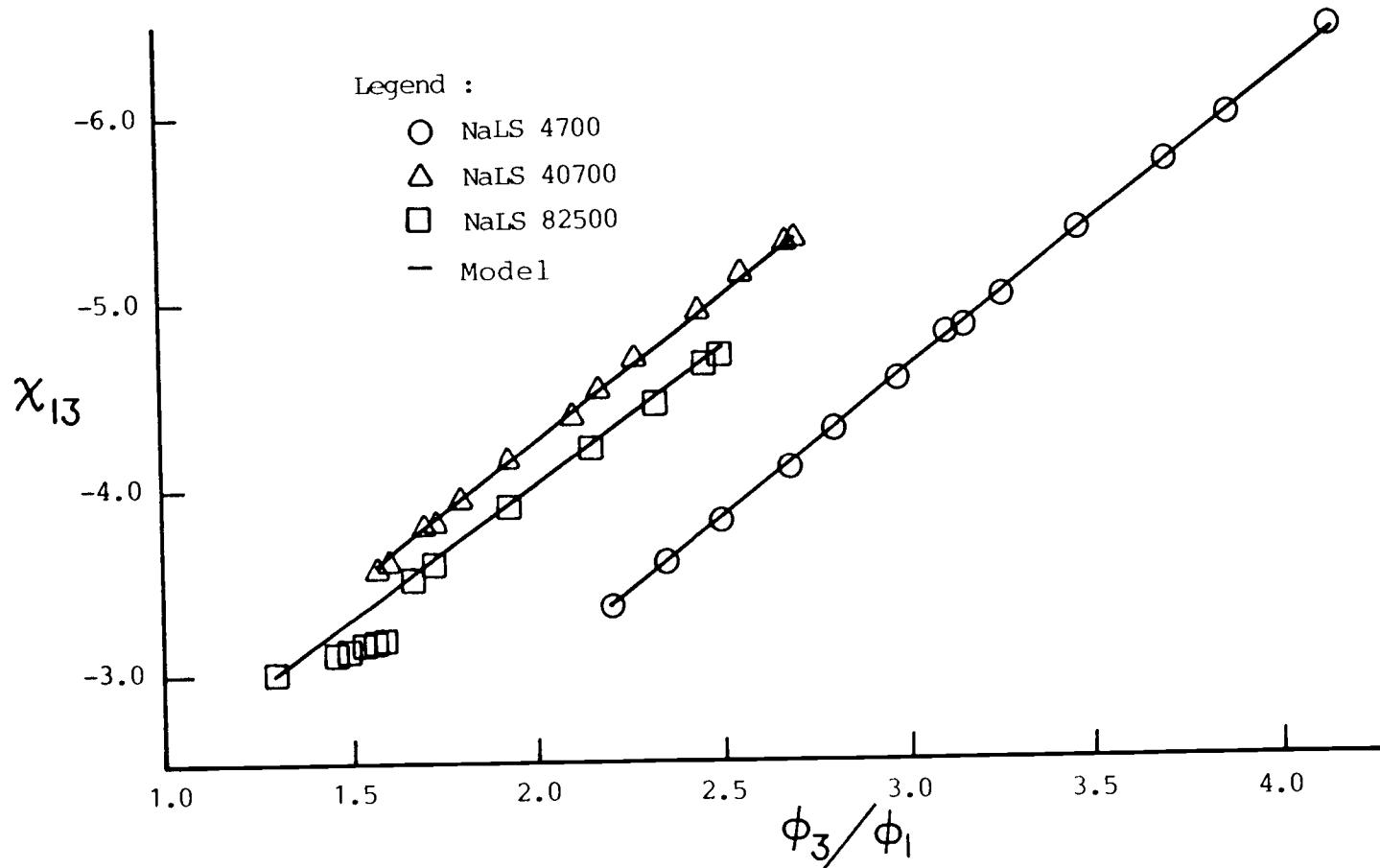


Figure 15. Interaction parameter χ_{13} as a function of ϕ_3/ϕ_1 at the cloud point ϕ_2

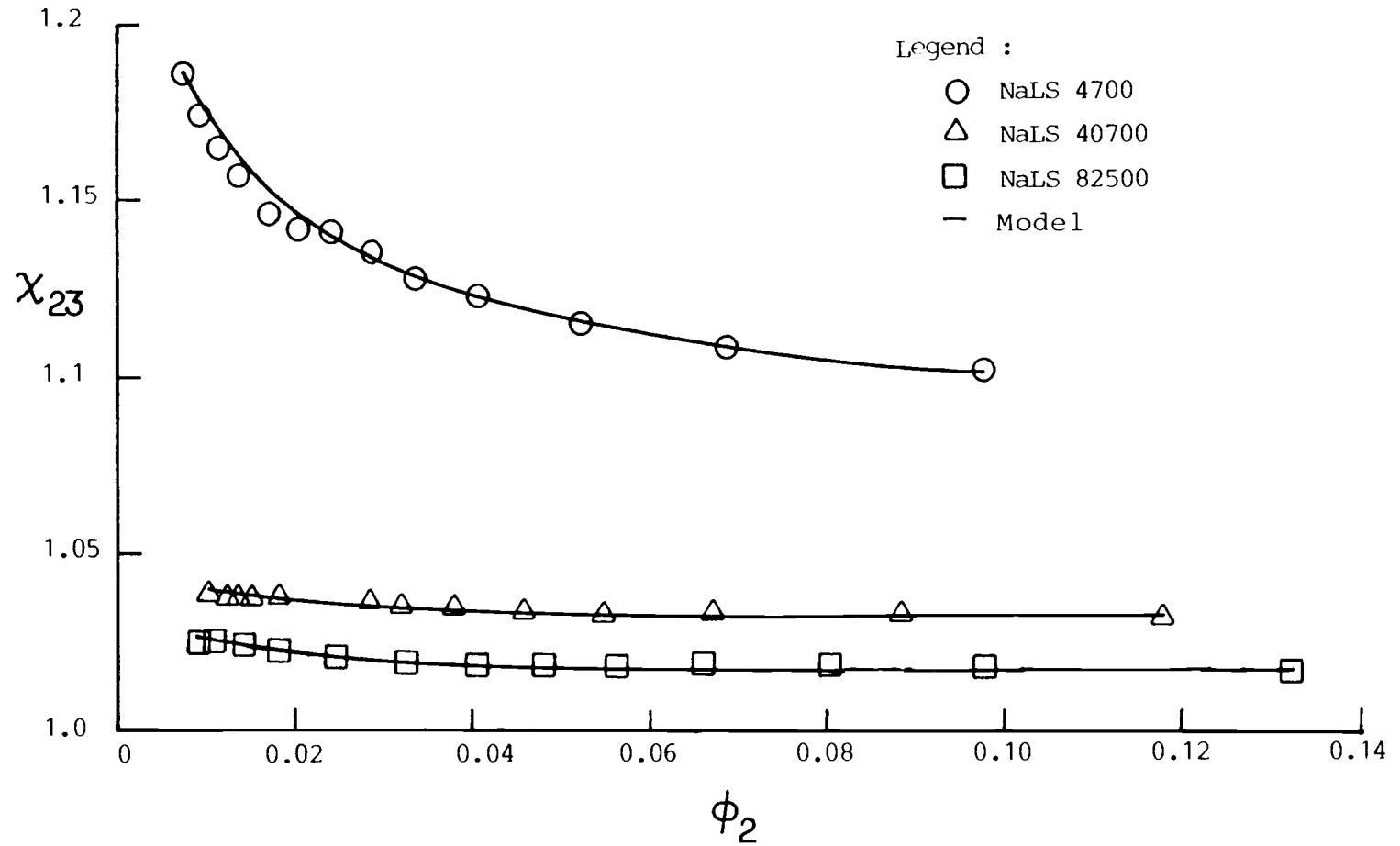


Figure 16. Interaction parameter χ_{23} as a function of ϕ_2 at the cloud point ϕ_3/ϕ_1 ratio

parameters between ethanol and NaLS indicate that ethanol is not a solvent for NaLS. Its magnitude is increased as ϕ_3/ϕ_1 increase (see Table 3), and it will never be close to 0.5. Thus from equation (8), the solubility of NaLS in ethanol is negligible and separation of NaLS from a water-NaLS-ethanol system will always occur as ethanol is added.

D. Application of the Calculated Flory - Huggins Equation Parameters to Solubility Prediction

For a specified NaLS fraction and a given solvent composition ϕ_3/ϕ_1 in the experimental range, ϕ_2 can be estimated by substituting the calculated values of X_{12} , X_{13} , X_{23} , ΔH , and T_2^0 into equation (24). Compared to the experimental ϕ_2 , the deviations are within 4 percent. Thus, the Flory - Huggins equation explains well the experimental findings on the present studied chemical system. Also, the non-linear regression algorithm used to correlate the experimental data does results in a good correlation as can be seen by the small residual for each data point (not shown in Table 3).

CONCLUSIONS

1. Fractionation by partial dissolution is a workable method for fractionating lignin sulfonates into different molecular weight fractions, especially when removing polysaccharides from the sample is desired. To get a narrower molecular weight distribution, it is recommended that the ethanol percentage difference between two consecutive runs be kept small, e.g., 2 - 3 percent.
2. The cloud point titration technique gives reproducible phase equilibrium data for the two systems used in this study and results for PEG are consistent with published data.
3. The Flory - Huggins equation for a monodisperse polymer results in a good correlation of the cloud point data for water-NaLS-ethanol system even though the NaLS fractions used in this study are polydisperse.
4. Physically significant values of X_{12} , X_{13} , and X_{23} were obtained. After combining with ΔH and T_2^0 , the solubility of a specified NaLS fraction in a mixed solvent for a given value of ϕ_3/ϕ_1 can be calculated.

RECOMMENDATIONS

1. Obtain interaction parameter for a larger number of Mw's. This could be done by one of the two methods.
 - A. By using partial dissolution and a narrower range of ethanol/water ratio to generate NaLS fraction with Mw's near 10000 and 20000.
 - B. By using preparative size exclusion chromatography to generate a series of samples with narrow molecular weight ranges.

The samples could be used to obtain X_{ij} values in the NaLS molecular weight range between 4700 and 40700 to give a more complete picture of the solubility behavior of the polydisperse system.

2. Mixing rules for estimating the solubility of polydisperse NaLS from the properties of narrow molecular weight fractions should be proposed and tested.
3. A separate calorimetric study should be done on the sodium lignin sulfonates dissolution process to obtain ΔH_m , ΔS_m , and ΔG_m . Use these values to evaluate the interaction parameter X_{ij} , to see if it is consistent with the present study.

4. The cloud point composition data could be analyzed using polyelectrolyte solution theory. This method might account for the strong ionic interaction between the ionized sites of the lignin sulfonate and water molecules.

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APPENDIX

A-1. Chemical Potential of Polymeric Solute in a Binary Solution

$$\Delta G_m = kT (N_1 \ln \phi_1 + N_2 \ln \phi_2 + XN_1 \phi_2)$$

$$\begin{aligned} \text{where } \phi_1 &= \frac{n_1 V_1}{n_1 V_1 + n_2 V_2} = \frac{(N_1/N_o) V_1}{(N_1/N_o) V_1 + (N_2/N_o) V_2} \\ &= \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \end{aligned}$$

$$\text{and } \phi_2 = \frac{N_2 V_2}{N_1 V_1 + N_2 V_2}$$

$$\mu_2 - \mu_2^o = \left(\frac{\partial \Delta G_m}{\partial N_2} \right)_{N_1}$$

$$\begin{aligned} &= kT \frac{\partial}{\partial N_2} \left(N_1 \ln \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} + N_2 \ln \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \right. \\ &\quad \left. + XN_1 \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \right) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial N_2} \left(N_1 \ln \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \right) &= N_1 \left(\frac{N_1 V_1 + N_2 V_2}{N_1 V_1} \cdot \frac{-N_1 V_1 V_2}{(N_1 V_1 + N_2 V_2)^2} \right) \\ &= \frac{-N_1 V_2}{N_1 V_1 + N_2 V_2} \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial N_2} \left(N_2 \ln \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \right) &= \ln \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} + N_2 \frac{N_1 V_1 + N_2 V_2}{N_2 V_2} \cdot \\ &\left(\frac{V_2}{N_1 V_1 + N_2 V_2} + \frac{-N_2 V_2 V_2}{(N_1 V_1 + N_2 V_2)^2} \right) \\ &= \ln \phi_2 + (1 - \phi_2) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial N_2} \left(X N_1 \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \right) &= X N_1 \left(\frac{V_2}{N_1 V_1 + N_2 V_2} - \frac{N_2 V_2 V_2}{(N_1 V_1 + N_2 V_2)^2} \right) \\ &= X \left(\frac{N_1 V_2}{N_1 V_1 + N_2 V_2} - \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \cdot \right. \\ &\quad \left. \frac{N_1 V_2}{N_1 V_2 + N_2 V_2} \right) \end{aligned}$$

Define the number of segments in a polymer chain, x_2

$$x_2 = \frac{V_2}{V_1} = \frac{M_w v_2}{V_1}$$

Substitute into the above equations

$$\begin{aligned} \frac{-N_1 V_2}{N_1 V_1 + N_2 V_2} &= \frac{-N_1 V_1 x_2}{N_1 V_1 + N_2 V_2} = -x_2 \phi_1 = -x_2 (1-\phi_2) \\ X \left(\frac{N_1 V_2}{N_1 V_1 + N_2 V_2} - \frac{N_2 V_2}{N_1 V_1 + N_2 V_2} \cdot \frac{N_1 V_2}{N_1 V_1 + N_2 V_2} \right) \\ &= X (x_2 (1-\phi_2) - \phi_2 x_2 (1-\phi_2)) \\ &= X x_2 (1-\phi_2)^2 \end{aligned}$$

Thus,

$$\begin{aligned} \mu_2 - \mu_2^{\circ} &= \left(\frac{\partial \Delta G_m}{\partial N_2} \right)_{N_1} \\ &= kT (-x_2 (1-\phi_2) + \ln \phi_2 + (1-\phi_2) + X x_2 (1-\phi_2)^2) \end{aligned}$$

Rearrange and convert into molar unit

$$\mu_2 - \mu_2^{\circ} = RT (\ln \phi_2 + (1-x_2)(1-\phi_2) + x_2 X (1-\phi_2)^2)$$

A2. Enthalpy Change of Dissolution of Polymeric Solute
in a Binary Solution

$$\Delta G = \mu_{2,\text{aggregate}} - \mu_{2,\text{solution}}$$

$$\frac{-\Delta G}{RT} = \frac{\mu_{2,\text{solu}} - \mu_{2,\text{aggr}}}{RT} \quad \dots\dots\dots(\text{A-2-1})$$

Integrate the following Gibbs - Helmholtz equation

$$\left(\frac{\partial (\Delta G/T)}{\partial T} \right)_P = \frac{-\Delta H}{T^2}$$

from T_2 , at which the solutes in solution and in the undissolved aggregates are in equilibrium, to T_2° , at which the polymer aggregates start to melt.

$$\int_{T_2}^{T_2^{\circ}} d(\Delta G/T) = \int_{T_2}^{T_2^{\circ}} \frac{-\Delta H}{T^2} dT \quad \dots\dots\dots(\text{A-2-3})$$

$$\int_{T_2}^{T_2^{\circ}} d(\Delta G/T) = \frac{\Delta G}{T_2^{\circ}}, \text{ because } \Delta G = 0 \text{ at equilibrium} \quad \dots\dots\dots(\text{A-2-4})$$

$$\int_{T_2}^{T_2^{\circ}} \frac{-\Delta H}{T^2} dT = \Delta H \left(\frac{1}{T_2^{\circ}} - \frac{1}{T_2} \right) \quad \dots\dots\dots(\text{A-2-5})$$

Combining equation (A-2-1), (A-2-3), (A-2-4), and (A-2-5)

$$\frac{\mu_2 - \mu_2^0}{R T} = \frac{-\Delta G}{R T_2^0} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_2^0} \right) \dots\dots\dots (A-2-6)$$

Where the chemical potential difference is given by equation (21) as

$$\frac{\mu_2 - \mu_2^0}{R T} = \ln \phi_2 - (x_2 - 1)(1 - \phi_2) + X x_2 (1 - \phi_2)^2 \dots\dots (21)$$

Combining equation (21) with equation (A-2-6), the following equation can be obtained.

$$\frac{1}{x_2} \ln \phi_2 - (1 - 1/x_2)(1 - \phi_2) + X(1 - \phi_2)^2 = \frac{\Delta H}{R x_2} \left(\frac{1}{T_2} - \frac{1}{T_2^0} \right)$$

A-3. Cloud point compositions of Water(1) - PEG(2) - Ethanol(3) system

PEG 8650			PEG 12600			PEG 22000		
ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3
0.0443	0.0707	0.8851	0.0445	0.0649	0.8906	0.0939	0.2022	0.7039
0.0368	0.0445	0.9188	0.0400	0.0489	0.9111	0.0566	0.0938	0.8496
0.0339	0.0352	0.9310	0.0370	0.0391	0.9239	0.0516	0.0726	0.8760
0.0315	0.0247	0.9439	0.0316	0.0213	0.9472	0.0451	0.0537	0.9012
0.0274	0.0146	0.9581	0.0275	0.0115	0.9611	0.0371	0.0341	0.9287
0.0242	0.0088	0.9670	0.0243	0.0048	0.9709	0.0316	0.0182	0.9502
0.0216	0.0054	0.9730	0.0217	0.0020	0.9763	0.0276	0.0052	0.9672
0.0196	0.0026	0.9778				0.0243	0.0025	0.9732
						0.0217	0.0012	0.9771

A-4. Calling Program for Flory - Huggins Equation Parameter
Calculation for Water - PEG - Ethanol System

```

C      CALCULATION OF WATER(1)-PEG(2)-ETHANOL(3) INTERACTION
C      PARAMETER WITHOUT SOLVENT COMPOSITION DEPENDENCE
C      USING IMSL SUBROUTINE ZXSSQ (NONLINEAR OPTIMIZATION
C      METHOD)

      PROGRAM POLY
      EXTERNAL FUNC
      INTEGER M,N,IXJAC,NSIG,MAXFN,IOPT,I,INFER,IER
      REAL PARM(4),X(5),F(6),XJAC(6,5),XJTJ(15),WORK(52),
*      EPS,DELTA,VF1(6),VF2(6),VF3(6),SN(6),
*      PEGMW,PEGSPV,R,SSQ
C      SN=NUMBER OF SEGMENTS OF PEG, R=GAS CONSTANT
      COMMON /SSQ/VF1,VF2,VF3,SN,R
      M=6
      N=5
      IXJAC=6
      NSIG=3
      EPS=0.0
      DELTA=0.0
      MAXFN=1000
      IOPT=1
C      VARIABLES IN FLORY - HUGGINS EQUATION
C      X(1)=X12
C      X(2)=X13
C      X(3)=X23
C      X(4)=Delta H
C      X(5)=Tf
      R=8.314
C      INPUT EXPERIMENTAL DATA AND INITIAL GUESS VALUE
C      OF X(I)
      OPEN (5,FILE='PEG1.DAT')
      READ (5,*) PEGMW,PEGSPV
      READ (5,*) (VF1(I),I=1,6)
      READ (5,*) (VF3(I),I=1,6)
      READ (5,*) (X(I),I=1,5)
C      CALCULATE AND PRINT CLOUD POINT VOLUME FRACTION
      7  FORMAT(1X,6F12.4)
      DO 30 K=1,6
      VF2(K)=1.-VF1(K)-VF3(K)
      SN(K)=PEGMW*PEGSPV/(57.33*(VF3(K)/(VF3(K)+VF1(K)))
*      +17.68*VF1(K)/(VF3(K)+VF1(K)))
      30 CONTINUE
      WRITE(*,7) (VF1(I),I=1,6)
      WRITE(*,7) (VF2(I),I=1,6)
      WRITE(*,7) (VF3(I),I=1,6)
      WRITE (*,7) (SN(I),I=1,6)

```

```
CALL ZXSSQ(FUNC,M,N,NSIG, EPS, DELTA, MAXFN, IOPT, PARM, X,  
*          SSQ, F, XJAC, IXJAC, XJTJ, WORK, INFER, IER)  
WRITE(*,7) (X(I), I=1, 5)  
WRITE(*,7) SSQ  
WRITE(*,7) (F(I), I=1; 6)  
STOP  
END  
SUBROUTINE FUNC(X, M, N, F)  
INTEGER M, N, I  
REAL X(N), F(M), VF1(6), VF2(6), VF3(6), SN(6), R  
COMMON /SSQ/VF1, VF2, VF3, SN, R  
DO 40 I=1, 6  
P1=LOG(VF2(I))  
P2=+(SN(I)-1.)*(1.-VF2(I))  
P3=SN(I)*(X(1)*VF1(I)+X(3)*VF3(I))*(1.-VF2(I))  
P4=SN(I)*(X(2)*VF1(I)*VF3(I))  
Y=(X(4)/R)*((1./298.)-(1./X(5)))  
F(I)=P1+P2+P3+P4-Y  
40 CONTINUE  
RETURN  
END
```

A-5. Cloud point composition of Water(1) - NaLS(2) - Ethanol system

NaLS 82500			NaLS 40700			NaLS 4700		
ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3	ϕ_1	ϕ_2	ϕ_3
0.3773	0.1321	0.4906	0.3391	0.1185	0.5424	0.2817	0.0986	0.6197
0.3662	0.0986	0.5352	0.3544	0.0885	0.5571	0.2772	0.0693	0.6535
0.3678	0.0805	0.5517	0.3428	0.0667	0.5905	0.2707	0.0526	0.6767
0.3619	0.0667	0.5714	0.3465	0.0551	0.5984	0.2604	0.0414	0.6982
0.3681	0.0558	0.5761	0.3399	0.0457	0.6144	0.2537	0.0341	0.7122
0.3724	0.0483	0.5793	0.3279	0.0382	0.6339	0.2449	0.0286	0.7265
0.3583	0.0405	0.6012	0.3133	0.0323	0.6544	0.2369	0.0244	0.7387
0.3541	0.0335	0.6124	0.3052	0.0281	0.6667	0.2357	0.0211	0.7432
0.3329	0.0250	0.6421	0.2997	0.0175	0.6828	0.2313	0.0173	0.7514
0.3101	0.0181	0.6718	0.2855	0.0150	0.6995	0.2205	0.0144	0.7651
0.2971	0.0142	0.6887	0.2765	0.0132	0.7103	0.2105	0.0110	0.7785
0.2856	0.0115	0.7029	0.2696	0.0118	0.7186	0.2033	0.0089	0.7878
0.2832	0.0086	0.7082	0.2679	0.0108	0.7213	0.1927	0.0072	0.8001

A-6. Calling Program (1) for Flory - Huggins EquationParameter Calculations for Water-NaLS-Ethanol System

```

C      CALCULATION OF WATER(1) - NaLS(2) - ETHANOL(3)
C      INTERACTION PARAMETER WITHOUT SOLVENT COMPOSITION
C      DEPENDENCE
C      USING IMSL SUBROUTINE ZXSSQ (NONLINEAR OPTIMIZATION
C      METHOD)

      PROGRAM POLY
      EXTERNAL FUNC
      INTEGER M,N,IXJAC,NSIG,MAXFN,IOPT,I,INFER,IER
      REAL PARM(4),X(5),F(13),XJAC(13,5),XJTJ(15),WORK(66),
*      EPS,DELTA,VF1(13),VF2(13),VF3(13),SN(13),NALSMW,
*      NALSSPV,R,SSQ
C      SN=NUMBER OF SEGMENTS OF NaLS, R=GAS CONSTANT
      COMMON /SSQ/VF1,VF2,VF3,SN,R
      M=13
      N=5
      IXJAC=13
      NSIG=3
      EPS=0.0
      DELTA=0.0
      MAXFN=1000
      IOPT=1
C      VARIABLES IN FLORY - HUGGINS EQUATION
C      X(1)=X12
C      X(2)=X13
C      X(3)=X23
C      X(4)=Delta H
C      X(5)=Tf
      R=8.314
C      INPUT EXPERIMENTAL DATA AND INITIAL GUESS VALUE
C      OF X(I)
      OPEN (5,FILE='NaLS1.DAT')
      READ (5,*) NaLSMW,NaLSSPV
      READ (5,*) (VF1(I),I=1,13)
      READ (5,*) (VF3(I),I=1,13)
      READ (5,*) (X(I),I=1,5)
C      CALCULATE AND PRINT CLOUD POINT VOLUME FRACTION
      7  FORMAT(1X,13F12.4)
      DO 30 K=1,13
      VF2(K)=1.-VF1(K)-VF3(K)
      SN(K)=NaLSMW*NaLSSPV/(57.33*(VF3(K)/(VF3(K)+VF1(K)))
*      +17.68*VF1(K)/(VF3(K)+VF1(K)))
      30 CONTINUE
      WRITE(*,7) (VF1(I),I=1,13)
      WRITE(*,7) (VF2(I),I=1,13)
      WRITE(*,7) (VF3(I),I=1,13)

```

```

WRITE (*,7) (SN(I),I=1,13)
C  VARIABLES CALCULATION BY IMSL SUBROUTINE
CALL ZXSSQ(FUNC,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,
*      SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
WRITE(*,7) (X(I),I=1,5)
WRITE(*,7) SSQ
WRITE(*,7) (F(I),I=1,13)
STOP
END
SUBROUTINE FUNC(X,M,N,F)
INTEGER M,N,I
REAL X(N),F(M),VF1(13),VF2(13),VF3(13),SN(13),R
COMMON /SSQ/VF1,VF2,VF3,SN,R
DO 40 I=1,13
P1=LOG(VF2(I))
P2=+(SN(I)-1.)*(1.-VF2(I))
P3=SN(I)*(X(1)*VF1(I)+X(3)*VF3(I))*(1.-VF2(I))
P4=SN(I)*(X(2)*VF1(I)*VF3(I))
Y=(X(4)/R)*((1./298.)-(1./X(5)))
F(I)=P1+P2+P3+P4-Y
40 CONTINUE
RETURN
END

```

A-7. Calling Program (2) for Flory - Huggins EquationParameters Calculations for Water-NaLS-Ethanol System

```

C      CALCULATION OF WATER(1)-NaLS(2)-ETHANOL(3)
C      INTERACTION PARAMETER WITH SOLVENT COMPOSITION
C      DEPENDENCE
C      USING IMSL SUBROUTINE ZXSSQ (NONLINEAR OPTIMIZATION
C      METHOD)

      PROGRAM POLY
      EXTERNAL FUNC
      INTEGER M,N,IXJAC,NSIG,MAXFN,IOPT,I,INFER,IER
      REAL PARM(4),X(6),F(13),XJAC(13,6),XJTJ(21),WORK(77),
*      EPS,DELTA,VF1(13),VF2(13),VF3(13),SN(13),NALSMW,
*      NALSSPV,R,SSQ,X12(13),X13(13),X23(13),DeltaH,Tf
C      SN=NUMBER OF SEGMENTS OF NaLS, R=GAS CONSTANT
      COMMON /SSQ/VF1,VF2,VF3,SN,R,DeltaH,Tf
      M=13
      N=6
      IXJAC=13
      NSIG=3
      EPS=0.0
      DELTA=0.0
      MAXFN=1000
      IOPT=1
C      VARIABLES IN FLORY - HUGGINS EQUATION
C      X12=A*VF3/VF1+B
C      X13=C*VF3/VF1+D
C      X23=E*VF3/VF1+F
C      X(1)=A
C      X(2)=B
C      X(3)=C
C      X(4)=D
C      X(5)=E
C      X(6)=F
C      X(7)=Delta H, FIXED
C      X(8)=Tf, FIXED
      R=8.314
C      INPUT EXPERIMENTAL DATA AND INITIAL GUESS VALUE
C      OF X(I)
      OPEN (5,FILE='NaLS1.DAT')
      READ (5,*) NaLSMW,NaLSSPV,DeltaH,Tf
      READ (5,*) (VF1(I),I=1,13)
      READ (5,*) (VF3(I),I=1,13)
      READ (5,*) (X(I),I=1,6)
C      CALCULATE AND PRINT CLOUD POINT VOLUME FRACTION
7      FORMAT(1X,13F12.4)
      DO 30 K=1,13
      VF2(K)=1.-VF1(K)-VF3(K)

```

```

      SN(K)=NaLSMW*NaLSSPV/(57.33*(VF3(K)/(VF3(K)+VF1(K)))
*      +17.68*VF1(K)/(VF3(K)+VF1(K)))
30  CONTINUE
      WRITE(*,7) (VF1(I),I=1,13)
      WRITE(*,7) (VF2(I),I=1,13)
      WRITE(*,7) (VF3(I),I=1,13)
      WRITE(*,7) (SN(I),I=1,13)
C   VARIABLES CALCULATION BY IMSL SUBROUTINE
      CALL ZXSSQ(FUNC,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,
*              SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      WRITE(*,7) (X(I),I=1,6)
      WRITE(*,7) DeltaH,Tf
      WRITE(*,7) SSQ
      WRITE(*,7) (F(I),I=1,13)
      DO 50 I=1,13
      X12(I)=X(1)*VF3(I)/VF1(I)+X(2)
      X13(I)=X(3)*VF3(I)/VF1(I)+X(4)
      X23(I)=X(5)*VF3(I)/VF1(I)+X(6)
50  CONTINUE
      WRITE(*,7) (X12(I),I=1,13)
      WRITE(*,7) (X13(I),I=1,13)
      WRITE(*,7) (X23(I),I=1,13)
      STOP
      END
      SUBROUTINE FUNC(X,M,N,F)
      INTEGER M,N,I
      REAL X(N),F(M),VF1(13),VF2(13),VF3(13),SN(13),R,
*      DeltaH,Tf
      COMMON /SSQ/VF1,VF2,VF3,SN,R,DeltaH,Tf
      DO 40 I=1,13
      P1=LOG(VF2(I))
      P2=+(SN(I)-1.)*(1.-VF2(I))
      P3=SN(I)*((X(1)*VF3(I)/VF1(I)+X(2))*VF1(I)
*      +(X(5)*VF3(I)/VF1(I)+X(6))*VF3(I))*(1.-VF2(I))
      P4=SN(I)*((X(3)*VF3(I)/VF1(I)+X(4))*VF1(I)*VF3(I))
      Y=(DeltaH/R)*((1./298.)-(1./Tf))
      F(I)=P1+P2+P3+P4-Y
40  CONTINUE
      RETURN
      END

```