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EXTRACTIONS DES LIGNOSULFONATES ET DES HYDRATES DE CARBONE
DE LA LIQUEUR RESIDUAIRE BISULFITIQUE A HAUT RENDEMENT.

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Chapter I

INTRODUCTION

1-1 Chemical Composition of Wood^(1,2)

Wood is very difficult to define chemically, because it is a complex heterogeneous product of nature made up of interpenetrating components, largely of high molecular weight. The major components are generally classified as cellulose, hemicellulose, lignin, and solvent-soluble substances (extractives); the amounts present vary with wood species. Table 1 shows the chemical composition of spruce wood and birch wood which may be taken to represent softwoods and hardwoods.⁽³⁾

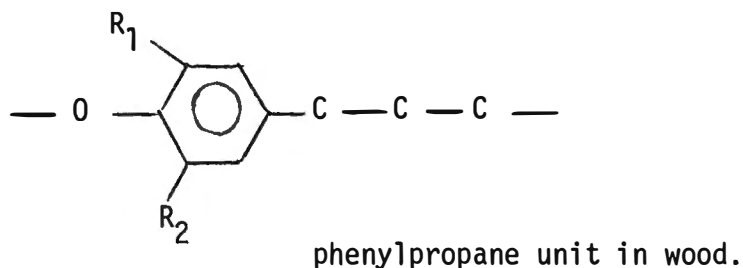
(1) Cellulose: it is a chain polymer composed solely of glucose or exactly of glucose anhydride units called glucan. It is comparatively resistant to extensive dissolution by pulping chemicals. This permits the removal of most of the lignin without too great a loss or degradation of the cellulose.

(2) Hemicellulose: it is a mixture of low-molecular-weight polysaccharide polymers. Hemicellulose polymers are composed of condensation products of the following major saccharide units: D-xylose, D-mannose, D-glucose, L-arabinose, D-galactose, D-glucuronic acid, and D-galacturonic acid. It is much more susceptible to acid hydrolysis.

Table 1. Chemical composition of spruce and birch wood.
(percent of dry wood)

		Spruce (<u>Picea abies</u>)	Birch (<u>Betula verrucosa</u>)
cellulose	glucan	44.3	37.5
	glucan		
	galactan	1.9	1.0
	mannan	10.3	0.5
hemicellulose	araban	0.5	0.5
	xylan	7.6	24.6
	uronic acid		
	anhydride	2.5	5.9
	acetyl	1.4	4.8
lignin and related substances		28.6	19.5
ash, extractives, protein, undetermined substances		3.5	5.9
		100.5	100.2

(3) Lignin: it is composed of a large number of repeating units (phenylpropane units).

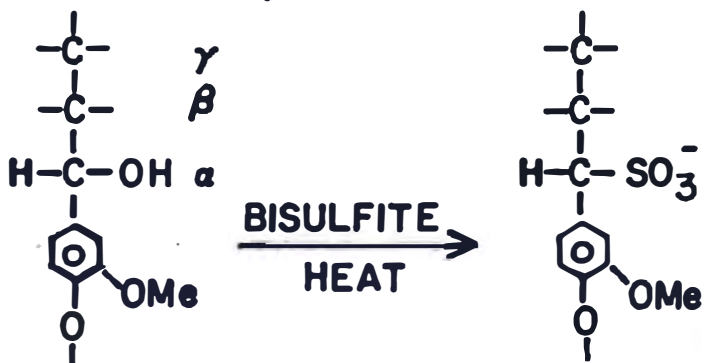


In softwood the units are mainly guaiacylpropane units ($R_1 = \text{OCH}_3$, $R_2 = \text{H}$), but there are also few p-hydroxyphenylpropane ($R_1 = R_2 = \text{H}$). Hardwood contains these units: $R_1 = R_2 = \text{OCH}_3$. The units are joined to each other by ether bonds and carbon-carbon bonds and form a tridimensional network. This large molecule is probably joined by ether bonds to hemicellulose components, and these hemicellulose components are in turn bound to cellulose molecules by hydrogen bonds. Besides the true high-molecular-weight lignin, wood contains also low-molecular-weight lignin-like compounds.

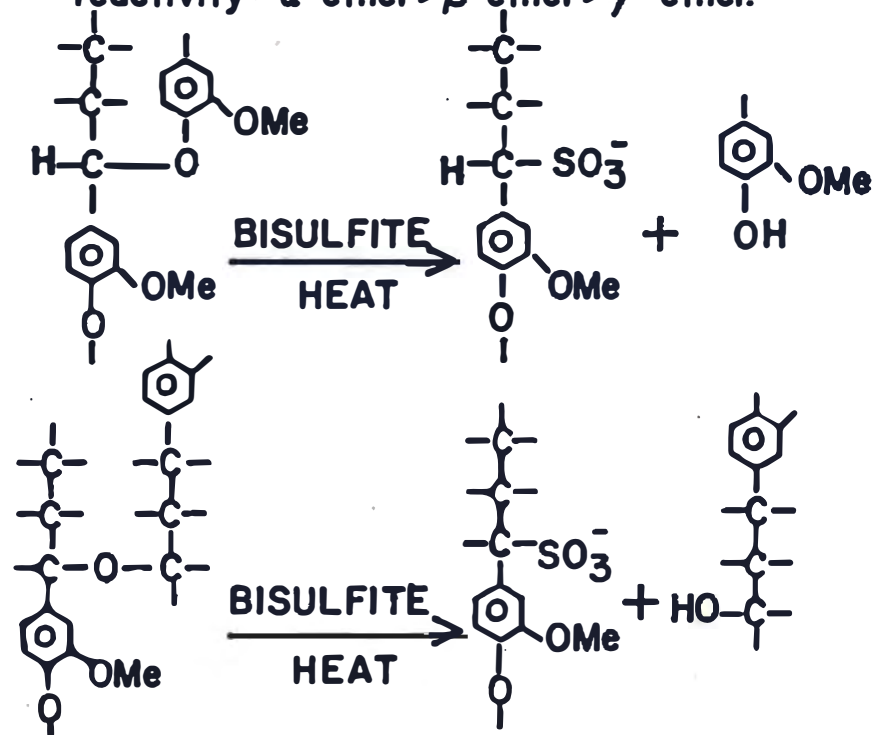
During bisulfite cooking lignin in wood undergoes sulfonation reaction at 130 to 140°C and converts into soluble lignosulfonates. The formation of sulfonate is shown in Figure 1.⁽¹⁾

The chemical structure of lignosulfonates has been studied for well over 100 years and even today its structure is not yet established. Goring⁽⁴⁾ indicated that the negatively-charged sulfonate groups near surface of the particle maintain its solubility in water. The molecular weight distribution extends from a few hundred up to about 100 000. The molecular

(A) Replacement of aliphatic hydroxy, usual order of reactivity: $\alpha\text{-OH} > \beta\text{-OH} > \gamma\text{-OH}$.



(B) Ether cleavage, usual order of reactivity: $\alpha\text{-ether} > \beta\text{-ether} > \gamma\text{-ether}$.



(C) Addition to ethylenic group.



Figure 1. Sulfonation of lignin during bisulfite cooking.

weight distribution is influenced by the wood species and processing conditions used. Gardon and Manson⁽⁵⁾ found that thirty percent of the lignosulfonates had a molecular weight between 3 700 and 5 000 and an equal amount had a molecular weight between 15 000 and 25 000. The aromatic constituents of lignosulfonates give an ultraviolet spectra in acid or neutral solution. The absorption maxima is situated at 280 nm as shown in Figure 2.

1-2 Methods of Pulp Manufacturing

The basic purpose of pulping is to loosen and separate the individual fiber cells from each other as they exist in wood. Once softened and separated, these fibers are in a much more adaptable state for paper-making operations.

The industry of pulp and paper utilizes principally two categories of pulps; one is mechanical pulp and the other is chemical pulp.

1-2-1 Mechanical pulping

The basic principles of manufacturing mechanical pulp are very simple. The wood is defibered by grinder or refiner in the presence of a large amount of water. The woods most commonly used are spruce, balsam fir, jackpine, western hemlock, poplar, and assorted hardwoods.

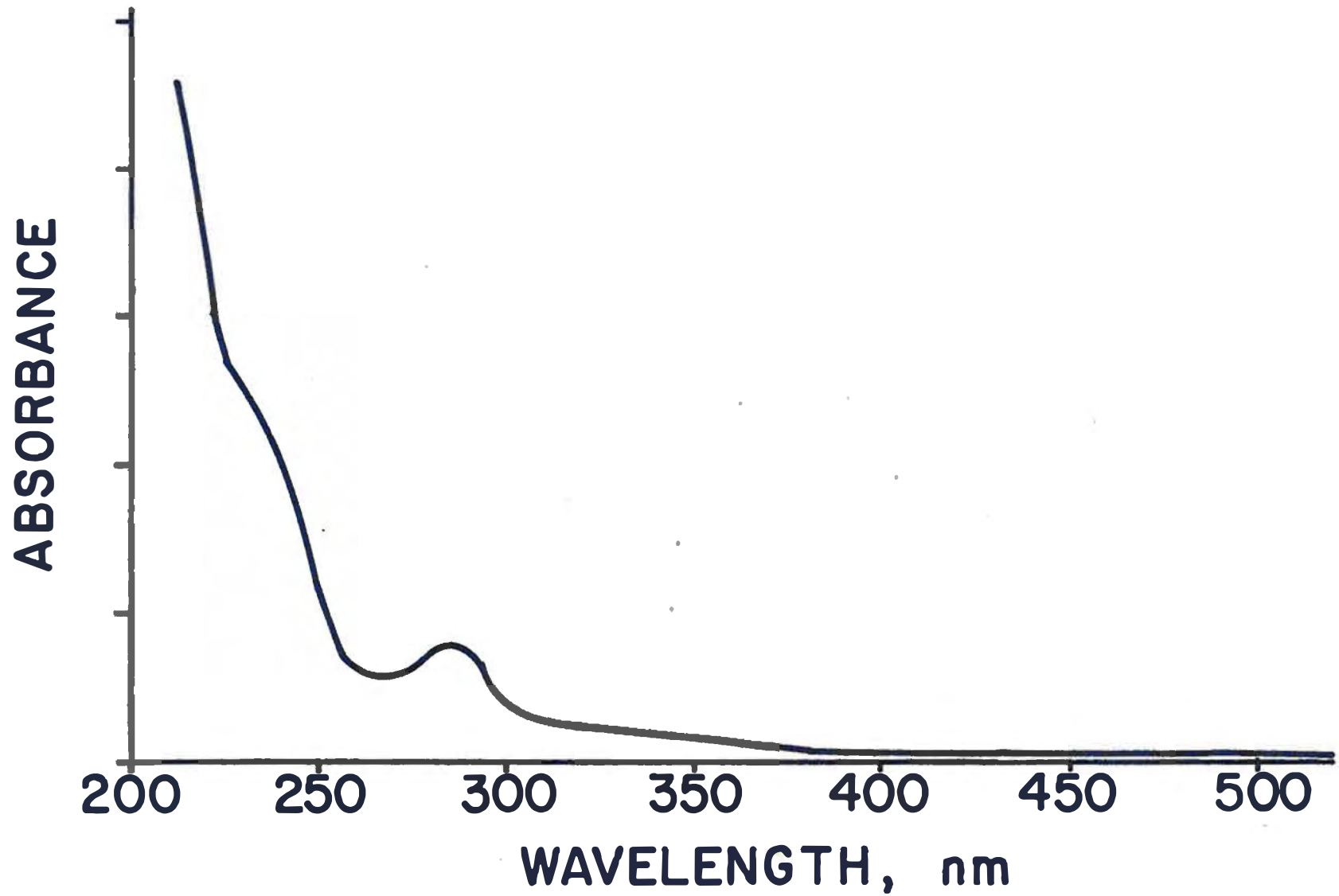


Figure 2. The ultraviolet spectra of lignosulfonates in water solution.

The yield of pulp ranges from 85% to 95% depending on the species, source, age, and moisture content of wood as well as on the operation conditions. Because of its low cost, softness, and absorbancy, mechanical pulps are used mainly for manufacturing print papers, toilet tissue, board containers, and dishes. Mechanical pulps are also mixed with chemical pulps for newsprint.

1-2-2 Chemical pulping

In chemical pulping, fiber separation is accomplished entirely by the expenditure of chemical energy. Pulp yield is normally in the range from 35% to 50% which depends on : (1) liquor composition, (2) cooking temperature , (3) cooking time, (4) cooking pressure, and (5) pH. The two major chemical pulping processes are the acid-sulfite and the alkaline-kraft processes. This was classified in terms of pH range. The nomenclature and process definition are given in Table 2.

Table 2. Nomenclature and process definition of chemical pulp.

Nomenclature	Predominant chemical agent in cooking liquor	Approx. initial pH at 25°C
Acid sulfite	$H_2SO_3 + XHSO_3$	1 - 2
Bisulfite	$XHSO_3$	2 - 6
Neutral sulfite	$XSO_3 + XCO_3$ (XOH or none)	6 - 9
Alkaline sulfite	$XSO_3 + XOH$ (or Na_2S)	10

X: the cation used; i.e., calcium, sodium, magnesium, or ammonium.

Acid sulfite, the original process, is used for the fine paper pulps, especially for dissolving and acetate grades which are used in the manufacture of rayon, acetate yarns and films.

Bisulfite pulping has found its most widespread use in producing particular paper-grade pulps and in providing high yield chemical pulp make-up for newsprint. The yield of this kind of pulp is normally about 70% and can be higher.

The Kraft process is now the dominant process, about 75% of the chemical pulp produced is from this process. Its versatility and flexibility make it suitable for using any wood species. Extractives, of certain wood species, which lead to pitch troubles in acid sulfite pulping are dissolved or dispersed by alkaline pulping liquor. Carbohydrates which tend to degrade in acidic medium are largely alkali-stable in the kraft process. When mixed with bleached softwood sulfite pulp, kraft pulp found its main use in fine papers. Since the color of this pulp before being bleached is much darker than unbleached sulfite pulp, the use of pulp in the unbleached state is largely confined to coarse wrapping, industrial papers, container boards, and base sheet with lighter-color liner.

1-3 Composition of Pulping Effluents.

In mechanical pulping where the yield ranges from 85% to 95%, the waste residue in the effluent leaving the system is chiefly in the form

of a very fine debris which could not be retained in the screening and cleaning system. The effluent also contains small amount of resin acids.

In the spent cooking liquor of kraft process, there contains: resin acids, fatty acids, turpentine, tall oil, alkali lignin, dimethyl sulfoxide and sugars from the degradation of hemicellulose.

The spent liquor from bisulfite process is sometimes diluted when leaving the digester. It contains 6% to 15% solids which come from the dissociation of wood material during cooking. Manufacturing one metric tonne of pulp produces eight cubic meters of spent liquor⁽⁶⁾ which contains carbohydrates and lignosulfonates, as the two principal constituents, and other constituents such as saccharic acids, hemicellulose, resins, organic acids, aldehydes and alcohols. The constituent composition may vary, depending on the species of wood, cooking time and temperature, and the base used. Table 3 gives an example for the composition of spent sulfite liquor obtained from the cooking of spruce⁽⁶⁾.

1-4 Actual Situation of the Sulfite Industry.

In Canada, there are thirty-six mills producing sulfite pulp. Most of them are a part of a newsprint complex; the others are dissolving-pulp mills. These mills are concentrated in Quebec, Ontario, and Atlantic regions. There are eighteen mills located in Quebec. To the author's knowledge, sixteen of these mills do not have any liquor treatment or byproducts recovery systems. Table 4 provides some information on mill size

distribution⁽⁷⁾ (the figures might not be completely up-to-date). Noticeable are the many mills of small and medium capacity.

Table 3. Composition of sulfite spent liquor obtained from the cooking of spruce.

Component	Concentration, g/l
Dissolved solids	100
Total sugars (as glucose)	15 - 22
Hexose	11 - 16
Pentose	4 - 6
Acetic acid	2 - 5
Sulfur (as SO ₂)	8 - 10
Total inorganic (free of SO ₂)	0.5 - 2.5
Organic (combined with SO ₂)	3 - 5
Lignosulfonates	50 - 65
Calcium	7 - 10
Miscellaneous	2 - 5

Table 4. Classification of the Canadian sulfite pulp mills, 1971.

Capacity range tpd*	No. of mills	Total capacity tpd
- 100	3	265
100 - 200	12	1868
200 - 300	12	3110
300 - 400	0	-
400 - 500	9	3960
500 -	0	-

* tpd : metric tonne per day.

In November 1971, regulations to limit the discharge of pollutants from the pulp and paper industry were promulgated. In order to face the anti-pollution regulations, the installation of abatement facilities or another alternative abatement measures must be realized. Because of the high capital cost required for installing a recovery system to recover chemicals and heat from the sulfite spent liquor, it may not be economically feasible for such old, small mills to install such a system. Alternative abatement measures, such as biological treatment, could involve high costs as well as increased energy requirements. Biological treatment could also result in the discharge of large amount of biological solids; and it would remove only a portion of the dissolved materials discharged from the cooking process. The sulfite sector of the pulp and paper industry poses the most difficult problem in pollution abatement research.

1-5 Purpose of the Study

The major pollutants in the sulfite spent liquor are lignosulfonates and carbohydrates. Carbohydrates are easily bio-oxidized by microorganisms and consume a lot of dissolved oxygen in a receiving water. Lignosulfonates break down biologically at an extremely slow rate. Biochemical oxygen demand (BOD) load ranges from 1430 to 1870 kg/tonne for high yield pulp and 1980 to 2640 kg/tonne for low yield pulp⁽⁸⁾. When dumped into a receiving water, high BOD loading can affect other kinds of aquatic lives which need oxygen for their survival. The spent liquor, therefore, requires a treatment before it being discharged to the rivers so as to reduce its BOD loading impact to an acceptable level on the environment.

Many physico-chemical treatment methods used to reduce the pollutants have been reported, employing techniques such as adsorption, ion-exchange, coagulation, flocculation, precipitation, and membrane separation. In addition to those methods, Enkvist et al.⁽⁹⁾ and Boggs⁽¹⁰⁾ described a method using organic solvents to isolate a mixture of sugars from calcium base sulfite spent liquors. Two patents^(11, 12) concerning the recovery of by-products from spent liquors by solvent extraction were granted.

The purpose of this work is to study the possible use of liquid-liquid extraction as a method to remove lignosulfonates or carbohydrates from the sodium base bisulfite spent liquor. If it is a good process with high efficiency of extracting lignosulfonates or carbohydrates, then, it might be adopted and used by sulfite mills to control water pollution.

Chapter II

EXPERIMENTAL

2-1 Solvents and Chemicals

Purity of solvents and chemicals used throughout the present work is shown in Table 5.

Table 5. Purity of solvents and chemicals

Solvent or chemical	Mark	Purity
Acetone	Anachemia chemical Ltd.	Reagent, A.C.S.
p-Dioxane	J.T. Baker Chemical Co.	98% (assay by G. C.)
Methanol	Anachemia chemical Ltd.	C. P.
Ethanol	Commercial Alcohols Ltd.	unmatured spirits
Sulfuric acid	J.T. Baker Chemical Co.	Baker analyzed reagent
Anthrone	Fisher Scientific Co.	Certified
Thiourea	J.T. Baker Chemical Co.	Baker analyzed reagent
Isopropanol	The McArthur Chemical Co. Ltd.	99%

(Cont'd)

Sodium chloride	Fisher Scientific Co	Certified, A.C.S.
Silver nitrate solution (N/10)	Fisher Scientific Co.	Certified
Lignosulfonates	Prepared in the present work	

2-2 Preparation of Concentrated Bisulfite Spent Liquor

Spent liquor, containing about 10% dissolved solids, was collected from the blow pit of a sodium-base bisulfite pulp mill. This liquor was concentrated in a concentration system to have a solids content of about 50%, resulting in a stock liquor which was used throughout the present work for all the series of experiments.

The system (shown in Figure 3) used to concentrate spent liquor consisted of a column which was composed of three concentric glass tubes, two condensers, and four receiving flasks. The outer annular section and the core tube of the column were for steam; and the inner annular section was packed with many small glass packing materials in form of helices. Dilute spent liquor was pumped from a reservoir to the packed section by vacuum suction and at a constant flow rate controlled by a flow meter. During concentration, water contained in the dilute liquor was evaporated and passed through the primary condenser to receiving flask C or D. The concentrated spent liquor went down to receiving flask A or B.

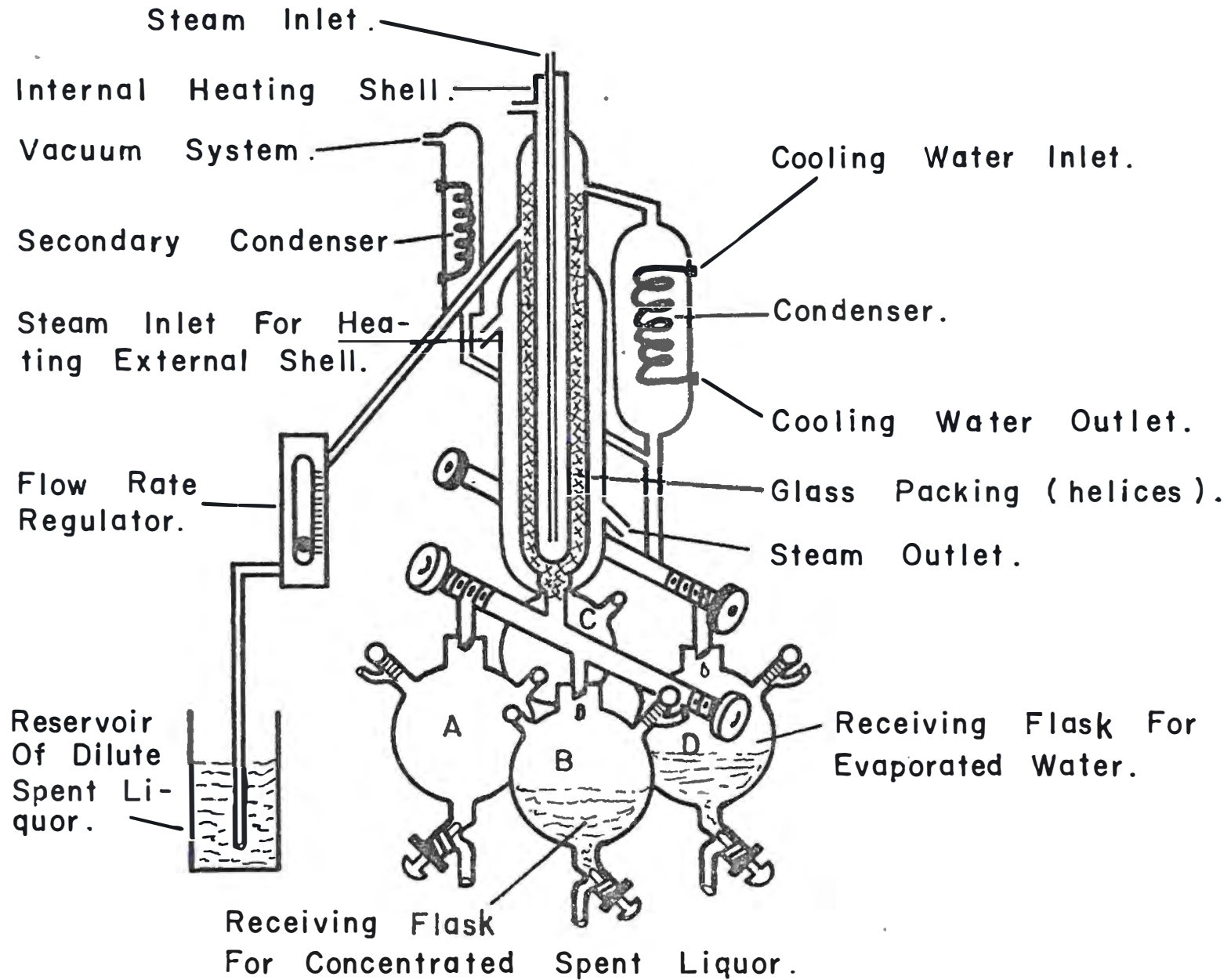


Figure 3. System for concentrating the bisulfite spent liquor.

2-3 Precipitation of Lignosulfonates from Bisulfite Spent Liquor

Since "pure" lignosulfonates can not be obtained from commercial companies and its properties may change with wood species and processing conditions used, the lignosulfonates used as "standard" were precipitated from the same spent liquor. This "standard" was used for all the experiments in the study.

pH value of the concentrated spent liquor in a beaker was adjusted to about 2.5 with hydrochloric acid and then the liquor was heated in a constant temperature water bath at 70°C. Afterward, sodium chloride was added slowly to the liquor with constant stirring using a glass rod, until its saturation point was reached. After that point, an excess of sodium chloride was added to the liquor, to secure the precipitation of lignosulfonates. The high viscous portion of the liquor was collected by centrifugation. The paste collected was dissolved in a minimum volume of hot distilled water and dialyzed in a cellophane membrane against distilled water of 70°C. The dialysis water was changed frequently and tested with silver nitrate solution until no silver chloride precipitated out. The dialyzed solution was dried at 65°C in an oven under a vacuum of about 102 kPa. The dry substance obtained was sodium base lignosulfonates.

2-4 Measurement of Total Solids in Spent Liquor⁽¹⁴⁾

2-4-1 Apparatus :

1. Vacuum oven (Fisher, Isotemp vacuum oven Model 281).
2. Glass weighing bottle, 70 mm ID x 30 mm height.

3. Glass beads, 1 mm diameter.
4. 150-mesh circular stainless-steel screen.

2-4-2 Procedures :

1. Dry and tare a weighing bottle containing 20 to 25 g glass beads and a circular stainless-steel screen.
2. For weak liquor (less than 20% solids), add enough liquor sample to the bottle to give 1 to 2 g of dry solids. For strong liquor (more than 20% solids), select a suitable dilution factor, then use the well-mixed, diluted liquor for measurement.
3. Attach the screen to the inside of the weighing bottle, without touching the sample solution.
4. Dry the bottle with sample at 65⁰C (oven temperature) for three hours under about 85 kPa vacuum, then one and half hour under about 102 kPa vacuum.
5. Cool sample in a dessiccator for about one hour and weigh it.
6. Make measurements in triplicate for each liquor sample, and take the average value.

2-5 Extraction

Spent liquors of desired dissolved solids contents were prepared by diluting the concentrated stock liquor with distilled water. Five solids

contents were used in the study and are given in Table 6.

Table 6. Solids content of bisulfite spent liquor used in all experiments

Spent liquor	Solids content, %
A	47.33
B	41.95
C	37.49
D	24.60
E	21.44

2-5-1 General

For each extraction experiment, 50 ml of liquor was put in a 125-ml cylindrical graduated separatory funnel, followed by the addition of the desired volume of solvent. After being shaken vigorously, the funnel was let stand still vertically for about half an hour; then, the different phases were separated.

A small portion of each phase was taken, and the quantities of water and solvent in the sample were measured by gas chromatography. The remaining portion was dried in a vacuum-drying oven (at 65⁰C). The dried material was weighed, and its absorbance at 280 nm was measured with a spectrophotometer.

2-5-2 Extraction at different pH's

The concentrated stock spent liquor had a pH value of 5.58. For a particular solids content, sample liquors with different pH's were prepared by adjusting the pH value of the original sample liquor with concentrated sulfuric acid or 10% sodium hydroxide solution. The pH value of a sample was measured with a Fisher Model 120 pH meter.

2-5-3 Extraction at different temperatures

Sample liquors and solvents were kept in a constant temperature water bath (Magic While constant temperature bath, Blue M. Electric Company, Blue Bland, Ill., U.S.A.) at least overnight, allowing them to be in equilibrium in temperature with the water. After being shaken, the funnel and its content were placed in the water bath for about one hour, letting the phases to separate.

2-6 Quantitative Analysis of Carbohydrates⁽¹⁵⁾

The quantitative analysis of carbohydrates in a sample was carried out using a colorimetric method. This method is based on the color reaction between carbohydrates and anthrone in a sulfuric acid medium, by measuring the absorbance of the reaction product at 620 nm.

2-6-1 Reagents :

1. The sulfuric acid used was prepared by adding one liter

of the reagent grade concentrated sulfuric acid to 50 ml of distilled water.

2. The 0.2% anthrone reagent stabilized with thiourea was made by dissolving 0.2 g of anthrone and 1 g thiourea in 100 ml sulfuric acid solution prepared above.

2-6-2 Procedures :

1. 2.5 ml of sample solution was added to a 10-cc test tube which was then covered with a glass marble.
2. The sample was cooled in a slush (mixture of water and crushed ice), as long as possible, until it attained the slush temperature.
3. 5 ml of reagent was added into the sample solution, stirred and mixed completely with a small glass rod. The mixture was allowed to be in equilibrium in temperature with the slush.
4. The test tube was transferred to a water bath at 95°C, and the reaction was carried for 2.5 minutes.
5. The test tube was taken out from the water bath and cooled in slush at least one minute.
6. Comparing with a blank, the absorbance at 620 nm was measured.

The amount of carbohydrates in a sample was calculated in terms of apparent glucose. During the reaction, reaction temperature and time had

to be controlled carefully.

2-7 Spectrophotometers

The absorbance of precipitated lignosulfonates was measured with a Unicam SP 1800 ultra-violet spectrophotometer. Scan speed was 1 nm/sec; chart speed was 10 sec/cm (expansion was 10 nm/cm). Absorbance was measured in the range from 210 to 700 nm. The reference was distilled water. All other absorbances were measured on a Zeiss spectrophotometer, Model PM2D.

2-8 Gas Chromatography

Quantities of water and organic solvent in the different phases were determined by gas chromatography⁽¹⁶⁾. A Perkin Elmer GC-900 gas chromatograph with hot wire detector was used throughout the study, employing a 360 cm x 6 mm I.D. stainless steel column packed with 5% Triton X-305 T40/60 chromatographic support. Helium was used as the carrier gas. For each sample, determination was made in duplicate. Area of the chromatogram was measured with a compensating polar planimeter (model 62005, Keuffel & Esser Co.). Weights of water and solvent in the sample were calculated in comparing the chromatogram areas of the sample with those of 5 μ l distilled water and 5 μ l organic solvent, respectively.

The operating conditions for the gas chromatograph were:

1. Temperature : injector - 150°C
manifold - 200°C
detector - 300°C
2. Programmed oven temperature : 1°C per minute from 50 to 75°C
3. Current of the detector : 175 mA
4. Attenuation : X128, X256 (for acetone)
5. Carrier gas : pressure - 50 kg/cm²
flow rate - 52 ml/min
6. Chart speed : 5 mm/min
7. Injected sample volume : 5 ul
8. Syringe : 10-ul Pressure-Lock series C liquid syringe (Precision sampling Corp., Baton Rouge, La. U.S.A.)

2-9 High Pressure Liquid Chromatography

A Waters Associates high pressure liquid chromatograph was used, which contained a Model 6000A solvent delivery system and a Model 440 absorbance detector. Analytical columns (stainless steel) were : 5 x 60 cm x 9.5 mm I.D.; one was packed with deactivated type AX Porasial (particle

size : 75-125 microns, pore diameter 100 Å), two with type BX (pore diameter : 100 - 200 Å), and two with type EX (pore diameter : 800 - 1000 Å). A technique of dry-packing was used to pack all five columns. The technique included : 1) a column was fixed vertically on a iron-stand, and 2) through a small funnel, a small portion of packing materials was successively added to the column, and 3) during each addition, the packed column was vibrated with a handle vibrator. After the packing was finished, these columns were connected to the chromatograph and eluted with solvent for a sufficient period of time to exclude air in the column. All samples were clarified, with a sample clarification kit, before injected into the column.

The operating conditions for the high pressure liquid chromatography were :

1. Flow rate of solvent : 3 ml/min
2. Pressure : 9 650 kPa - 11 000 kPa
3. Detector : UV, absorbance fixed at 254 nm
4. Chart speed : 2.5 mm/min
5. Sample concentration : about 0.25%

2-10 Recovery of Carbohydrates by Ultrafiltration

Ultrafiltration is a physical method of separating different substances in solution by molecular size and conformation. Carbohydrates in bisulfite liquors are, in general, in form of oligosaccharides and polysaccharides with small or large molecules. Lignosulfonates, on the other hand, are

large molecules. One third of the lignosulfonates had a mean molecular weight between 3 700 and 5 000; and an equal amount had a molecular weight between 15 000 and 25 000. Thus, ultrafiltration appears to be a potential, useful method to separate the carbohydrates. For verification, a sample solution was prepared by dissolving one gram of dry solids from spent liquor A in 100 ml of distilled water. Another eight sample solutions of the same concentration were prepared using the dry solids from the different phases obtained after extracting liquor A (pH = 5.58) with different organic solvents. The extraction was carried out at a solvent-liquor volume ratio of 1 to 1.

The ultrafiltration was performed inside a beaker wherein a filter unit (Pellicon type PTGC membrane, manufactured by Millipore Corp., U.S.A., membrane area 11 cm², dimensions 50 x 11 mm diameter, sample capacity is approximately 100 ml per unit) was clamped and fixed horizontally so that the entire filter area remained submerged and active for the maximal period of time. The filter unit was connected to a vacuum source (the whole system is shown in Figure 4).

The sample solution was stirred with a magnetic stirrer during filtration. Both the filtrate and the retentate were collected. These solutions were dried in a vacuum-drying oven and weighed. The amount of lignosulfonates was determined by the absorbance at 280 nm, and the carbohydrates by the method of the anthrone reaction. The amount of carbohydrates was calculated in terms of apparent glucose.

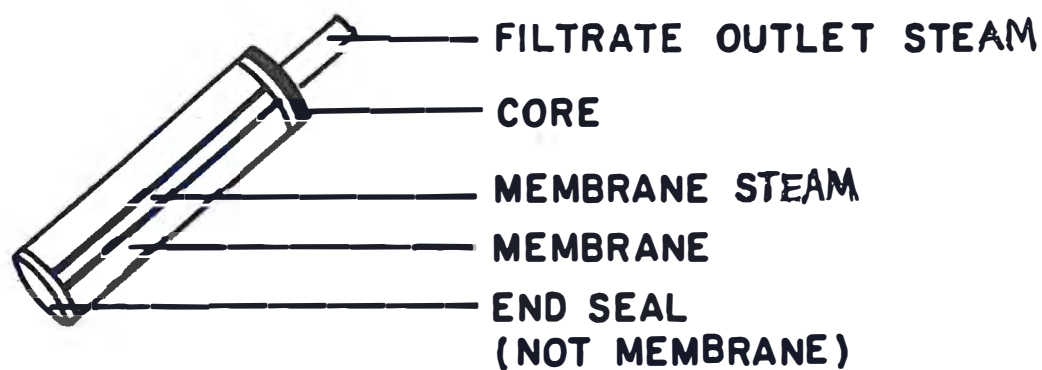
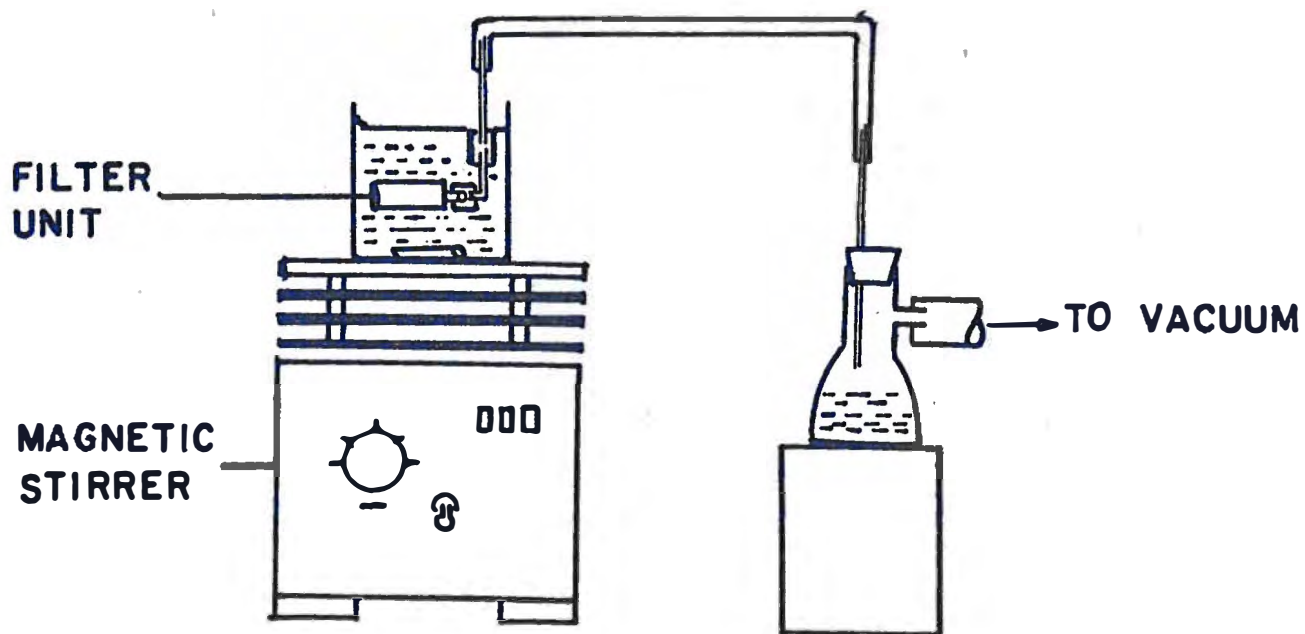


Figure 4. System of ultrafiltration.

Chapter III

RESULTS

3-1 Absorptivity of Lignosulfonates

As seen from Figure 5, the data obtained in the present study obeyed the Lambert Beer's law :

$$A = a \times c \times l$$

where

- A : absorbance
- a : absorptivity
- c : concentration, g/l
- l : optical path, cm

The absorptivity of lignosulfonates at 280 nm :

$$\begin{aligned} a &= \frac{\text{absorbance } (A_{280}) \times \text{cm}^{-1}}{\text{dry matter content (mg/ml)}} \\ &= 11.5 \end{aligned}$$

This value of absorptivity was comparable with 11.4 obtained by Forss⁽¹⁷⁾.

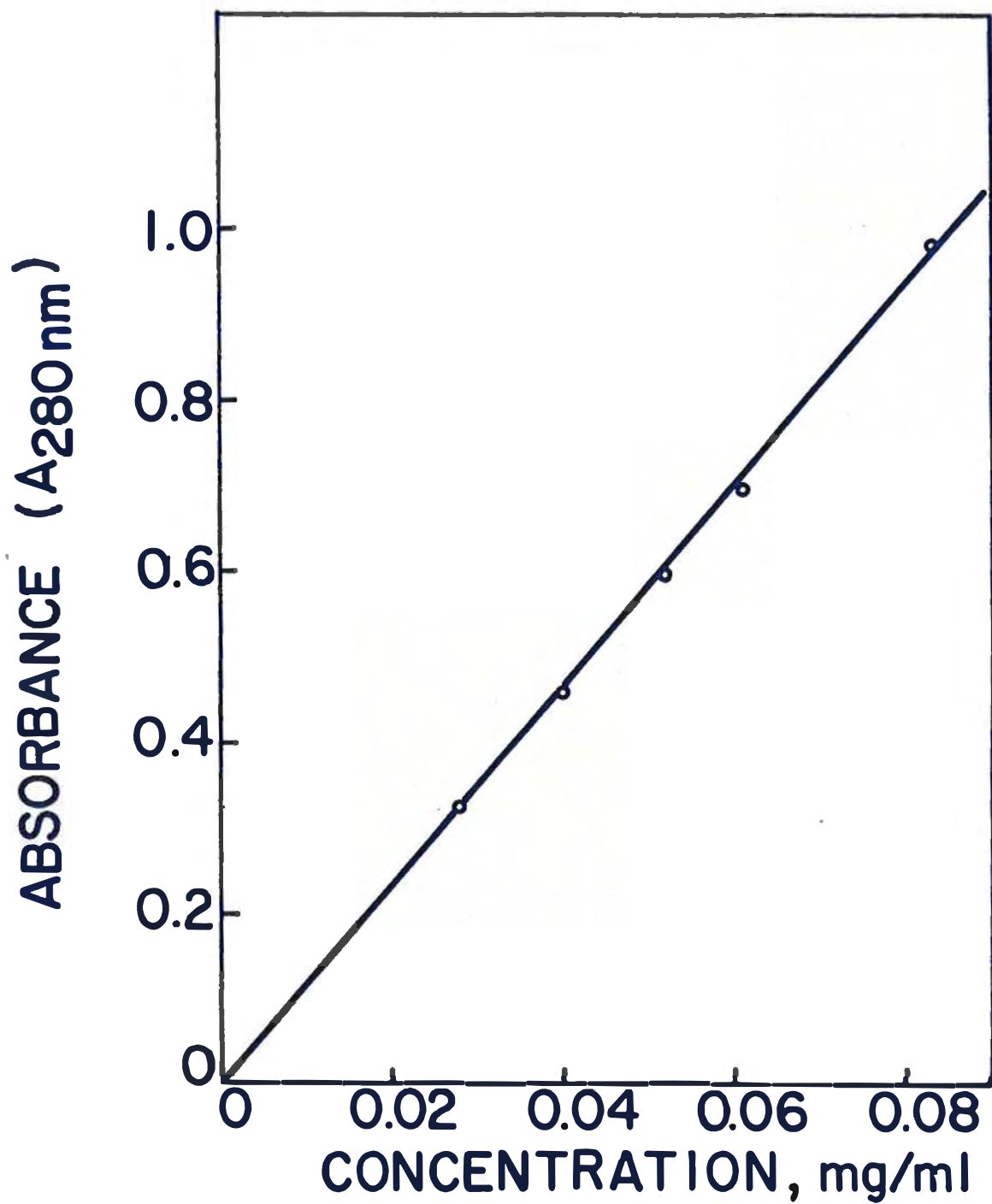


Figure 5. The absorbance at 280 nm as a function of the concentration of lignosulfonates.

3-2 Material Balance

The law of conservation of matter states that matter can not be created or destroyed. During the extraction, material balance must hold over the entire process. All materials entering in the process must be equal to the sum of the substances distributed in the different phases.

Before extraction, the substances entering in the process were :

$$W + S + H$$

where W : weight of total dry solids, g,
 S : weight of solvent used, g,
 H : weight of water contained in the spent liquor, g.

After extraction, there were two phases. The upper phase contained :

$$W_u + S_u + H_u$$

where W_u : weight of dry solids in the upper phase, g,
 S_u : weight of solvent in the upper phase, g,
 H_u : weight of water in the upper phase, g,

and the lower phase contained:

$$W_l + S_l + H_l$$

where W_l : weight of dry solids in the lower phase, g,
 S_l : weight of solvent in the lower phase, g,
 H_l : weight of water in the lower phase, g,

If the material balance holds, the sum of

$$W_u + S_u + H_u + W_l + S_l + H_l \quad \text{must be equal to} \quad W + S + H.$$

In the following, the material balance made for the extraction of a liquor containing 28.35% solids and pH = 5.58 with isopropanol, at 20°C and a volume ratio of 1/1, is given as an example :

Before extraction :

$$W = 15.909 \text{ g}, \quad S = 39.232 \text{ g}, \quad H = 40.672 \text{ g}$$

After extraction :

$$W_u = 11.050 \text{ g}, \quad S_u = 34.749 \text{ g}, \quad H_u = 24.078 \text{ g}$$

$$W_l = 4.670 \text{ g}, \quad S_l = 4.789 \text{ g}, \quad H_l = 13.990 \text{ g}$$

The sums were :

$$W + S + H = 95.813 \text{ g}$$

$$W_u + S_u + H_u + W_l + S_l + H_l = 93.326 \text{ g}$$

This result demonstrated that the material balance holds within the experimental errors.

3-3 Calculations and Determinations

The percentage of liquor solids distributed in different phases was calculated as follows :

$$\% \text{ solids} = \frac{W_u \text{ or } W_l \text{ or } W_i}{W} \times 100 \quad (1)$$

(W_i : weight of dry solids in the interphase, g; if such a phase existed).

The weight of lignosulfonates in the sample was determined from the measurement of absorbance at 280 nm :

$$A = a \times c \times l = a \times (W_L/V) \times l \quad (2)$$

$$W_L = AV/al \quad (3)$$

where W_L : weight of lignosulfonates, mg,
 V : volume, ml
 A : absorbance at 280 nm,
 a : absorptivity, 11.5,
 l : optical path, 1 cm

The relative amounts of lignosulfonates distributed in the upper and lower phases, expressed in terms of % lignosulfonates content with respect to the solids weight in each phase, were also determined from the measurements of absorbances at 280 nm. They were denoted by W_{Lu}/W_u and W_{Ll}/W_l , where W_{Lu} and W_{Ll} were the weights of lignosulfonates in the upper and lower phases, respectively. Lignosulfonates in the two phases were then calculated as :

$$\begin{aligned} & \text{Weight of lignosulfonate } (W_{Lu} \text{ or } W_{Ll}) \\ & = (W_u \text{ or } W_l) \times (W_{Lu}/W_u \text{ or } W_{Ll}/W_l) \quad (4) \end{aligned}$$

The percentage of lignosulfonates, based on the weight of lignosulfonates in the liquor sample, in the upper and lower phases was calculated as follows :

$$\% \text{ lignosulfonates } (W_{Lu}/W_L) \text{ or } (W_{Ll}/W_L) \times 100 \quad (5)$$

3-4 Effect of Volume Ratio of Solvent to Spent Liquor

In the experiments Set I, there were five series. The first series was for spent liquor A which was extracted with five organic solvents (isopropanol, acetone, ethanol, dioxane, and methanol) at 20°C. The pH value of the liquor was 5.58. Four solvent-liquor volume ratios were used : 1.5, 1.0, 0.75, and 0.5.

The second to the fifth series were for spent liquors B, C, D, and E, respectively. These liquors were extracted with the same solvents as mentioned above, and under the same conditions. Spent liquors A, B, C, D, and E contained different percent solids, as indicated in Chapter II (Table 6).

Tables 7, 8, 9, and 10 present the volume of spent liquor used, weight of total solids, solids content of spent liquor, weight of lignosulfonates, density of solvent used, and the results obtained for experiments Set I, such as weight of solids, percent solids, lignosulfonates content, weight of lignosulfonates, percent lignosulfonates contained in the different phases.

The fifth series of experiment Set I failed, thus no results is presented.

3-5 Effect of Solvent

In the operation of solvent extraction, two components miscible in all proportions can be partially separated by the addition of a third liquid component which produces a region of immiscibility. A solvent is selective for a given solute when the mass fraction of the solute in the extract phase (solvent rich phase) is greater than in the raffinate phase where both mass fractions are expressed on an extracting solvent-free basis⁽¹⁸⁾.

The selectivity diagram for a given sample liquor was plotted as the mass of lignosulfonates (A) per unit mass of [A + B (water)] in the lower (raffinate) phase against the mass of lignosulfonates per unit mass of [A + B] in the upper (extract) phase.

Effect of solvent on extraction at 20⁰C and pH(liquor) = 5.58 can be seen from selectivity diagram. The selectivity diagrams for spent liquors A, B, C, and D are represented in Figures 6, 7, 8, and 9, respectively for the solvent-liquor volume ratios studied.

Table 7. Results obtained for the first series of experiments Set I, spent liquor A: extracted with different organic solvents at 20°C and pH(liquor) = 5.58, using several volume ratios.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
AI	50	27.977	47.33	14.124	0.7824	0.7891	0.7869	1.0325
AA	50	27.440	47.33	15.106				
AE	50	27.440	47.33	15.106				
AD	50	27.440	47.33	15.106				
Sample	Solvent, v/v liquor	solvent	Solids (I) g, (W _u & W _l)	% solids W _u or W _l W	Lignosulfon- ates content, % (II) (by ab- sorbance) W _{Lu} /W _u and W _{Ll} /W _l	Lignosulfon- ates, g (I x II) W _{Lu} & W _{Ll}	% lignosul- fonates, W _{Lu} /W _L & W _{Ll} /W _L	
AI1-u*	1.5	IPA***	1.631	5.83	81.18	1.324	7.08	
AI1-l**			26.544	94.88	47.75	12.676	89.75	
AI2-u	1.0	IPA	1.712	6.12	84.40	1.445	10.23	

u* stands for upper phase
l** stands for lower phase
IPA*** stands for isopropanol

Table 7 (Cont'd)

AI2-1	1.0	IPA	26.682	95.37	44.77	11.945	84.57
AI3-u	0.75	IPA	2.057	7.35	86.39	1.777	12.58
AI3-1			23.788	85.03	48.17	11.459	81.13
AI4	0.5	IPA	(one phase)				
AA1-u	1.5	Acetone	2.723	9.93	94.04	2.562	16.96
AA1-1			25.441	92.71	47.61	12.113	80.18
AA2-u	1.0	Acetone	3.501	12.76	91.17	3.192	21.13
AA2-1			23.544	85.80	47.35	11.148	73.80
AA3-u	0.75	Acetone	4.623	16.85	88.34	4.084	27.03
AA3-1			22.279	81.19	47.20	10.516	69.61
AA4-u	0.5	Acetone	12.663	46.15	70.17	8.886	58.82
AA4-1			13.278	48.39	36.97	4.909	32.49
AE2-u	1.0	Ethanol	9.038	32.94	77.13	6.971	46.15
AE2-1			17.381	63.34	38.17	6.634	43.92
AE3-u	0.75	Ethanol	13.182	48.04	73.75	9.722	64.36
AE3-1			14.695	53.55	33.96	4.990	33.04
AE4	0.5	Ethanol	(one phase)				
AD1-u	1.5	Dioxane	3.923	13.69	82.64	3.242	23.14
AD1-i*			7.699	26.87	75.16	5.787	39.13
AD1-1			16.936	59.10	30.72	5.203	35.18
AD2-u	1.0	Dioxane	9.032	31.52	84.46	7.628	51.58

* stands for interphase

Table 7 (Cont'd)

AD2-i			2.541	8.67	75.15	1.910	12.91
AD2-1			17.013	59.37	27.25	4.636	31.35
AD3-u	0.75	Dioxane	15.092	52.67	72.94	11.008	74.43
AD3-1			13.307	46.44	22.21	2.955	19.98
AD4-u	0.5	Dioxane	19.641	68.54	57.60	11.313	76.49
AD4-1			9.018	31.47	29.23	2.636	17.82

Table 8. Results obtained for the second series of experiments Set I, spent liquor B : extracted with different organic solvents at 20°C and pH(liquor) = 5.58, using several volume ratios.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
BI	50	24.985	41.95	12.870	0.7824	0.7882	0.7881	1.0294
BA	50	23.963	41.95	12.820				
BE	50	23.963	41.95	12.820				
BD	50	23.963	41.95	12.820				
Sample	Solvent Liquor, v/v	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by ab- sorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I x II) $\frac{W_{Lu}}{W_u}$ & $\frac{W_{Ll}}{W_l}$	% lignosul- fonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$	
BII-u	1.5	IPA	1.987	7.95	79.42	1.578	12.33	
BI1-1			21.900	87.65	47.25	10.348	80.40	
BI2-u	1.0	IPA	1.886	7.55	85.05	1.604	12.46	
BI2-1			22.559	90.29	48.59	10.961	85.17	
BI3-u	0.75	IPA	2.749	11.00	79.05	2.173	16.88	
BI3-1			21.538	86.20	46.06	9.922	77.09	

Table 8. (Cont'd)

BI4	0.5	IPA	(one phase)				
BA1-u	1.5	Acetone	3.438	14.35	86.32	2.968	23.15
BA1-l			20.419	85.21	46.62	9.520	74.25
BA2-u	1.0	Acetone	5.301	22.12	77.24	4.094	31.94
BA2-l			18.394	76.76	46.39	8.533	78.00
BA3-u	0.75	Acetone	9.692	40.45	81.57	7.906	61.67
BA3-l			14.251	59.47	33.69	4.801	37.45
BA4-u	0.5	Acetone	16.844	70.29	57.55	9.693	75.61
BA4-l			6.620	27.63	33.27	2.202	17.18
BE1-u	1.5	Ethanol	6.283	26.22	72.75	4.571	35.65
BE1-l			18.304	76.38	40.72	7.453	58.14
BE2-u	1.0	Ethanol	9.638	40.22	69.57	6.705	52.30
BE2-l			14.155	59.07	36.77	5.205	40.60
BE3-u	0.75	Ethanol	12.878	53.74	63.72	8.206	64.01
BE3-l			11.510	48.03	29.73	3.422	26.69
BE4	0.5	Ethanol	(one phase)				
BD1-u	1.5	Dioxane	5.530	23.08	83.59	4.623	36.06
BD1-i			3.867	16.14	73.00	2.820	22.00
BD1-l			13.847	57.78	30.13	4.172	32.54
BD2-u	1.0	Dioxane	10.535	43.96	76.52	8.061	62.88
BD2-l			12.404	51.76	24.32	3.016	23.52
BD3-u	0.75	Dioxane	15.072	62.89	72.48	10.924	85.21
BD3-l			9.610	40.12	21.65	2.082	16.24
BD4	0.5	Dioxane	(one phase)				

Table 9. Results obtained for the third series of experiments Set I, spent liquor C :
 extracted with different organic solvents at 20°C and pH(liquor) = 5.58, using
 several volume ratios.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
CI	50	21.430	37.49	10.512	0.7824	0.7893	0.7839	1.0320
CA	50	20.915	37.49	11.099				
CE	50	20.915	37.49	11.099				
CD	50	20.915	37.49	11.099				
Sample	Solvent, Liquor v/v	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I x II) W_{Lu} & W_{Ll}	% lignosul- fonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$	
CI1-u	1.5	IPA	2.183	10.19	82.61	1.803	17.15	
CI1-l			18.272	85.26	43.82	8.009	76.19	
CI2-u	1.0	IPA	2.794	13.04	87.91	2.456	23.26	
CI2-l			16.609	77.50	46.91	7.791	74.12	

Table 9. (Cont'd)

CI3-u	0.75	IPA	3.154	14.72	76.19	2.404	22.87	
CI3-1			17.525	81.78	44.13	7.733	73.56	
CI4-u	0.5	IPA	3.905	18.22	70.20	2.741	26.07	
CI4-1			16.665	77.76	39.12	6.519	62.01	
CA1-u	1.5	Acetone	4.635	22.16	81.96	3.799	34.23	
CA1-1			16.001	76.50	45.17	7.228	65.12	
CA2-u	1.0	Acetone	7.403	35.39	78.00	5.774	52.02	
CA2-1			12.974	62.03	37.11	4.815	43.38	
CA3-u	0.75	Acetone	11.292	53.99	74.04	8.360	75.32	
CA3-1			9.433	45.10	28.70	2.707	24.39	
CA4-u	0.5	Acetone	17.957	85.86	53.82	9.664	87.07	
CA4-1			2.570	12.29	27.60	0.709	6.39	
CE1-u	1.5	Ethanol	6.766	32.35	75.39	5.101	45.96	
CE1-1			13.750	65.74	42.47	5.839	52.61	
CE2-u	1.0	Ethanol	10.395	49.70	73.31	7.621	68.66	
CE2-1			10.754	51.42	32.00	3.441	31.00	
CE3-u	0.75	Ethanol	14.247	68.12	58.13	8.282	74.61	
CE3-1			6.453	30.85	28.61	1.846	16.63	
CE4	0.5	Ethanol	(one phase)					
CD1-u	1.5	Dioxane	6.533	31.24	76.65	5.001	45.12	
CD1-i			3.006	14.66	71.44	2.190	19.73	
CD1-1			10.816	51.71	36.04	3.898	35.12	

Table 9. (Cont'd)

CD2-u	1.0	Dioxane	8.918	42.64	74.35	6.631	59.74
CD2-1			10.217	48.85	33.28	3.400	30.63
CD3-u	0.75	Dioxane	12.667	60.56	60.98	7.724	69.59
CD3-1			8.061	38.57	30.66	2.471	22.27
CD4	0.5	Dioxane	(one phase)				

Table 10. Results obtained for the fourth series of experiments Set I, spent liquor D: extracted with different organic solvents at 20°C and pH(liquor) = 5.58, using several volume ratios.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
DI	50	13.827	24.60	7.104	0.7824	0.7881	0.7861	1.0332
DA	50	13.076	24.60	6.718				
DE	50	13.076	24.60	6.718				
DD	50	13.076	24.60	6.718				

Sample	Solvent Liquor, v/v	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I x II) W _{Lu} & W _{Ll}	% lignosul- fonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$
DI1-u	1.5	IPA	3.273	23.59	65.77	2.153	30.31
DI1-l			10.035	72.34	46.01	4.617	64.99
DI2-u	1.0	IPA	4.848	35.06	65.47	3.174	44.68
DI2-l			8.291	59.96	41.25	3.420	48.14
DI3-u	0.75	IPA	7.431	53.57	55.86	4.151	58.43
DI3-l			5.858	42.23	38.49	2.255	31.74

Table 10. (Cont'd)

DI4	0.5	IPA	(one phase)				
DA1-u	1.5	Acetone	6.079	46.49	70.62	4.293	63.30
DA1-1			6.561	50.18	32.08	2.105	31.33
DA2-u	1.0	Acetone	8.389	64.16	69.24	5.809	86.46
DA2-1			4.293	32.83	19.98	0.858	12.77
DA3	0.75	Acetone	(one phase)				
DA4	0.5	Acetone	(one phase)				
DE1-u	1.5	Ethanol	6.976	53.35	65.00	4.534	67.49
DE1-1			5.982	45.78	36.51	2.184	32.50
DE2-u	1.0	Ethanol	9.436	72.16	58.62	5.531	82.33
DE2-1			3.640	27.84	32.60	1.187	17.66
DE3	0.75	Ethanol	(one phase)				
DE4	0.5	Ethanol	(one phase)				
DD1-u	1.5	Dioxane	7.911	60.50	62.98	4.982	74.16
DD1-1			5.146	39.35	33.73	1.736	20.48
DD2-u	1.0	Dioxane	10.316	78.89	58.35	6.019	89.60
DD2-1			2.670	20.42	26.18	0.699	10.40
DD3	0.75	Dioxane	(one phase)				
DD4	0.5	Dioxane	(one phase)				

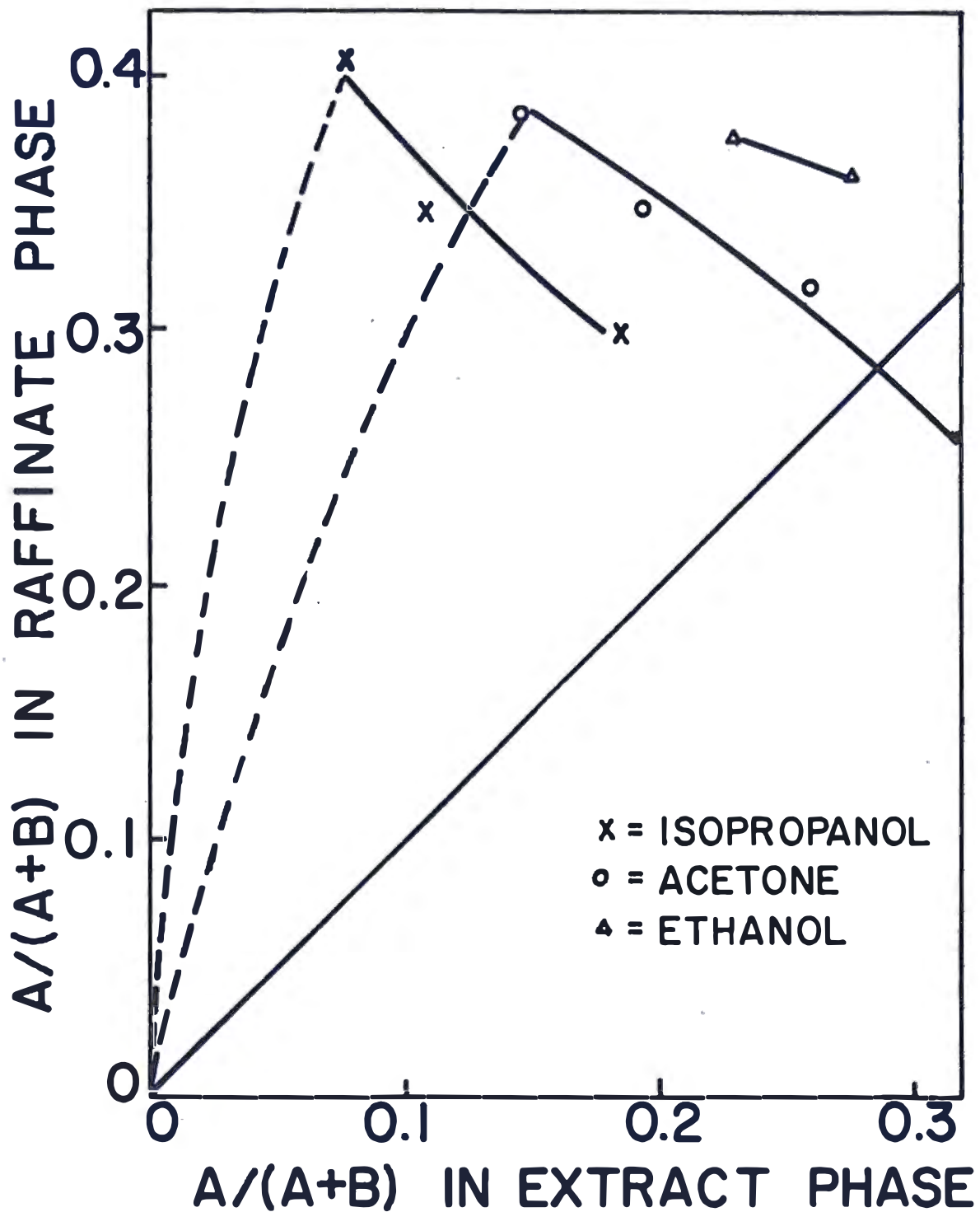


Figure 6. Selectivity diagram for spent liquor A at 20°C and $\text{pH}(\text{liquor}) \approx 5.58$. A is mass of lignosulfonates, B is mass of water.

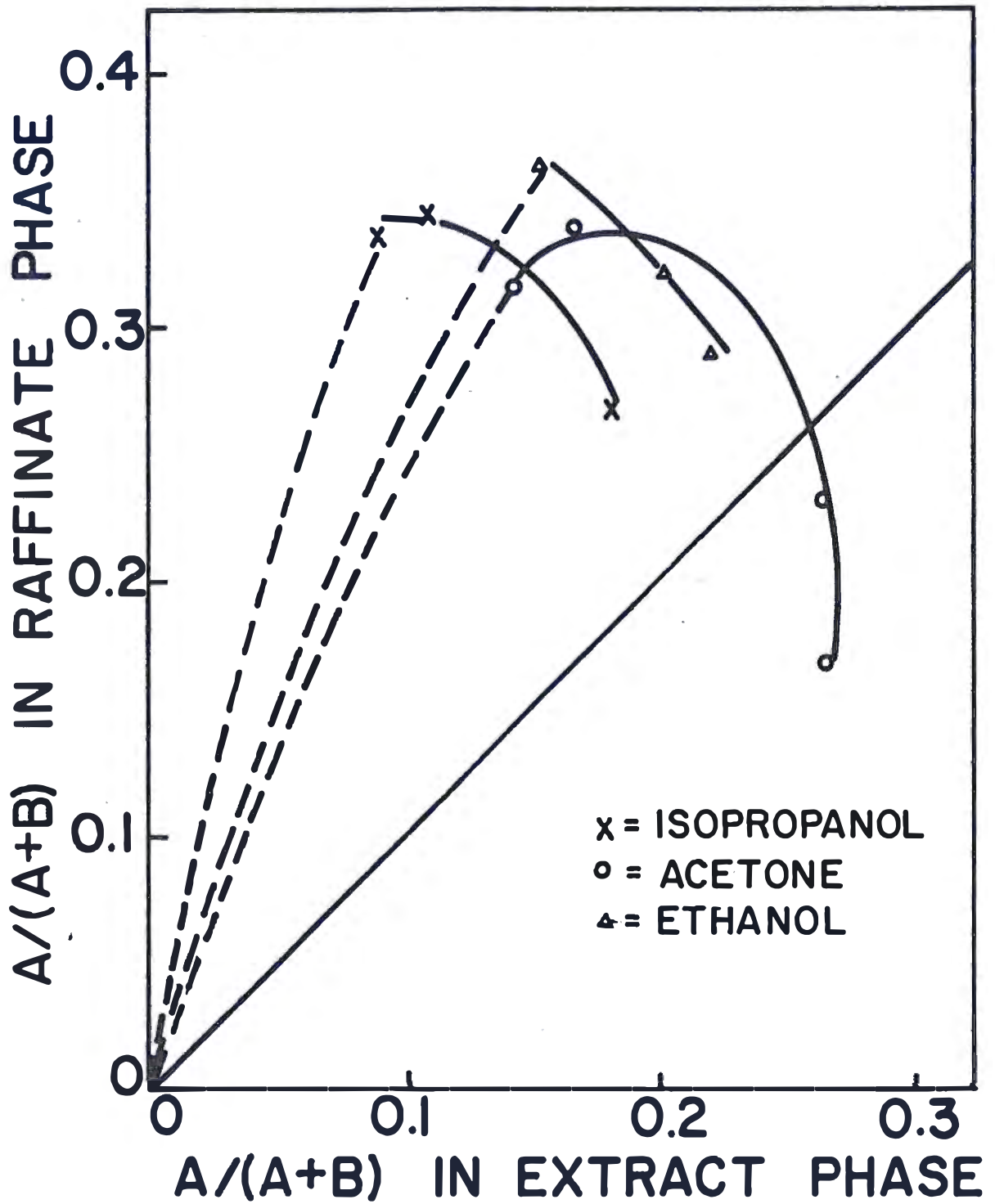


Figure 7. Selectivity diagram for spent liquor B at 20°C and pH(liquor)=5.58. A is mass of lignosulfonates, B is mass of water.

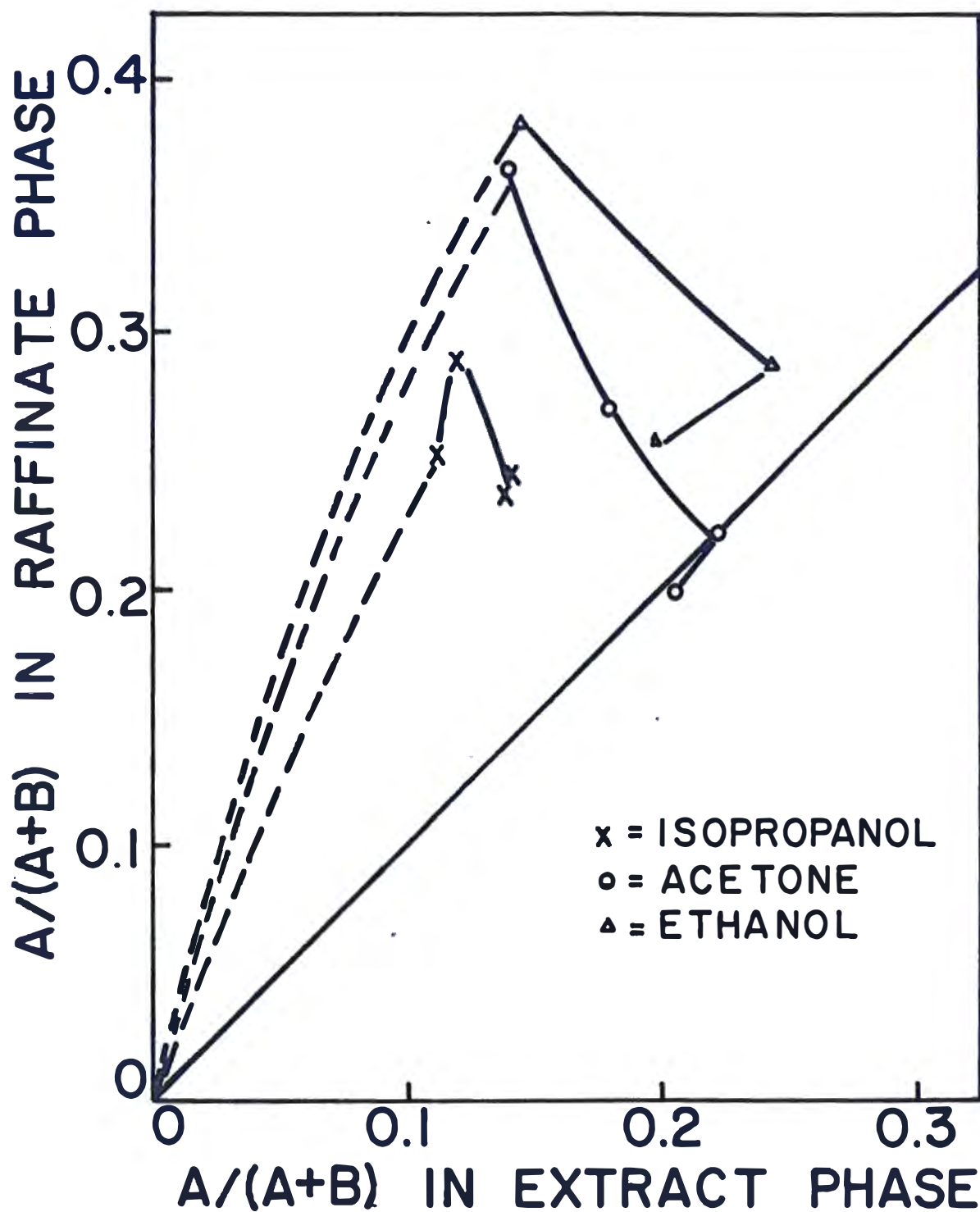


Figure 8. Selectivity diagram for spent liquor C at 20°C and pH(liquor)=5.58. A is mass of lignosulfonates, B is mass of water.

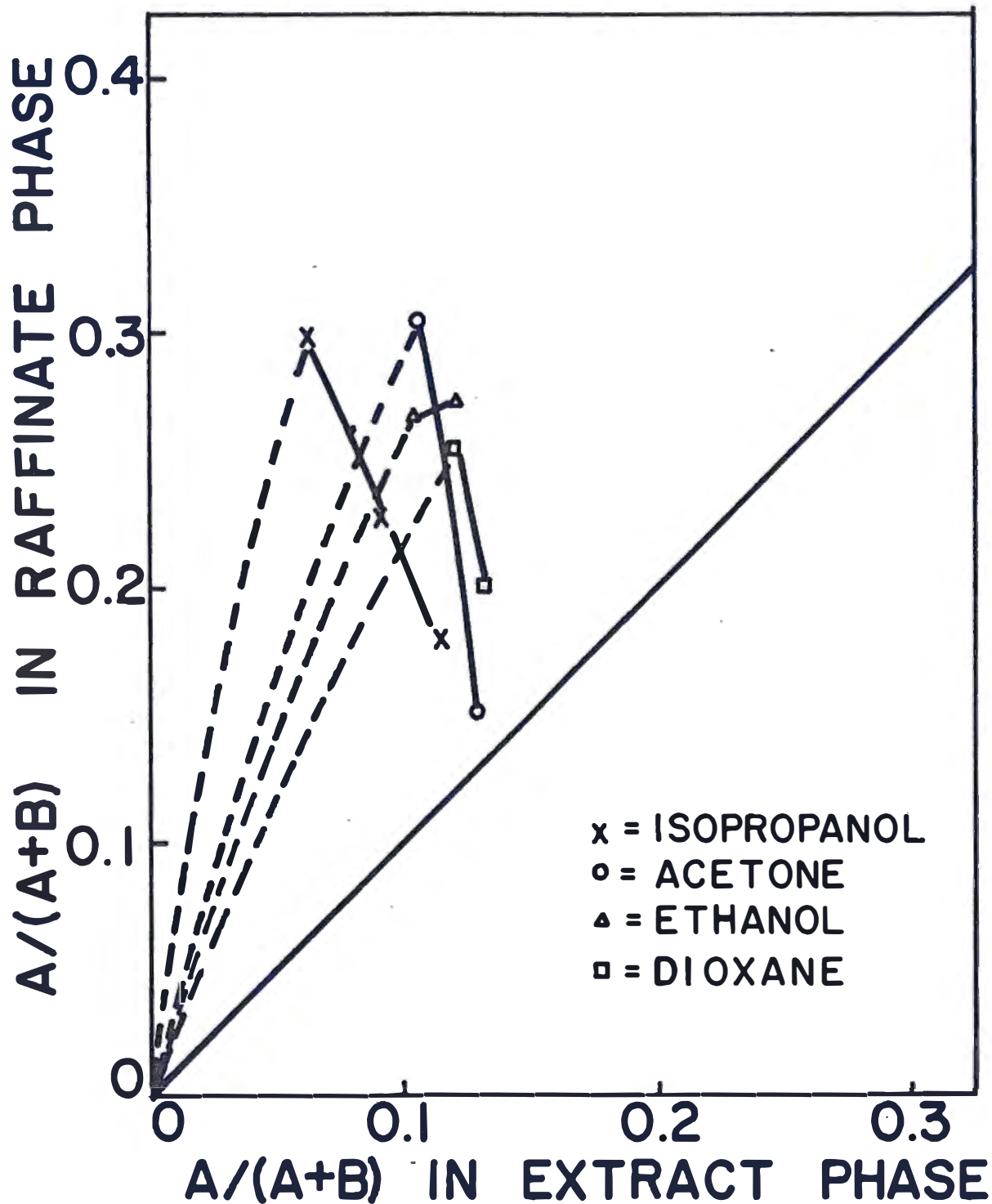


Figure 9. Selectivity diagram for spent liquor D at 20°C and pH(liquor) = 5.58. A is mass of lignosulfonates, B is mass of water.

3-6 Effect of pH of the Spent Liquor

In the experiments Set II, the effect of pH of spent liquor on extraction efficiency was studied. Three series of experiments were conducted. Each series included pH's: 9.0, 7.0, 3.5, and 1.0; and each sample liquor was extracted at 20°C with four organic solvents using a solvent-liquor volume ratio of 1/1. All results obtained are represented in Tables 11, 12, and 13.

3-7 Effect of Temperature

The experiments Set III, which included four series, studied the effect of temperature on extraction efficiency. Extractions were carried out with four organic solvents, at pH(liquor) = 5.58 and using a volume ratio of 1 to 1. Except for the extractions with acetone, which were operated at 40°C and 50°C, operating temperatures for other solvents were 40°, 50°, 60°, and 70°C. The results obtained for this set are shown in Tables 14 - 17.

Table 11. Results obtained for the first series of experiments Set II, spent liquor A :
 extracted with different organic solvents at 20°C and several pH's(liquor),
 using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

SPENT LIQUOR					DENSITIES OF SOLVENT			
Sample	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
A5	50	27.806	47.33	13.522	0.7841	0.7879	0.7899	1.3036
A6	50	27.070	47.33	13.337				
A7	50	27.404	47.33	13.738				
A8	50	27.194	47.33	-				
Sample	pH(liquor)	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I x II) W _{Lu} & W _{Ll}	% lignosul- fonates, $\frac{W_{Ll}}{W_L}$ & $\frac{W_{Lu}}{W_L}$	
AI5-u	9.0	IPA	1.455	5.23	87.57	1.274	9.42	
AI5-1			25.623	92.18	48.33	12.383	91.58	
AI6-u	7.0	IPA	1.688	6.23	66.69	1.126	8.44	
AI6-1			25.452	94.02	48.99	12.469	93.49	
AI7-u	3.5	IPA	2.116	7.72	57.70	1.221	8.87	
AI7-1			24.315	88.72	46.87	11.396	82.96	

Table 11. (Cont'd)

AI8-u	1.0	IPA	3.354	12.33			
AI8-1			23.525	86.51			
AA5-u	9.0	Acetone	3.174	11.41	86.41	2.742	20.28
AA5-1			24.215	87.09	40.65	9.842	72.78
AA6-u	7.0	Acetone	3.491	12.93	74.55	2.602	19.51
AA6-1			23.571	87.07	47.03	11.085	83.12
AA7-u	3.5	Acetone	5.446	19.87	85.64	4.664	33.95
AA7-1			21.333	77.85	39.83	8.497	61.85
AA8-u	1.0	Acetone	6.878	25.29			
AA8-1			20.356	74.86			
AE5-u	9.0	Ethanol	7.242	26.04	77.56	5.617	41.54
AE5-1			20.033	72.04	39.96	8.005	59.20
AE6-u	7.0	Ethanol	8.102	29.93	72.29	5.857	43.92
AE6-1			19.553	72.23	36.54	7.144	53.57
AE7-u	3.5	Ethanol	9.603	35.04	66.81	6.416	46.70
AE7-1			16.680	60.87	35.92	5.991	43.61
AE8-u	1.0	Ethanol	12.060	36.77			
AE8-1			15.418	56.70			
AD5-u	9.0	Dioxane	5.391	19.39	80.70	4.531	32.18
AD5-1			21.734	78.16	43.46	9.445	78.29
AD6-u	7.0	Dioxane	7.715	28.49	74.17	5.722	42.90
AD6-1			19.902	73.52	43.03	8.564	64.08

Table 11 (Cont'd)

AD7-u	3.5	Dioxane	13.524	49.35	68.43	9.254	67.36
AD7-1			14.011	51.13	31.72	4.444	32.35
AD8-u	1.0	Dioxane	15.761	57.96			
AD8-1			10.506	38.63			

Table 12. Results obtained for the second series of experiments Set II, spent liquor C : extracted with different organic solvents at 20°C and several pH's(liquor), using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

SPENT LIQUOR					DENSITIES OF SOLVENT			
Sample	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
C5	50	20.440	37.49	10.308	0.7844	0.7874	0.7861	-
C6	50	20.854	37.49	10.283				
C7	50	20.344	37.49	11.262				
C8	50	20.632	-					
Sample	pH (Liquor)	Solvent	Solids (I) g, (W _u & W _l)	% solids W _u or W _l	Lignosulfon- ates content, % (II) (by absorbance) W _{Lu} /W _u and W _{Ll} /W _l	Lignosulfon- ates, g (I x II) W _{Lu} & W _{Ll}	% lignosul- fonates, W _{Lu} /W _L & W _{Ll} /W _L	
CI5-u	9.0	IPA	2.058	10.07	86.40	1.778	17.25	
CI5-l			17.635	86.27	50.40	8.888	86.22	
CI6-u	7.0	IPA	2.261	10.84	74.08	1.675	16.28	
CI6-l			17.383	83.35	50.25	8.735	84.93	
CI7-u	3.5	IPA	3.327	16.35	74.64	2.483	22.05	
CI7-l			16.622	81.71	48.19	8.010	71.12	
CI8			(one phase)					

Table 12 (Cont'd)

CA5-u	9.0	Acetone	6.608	32.33	77.97	5.152	49.98
CA5-1			13.699	67.02	37.88	5.189	50.34
CA6-u	7.0	Acetone	6.758	32.41	71.19	4.811	46.79
CA6-1			13.443	64.46	36.38	4.891	47.56
CA7-u	3.5	Acetone	8.962	44.15	84.18	7.544	66.99
CA7-1			10.860	53.38	24.86	2.699	23.97
CA8-u	1.0	Acetone	8.705	42.19			
CA8-1			10.964	53.14			
CE5-u	9.0	Ethanol	9.020	44.13	68.63	6.190	60.05
CE5-1			11.534	56.42	33.49	3.863	37.47
CE6-u	7.0	Ethanol	10.112	48.49	73.89	7.472	72.66
CE6-1			11.698	56.09	30.22	3.535	34.37
CE7-u	3.5	Ethanol	10.449	49.15	80.71	8.433	74.88
CE7-1			9.647	47.42	23.70	2.286	20.31
CE8-u	1.0	Ethanol	11.871	57.54			
CE8-1			7.943	38.50			

Table 13. Results obtained for the third series of experiments Set II, spent liquor D : extracted with different organic solvents at 20°C and several pH's(liquor), using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
D5	50	13.662	24.60	7.137	0.7833	0.7860	0.7862	1.0293
D6	50	13.690	24.60	7.043				
D7	50	13.386	24.60	7.105				
D8	50	13.900	24.60					
Sample	pH (liquor)	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I x II) $\frac{W_{Lu}}{W_u}$ & $\frac{W_{Ll}}{W_l}$	% lignosul- fonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$	
DI5-u	9.0	IPA	3.706	22.52	70.00	2.594	35.72	
DI5-l			9.148	66.96	41.72	3.817	53.47	
DI6-u	7.0	IPA	3.994	29.17	74.17	2.962	42.06	
DI6-l			9.022	65.90	43.32	3.908	55.49	

Table 13 (Cont'd)

DI7-u	3.5	IPA	4.579	34.21	73.27	3.355	47.22
DI7-1			9.388	70.13	39.37	3.696	52.02
DI8-u	1.0	IPA	6.468	46.53			
DI8-1			7.061	50.79			
DA5-u	9.0	Acetone	7.319	53.57	71.27	5.216	73.09
DA5-1			6.307	46.16	25.78	1.626	22.78
DA6-u	7.0	Acetone	7.730	56.46	69.77	5.393	76.57
DA6-1			5.182	37.85	26.30	1.363	19.35
DA7-u	3.5	Acetone	8.119	60.65	72.95	5.923	83.36
DA7-1			5.146	38.44	22.75	1.170	16.48
DA8	1.0	Acetone	(one phase)				
DE5-u	9.0	Ethanol	8.832	64.65	66.38	5.863	82.15
DE5-1			4.878	35.70	25.77	1.257	17.61
DE6-u	7.0	Ethanol	9.648	70.47	62.45	6.044	85.81
DE6-1			3.912	28.58	24.87	0.973	13.81
DE7-u	3.5	Ethanol	9.776	73.03	66.19	6.471	91.07
DE7-1			3.685	27.53	21.43	0.790	10.22
DE8	1.0	Ethanol	(one phase)				
DD5-u	9.0	Dioxane	10.366	75.87	57.06	5.915	82.88
DD5-1			2.993	21.91	16.65	0.498	6.98
DD6-u	7.0	Dioxane	10.495	76.62	62.13	6.521	92.57
DD6-1			3.160	23.08	14.71	0.465	6.59

Table 13. (Cont'd)

DD7-u	3.5	Dioxane	11.854	88.56	55.87	6.623	93.31
DD7-1			2.145	16.02	15.07	0.323	4.55
DD8	1.0	Dioxane	(one phase)				

Table 14. Results obtained for the first series of experiments Set III, spent liquor A :
 extracted with different organic solvents at several temperatures and pH(liquor)=
 5.58, using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
A9	50	28.058	47.33	14.413	0.7747	0.7749	0.7782	1.0206
A10	50	29.655	47.33	14.854	0.7672	0.7708	0.7735	1.0389
A11	50	28.255	47.33	14.291	0.7634		0.7670	1.0091
A12	50	27.395	47.33	14.073	0.7575		0.7656	1.0010
Sample	temperature °C	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I x II) W _{Lu} & W _{Ll}	% lignosul- fonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$	
A12-u	20	IPA	1.712	6.12	84.80	1.445	10.23	
A12-l			26.682	95.37	44.77	11.945	84.57	
A19-u	40	IPA	1.668	5.95	83.84	1.398	9.70	
A19-l			24.983	89.04	49.04	12.252	85.00	
A110-u	50	IPA	1.798	6.06	76.87	1.382	9.31	
A110-i			7.671	25.87	49.07	3.764	25.34	

Table 14. (Cont'd)

AI10-1			18.812	63.44	51.96	9.709	65.36
AI11-u	60	IPA	2.192	7.76	82.83	1.816	12.70
AI11-i			2.103	7.44	52.87	1.112	7.78
AI11-1			22.750	80.52	44.93	10.221	71.52
AI12-u	70	IPA	2.084	7.61	91.15	1.899	13.50
AI12-i			1.554	3.65	62.19	0.966	6.88
AI12-1			24.096	87.96	47.57	11.463	81.45
AA2-u	20	Acetone	3.501	12.76	91.17	3.192	21.13
AA2-1			23.544	85.80	47.35	11.148	73.80
AA9-u	40	Acetone	2.896	10.32	80.95	2.344	16.27
AA9-1			23.517	83.81	49.57	11.657	80.88
AA10-u	50	Acetone	2.275	7.67	87.04	1.980	13.33
AA10-1			27.186	91.67	47.53	12.922	86.99
AE2-u	20	Ethanol	9.038	32.94	77.13	6.971	46.15
AE2-1			17.381	63.34	38.17	6.634	43.92
AE9-u	40	Ethanol	10.297	36.70	79.35	8.171	56.69
AE9-1			16.979	60.52	36.30	6.163	42.76
AE10-u	50	Ethanol	12.287	41.43	72.26	8.879	59.77
AE10-1			15.758	53.14	33.07	5.211	35.88
AE11-u	60	Ethanol	12.173	43.08	73.75	8.978	62.82
AE11-1			13.868	49.08	32.69	4.533	31.72

Table 14. (Cont'd)

AE12-u	70	Ethanol	12.014	43.86	75.72	9.097	64.64
AE12-1			14.054	51.30	31.28	4.396	31.24
AD2-u	20	Dioxane	9.032	31.52	84.46	7.628	51.58
AD2-i			2.541	8.67	75.15	1.910	12.91
AD2-1			17.013	59.37	27.25	4.636	31.35
AD9-u	40	Dioxane	4.080	14.54	87.49	3.569	24.76
AD9-i			5.349	19.10	67.15	3.592	24.92
AD9-1			18.425	65.67	32.68	6.021	41.78
AD10-u	50	Dioxane	3.873	13.06	89.42	3.463	23.32
AD10-i			9.001	30.37	70.37	6.339	42.67
AD10-1			15.236	51.38	26.36	4.016	27.04
AD11-u	60	Dioxane	3.025	10.71	93.83	2.838	19.86
AD11-i			8.596	30.42	71.76	6.168	43.16
AD11-1			16.950	59.99	31.85	5.399	37.77
AD12-u	70	Dioxane	2.739	9.99	89.86	2.461	17.49
AD12-i			6.845	24.99	73.89	5.058	35.94
AD12-1			16.765	61.20	31.02	5.201	36.95

Table 15. Results obtained for the second series of experiments Set III, spent liquor B : extracted with different organic solvents at several temperatures and pH(liquor)=5.58, using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
B5	50	24.675	41.95	12.710	0.7747	0.7749	0.7782	1.0206
B6	50	24.138	41.95	13.040	0.7672	0.7708	0.7735	1.0389
B7	50	24.158	41.95	12.859	0.7634		0.7670	1.0091
B8	50	23.508	41.95	12.510	0.7575		0.7656	1.0010
Sample	Temperature °C	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfonates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfonates, g (I x II) W _{Lu} & W _{Ll}	% lignosulfonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$	
BI2-u	20	IPA	1.886	7.55	85.05	1.604	12.46	
BI2-l			22.559	90.29	48.59	10.961	85.17	
BI5-u	40	IPA	2.271	9.20	74.71	1.696	13.35	
BI5-l			23.021	93.30	47.95	11.039	86.85	
BI6-u	50	IPA	2.552	10.57	77.84	1.988	15.23	
BI6-l			21.002	86.88	49.10	10.312	79.06	

Table 15. (Cont'd)

BI7-u	60	IPA	2.637	10.92	91.62	2.417	18.79
BI7-1			20.488	84.81	49.35	10.111	78.63
BI8-u	70	IPA	2.672	11.39	91.13	2.438	19.50
BI8-1			20.559	87.46	48.16	9.901	79.15
BA2-u	20	Acetone	5.301	22.12	77.24	4.094	31.94
BA2-1			18.394	76.76	46.39	8.533	78.00
BA5-u	40	Acetone	4.246	17.21	81.25	3.450	27.11
BA5-1			20.124	81.56	38.41	7.730	60.82
BA6-u	50	Acetone	3.803	15.75	84.64	3.219	24.68
BA6-1			20.106	83.30	47.88	9.627	73.81
BE2-u	20	Ethanol	9.638	40.22	69.57	6.705	52.30
BE2-1			14.155	59.07	36.77	5.205	40.60
BE5-u	40	Ethanol	12.111	49.08	69.89	8.464	66.59
BE5-1			12.045	48.81	32.88	3.960	31.16
BE6-u	50	Ethanol	12.632	52.34	67.83	8.569	65.69
BE6-1			10.781	44.66	29.70	3.202	24.55
BE7-u	60	Ethanol	12.444	51.51	71.46	8.893	69.15
BE7-1			10.147	42.00	28.33	2.874	22.35
BE8-u	70	Ethanol	13.652	58.08	77.52	10.583	84.60
BE8-1			8.683	37.66	26.55	2.305	18.43

Table 15. (Cont'd)

BD2-u	20	Dioxane	10.535	43.96	76.52	8.061	62.88
BD2-l			12.404	51.76	24.32	3.016	23.52
BD6-u	50	Dioxane	8.139	33.72	77.04	6.270	48.07
BD6-i			2.838	11.76	65.31	1.853	14.21
BD6-l			13.319	57.66	28.01	3.731	28.60
BD7-u	60	Dioxane	9.146	37.86	73.75	6.745	52.45
BD7-i			4.078	16.88	65.40	2.667	20.74
BD7-l			11.653	48.24	30.29	3.530	27.45
BD8-u	70	Dioxane	4.842	20.60	74.62	3.613	28.88
BD8-i			5.164	21.97	71.52	3.693	29.52
BD8-l			12.865	54.73	31.34	4.032	32.23

Table 16. Results obtained for the third series of experiments Set III, spent liquor C : extracted with different organic solvents at several temperatures and pH(liquor)= 5.58, using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

Sample	SPENT LIQUOR				DENSITIES OF SOLVENT			
	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
C9	50	22.250	37.49	10.604	0.7747	0.7749	0.7782	1.0206
C10	50	20.638	37.49	10.632	0.7672	0.7708	0.7735	1.0389
C11	50	21.471	37.49	11.350	0.7634		0.7670	1.0091
C12	50	21.528	37.49	11.041	0.7575		0.7656	1.0010

Sample	Temperature °C	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfonates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfonates, g (I x II) W _{Lu} & W _{Ll}	% lignosulfonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$
CI2-u	20	IPA	2.794	13.04	87.91	2.456	23.36
CI2-l			16.609	77.50	46.91	7.791	74.12
CI9-u	40	IPA	2.659	11.95	64.98	1.728	16.30
CI9-l			18.287	82.19	44.28	8.097	76.36

Table 16. (Cont'd)

CI10-u	50	IPA	3.086	14.95	76.94	2.374	22.33
CI10-i			0.438	2.12	51.17	0.224	2.11
CI10-1			15.785	76.49	46.08	7.274	68.41
CI11-u	60	IPA	3.147	14.66	86.67	2.728	24.03
CI11-1			18.179	84.66	45.22	8.220	72.43
CI12-u	70	IPA	3.270	15.19	86.66	2.834	25.67
CI12-1			17.034	79.17	47.72	8.133	73.66
CA2-u	20	Acetone	7.403	35.39	78.00	5.774	52.02
CA2-1			12.974	62.03	37.11	4.815	43.38
CA9-u	40	Acetone	6.930	33.19	81.17	5.625	53.04
CA9-1			13.974	62.68	37.86	5.280	49.79
CA10-u	50	Acetone	5.151	24.96	75.87	3.908	36.76
CA10-1			15.725	76.19	48.75	7.666	72.10
CE2-u	20	Ethanol	10.395	49.70	73.31	7.621	68.66
CE2-1			10.754	51.42	32.00	3.441	31.00
CE9-u	40	Ethanol	11.426	51.35	66.62	7.612	71.78
CE9-1			8.825	39.66	26.90	2.374	22.38
CE10-u	50	Ethanol	12.890	62.46	66.58	8.582	80.72
CE10-1			7.808	37.83	26.22	2.047	19.25

Table 16. (Cont'd)

CE11-u	60	Ethanol	13.157	61.28	69.19	9.103	80.20
CE11-1			6.602	30.75	28.09	1.855	16.34
CE12-u	70	Ethanol	13.231	61.46	66.15	8.752	79.27
CE12-1			6.434	30.55	26.16	1.683	15.24
CD2-u	20	Dioxane	8.918	42.64	74.35	6.631	59.74
CD2-1			10.217	48.85	33.28	3.400	30.63
CD9-u	40	Dioxane	6.765	30.40	79.18	5.357	50.51
CD9-1			16.399	73.71	25.04	4.106	38.72
CD10-u	50	Dioxane	10.452	50.71	71.52	7.485	70.40
CD10-1			9.527	46.17	24.39	2.324	21.86
CD11-u	60	Dioxane	9.839	45.82	73.48	7.230	63.70
CD11-1			10.562	49.19	27.17	2.870	25.29
CD12-u	70	Dioxane	8.503	39.50	75.57	6.426	58.20
CD12-1			11.287	52.43	30.85	3.482	31.54

Table 17. Results obtained for the fourth series of experiments Set III, spent liquor D : extracted with different organic solvents at several temperatures and pH(liquor)= 5.58, using a volume ratio of 1 to 1.

Volume of liquor used and other physical data :

SPENT LIQUOR					DENSITIES OF SOLVENT			
Sample	Volume used cm ³	Total solids g, (W)	Solids content %	Lignosulfonates g, (W _L)	Isopropanol	Acetone	Ethanol	Dioxane
D9	50	13.487	24.60	7.098	0.7747	0.7749	0.7782	1.0206
D10	50	13.010	24.60	7.098	0.7672	0.7708	0.7735	1.0389
D11	50	13.548	24.60	7.130	0.7634		0.7670	1.0091
D12	50	12.748	24.60	6.709	0.7575		0.7656	1.0010

Sample	Temperature °C	Solvent	Solids (I) g, (W _u & W _l)	% solids $\frac{W_u \text{ or } W_l}{W}$	Lignosulfon- ates content, % (II) (by absorbance) $\frac{W_{Lu}}{W_u}$ and $\frac{W_{Ll}}{W_l}$	Lignosulfon- ates, g (I xII) W _{Lu} & W _{Ll}	% lignosul- fonates, $\frac{W_{Lu}}{W_L}$ & $\frac{W_{Ll}}{W_L}$
DI2-u	20	IPA	4.848	35.06	65.47	3.174	44.68
DI2-l			8.291	59.96	41.25	3.420	48.14
DI9-u	40	IPA	4.454	33.03	64.20	2.860	40.29
DI9-l			9.173	68.01	43.24	3.966	55.88

Table 17. (Cont'd)

DI10-u	50	IPA	3.969	30.50	70.16	2.784	39.23
DI10-1			8.637	66.38	43.70	3.774	53.17
DI11-u	60	IPA	4.599	33.94	76.81	3.532	49.54
DI11-1			7.648	56.45	41.61	3.182	44.63
DI12-u	70	IPA	4.735	37.15	68.17	3.228	48.12
DI12-1			7.355	57.70	44.70	3.287	49.01
DA2-u	20	Acetone	8.389	64.16	69.24	5.809	86.46
DA2-1			4.293	32.83	19.98	0.858	12.77
DA9-u	40	Acetone	9.041	67.04	64.64	5.845	82.34
DA9-1			4.362	32.34	21.69	0.946	13.33
DA10-u	50	Acetone	8.625	66.30	65.94	5.687	80.12
DA10-1			3.874	29.78	23.99	0.929	13.09
DE2-u	20	Ethanol	9.436	72.16	58.62	5.531	82.33
DE2-1			3.640	27.84	32.60	1.183	17.66
DE9-u	40	Ethanol	10.846	80.41	57.08	6.191	87.21
DE9-1			2.259	16.75	26.25	0.592	8.35
DE10-u	50	Ethanol	11.382	87.49	58.52	6.661	93.84
DE10-1			1.054	8.10	29.24	0.308	4.34
DE11-u	60	Ethanol	12.019	88.72	55.12	6.625	92.92
DE11-1			0.962	7.10	25.74	0.248	3.47

Table 17. (Cont'd)

DE12-u	70	Ethanol	12.147	95.29	54.21	6.585	98.15
DE12-1			0.854	6.70	30.77	0.261	3.91
DD2-u	20	Dioxane	10.316	78.89	58.35	6.019	89.60
DD2-1			2.670	20.42	26.18	0.699	10.40
DD9-u	40	Dioxane	10.475	77.66	66.97	7.015	98.83
DD9-1			2.713	20.11	16.08	0.436	6.14
DD10-u	50	Dioxane	10.926	83.98	54.02	5.902	83.15
DD10-1			2.850	21.91	18.71	0.533	7.51
DD11-u	60	Dioxane	10.589	78.16	58.25	6.168	86.51
DD11-1			2.437	17.99	13.44	0.328	4.59
DD12-u	70	Dioxane	10.168	79.76	59.06	6.005	89.51
DD12-1			2.288	17.95	19.34	0.442	6.60

3-8 Recovery of Carbohydrates by Ultrafiltration

Table 18 shows the results for the recovery of carbohydrates from nine samples treated by ultrafiltration. The amount of carbohydrates presented was expressed in terms of apparent glucose. The absorptivity of glucose at 620 nm was 3.8 absorbance/(mg cm⁻²).

The average duration of ultrafiltration for upper phase samples was 16 hours and 45 minutes, and that for lower-phase samples 6 hours. The operation duration depended on the filtration rate of the sample solution.

3-9 Phase Equilibrium Diagram⁽¹⁹⁾

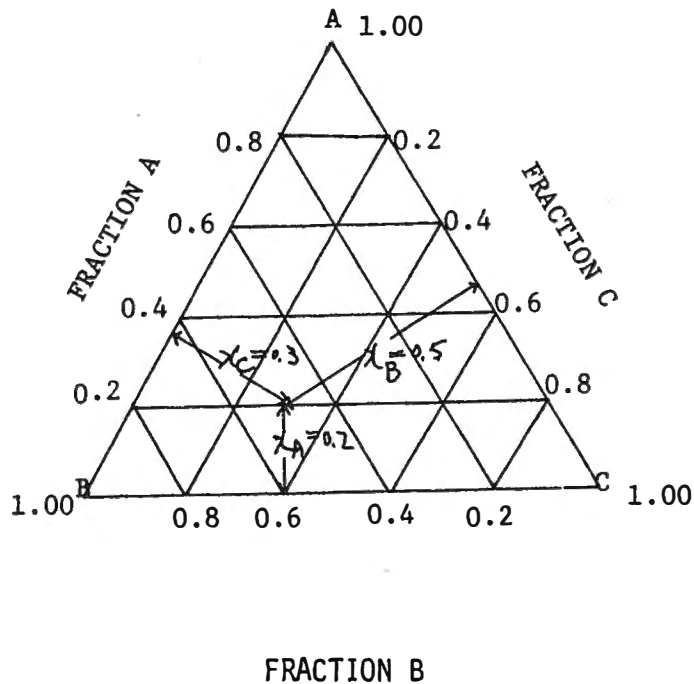
In liquid extraction, the phase equilibria of interest are those showing the distribution of a solute (A) between two immiscible or partially miscible liquids (B) and (C). Two cases should be considered: (1) the mutual solubility of liquids B and C is negligible even in the presence of component A, and (2) this solubility can not be ignored.

In the first case, when equilibrium is reached, the phase of B (plus some dissolved A) contains practically no C and the phase of C (plus A) practically no B. The equilibrium becomes a simple relation between the concentrations of solute in the two phases. The equilibrium curve is the usual X_e vs Y_e plot, with X_e and Y_e defined as the mass fractions of solute A in the phases B and C, respectively.

Table 18. Results obtained for recovery of carbohydrates by ultrafiltration.

Sample	duration of ultrafiltration	Substance does not pass through the filter			Substance passes through the filter		
		% (base on original sample wt.)	lignosulfonates, g	carbohydrates, g (in terms of apparent glucose)	% (base on original sample wt.)	lignosulfonates, g	carbohydrates, g (in terms of apparent glucose)
A	11 h	70.50		0.227	32.50		0.146
AI2-u	16 h 45 min	81.74	0.800	0.091	9.53	0.059	0.013
AI2-1	6 h	68.73	0.408	0.259	23.01	0.181	0.117
AA2-u	16 h 45 min	66.10	0.631	0.056	33.20	0.205	0.031
AA2-1	6 h 10 min	76.50	0.453	0.290	29.30	0.197	0.132
AE2-u	17 h	68.15	0.695	0.092	23.12	0.094	0.049
AE2-1	6 h	66.67	0.372	0.314	33.63	0.206	0.115
AD2-u	16 h 45 min	74.63	0.744	0.116	23.38	0.102	0.012
AD2-1	6 h	59.54	0.243	0.287	36.58	0.210	0.108

When the mutual solubility of diluent B and solvent C can not be neglected, the solubility and equilibrium relationships are often shown on triangular coordinates. In this method of plotting, the composition of any three-component mixture can be shown by a point lying inside an equilateral triangle, as shown in the following figure.



Triangular coordinates

The triangular diagram has certain characteristics. Concentrations represented by this diagram are based on the entire mixture, not on one or two components. Then the concentrations of the three components in each phase must add to unity, i.e. :

$$x_A + x_B + x_C = 1 \quad \text{and} \quad y_A + y_B + y_C = 1$$

Either mole fractions or mass fractions may be used; however, the unit in mass fraction is more commonly used.

The sum of mass fraction concentrations correlates with the diagram by the geometric principle that the sum of the perpendicular distances from any point to the three sides of an equilateral triangle equals the altitude of the triangle. Thus, if the altitude is taken as unity the perpendicular distances from any point to the sides automatically add to unity, and these distances can be used to represent the individual concentrations of the three components.

Equilibria in triangular diagrams are shown by tie-lines. These are usually straight lines connecting points on the two solubility curves (extracte and raffinate). Tie lines decrease in length as the solubility curves approach each other, and vanish at the plait point where the two phases become identical.

From the results (shown in tables 19 - 29) obtained for the distribution of solids, water, and solvent in the upper and lower phases, the solubility and equilibrium relationships studied as a function of solvent, temperature and volume ratio were presented by equilibrium diagrams. These diagrams are presented in figures 10 - 26.

Table 19. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the first series of experiments Set I, spent liquor A: extracted with different organic solvents at 20°C and pH(liquor) = 5.58, using several volume ratios.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
AI1-u	81	1.631	15.831	49.860
AI1-1	42	26.544	18.743	8.820
AI2-u	53	1.712	12.068	29.792
AI2-1	47	26.682	22.506	9.328
AI3-u	30	2.057	7.901	16.244
AI3-1	41	23.788	26.673	12.705
AA1-u	78	2.732	14.808	47.548
AA1-1	44	25.441	19.361	8.727
AA2-u	53	3.501	13.212	28.497
AA2-1	44	23.544	20.743	9.169
AA3-u	40	4.623	11.755	19.644
AA3-1	45	22.279	22.820	8.968
AA4-u	43	12.663	18.663	12.929
AA4-1	31	13.278	15.049	5.512
AE1-u	85	8.560	21.191	44.051
AE1-1	37	18.880	(13.270)	(14.965)
AE2-u	70	9.038	23.501	33.237
AE2-1	27	17.381	(10.960)	(6.107)
AE3-u	63	13.182	25.613	22.767
AE3-1	22	14.695	(8.848)	(6.348)
AD1-u	76	3.923	14.129	59.695
AD1-i	20	7.699	6.837	9.906
AD1-1	27	16.936	12.962	7.237
AD2-u	60	9.032	18.330	38.317
AD2-i	9	2.541	3.086	4.265
AD2-1	29	17.013	13.259	7.050

Table 19. (Cont'd)

AD3-u	63	15.092	23.524	32.554
AD3-1	23	13.307	11.998	5.591
AD4-u	56	19.641	26.183	22.189
AD4-1	18	9.018	9.542	4.241

Table 20. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the second series of experiments Set I, spent liquor B: extracted with different organic solvents at 20°C and pH(liquor)=5.58, using several volume ratios.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
BI1-u	83	1.987	16.250	50.211
BI1-l	41	21.900	20.512	8.349
BI2-u	51	1.886	15.936	30.854
BI2-l	49	22.559	20.828	8.266
BI3-u	32	2.749	9.721	17.247
BI3-l	54	21.538	27.041	11.702
BA1-u	85	3.438	17.552	53.123
BA1-l	38	20.419	20.572	6.593
BA2-u	62	5.301	19.966	34.633
BA2-l	36	18.394	16.502	4.132
BA3-u	56	9.692	21.517	21.993
BA3-l	29	14.251	(16.022)	(7.169)
BA4-u	57	16.844	26.345	15.843
BA4-l	16	6.620	11.194	3.861
BE1-u	97	6.283	24.541	48.987
BE1-l	27	18.304	(12.992)	(10.116)
BE2-u	74	9.638	26.133	32.952
BE2-l	24	14.155	10.995	5.244
BE3-u	67	12.878	28.705	24.790
BE3-l	18	11.510	8.422	3.839
BD1-u	83	5.530	19.669	56.896
BD1-i	17	3.867	5.317	7.737
BD1-l	24	13.847	10.796	5.933
BD2-u	78	10.535	25.558	44.878
BD2-l	21	12.404	10.675	5.192
BD3-u	69	15.072	28.140	34.319
BD3-l	16	9.610	8.660	3.596

Table 21. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the third series of experiments Set I, spent liquor C: extracted with different organic solvents at 20°C and pH(liquor)=5.58, using several volume ratios.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
CI1-u	87	2.183	14.412	42.543
CI1-1	37	18.272	23.557	16.260
CI2-u	55	2.794	17.697	28.257
CI2-1	28	16.609	19.019	10.838
CI3-u	52	3.154	14.841	20.208
CI3-1	33	17.525	23.911	8.193
CI4-u	31	3.905	17.200	14.451
CI4-1	43	16.665	20.391	4.944
CA1-u	92	4.635	26.874	50.160
CA1-1	30	16.001	12.530	8.320
CA2-u	72	7.403	26.262	33.444
CA2-1	25	12.974	13.014	4.354
CA3-u	66	11.292	29.160	26.544
CA3-1	19	9.433	9.259	2.987
CA4-u	68	17.957	37.768	16.675
CA4-1	6	2.570	2.842	1.896
CE1-u	103	6.766	29.724	51.792
CE1-1	20	13.750	(9.414)	(7.299)
CE2-u	81	10.395	30.926	37.830
CE2-1	17	10.754	8.503	2.516
CE3-u	74	14.247	33.406	28.479
CE3-1	11	6.453	5.273	1.861
CD1-u	96	6.533	25.974	67.481
CD1-i	10	3.006	3.285	4.609
CD1-1	18	10.816	8.740	4.633
CD2-u	84	8.918	31.250	47.107
CD2-1	15	10.217	7.899	3.342
CD3-u	75	12.667	34.424	35.723
CD3-1	11	8.061	5.473	2.197

Table 22. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the fourth series of experiments Set I, spent liquor D: extracted with different organic solvents at 20°C and pH(liquor)=5.58, using several volume ratios.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
DI1-u	105	3.273	31.664	54.299
DI1-1	19	10.035	10.724	3.527
DI2-u	79	4.848	31.538	34.454
DI2-1	20	8.291	11.592	3.617
DI3-u	70	7.431	32.331	25.510
DI3-1	15	5.858	10.275	2.891
DA1-u	108	6.079	35.630	53.552
DA1-1	14	6.561	7.018	(5.554)
DA2-u	89	8.389	39.173	37.345
DA2-1	9	4.293	4.783	1.529
DE1-u	114	6.976	37.975	53.960
DE1-1	10	5.982	(5.979)	(4.996)
DE2-u	91	9.436	40.297	36.721
DE2-1	7	3.640	3.159	1.420
DD1-u	114	7.911	36.165	74.878
DD1-1	10	5.146	5.073	2.176
DD2-u	93	10.316	39.368	50.069
DD2-1	5	2.670	2.781	1.174

Table 23. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the first series of experiments Set II, spent liquor A: extracted with different organic solvents at 20°C and several pH's (liquor), using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
AI5-u	54	1.455	12.598	33.190
AI5-1	45	25.623	21.767	5.907
AI6-u	56	1.688	12.588	34.419
AI6-1	44	25.452	21.963	5.162
AI7-u	54	2.116	13.172	32.882
AI7-1	44	24.315	21.962	5.900
AI8-u	54	3.354	13.340	32.285
AI8-1	45	23.523	-	-
AA5-u	57	3.174	16.093	32.784
AA5-1	41	24.215	17.670	6.998
AA6-u	55	3.491	14.414	31.470
AA6-1	44	23.571	20.181	8.103
AA7-u	61	5.446	17.527	32.897
AA7-1	37	21.333	16.506	6.485
AA8-u	62	6.878	18.752	33.437
AA8-1	36	20.356	15.332	6.475
AE5-u	69	7.242	23.133	35.618
AE5-1	30	20.033	11.859	4.350
AE6-u	68	8.102	22.359	34.666
AE6-1	30	19.553	12.013	4.465
AE7-u	72	9.603	23.782	35.854
AE7-1	25	16.680	11.196	4.102
AE8-u	74	12.060	24.631	37.081
AE8-1	24	15.418		
AD5-u	51	5.391	12.731	34.688
AD5-1	48	21.734	21.524	16.567
AD6-u	55	7.715	14.823	35.434
AD6-1	44	19.902	19.309	15.520

Table 23. (Cont'd)

AD7-u	74	13.524	22.422	45.683
AD7-l	24	14.011	11.680	5.522
AD8-u	79	15.761	24.503	46.952
AD8-l	20	10.506		

Table 24. Results obtained for the distribution of volume, solids, water, and solvent in different phases, for the second series of experiments Set II, spent liquor C: extracted with different organic solvents at 20°C and several pH's (liquor), using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
CI5-u	58	2.058	15.791	29.122
CI5-1	42	17.635	24.112	8.994
CI6-u	57	2.261	15.281	28.834
CI6-1	42	17.383	23.929	9.625
CI7-u	69	3.327	19.840	31.755
CI7-1	30	16.622	19.027	6.480
CA5-u	71	6.608	23.183	34.077
CA5-1	27	13.699	16.554	4.662
CA6-u	71	6.758	22.263	33.714
CA6-1	27	13.443	16.033	5.408
CA7-u	76	8.962	25.402	37.103
CA7-1	22	10.860	13.828	2.970
CA8-u	77	8.705	25.736	35.464
CA8-1	21	10.964	12.713	3.662
CE5-u	80	9.020	30.690	37.502
CE5-1	19	11.534	9.030	1.874
CE6-u	80	10.112	31.727	37.923
CE6-1	19	11.698	9.013	1.951
CE7-u	82	10.449	31.105	36.928
CE7-1	16	9.647	8.336	2.907
CE8-u	75	11.871	29.938	33.578
CE8-1	23	7.943	9.747	6.178

Table 25. Results obtained for the distribution of volume, solids, water, and solvent in different phases. for the third series of experiments Set II, spent liquor D: extracted with different organic solvents at 20°C and several pH's (liquor), using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
DI5-u	72	3.706	26.446	34.255
DI5-1	27	9.148	17.004	3.915
DI6-u	78	3.994	29.068	35.901
DI6-1	21	9.022	13.116	2.804
DI7-u	78	4.579	28.859	35.493
DI7-1	20	9.388	-	-
DA5-u	86	7.319	37.135	38.431
DA5-1	13	6.307	7.684	1.360
DA6-u	87	7.730	37.124	37.712
DA6-1	11	5.182	6.163	1.778
DA7-u	88	8.119	38.447	38.472
DA7-1	20	5.146	-	-
DE5-u	86	8.832	39.082	36.201
DE5-1	12	4.878	5.690	1.894
DE6-u	91	9.648	40.825	38.528
DE6-1	8	3.912	4.242	0.748
DE7-u	90	9.776	40.611	37.975
DE7-1	9	3.685	-	-
DD5-u	90	10.366	37.993	48.935
DD5-1	9	2.993	4.981	1.593
DD6-u	92	10.495	37.929	50.022
DD6-1	7	3.160	3.683	1.267
DD7-u	92	11.854	39.140	48.769
DD7-1	6	2.145	3.485	1.408

Table 26. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the first series of experiments Set III, spent liquor A: extracted with different organic solvents at several temperatures and pH(liquor) = 5.58, using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
AI9-u	49	1.668	11.869	29.479
AI9-1	50	24.983	22.990	8.076
AI10-u	46	1.798	10.403	24.579
AI10-i	22	7.671	(9.263)	(10.397)
AI10-1	30	18.812	14.384	3.386
AI11-u	48	2.192	9.738	28.937
AI11-i	15	2.103	5.748	3.934
AI11-1	36	22.750	17.717	4.228
AI12-u	53	2.084	12.306	30.686
AI12-i	8	1.554	(2.013)	(2.578)
AI12-1	39	24.096	20.121	4.584
AA9-u	52	2.896	11.919	30.394
AA9-1	46	23.517	20.912	9.471
AA10-u	52	2.275	11.839	31.285
AA10-1	47	27.186	21.639	8.616
AE9-u	72	10.297	24.035	31.748
AE9-1	26	16.979	10.716	5.730
AE10-u	74	12.287	23.330	33.484
AE10-1	24	15.758	10.120	4.879
AE11-u	76	12.173	23.276	33.062
AE11-1	23	13.868	10.617	3.320
AE12-u	76	12.014	23.778	34.878
AE12-1	23	14.054	9.671	3.152

Table 26 (Cont'd)

AD9-u	50	4.080	12.704	36.628
AD9-i	17	5.349	6.145	5.617
AD9-1	33	18.425	15.479	7.865
AD10-u	46	3.873	12.395	33.241
AD10-i	25	9.001	9.912	8.751
AD10-1	28	15.236	13.796	8.852
AD11-u	49	3.025	11.862	34.390
AD11-i	21	8.596	9.465	7.807
AD11-1	30	16.950	14.720	8.422
AD12-u	48	2.739	11.588	35.522
AD12-i	22	6.845	8.809	8.647
AD12-1	30	16.765	14.368	7.001

Table 27. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the second series of experiments Set III, spent liquor B: extracted with different organic solvents at several temperatures and pH(liquor) = 5.58, using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
BI5-u	56	2.271	15.735	31.485
BI5-1	44	23.021	21.677	7.376
BI6-u	62	2.552	16.693	33.204
BI6-1	37	21.002	20.196	4.637
BI7-u	62	2.637	18.401	36.406
BI7-1	37	20.488	18.765	3.476
BI8-u	62	2.672	16.118	32.524
BI8-1	37	20.559	20.266	3.946
BA5-u	59	4.246	18.482	32.918
BA5-1	39	20.124	19.517	6.735
BA6-u	56	3.803	15.387	28.822
BA6-1	42	20.106	20.117	9.181
BE5-u	81	12.111	29.448	34.712
BE5-1	18	12.045	8.022	2.839
BE6-u	81	12.632	28.872	33.996
BE6-1	18	10.781	7.846	3.383
BE7-u	83	12.444	30.205	36.275
BE7-1	16	10.147	7.953	2.573
BE8-u	84	13.652	29.796	34.713
BE8-1	15	8.683	6.307	1.990
BD6-u	71	8.139	21.591	42.088
BD6-i	10	2.838	4.696	2.879
BD6-1	19	13.319	10.020	5.471
BD7-u	62	9.146	18.748	38.340
BD7-i	12	4.078	4.450	3.369
BD7-1	26	11.653	14.832	7.003

Table 27. (Cont'd)

BD8-u	55	4.842	15.545	36.480
BD8-i	17	5.164	6.340	5.638
BD8-1	28	12.865	15.059	5.675

Table 28. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the third series of experiments Set III, spent liquor C: extracted with different organic solvents at several temperatures and pH(liquor) = 5.58, using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
CI9-u	60	2.659	17.736	32.141
CI9-1	40	18.287	21.460	5.934
CI10-u	64	3.086	18.883	32.816
CI10-1	33	15.785	19.595	4.668
CI11-u	62	3.147	18.401	34.271
CI11-1	36	18.179	20.422	4.792
CI12-u	65	3.270	19.813	32.540
CI12-1	35	17.034	19.796	4.495
CA9-u	68	6.930	25.717	30.261
CA9-1	29	13.974	13.294	7.319
CA10-u	66	5.151	22.545	33.042
CA10-1	33	15.725	16.296	6.282
CE9-u	81	11.426	31.714	35.086
CE9-1	18	8.825	7.315	2.924
CE10-u	84	12.890	32.875	34.967
CE10-1	15	7.808	6.455	2.557
CE11-u	87	13.157	34.371	37.312
CE11-1	12	6.602	5.649	1.830
CE12-u	88	13.231	34.371	37.705
CE12-1	11	6.434	4.888	1.723
CD9-u	81	6.765	28.911	45.274
CD9-1	18	16.399	9.766	6.034
CD10-u	78	10.452	28.824	45.357
CD10-1	21	9.527	11.316	6.046
CD11-u	77	9.839	29.312	44.255
CD11-1	22	10.562	11.442	5.992
CD12-u	72	8.503	26.851	41.785
CD12-1	27	11.287	(12.993)	(8.267)

Table 29. Results obtained for the distribution of volume, solids, water, and solvent in different phases for the fourth series of experiments Set III, spent liquor D: extracted with different organic solvents at several temperatures and pH(liquor) = 5.58, using a volume ratio of 1 to 1.

DISTRIBUTION				
Sample	Volume, cm ³	Solids, g	Water, g	Solvent, g
DI9-u	78	4.454	30.524	35.355
DI9-1	22	9.173	13.051	3.006
DI10-u	77	3.969	28.967	34.510
DI10-1	22	8.637	13.145	3.259
DI11-u	76	4.599	28.837	35.702
DI11-1	22	7.648	12.893	3.100
DI12-u	78	4.735	29.875	33.101
DI12-1	22	7.355	14.364	3.640
DA9-u	87	9.041	36.226	36.405
DA9-1	10	4.362	6.036	1.793
DA10-u	88	8.625	37.248	37.226
DA10-1	10	3.874	5.532	1.340
DE9-u	94	10.846	41.405	36.867
DE9-1	5	2.259	2.458	1.079
DE10-u	97	11.382	42.138	37.849
DE10-1	2	1.054	(0.747)	(0.824)
DE11-u	98	12.019	42.188	37.581
DE11-1	1	0.962	(0.534)	(0.767)
DE12-u	96	12.147	40.939	38.001
DE12-1	3	0.854	(2.204)	(0.270)
DD9-u	93	10.475	40.543	49.479
DD9-1	6	2.713	2.900	1.574
DD10-u	92	10.926	38.955	49.862
DD10-1	7	2.850	3.881	1.383
DD11-u	94	10.589	39.954	49.925
DD11-1	6	2.437	3.475	1.821
DD12-u	93	10.168	39.064	48.833
DD12-1	6	2.288	3.486	1.694

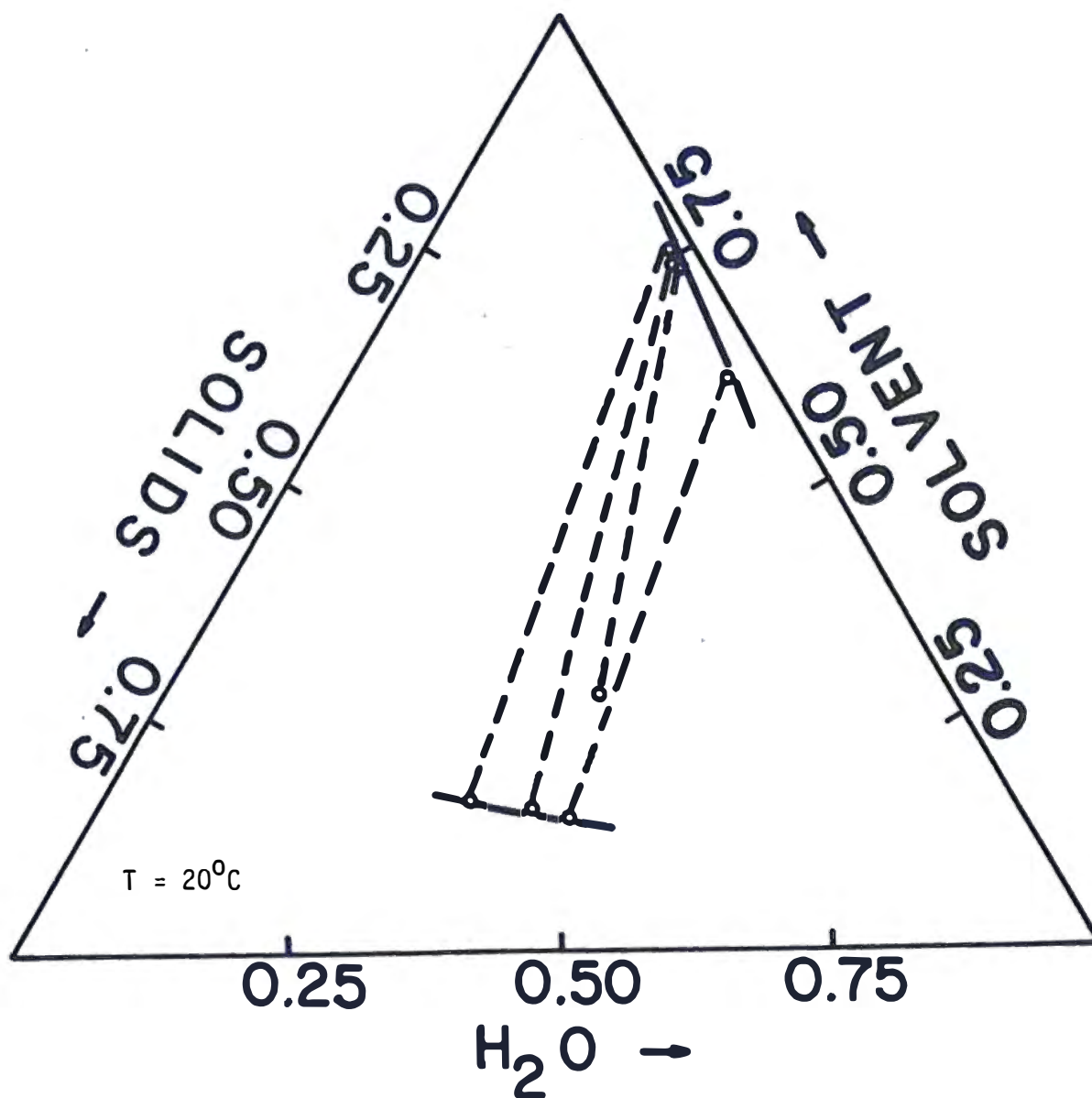


Figure 10. Phase equilibrium diagram for experiments Set I for volume ratio of 1.5 to 1, solvent : isopropanol.

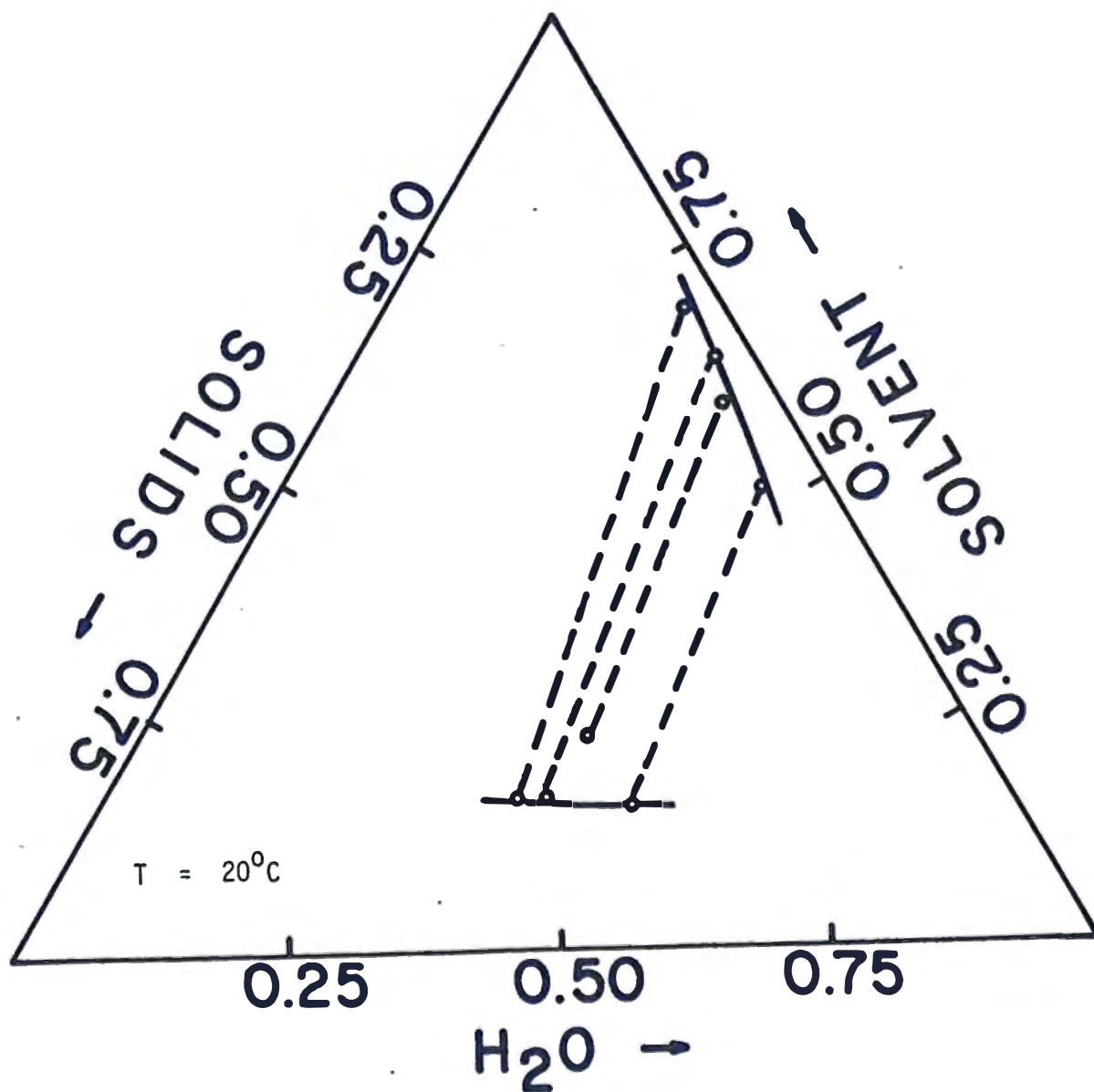


Figure 11. Phase equilibrium diagram for experiments Set I for volume ratio of 1 to 1, solvent : isopropanol.

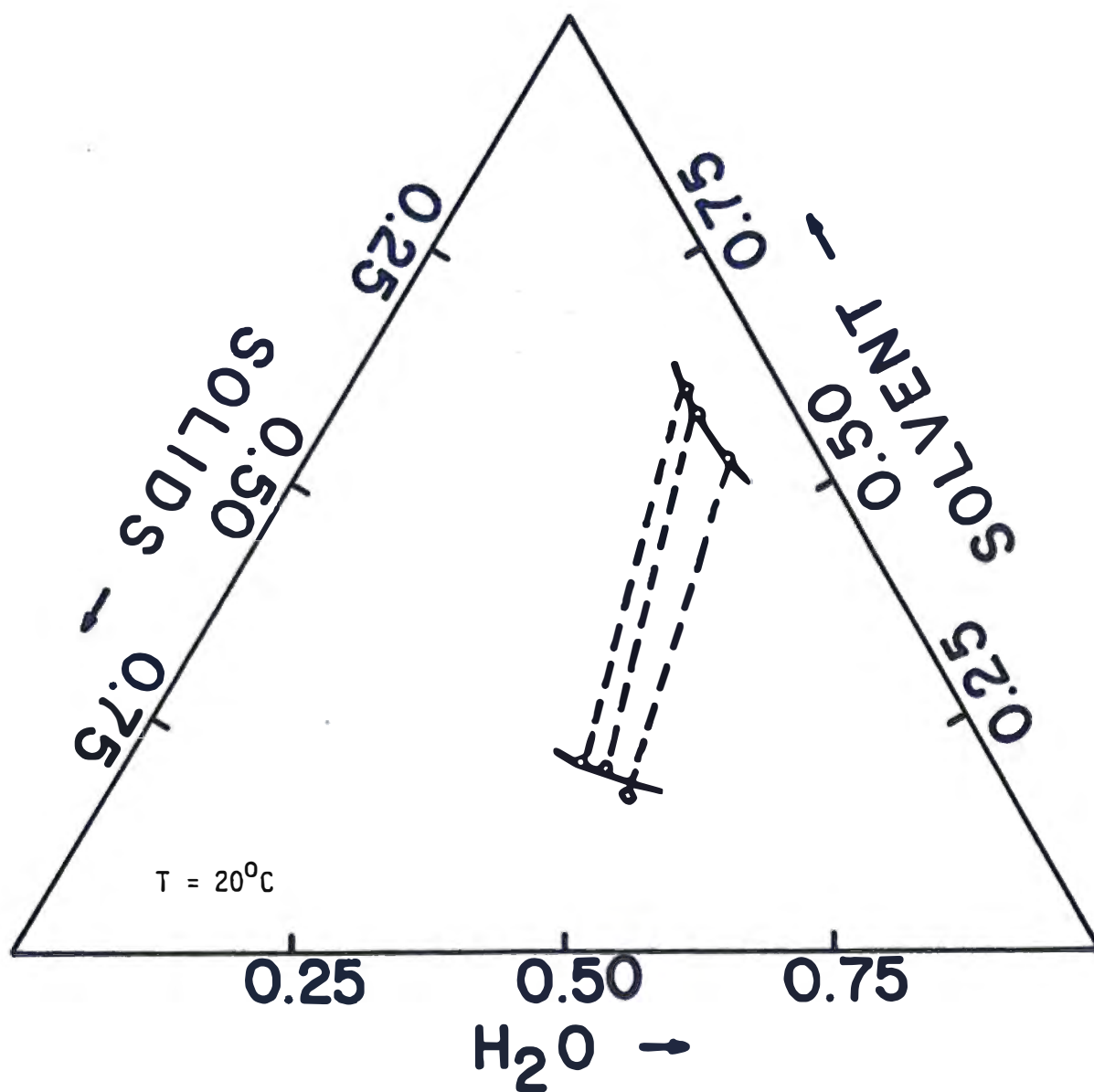


Figure 12. Phase equilibrium diagram for experiments Set I for volume ratio of 0.75 to 1, solvent : isopropanol.

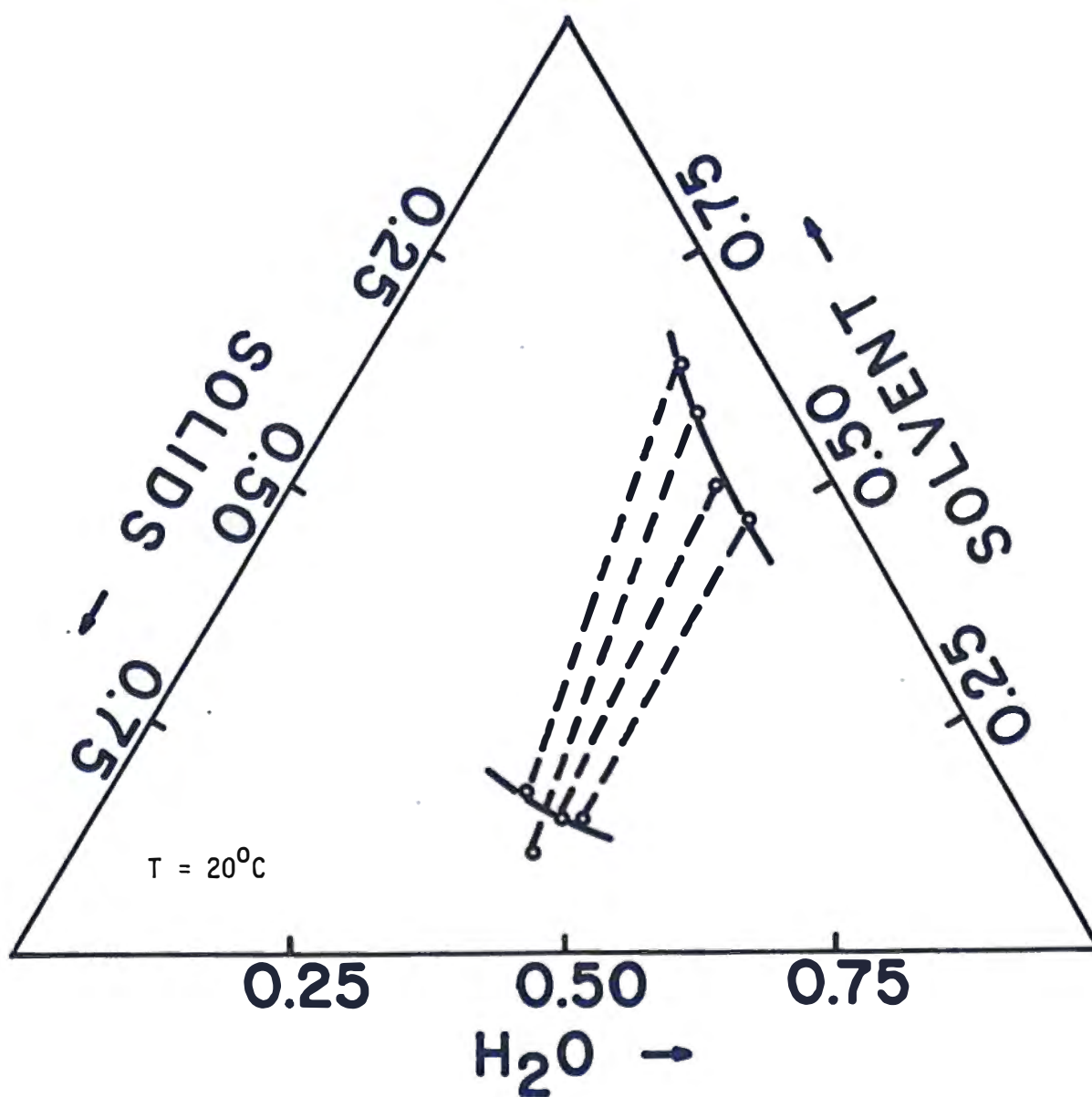


Figure 13. Phase equilibrium diagram for experiments Set I for volume ratio of 1 to 1, solvent : acetone.

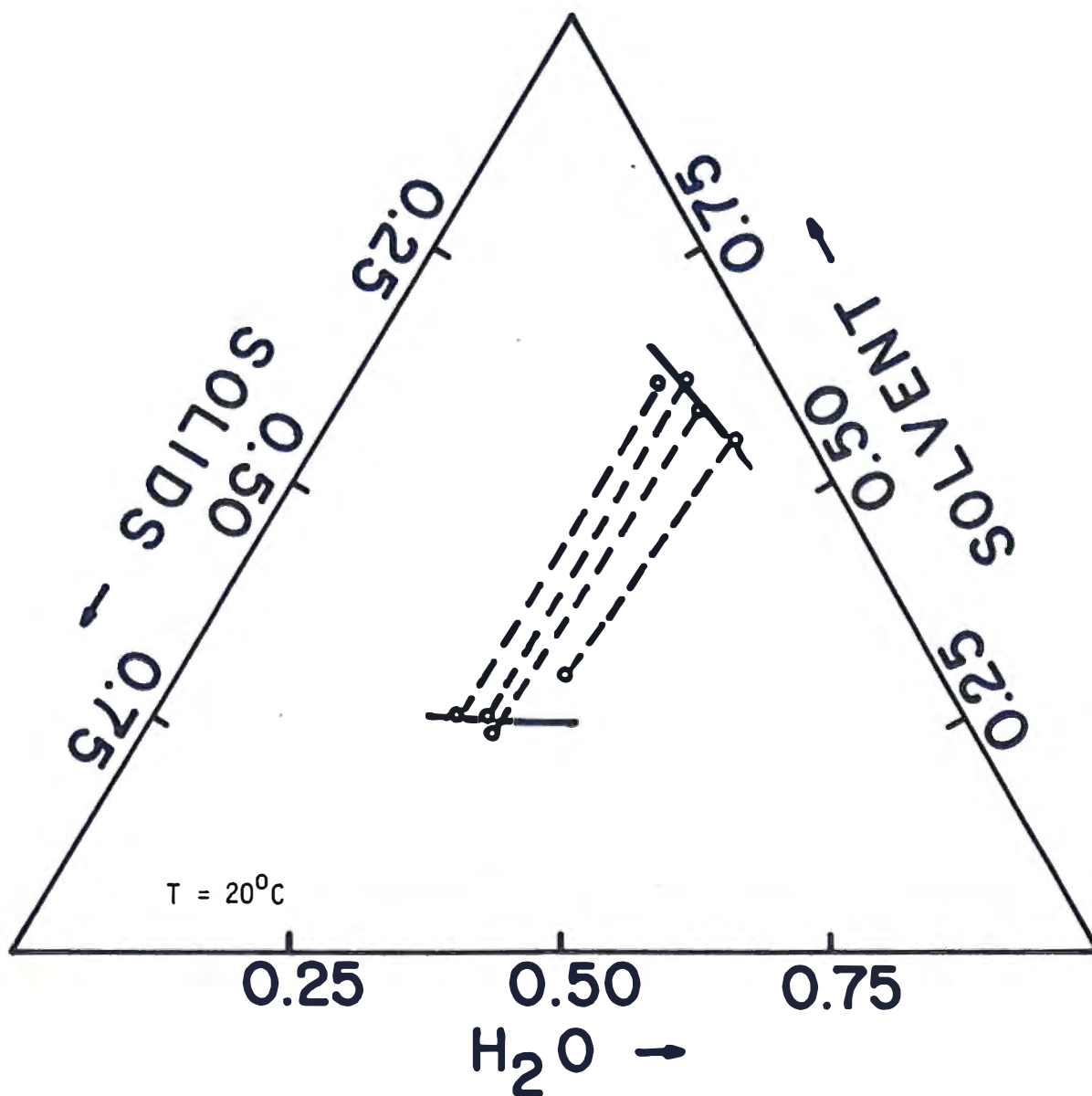


Figure 14. Phase equilibrium diagram for experiments Set I for volume ratio of 1.5 to 1, solvent : ethanol.

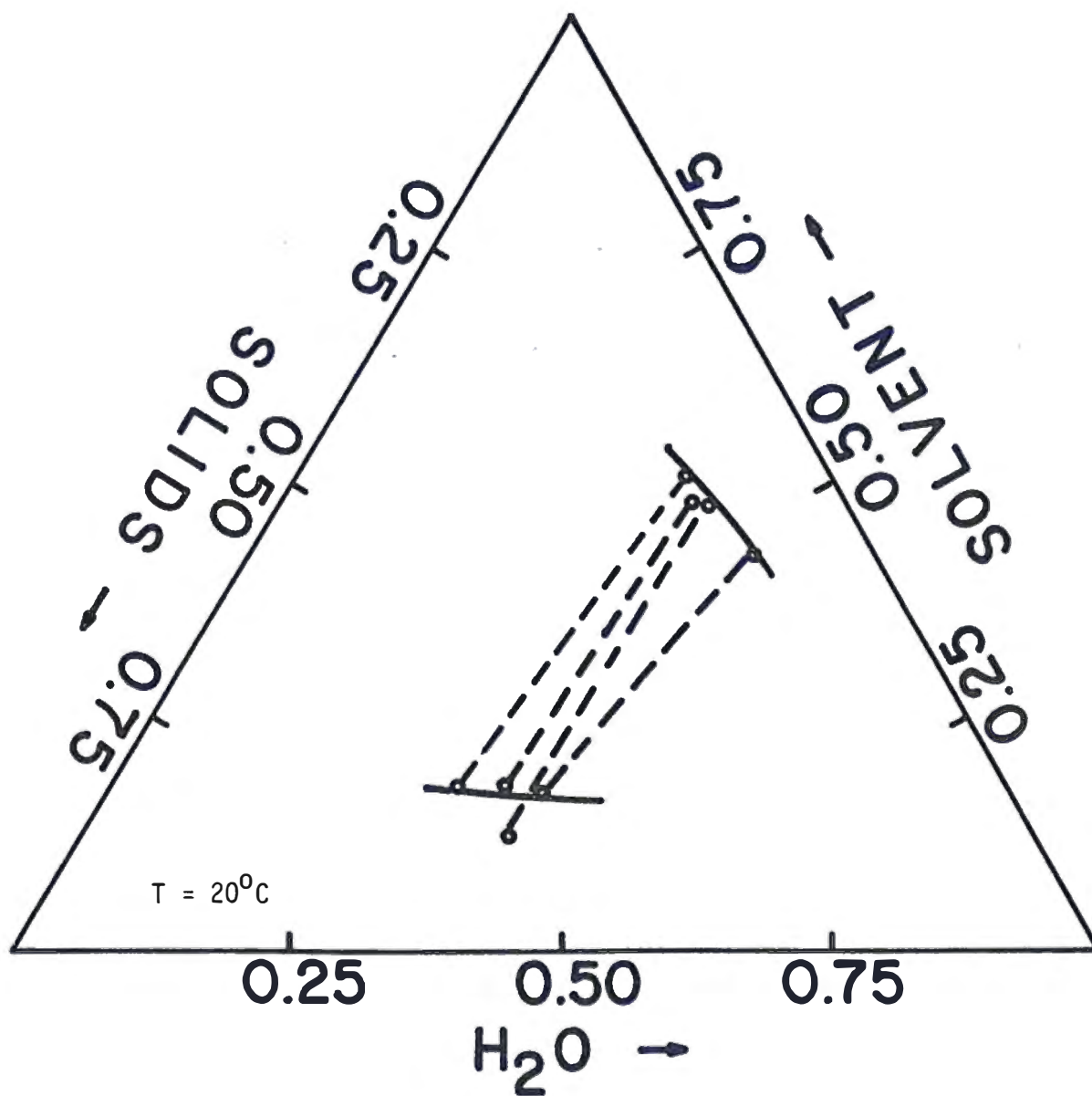


Figure 15. Phase equilibrium diagram for experiments Set I for volume ratio of 1 to 1, solvent : ethanol.

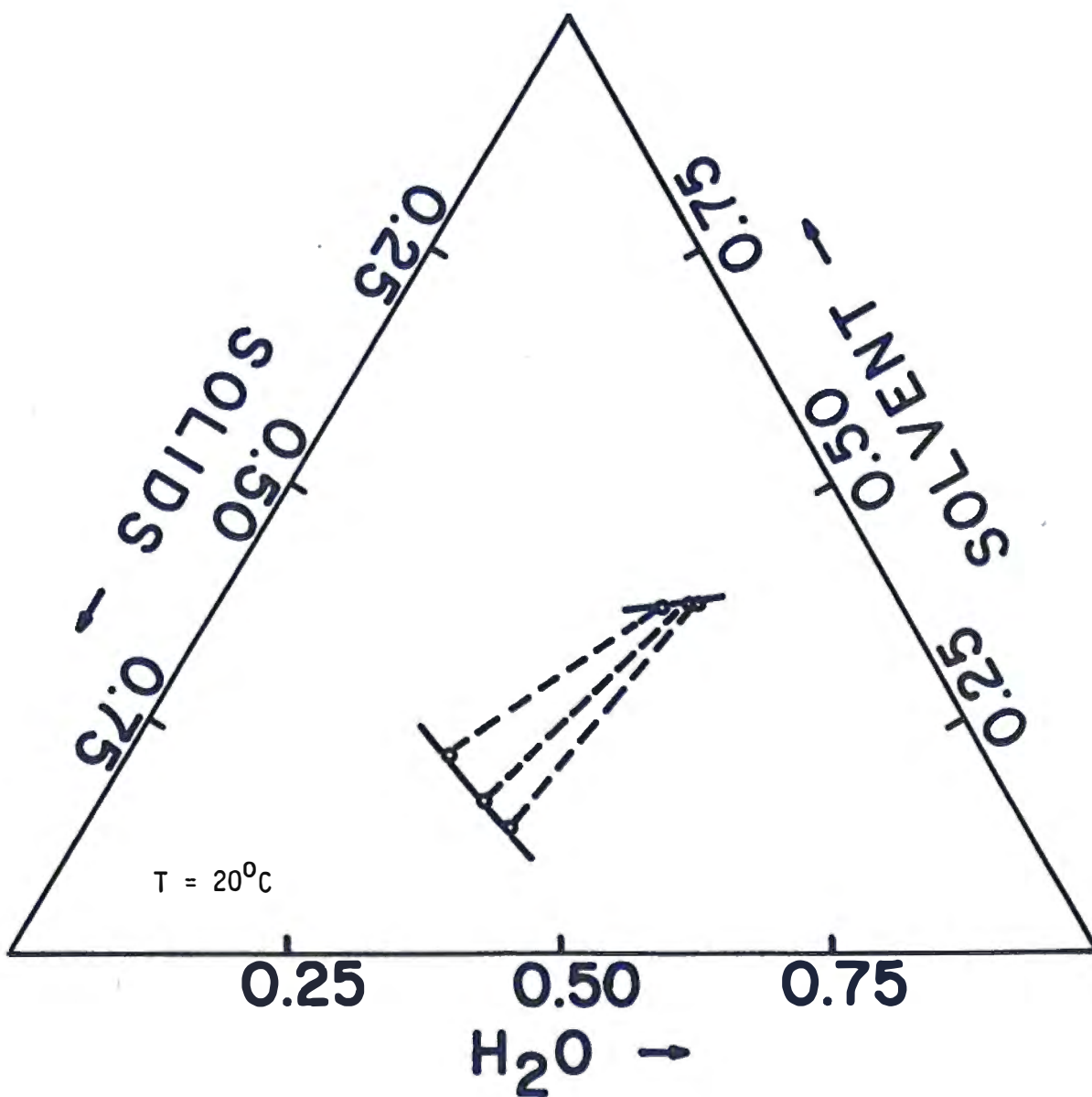


Figure 16. Phase equilibrium diagram for experiments Set I for volume ratio of 0.75 to 1, solvent : ethanol.

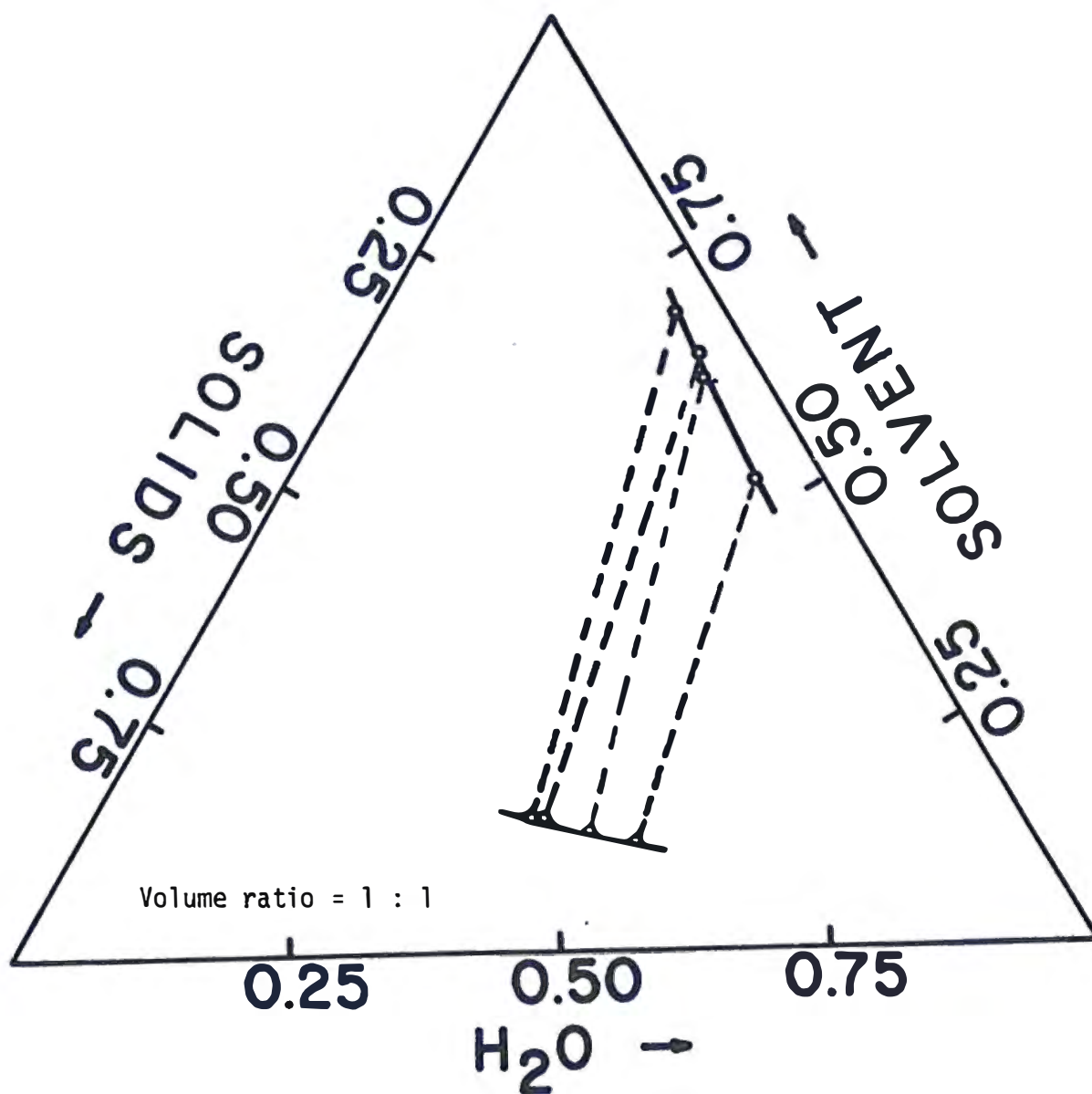


Figure 17. Phase equilibrium diagram for experiments Set III for temperature of 40°C, solvent : isopropanol.

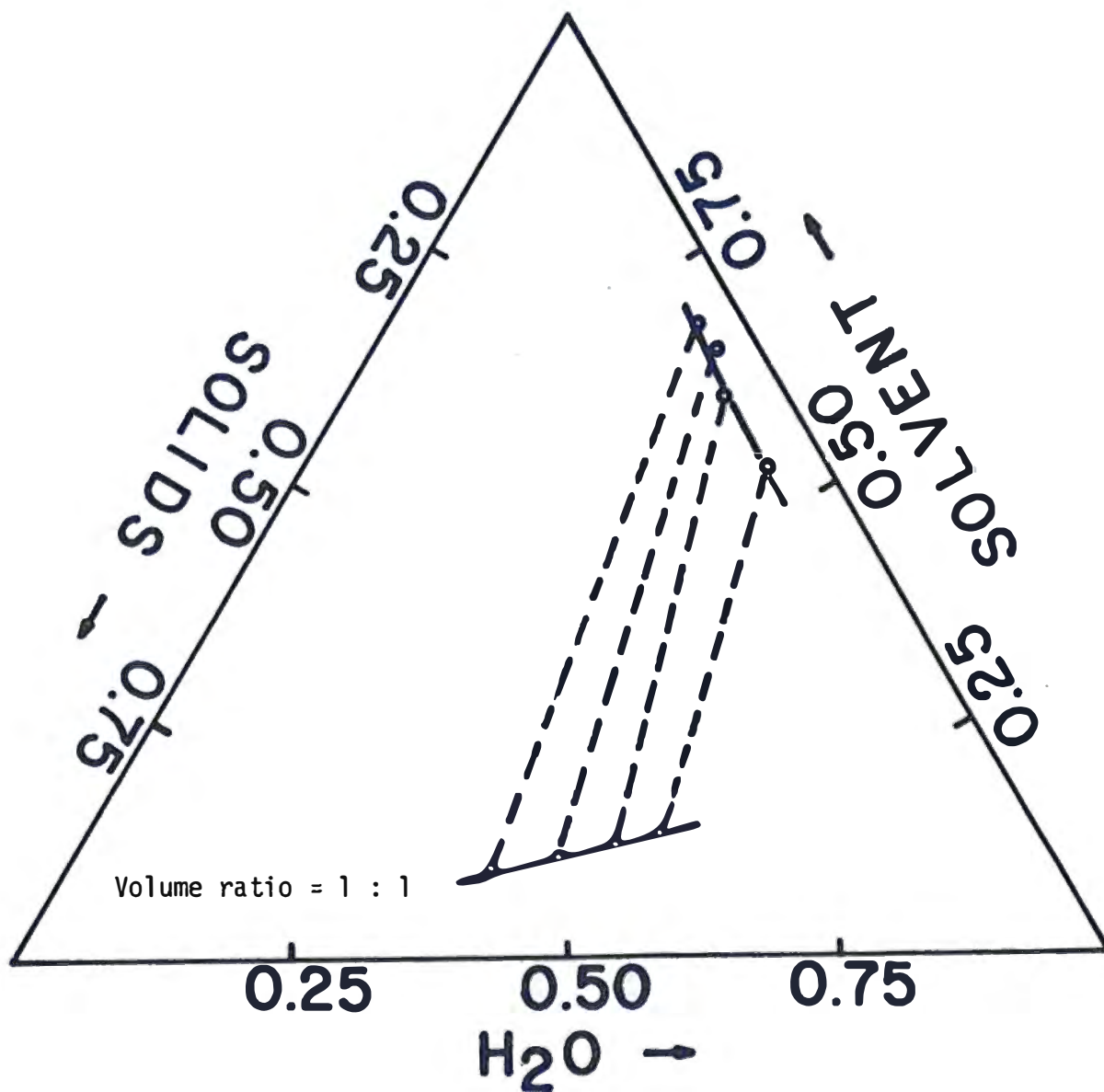


Figure 18. Phase equilibrium diagram for experiments Set III for temperature of 50°C, solvent : isopropanol.

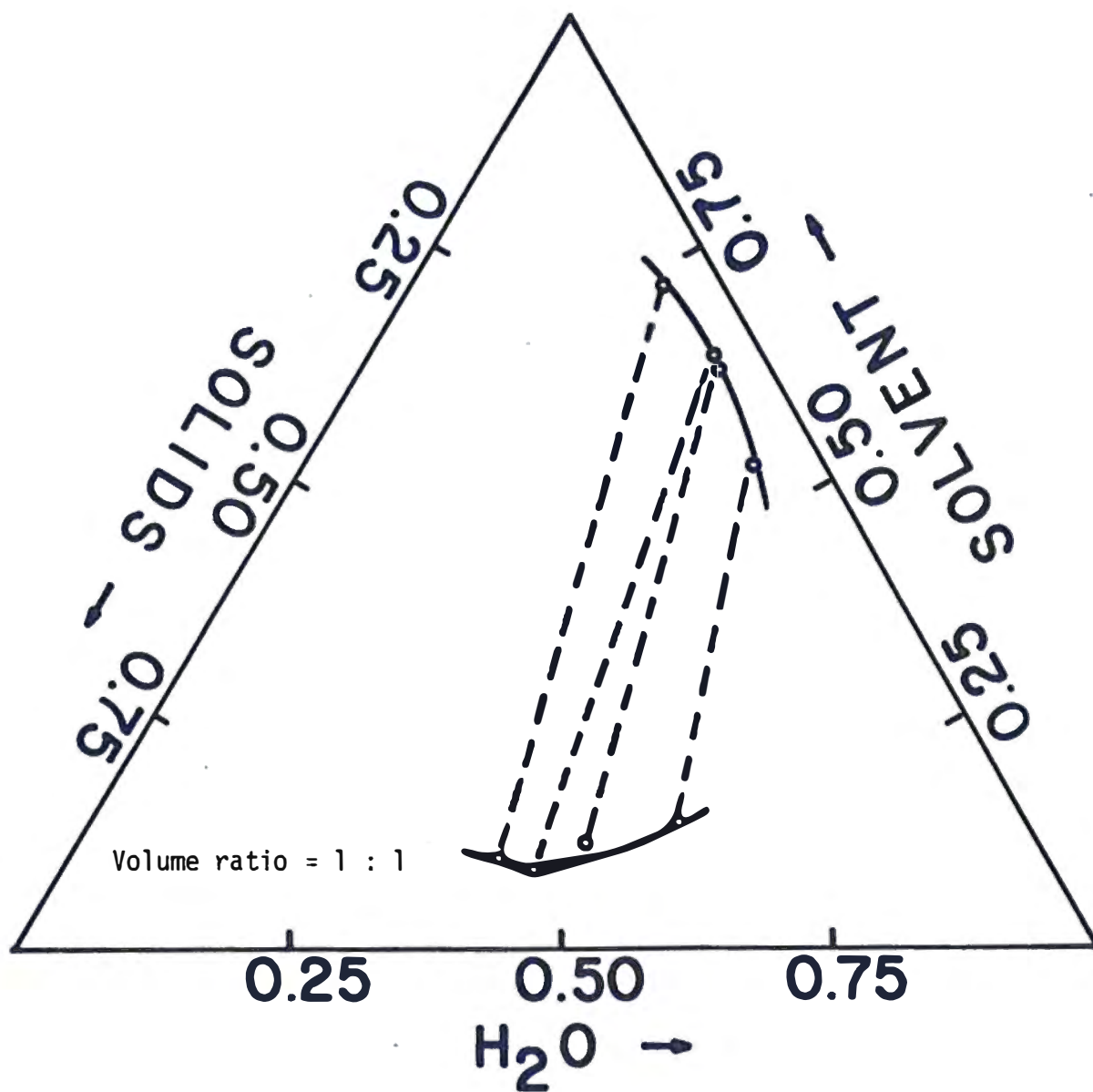


Figure 19. Phase equilibrium diagram for experiments Set III for temperature of 60°C, solvent : isopropanol.

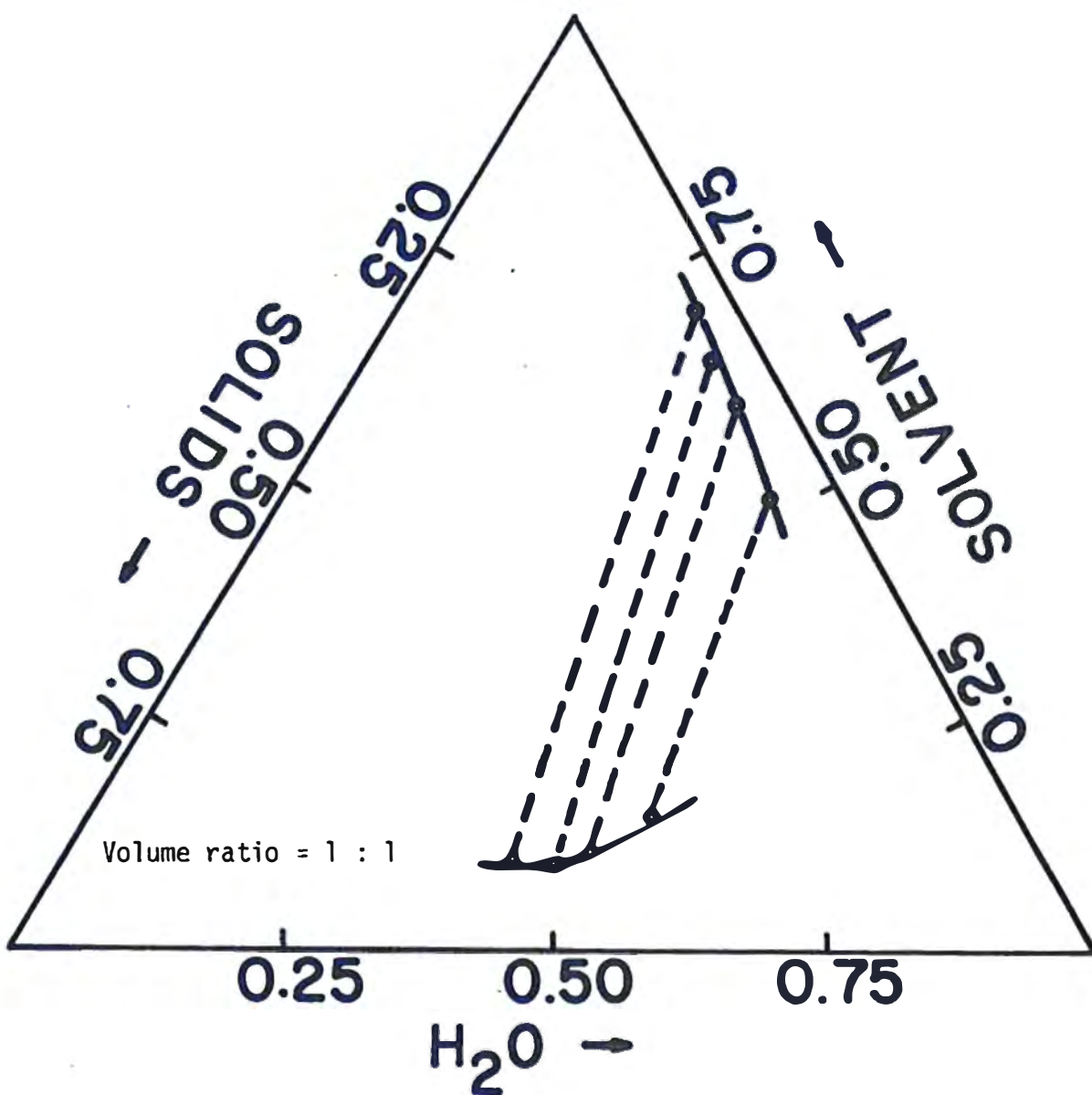


Figure 20. Phase equilibrium diagram for experiments Set III for temperature of 70°C , solvent : isopropanol.

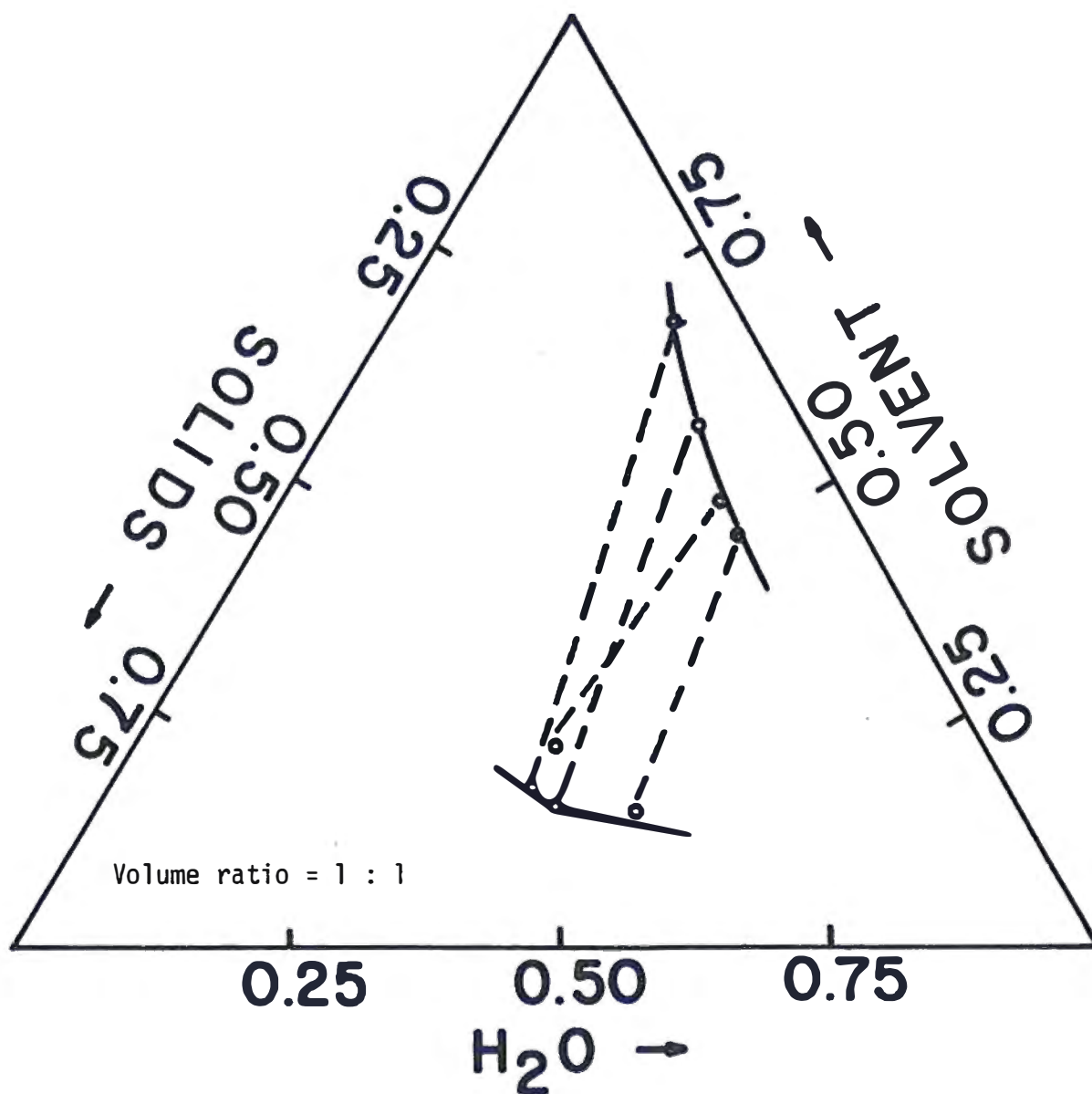


Figure 21. Phase equilibrium diagram for experiments Set III for temperature of 40°C , solvent : acetone.

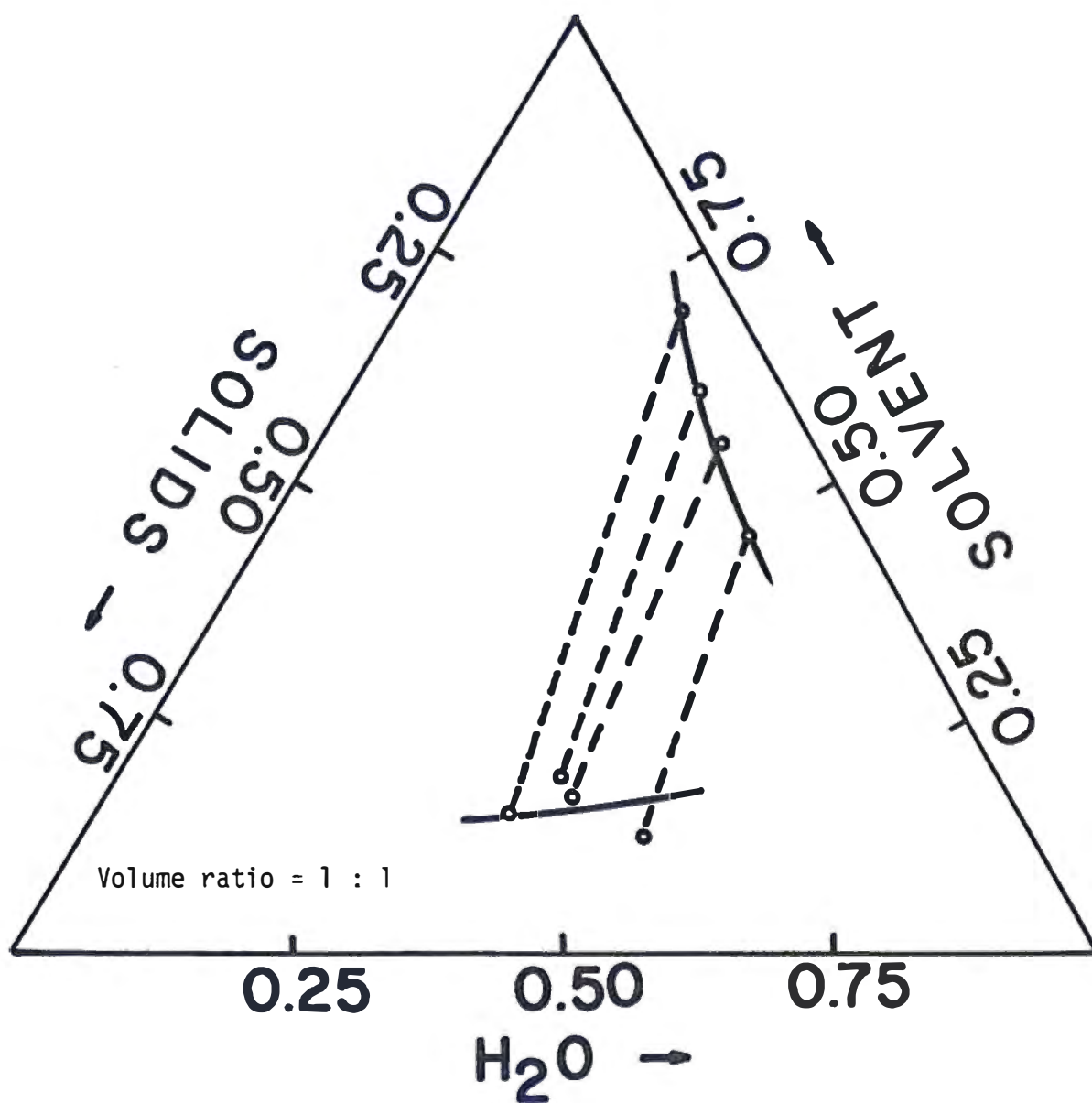


Figure 22. Phase equilibrium diagram for experiments Set III for temperature of 50°C , solvent : acetone.

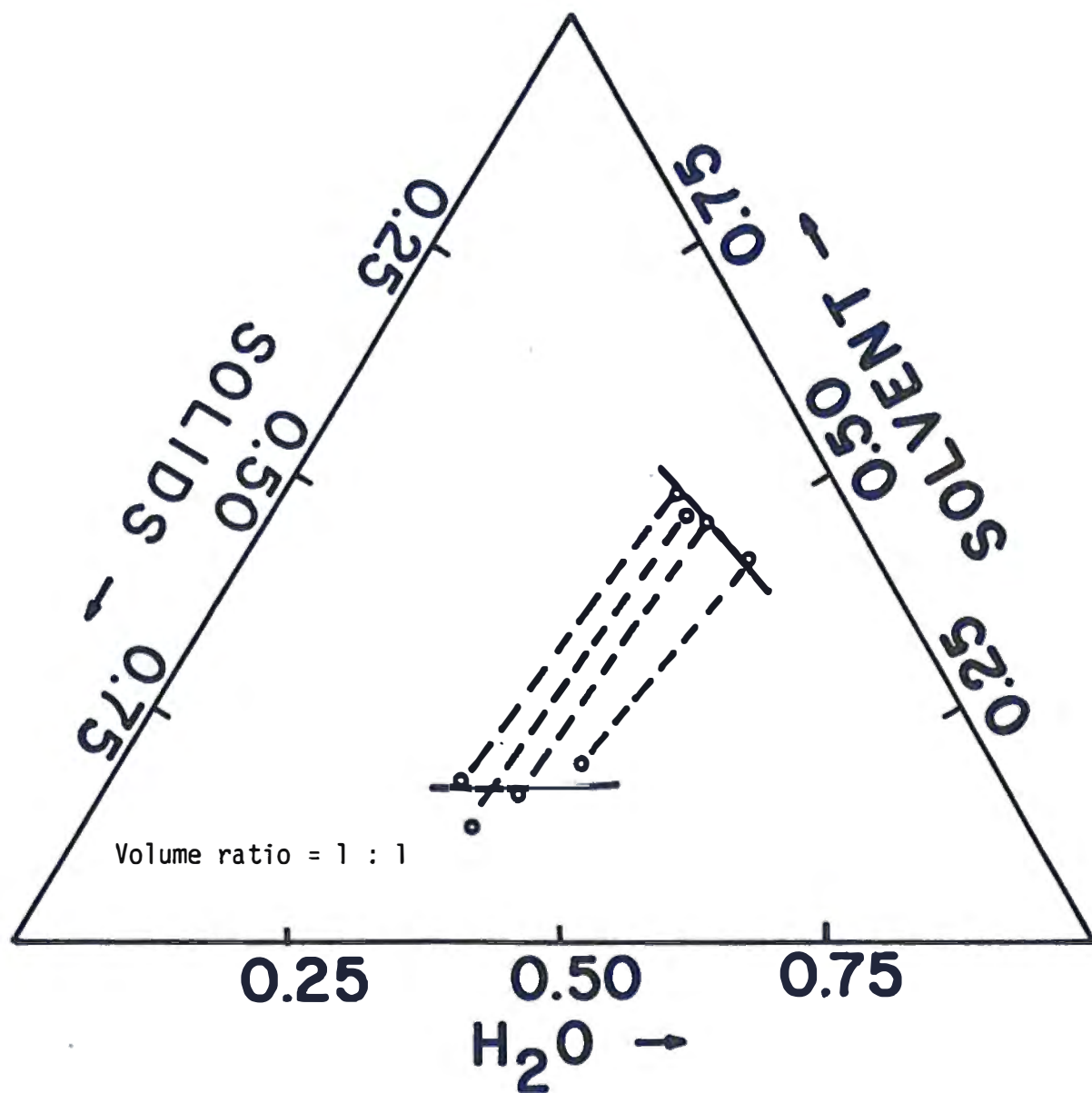


Figure 23. Phase equilibrium diagram for experiments Set III for temperature of 40°C, solvent : ethanol.

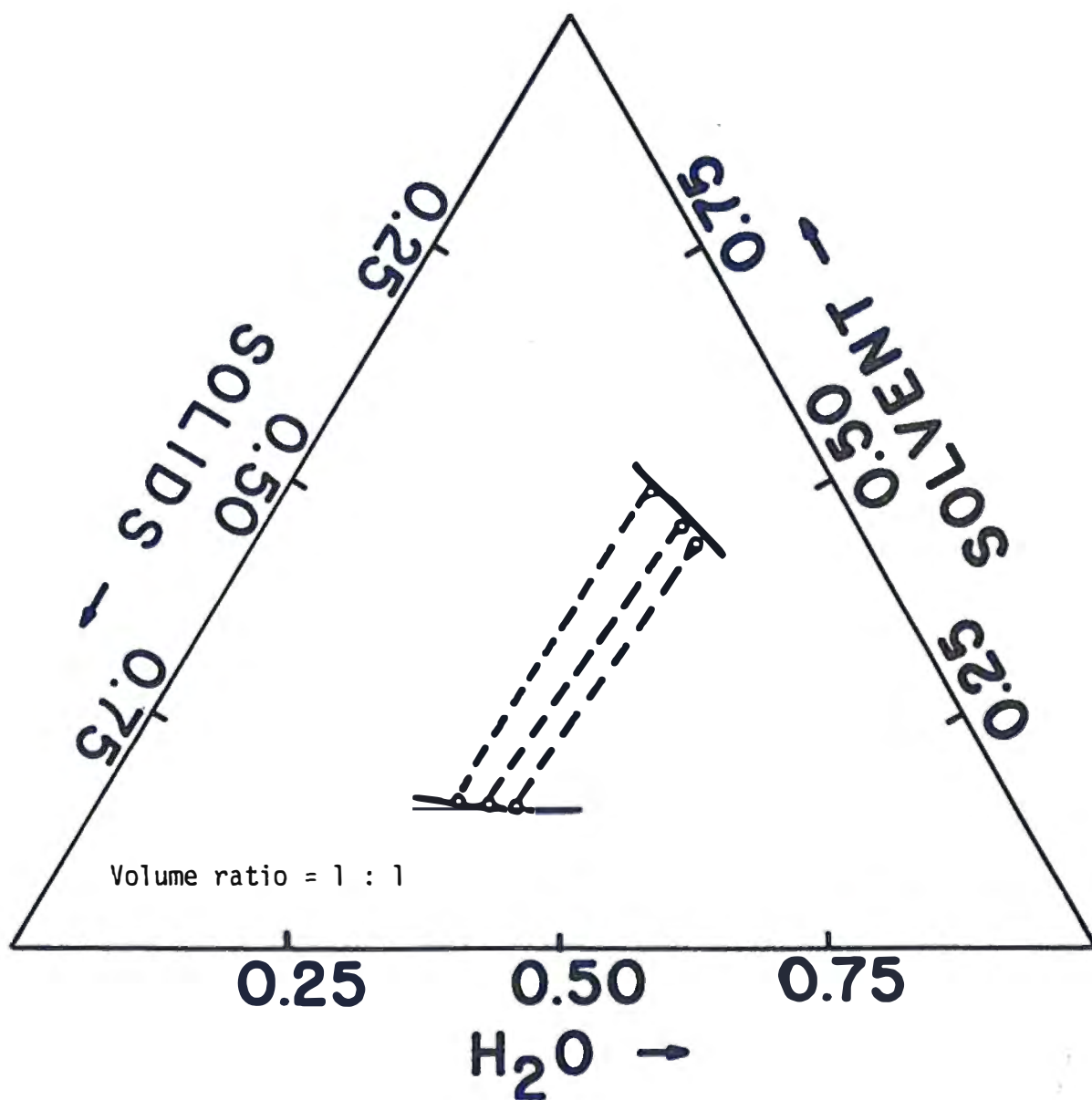


Figure 24. Phase equilibrium diagram for experiments Set III for temperature of 50°C, solvent : ethanol.

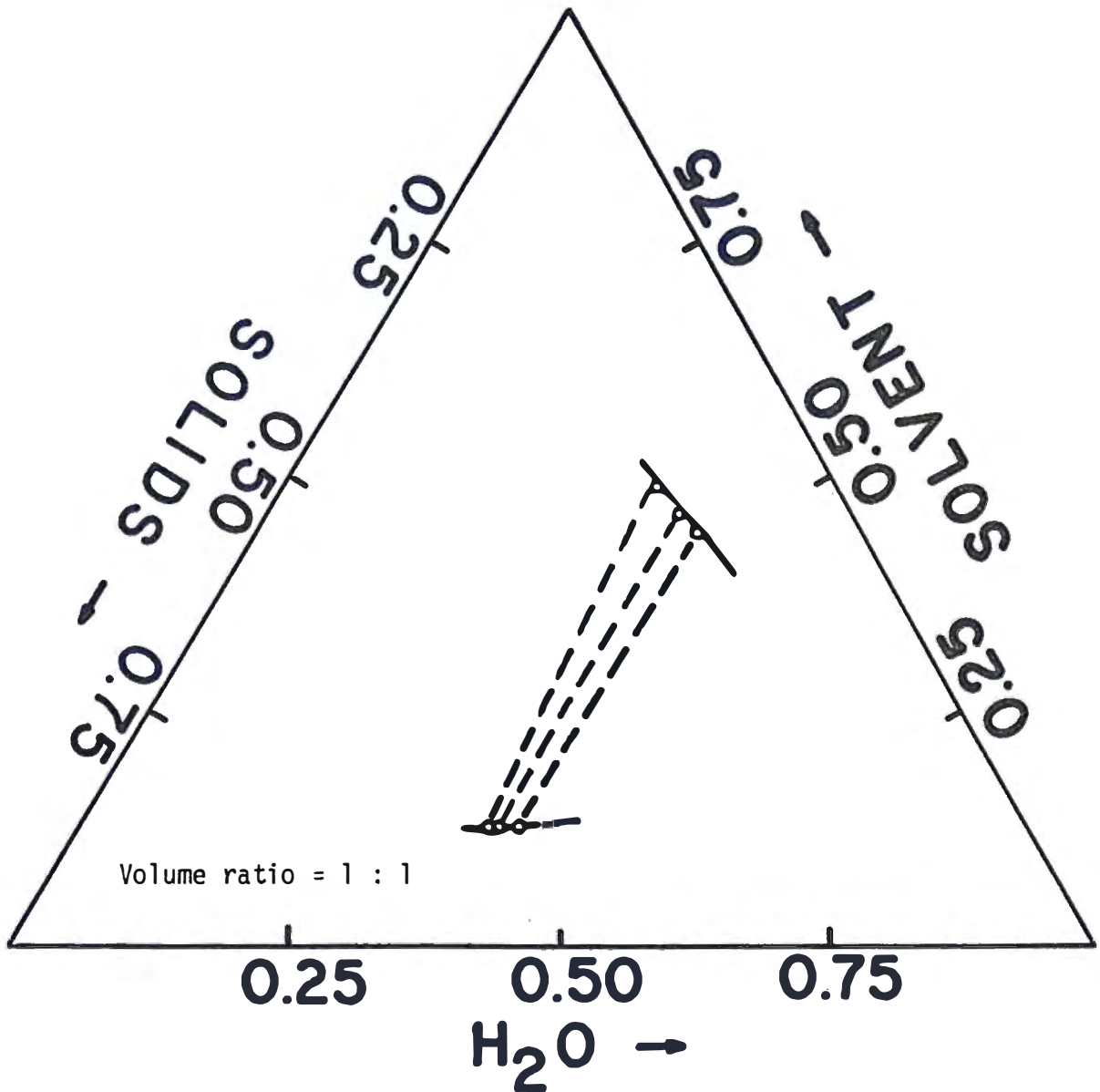


Figure 25. Phase equilibrium diagram for experiments Set III for temperature of 60°C, solvent : ethanol.

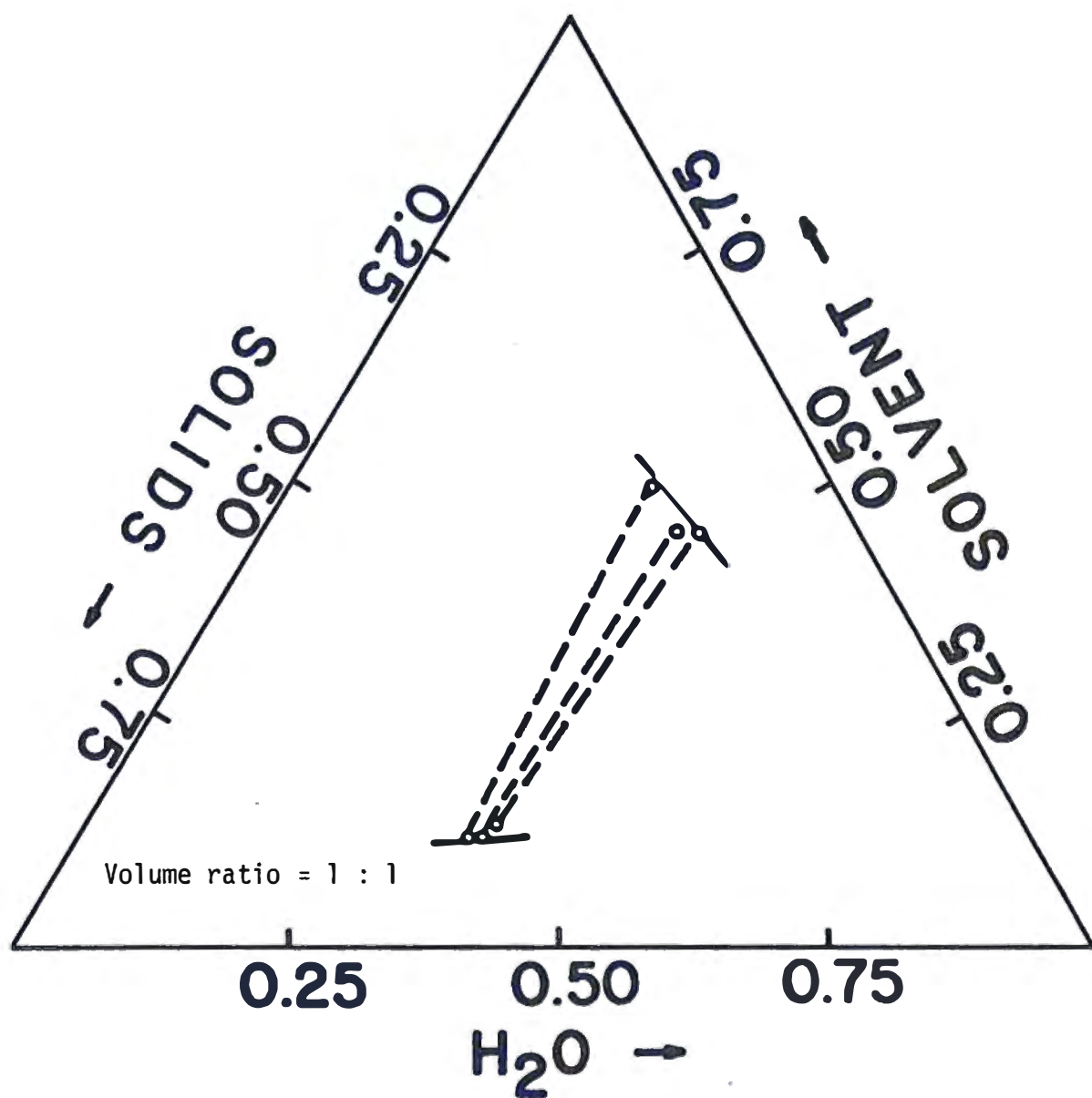


Figure 26. Phase equilibrium diagram for experiments Set III for temperature of 70°C, solvent : ethanol.

Chapter IV

DISCUSSION

4-1 Effect of Volume Ratio of Solvent to Spent Liquor on Extraction

From Tables 7 to 10 and Figures 10 to 16, it can be seen that the solubility of solute in spent liquor in the phases varied with the solids concentration, the volume ratio of solvent to spent liquor (S/SL), and the property of the solvent. The organic solvents studied were miscible easily with spent liquor at lower volume ratio of solvent to spent liquor. In most cases, no separation of phases was observed when the volume ratio of S/SL was less than 0.5 to 1; the several exceptions were: (1) spent liquor A extracted with dioxane, (2) spent liquor C extracted with isopropanol, and (3) spent liquors containing solids content higher than 37.49% extracted with acetone.

With the data reported in Tables 7 to 10, the percent solids and percent lignosulfonates content in the upper phase were plotted versus S/SL ratio for various experimental conditions. The curves plotted are shown in figures 27 to 30. Figures 27, 28 and 30 indicate that, for a given sample liquor, the amount of dry solids in the upper phase increased, in general, as the S/SL ratio decreased. When using isopropanol as an extracting solvent, the percent solids in the upper phase changed slightly with the

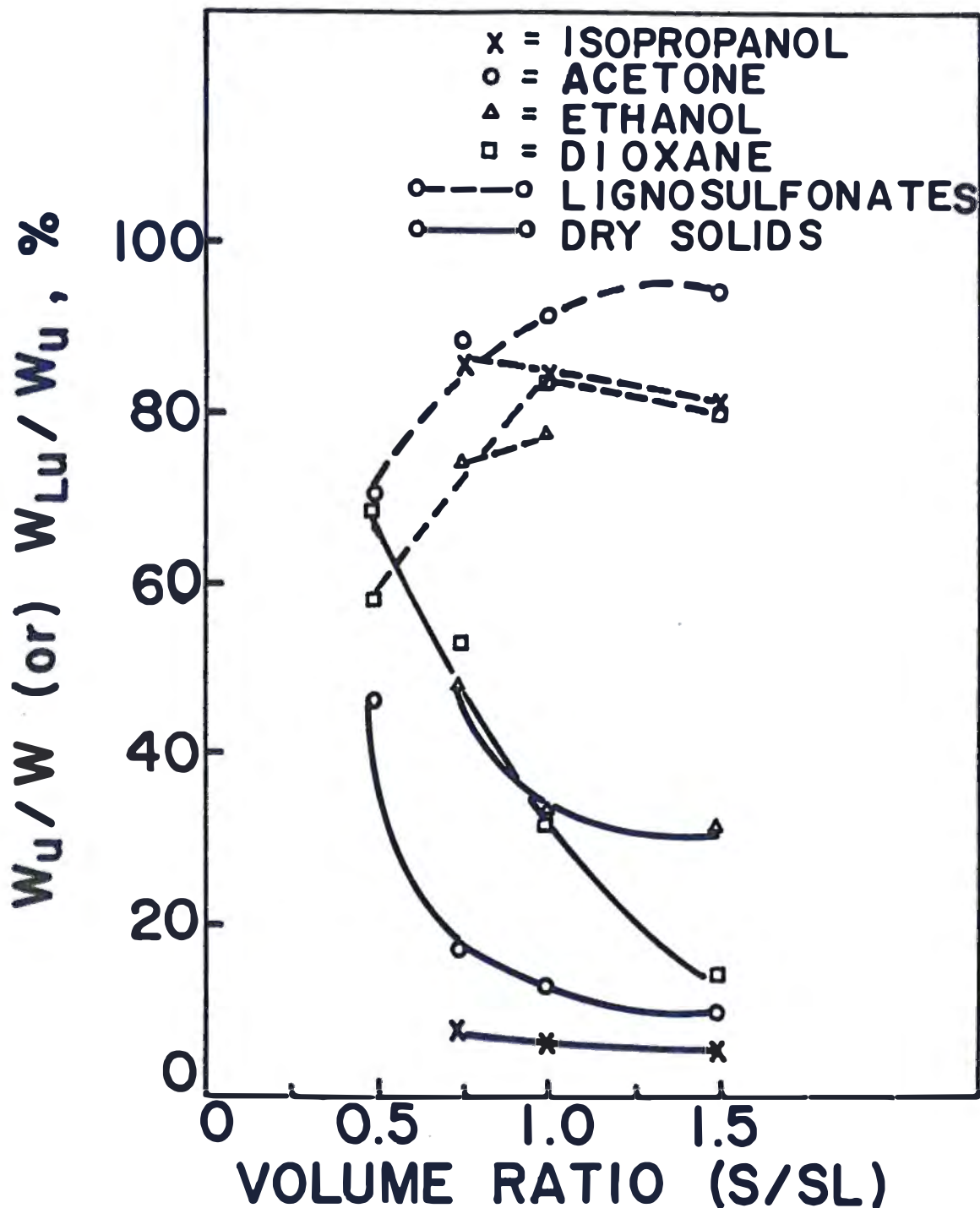


Figure 27. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of volume ratio of solvent to spent liquor for the first series of experiments Set I : spent liquor A was extracted with different organic solvents at 20°C and pH(liquor)= 5.58, using several volume ratios.

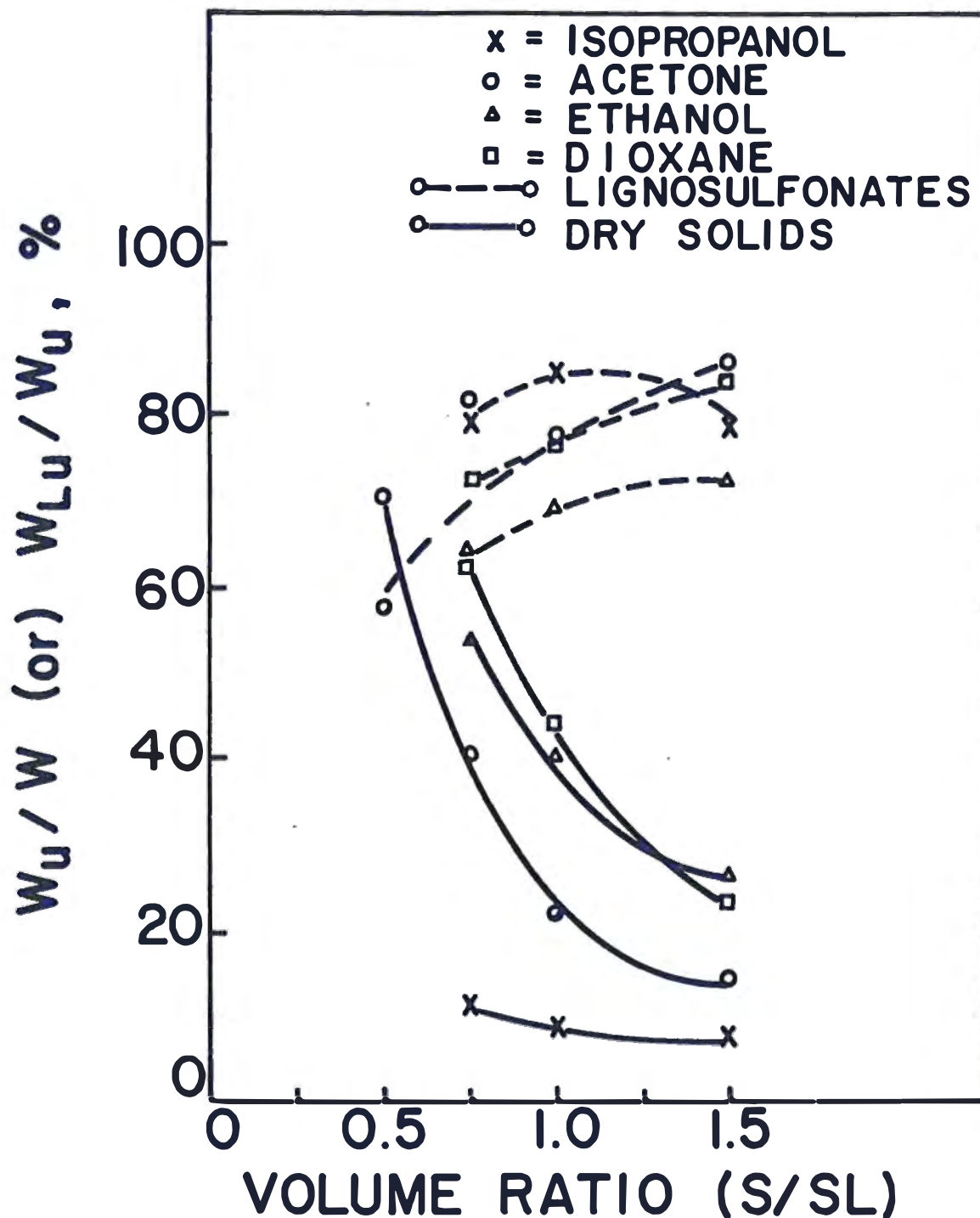


Figure 28. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of volume ratio of solvent to spent liquor for the second series of experiments Set I.: spent liquor B was extracted with different organic solvents at 20°C and $\text{pH}(\text{liquor}) = 5.58$, using several volume ratios.

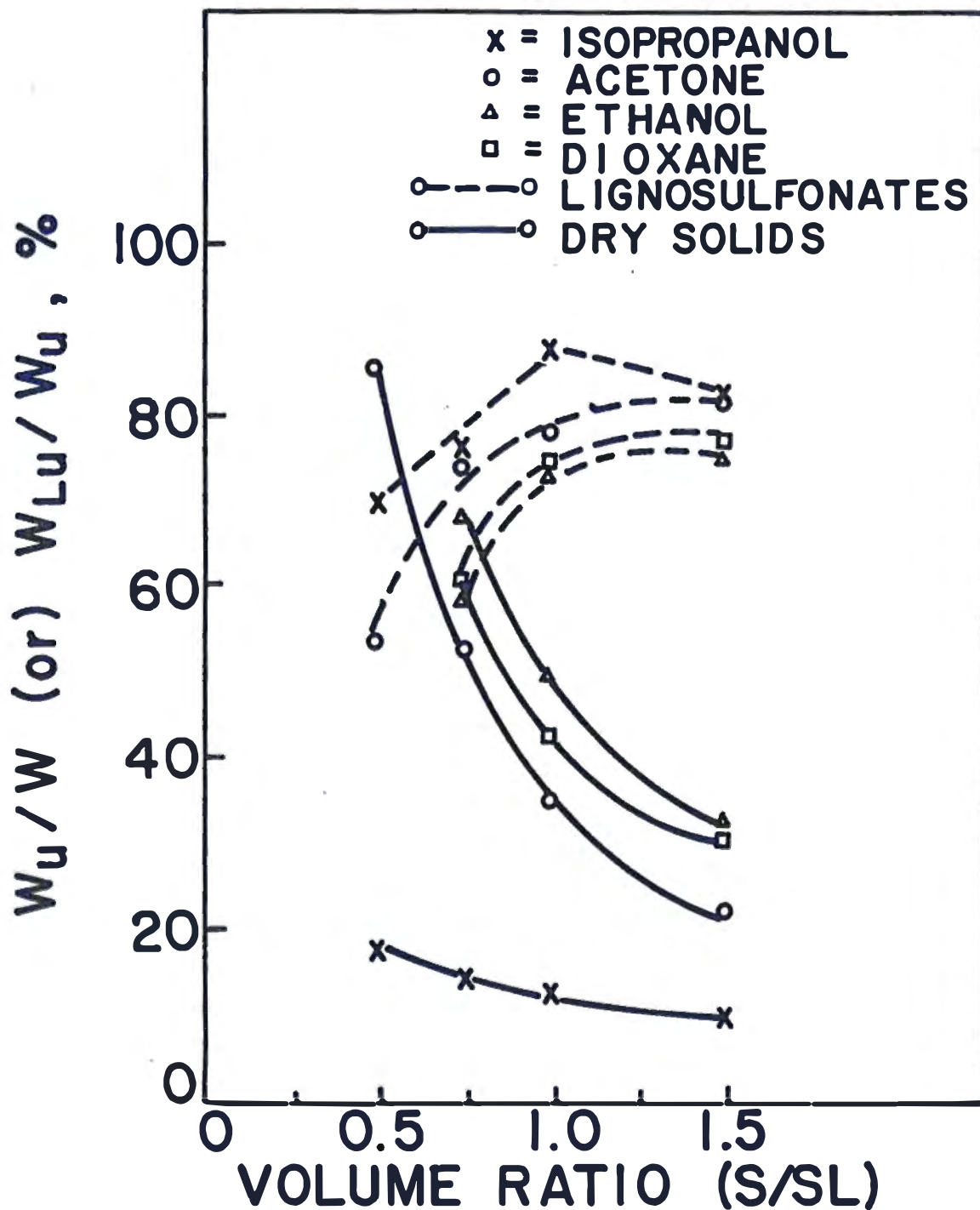


Figure 29. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of volume ratio of solvent to spent liquor for the third series of experiments Set I : spent liquor C was extracted with different organic solvents at 20°C and $\text{pH}(\text{liquor}) = 5.58$, using several volume ratios.

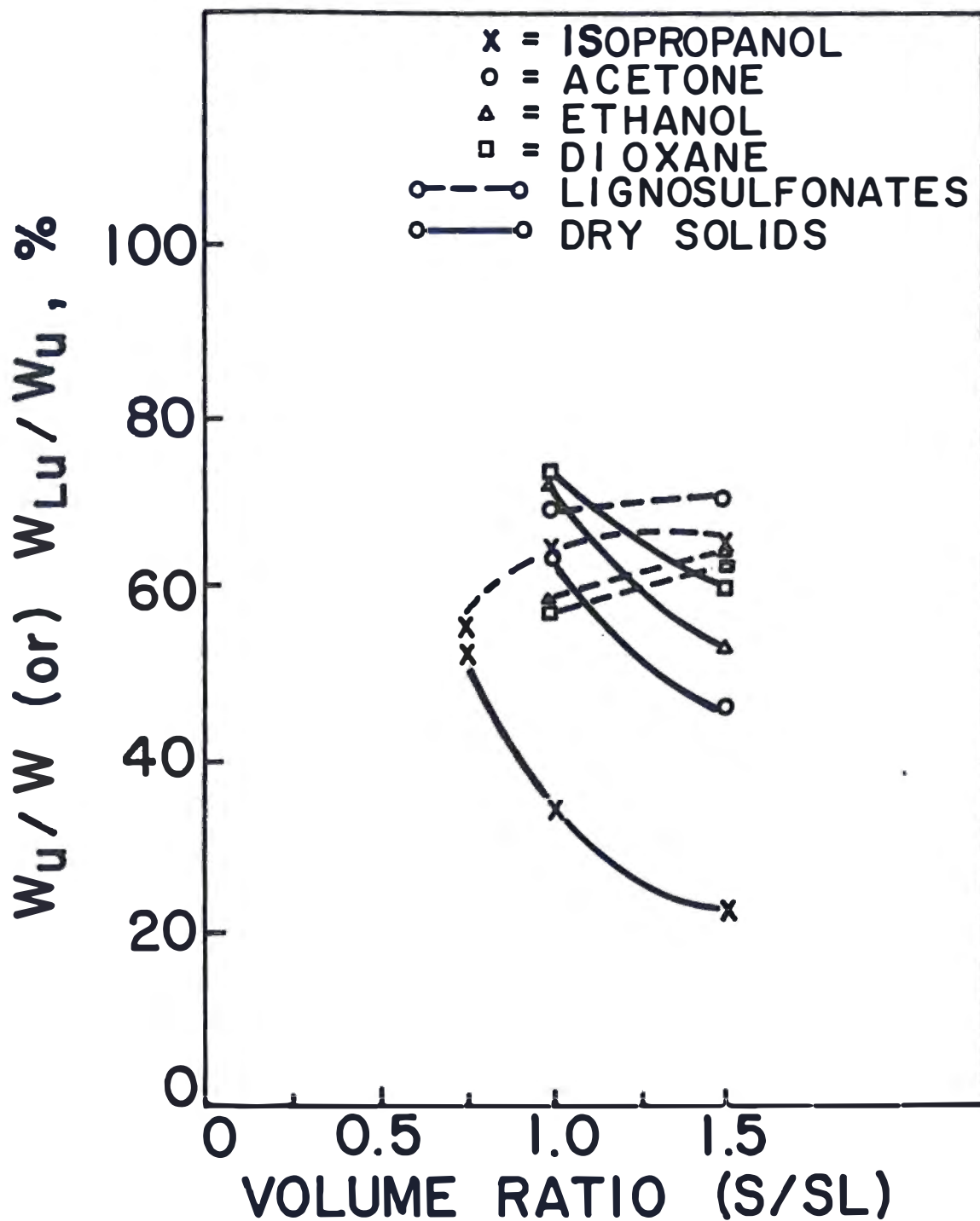


Figure 30. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of volume ratio of solvent to spent liquor for the fourth series of experiments Set I : spent liquor \underline{D} was extracted with different organic solvents at 20°C and $\text{pH}(\text{liquor}) = 5.58$, using several volume ratios.

S/SL ratio; while using another solvents such as acetone, ethanol, and dioxane, the amount of dry solids in the upper phase augmented rapidly when diminishing the S/SL ratio. The curves of percent lignosulfonates content show about the same trend as those for the percent solids. Also from these figures, isopropanol is seen to have the best efficiency of extracting lignosulfonates from sample liquors when using a volume ratio of 1. From the results (tables 7 - 10) of distributions of water and solvent in the different phases, it can be seen that, in most cases, the upper phase was the solvent rich phase. When the S/SL ratio decreased, water content in this phase increased.

For spent liquor D, there were two phases only when it was extracted with organic solvents at higher volume ratio of S/SL (1.5 to 1 and 1 to 1). As shown in Figure 30, there was no significant change in the percent lignosulfonates content distribution while changing the S/SL ratio when using acetone or isopropanol as solvent. For spent liquor E of which the solids content was 20.44%, two phases could not form when this liquor was extracted with any of the solvents used in this study.

At higher volume ratio of S/SL, viscosity of the lower phase was observed to increase with the solids concentration in a sample liquor. High viscosity caused discharge problem when discharging the lower phase from the separatory funnel.

For sample liquors extracted with isopropanol, the time for phase separation must be kept within one hour. If this time was more than one hour,

an interface between the upper and lower phases would occur; thus, a clear phase separation could not be obtained. During mixing an extracting solvent with a sample liquor, too vigorous shaking of the separatory funnel should be avoided, to prevent such an interface phase from occurring.

When using dioxane as an extracting solvent for spent liquors A, B, and C, with a volume ratio of $S/SL = 1.5$, three clear phases were formed. For spent liquor A, three clear phases were also obtained, when using a volume ratio of $S/SL = 1$.

4-2 Effect of Solvent on Extraction

In choosing a solvent for a liquid-extraction process, there are several principles that can be used as a guide. The following are the requirements of a useful extraction solvent :

- (1) high selectivity: capable of extracting one component of a solution in preference to another.
- (2) large capacity: dissolving relatively large quantities of the preferentially extracted solute.
- (3) high recoverability: permitting re-use of the solvent.
- (4) reasonable in cost and commercially available.
- (5) low toxicity.

The selectivity was ordinarily studied first in deciding the applicability of a solvent.

The property of selectivity may be demonstrated by plotting of a selectivity diagram. For a ternary system, the more highly selective the solvent, the greater will be the curve divergence from the 45° diagonal. If the curve coincides with the 45° diagonal, no separation is possible.

The selectivity diagrams shown in Figures 6 to 9 indicate that, at 20°C and $\text{pH}(\text{liquor}) = 5.58$, isopropanol was the most selective solvent among the solvents studied for the solute: the lignosulfonates, when the solids content of spent liquor was 24% or more than 40%. For spent liquor C, solids content = 37.49%, the selectivities of all solvents used were almost the same. Use of isopropanol as a solvent to extract lignosulfonates was favourable for spent liquors with higher solids content.

As mentioned before (section 4-1), three phases appeared when using dioxane as a solvent at S/SL ratios of 1.5/1 and 1/1; it was, therefore, impossible to compare the selectivity of this solvent with those of other solvents in the same diagram such as Figures 6 to 8. However, for spent liquor D, two phases separation could be obtained with dioxane, and comparison of selectivity was able to be made, as shown in Figure 9. From this figure, it can be seen that dioxane is the least selective solvent for lignosulfonates.

In most cases, methanol was not a good solvent. When adding methanol to spent liquor and mixing them well by shaking, a very fine solids appeared. These solids were suspended in the solution, they took a very long time to settle down. To correct this problem, extractions at different liquor pH's and temperatures were studied. Unfortunately there was no improvement.

4-3 Effect of pH of Spent Liquor on Extraction.

It was believed that emulsions may sometimes be broken by changing the pH of a solution by adding acid or base. To prove this was one of the purposes for the experiments Set II. In the experiments of using isopropanol as the extracting solvent, it was noted that an interface phase would occur if the liquor pH value was equal to 5.58. At other pH values, however, regardless of the length of the phase separation time, such a phase did not form. There was another very interesting result found from the experiments when spent liquor A (pH = 5.58) was extracted with dioxane, three clear phases were observed; after changing the pH either to the base or to the acid side, there were only two phases.

In order to study the effect of liquor pH on the distributions of dissolved solids and lignosulfonates, the percent solids and the percent lignosulfonates content in the upper phase were plotted as a function of liquor pH value; and the curves so plotted are shown in Figures 31, 32 and 33. It can be seen from these figures that change in liquor pH value had no

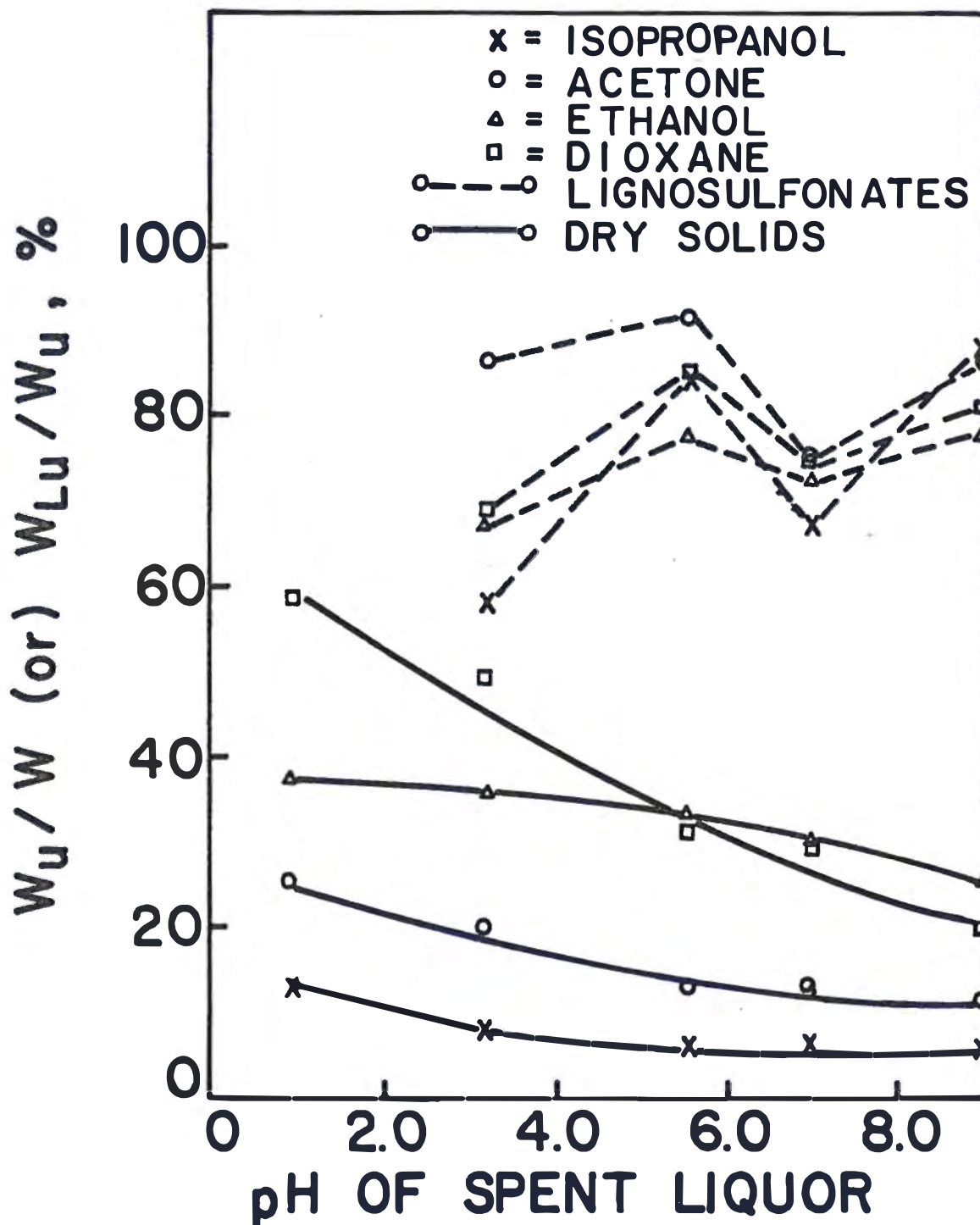


Figure 31. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of pH value of spent liquor for the first series of experiments Set II: spent liquor A was extracted with different organic solvents at 20°C and several pH's(liquor), using a volume ratio of 1 to 1.

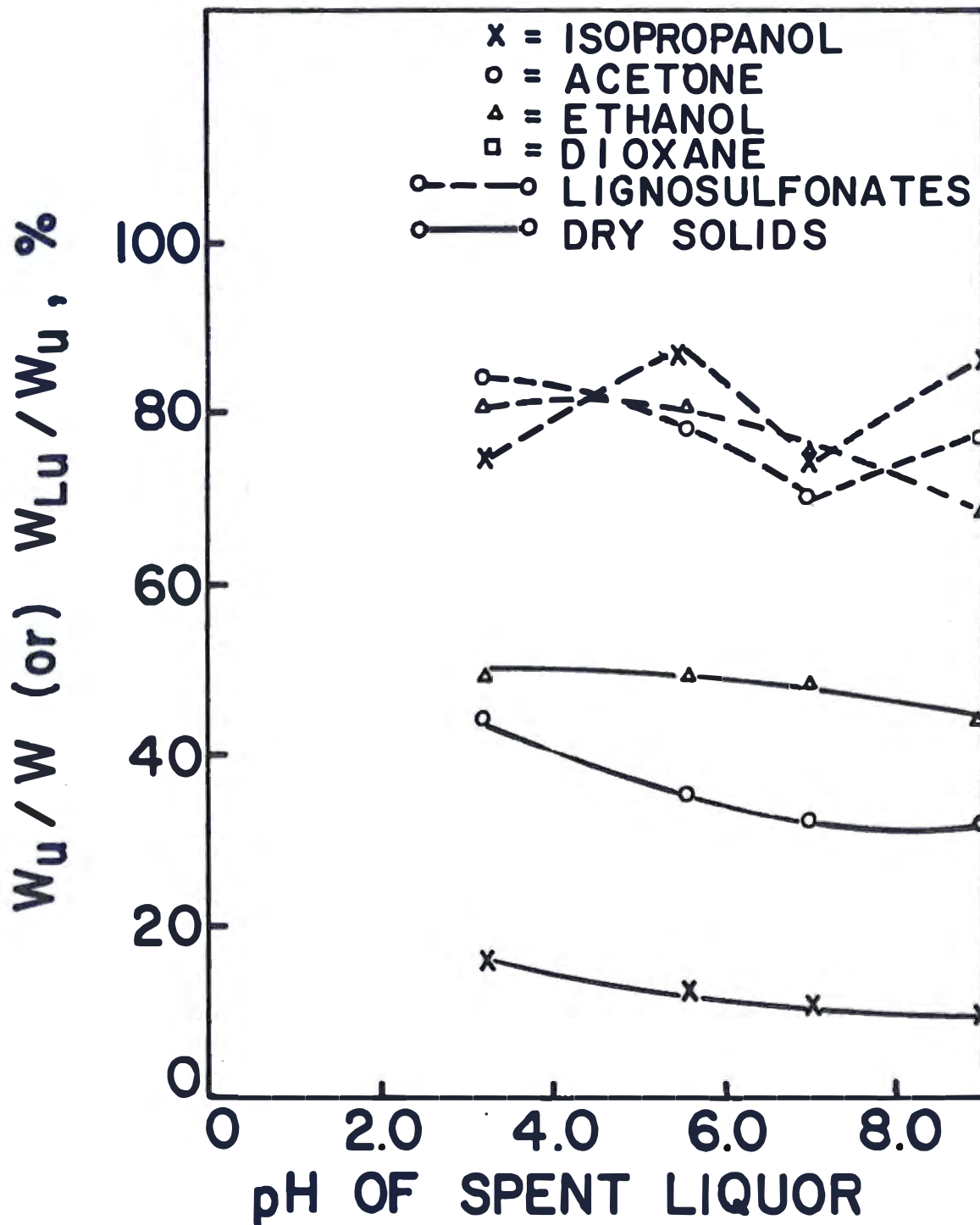


Figure 32. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of pH value of spent liquor for the second series of experiments Set II : spent liquor \bar{C} was extracted with different organic solvents at 20°C and several pH's(liquor), using a volume ratio of 1 to 1.

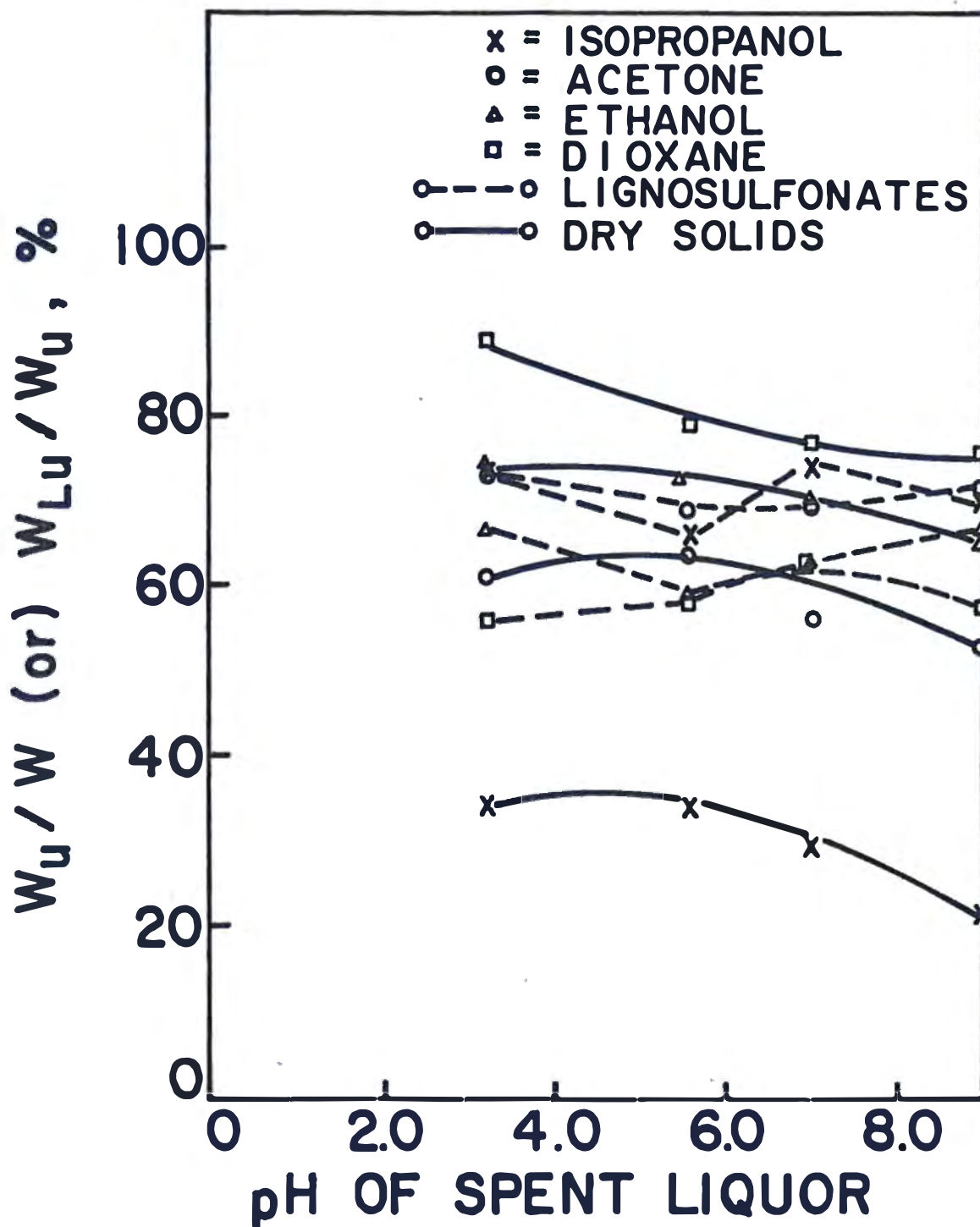


Figure 33. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of pH value of spent liquor for the third series of experiments Set II : spent liquor D was extracted with different organic solvents at 20°C and several pH's(liquor), using a volume ratio of 1 to 1.

pronounced influence on both distributions. An exception was observed for spent liquor A when extracted with dioxane (see Figure 31); in this case, the solids content of the upper phase dropped considerably when the pH value changed from 1.0 to 9.0. As regards to the separation of carbohydrates and lignosulfonates, change in liquor pH value did not increase the separation efficiency.

For spent liquors A and C (Figures 31 and 32), a change in pH from the original value of 5.58 would generally decrease slightly the percent lignosulfonates content of the upper phase; while for spent liquor D, (Figure 33) a slight increase in W_{Lu}/W_u was observed as the liquor pH value changed. Nevertheless, the effect was not very significant.

When spent liquor was strongly acidified with sulfuric acid, all the organic salts in it turned into the organic acids plus sodium sulfate. With pH value of the spent liquor equal to 1.0, some chemicals crystallized out during the extraction. These crystals could be considered to be sodium sulfate, which was soluble in water and insoluble in alcohols and other organic solvents. On the other hand, some components contained in the spent liquor might be denatured due to strong acidification by H_2SO_4 . The substance obtained after drying the acidified liquor was dark-brown and partially soluble in water. The insoluble substance swelled and looked like jelly. It was suggested that, under strong acidic condition, lignosulfonates might be cross-linked themselves.

In some cases the phase equilibrium also changed under this acidic condition (pH = 1.0). For example, when spent liquor C was extracted with isopropanol, spent liquor D extracted with acetone, ethanol, or dioxane, there was only one phase instead of two.

4-4 Effect of Temperature on Extraction

It is known that solubility, generally, increases with temperature. In the present study, solubilities of dissolved solids and liginosulfonates were expressed as the percent solids and the percent liginosulfonates content in the upper phase and their variations with temperature are shown in Figures 34 to 37.

Figure 34 shows the case for spent liquor A. Dry solids in the upper phase increased slightly with increasing temperature when isopropanol and ethanol were used as the extracting solvents; while for acetone and dioxane, the solids content decreased with increasing temperature. Especially for dioxane, percent solids decreased rapidly when temperature raised from 20⁰C to 40⁰C; afterward, it decreased slowly. From the view point of extracting liginosulfonates it is better to carry out the extraction at high temperature than at low temperature with the exception when ethanol was used as the extracting solvent. Among the solvents used, dioxane was the most selective for liginosulfonates at temperature higher than 20⁰C; as an example, at 60⁰C, the liginosulfonates content of the upper phase was as high as 95%.

Figures 35 and 36 show that the temperature effect for spent liquors B and C was similar. When using isopropanol as the extracting solvent, lignosulfonates content dropped rapidly to a minimum (Fig. 36) at 40°C and it increased rapidly again afterward. The effect of temperature was not obvious when acetone, ethanol, or dioxane were served as the extracting solvent.

Figure 37 shows the results for spent liquor D whose solids content was rather low (i.e., 24.6%). When this liquor was extracted with ethanol, the solids content of the upper phase increased considerably with increasing temperature. At the same time, the volume fraction of the upper phase also increased with increasing temperature. At 70°C, for example, about 5% (by volume, referred to the total volume of the two phases) of liquid was in the lower phase. For other solvents used in this series of experiments, the temperature effect was not pronounced.

Temperature effect on extraction can also be seen from the comparison of the phase equilibrium diagrams plotted at various temperatures in Figures 17 to 26. These figures show that, when using ethanol as the solvent, the area of immiscibility diminishes as the temperature increases; while for other solvents, the variation is not so obvious.

4-5 Recovery of Carbohydrates by Ultrafiltration

The main purpose of this work was to study the use of solvent extraction as a means for the separation of lignosulfonates or carbohydrates from

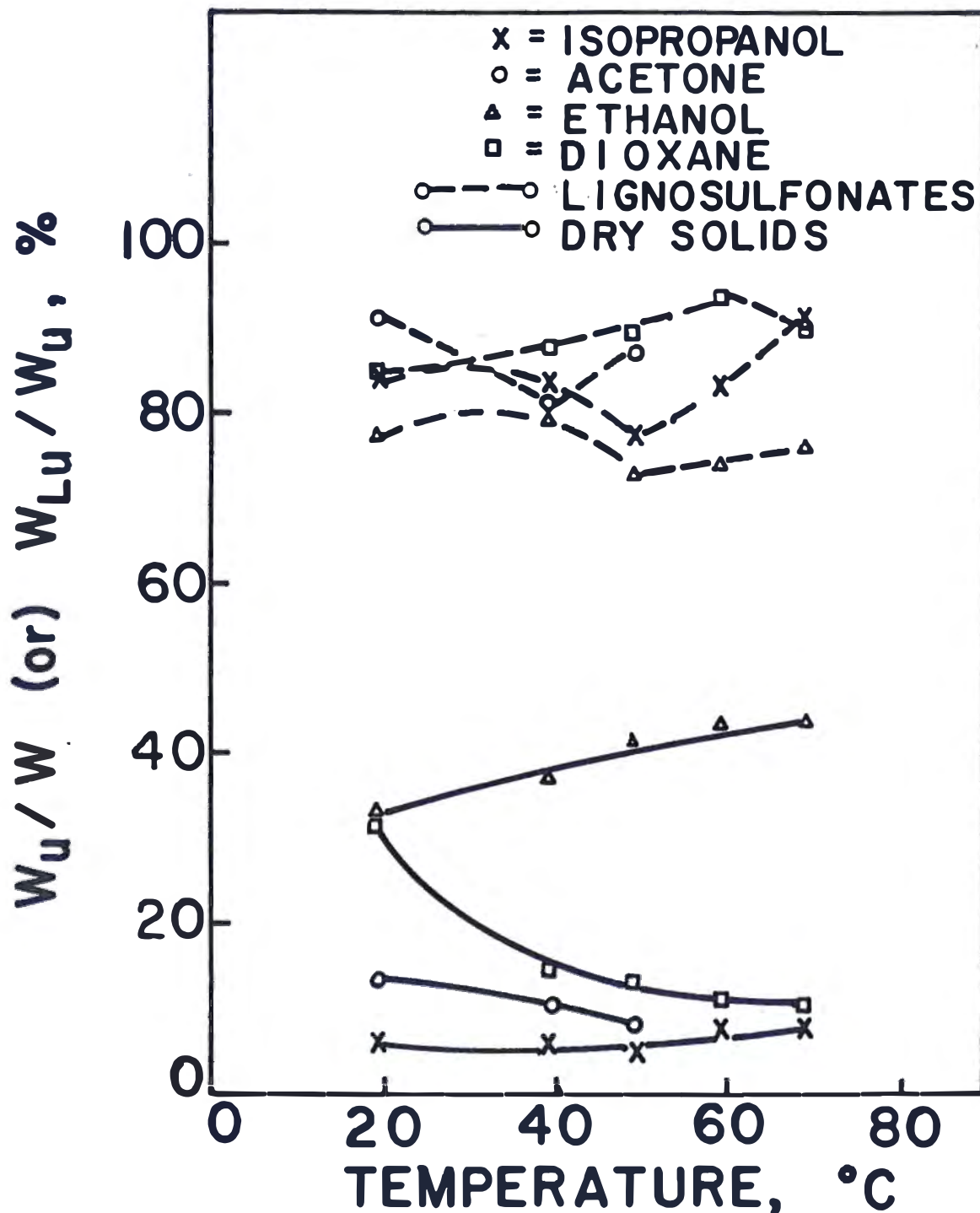


Figure 34. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of temperature for the first series of experiments Set III : spent liquor A was extracted with different organic solvents at several temperatures and $\text{pH}(\text{liquor}) = 5.58$, using a volume ratio of 1 to 1.

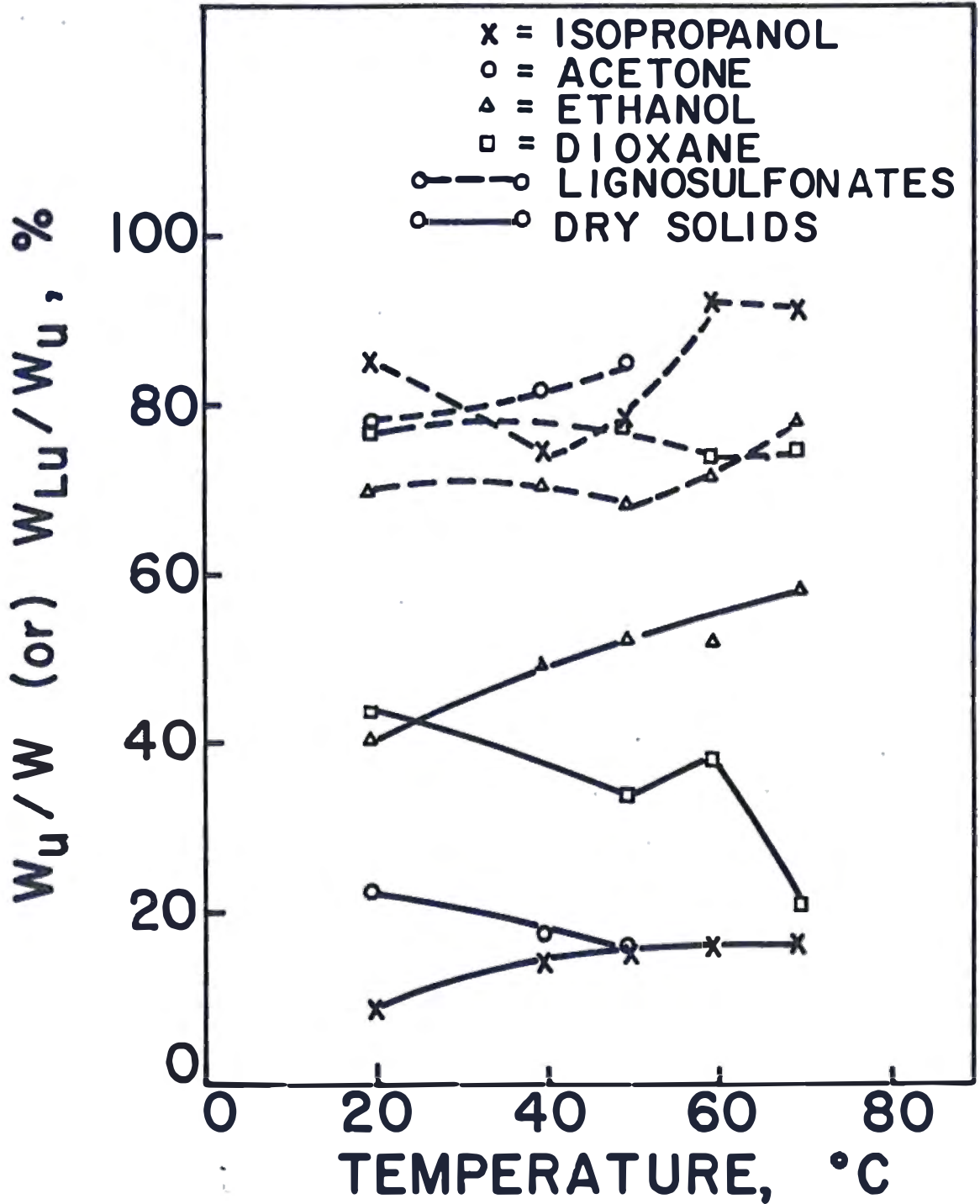


Figure 35. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of temperature for the second series of experiments Set III : spent liquor B was extracted with different organic solvents at several temperatures and $\text{pH}(\text{liquor}) = 5.58$, using a volume ratio of 1 to 1.

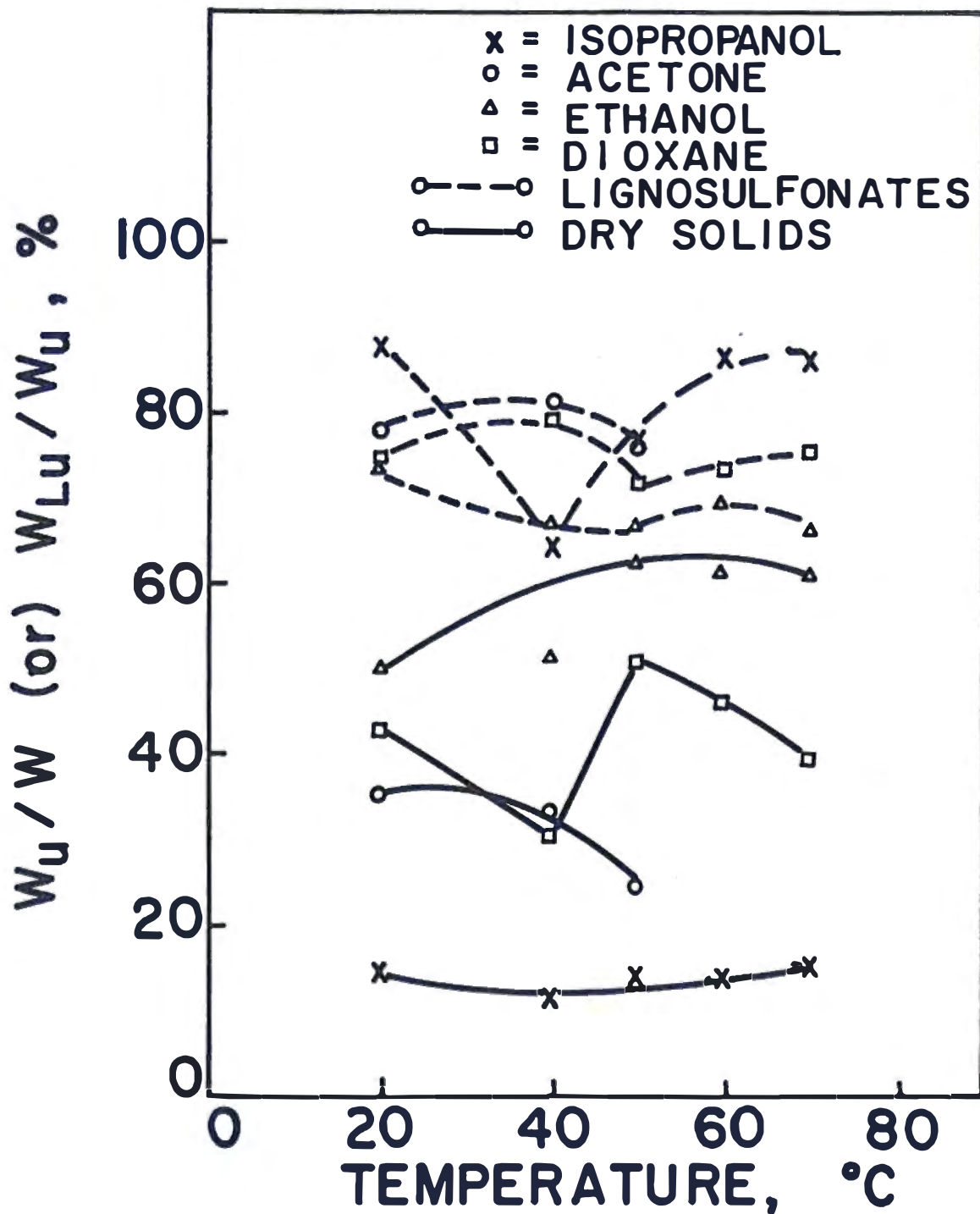


Figure 36. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of temperature for the third series of experiments Set III : spent liquor C was extracted with different organic solvents at several temperatures and $\text{pH}(\text{liquor}) = 5.58$, using a volume ratio of 1 to 1.

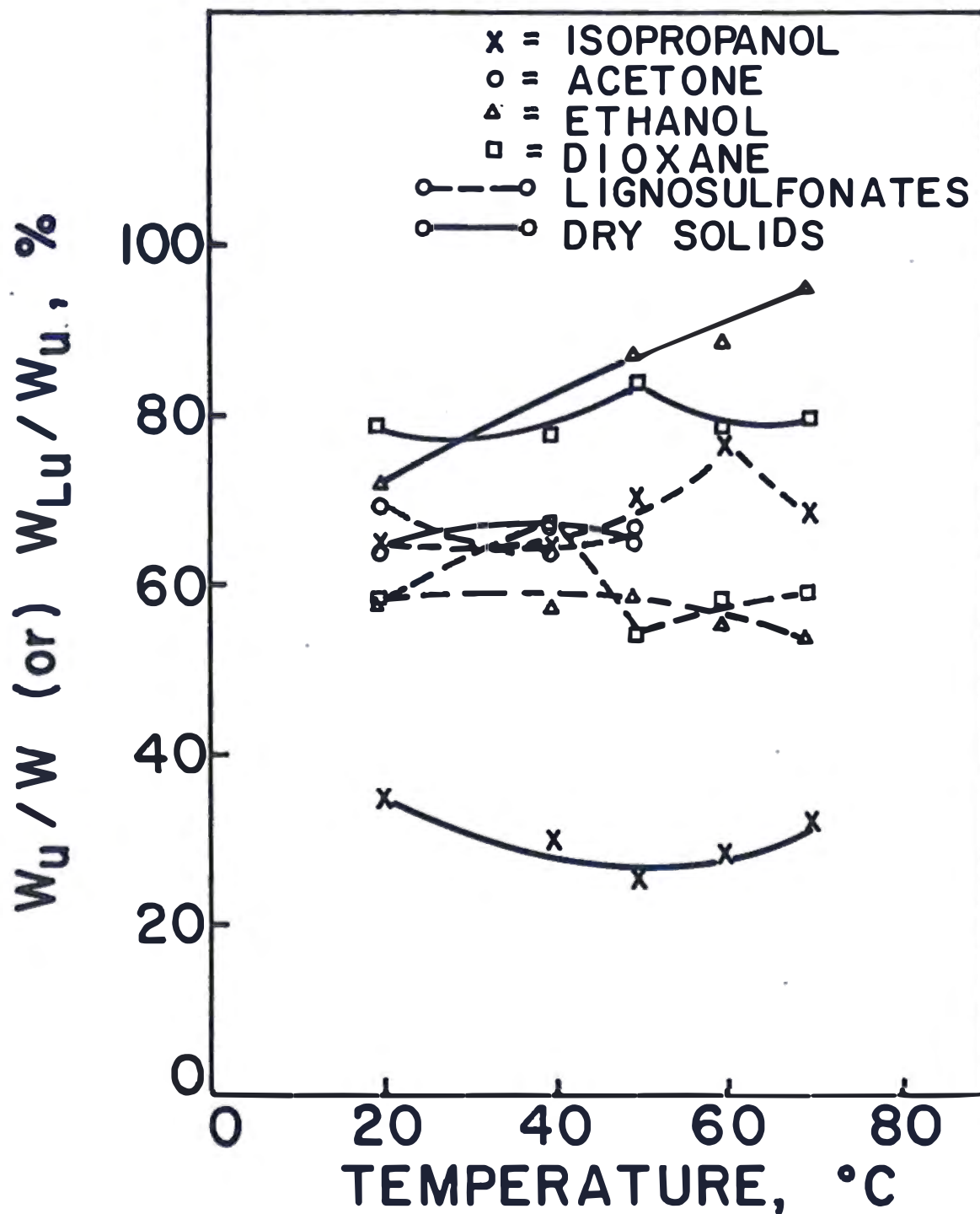


Figure 37. Plots of (g solids in upper phase, W_u)/(g total solids, W) and (g lignosulfonates in upper phase, W_{Lu})/(g solids in upper phase, W_u) as a function of temperature for the fourth series of experiments Set III: spent liquor D was extracted with different organic solvents at several temperatures and $\text{pH}(\text{liquor}) = 5.58$, using a volume ratio of 1 to 1.

the spent liquor under study. Therefore, only a few tests on the separation by means of ultrafiltration were conducted. One advantage in using this method is that the approximate distribution of molecular weights of lignosulfonates could be obtained. In the sample obtained from the upper phase, when spent liquor was extracted with isopropanol, the amount of the higher molecular weight compounds was 10% more in comparison with other samples which were obtained with acetone, ethanol, or dioxane.

The membrane filter used permits substance having molecular weight less than 10 000 to pass through. Carbohydrates ordinarily are small molecules ; thus, they could pass the membrane. According to the results shown in Table 17, a certain amount of carbohydrates still remained in the sample solution (they did not pass through the filter), especially for the samples obtained from the lower phases. From these results, the supposition made by Forss³ might be true that lignosulfonates have the possibility to form a complex with carbohydrates through an ether bond. Actually, no direct proof has been reported in supporting this supposition; moreover, the real structure of lignosulfonates has not yet been well understood.

4-6 Viscometry and High Pressure Liquid Chromatography

4-6-1 Viscometry

In order to study the relationship between extraction efficiency and molecular weight of lignosulfonates, several methods were tried for the determination of the molecular weight. The method by the measurement of

viscosity could not be used, because the solubility of lignosulfonates in most organic solvents was extremely small or nearly zero. Even in water solution, the solubility of lignosulfonates also had a limit; turbidity occurred when the lignosulfonates concentration was increased above 5%. In using this method, sample solution had to be prefiltered before the test, to remove any small particles which influenced the viscosity of the test solution. The solids concentration of a sample solution thus could be changed after filtration, if there was some insoluble material in the solution. When concentration of solution changed, the viscosity also changed at the same time; it was, therefore, difficult to obtain a precise molecular weight for the solute.

4-6-2 High pressure liquid chromatography.

In recent years, high pressure liquid chromatography has been demonstrated to be a simple, precise, and rapid method for the separation of substances with different molecular weight. In this study the gel permeation involved in the high pressure liquid chromatography was also used to determine the molecular weight distribution of lignosulfonates in different samples.

A difficulty in using this method was that lignosulfonates of high molecular weights often deposited by adsorption on the packing material, such as deactivated glass beads (Porasil), when using distilled water as the eluant. The chromatogram changed each time when the same amount of sample was injected into the column.

Changing the packing material of columns or changing the eluting solvent was one way to remove the disadvantage of this method. To the author's knowledge, there are three sorts of packing materials, sold by the Waters Associates Co., which can be used for gel permeation purpose. They are Styragel, Poragel, and deactivated Porasil; except for the last one, the other two were comparatively suitable for organic solvents. Because of the solubility of lignosulfonates, deactivated Porasil was used as the packing material and a mixture of distilled water and methanol by a volume ratio of 9:1 or 8.5:1.5 was used as the eluant.

When the adsorption problem was solved to a great degree by changing the eluant, another problem was introduced in the system: air bubbles entered the liquid chromatograph system and rested in the columns, detector, or pump frequently. Therefore, distilled water and methanol were degased by boiling them individually then mixed in a desired volume ratio; or the solvent mixture was stirred with a magnetic stirrer during the operation of the instrument.

4-7 Phase Equilibrium Diagram.

Phase equilibrium diagram was established with the solubility curves plotted for the two phases: the upper (extract) and the lower (raffinate). When dioxane was used as the extracting solvent three clear phases occurred at high liquor solids concentration when using S/SL ratios of 1.5 and 1. The tie line which connected the three equilibrium points was not a straight

line. The phase equilibria of these systems could, therefore, not be represented by the same equilibrium diagrams as for the cases where there were only two phases.

As for the abnormality in the experimental results involving acetone (Figure 21), it was considered to be caused by experimental error. Because of its high volatility, acetone might easily be lost by evaporation during the manipulation of sample. Consequently, the inaccurate result was obtained in the determination of the partition of water and acetone by gas chromatography. Especially, when the sample size was very small, any tiny error in volume might change the phase equilibrium diagram considerably.

Chapter V

CONCLUSIONS

The results of the presented study suggested that, among the four organic solvents used, isopropanol appeared to be the most selective solvent for extracting the lignosulfonates contained in the bisulfite spent liquor studied. When the volume ratio of solvent to spent liquor was 1 to 1, the percent of lignosulfonates content in the solvent-rich phase reached a maximum. But the yield of lignosulfonates was too low for practical application. Changing the operating conditions such as liquor pH and operating temperature could not improve the yield. Furthermore, in view of economy, for a unit amount of solvent used, the yield of lignosulfonates was comparatively low. As a result, the process of liquid extraction can not be considered for commercial application for the bisulfite liquor studied.

These results also suggested the possibility of having a certain amount of lignosulfonates-carbohydrates complexes in the liquor studied. This suggestion indeed leads to an idea about the extraction process although no definite conclusion can be drawn concerning the efficiency of separating lignosulfonates and carbohydrates. The idea is presented below. If it is true that there is a certain amount of lignosulfonates and

carbohydrates bound together to form complex compounds, good or satisfactory separation of these two components would never occur even with the use of other organic solvents or with the change of operating conditions such as temperature, pH value of the spent liquor, solvent-liquor ratio, and multiple-stage extraction. This is because the dry material contained in both phases, extract and raffinate, contains complexes of which the bonding between the constituting components can not be separated with simple physical means. Consequently, if the existence of complex compounds in spent liquor is true, the approach suggested for future study to increase the separation efficiency consists of two stages: the first stage is to find a convenient and economic method, either chemical or physical if possible, which can break down the bonding between these two components; then, the second is to separate them by liquid extraction.

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