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Equilibrium data for the sucrose-potassium chloride-water system were taken for Dowex 50 W X 4 resin at 90° C. The sugar concentration was varied from 0% to 60% by weight, and the salt content, from 0% to 6% by weight. Because shrinkage of the resin due to salt absorption was noted, the bulk volume of the resin was determined for the same ranges of sugar and salt concentrations.

It was found that as the sugar concentration increased, the absorption of sugar increased, and the absorption of sugar decreased with increasing salt concentrations. The distribution coefficient, the ratio of the concentration of the solute in the liquid in the resin phase to the concentration of the solute in the liquid outside of the resin was found to increase with increasing sucrose concentrations as would be expected for a nonionic substance. The decreased absorption of sucrose with increasing salt concentration is caused by shrinkage of the resin, and a consequent decrease in capacity.

PHASE EQUILIBRIA FOR THE SUCROSE-POTASSIUM CHLORIDE-WATER SYSTEM ON DOWEX 50 W X 4 RESIN (K^+) AT 90°C

by

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INTRODUCTION

Economic conditions in the United States (24) make it desirable to recover sugar from beet molasses, which contain about 50% sugar (Appendix C). However, as beet molasses has many uses, it is essential that any process for the recovery of sugar be economically competitive with other uses of beet molasses.

Ten years ago the process of ion exclusion was developed (25). Ion exclusion is a unit operation which separates ionic from nonionic components. At that time it was not an economical process to use for the separation of sugar and salt from molasses, although further research indicated that the process might be developed and made economically feasible if it could be operated as a continuous process. In order that a continuous recovery process could be designed and operated on a pilot-plant scale, equilibrium data for the system were needed. It was the purpose of this research to provide these data.

This thesis describes the system sucrose-potassium chloride-water on Dowex 50 W X 4 ion exchange resin. This system was chosen because potassium chloride is one of the major impurities which retards the crystallization of sugar in molasses (17). Commercial granulated sugar (99% sucrose) and technical grade potassium

chloride were used because it was proposed to use the same materials on a pilot plant study of a continuous counter-current ion exclusion process (13).

The effect of temperature on the absorption of sucrose in the resin was studied. On the basis of the results of this study, a temperature of 90° C was selected as desirable, and equilibrium data were taken at this temperature. Because the absorption of salt and sugar causes a shrinkage in the resin volume, the effects of salt and sugar concentrations on the resin volume were also determined.

LITERATURE SURVEY

Wheaton and Bauman (25) discussed the theory of ion exclusion and its potential applications in 1953. They performed chromatographic separations of certain organic compounds from some ionic impurities. However, because of insufficient knowledge of the factors affecting K_d, the distribution coefficient (ratio of the concentration of the solute inside the resin to the concentration outside the resin phase), they were unable to separate sugar from salt in molasses.

Simpson and Wheaton (20) gave a good resumé of the effects of a number of variables on the efficiency of ion exclusion chromatographic separations -- particle size, flow rate, cross linkage and feed volume to column volume ratio -- for ethylene glycol as a test compound. Simpson and Bauman (19) described a procedure for recycling effluents from a chromatographic ion exclusion separation of ethylene glycol from sodium chloride which could possibly be adapted to sugar liquor purification.

By varying flow rate, resin particle size, feed volume and percentage of divinyl benzene in the case of Dowex resin, Asher (1) was able to vary the distribution coefficient of a component and make chromatographic separations. He studied the sodium chloride-dextrose system. Better separation was obtained at higher temperatures, and the possibility of color removal from molasses by ion

exclusion was also confirmed. All of the above authors got better chromatographic separations with lower flow rates, smaller particle size and lower crosslinkage in the resin.

A more recent publication by Norman, Rorabaugh and Keller (15) discussed some of the variables and advantages of ion exclusion as applied to sugar-juice purification. They also proposed operating requirements for a continuous Higgin's contactor which might be used to purify sugar beet thick juice diluted to 40% by weight.

Stark (21) investigated the chromatographic separation of impurities other than salts and colored materials present in molasses, for example amino acids and salts of weak acids. Impurities carrying nitrogen compounds were eluted after the sucrose, so further purification was achieved. He concluded that the best separation of impurities from molasses is done with Dowex 50 W X 4 resin at 90^{o} C.

THEORY

The process of separation of ionic from nonionic substances using ion exclusion is only a little over ten years old (25, 26). Ion exclusion purification arose from the observation that at equilibrium the concentration of a strong electrolyte is lower within the aqueous portion of the resin phase than in the surrounding solution. Non-ionized or weakly ionized compounds generally have a relatively high concentration within the resin bead. Ion exclusion depends primarily on the following factors: Donnan equilibrium, the distribution coefficient, and the nature of the resin. These factors are discussed in the following sections.

Donnan Equilibrium - Potential

The phenomenon of ion exclusion is well explained by Donnan's theory of membrane equilibrium (1). The membrane separates two electrolytes, one of which contains an ion which does not diffuse through the membrane. Suppose that on one side of the membrane there is NaCl, and on the other side, NaR, where R is impermeable to the membrane. Donnan showed that equilibrium is established only when

$$(Na)^+_1 \times (Cl)^-_1 = (Na)^+_2 \times (Cl)^-_2 \qquad (1)$$

Where $(Na)^+$ and $(Cl)^-$ are the concentrations of cations and anions in

solutions (1) which contains no R^- and (2) which contains R^-.

Suppose that when equilibrium is established, in solution (1) we have

$$(Na)_1^+ = (Cl)_1^- = X$$

and in solution (2)

$$(Cl)_2^- = Y$$

$$(R)_2^- = Z$$

$$(Na)_2^+ = (Y + Z)$$

Then from equation (1)

$$X^2 = Y(Y + Z)$$

Thus, for any non-zero value of Z, X is greater than Y, or at equilibrium the concentration of anions in the resin phase is greater than that in the solution. Because of the higher concentration of anions in the resin phase, there is a lower potential than that in the solution (23). Thus, a potential difference is developed. It can be represented as:

$$E = \frac{RT}{F} \ln \frac{X}{Y} \quad \text{or} \quad E = \frac{RT}{F} \ln \frac{\alpha_x}{\alpha_y}$$

Where R = gas constant

T = absolute temperature

F = Faraday's constant

α_x and α_y = The activities of the ions on the two sides of the membranes.

The existence of a Donnan potential can also be explained in another way. A cation exchanger will have a fixed amount of cations on its surface. When it is contacted with a given solution, the concentration of cations on the resin is higher than that in the solution. In addition, before equilibrium is attained the concentration of anions in the resin is lower than in the solution. Thus, due to the concentration difference cations diffuse out of the resin and anions diffuse in. The first few ions which diffuse thus build up an electrical potential difference between the two phases. This so called "Donnan Potential" pulls the cations back into the resin and the anions back into the solution. An equilibrium is established in which the tendency of the ions to level out the existing concentration difference is balanced by the action of the electric field. At this point, no more anions -- or cations from the law of electroneutrality -- will enter the resin. In short, after equilibrium is attained, the resin phase excludes any more electrolyte.

Helfferich (8) explains the effects of solution concentration, ionic valences of the solute, and the capacity and degree of crosslinking of the resin on the Donnan potential.

Effect of Solution Concentration

According to the Donnan-membrane theory, there is a greater concentration of anions in the resin phase than in the solution at

equilibrium. The Donnan potential is greater when the concentration difference between the resin and the solution is larger, and thus, because of the large number of anions in the resin, there is less migration of anions to the resin. This is also true for the cations because of the law of electroneutrality. Therefore there is a better exclusion. If the concentration of the outer solution is high, less cations will diffuse out, and therefore, there is a lower potential. Due to the lower potential the exclusion of electrolyte from the resin is less.

Effect of Valency

When the valency of the cation is higher the Donnan potential required to balance the tendency of the cation to diffuse into the solution is smaller. With a smaller Donnan potential, electrolyte exclusion is less efficient. On the other hand a given Donnan potential excludes the anions more efficiently when the anion's valence is higher. Consequently electrolyte exclusion is more efficient with cations of low valence. For example Na_2SO_4 is more strongly excluded by a cation exchanger than NaCl, and NaCl is more strongly excluded than $CaCl_2$. For an anion exchanger the sequence is the opposite.

Effect of Capacity and Crosslinkage

The Donnan potential increases with decreasing external and increasing internal cation concentration. Cation concentration in the resin phase is high when the resin has a high exchange capacity and is highly crosslinked.

Helfferich (8) concludes that the exclusion is favored by low concentration of the solution, high capacity crosslinking of the resin, low valence of the cation and high valence of the anion.

Distribution Coefficient

The nonelectrolyte in contact with the ion exchange resin will see no Donnan potential barrier to its solution within the resin phase. If the resin phase is viewed as simply a second solution phase, entirely similar to the outer solution, but separated from it by a boundary through which the nonelectrolyte can freely pass, it would be expected that the equilibrium concentration of solute in both solutions would be the same. It also follows from these suppositions that all nonelectrolytes would show identical distributions between the resin and solution. Experimental measurements of the nonelectrolyte distribution factor, however, have shown this reasoning to be faulty (26).

The distribution coefficient K_d is defined as $\frac{C^r}{C}$, where C^r is the

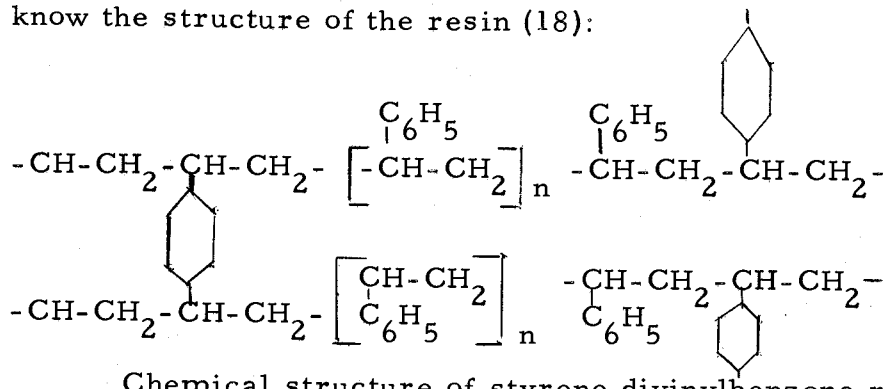
concentration of the solute in the liquid within the resin, and C is the concentration of the solute in the liquid outside of the resin. The K_d value is normally of the order of 0. 1 for highly ionized solutes such as sodium chloride, hydrocloric acid, etc., in dilute solution. However, the same dilute concentration of the nonionic species gives rise to values of K_d from 0. 2 to 1. 2 and greater. The value of K_d is dependent upon resin type, ionic form and, in many cases, upon the concentration of the solutes in contact with the resin. It also depends on the crosslinkage of the resin. The K_d values for 16%, 8% and 1% crosslinked Dowex 50 W resin were 0. 33, 0. 62 and 0. 88 respectively. This indicates that K_d approaches one as crosslinkage is decreased. These were determined with 5% ethylene glycol solution (26).

The K_d of most nonionic materials increases with increased concentrations. For example the K_d of ethylene glycol increases from approximately 0. 50 to 0. 75 when the outside solution concentration is increased from 4% to 20% for the sodium form of Dowex 50 X 8 resin. On the other hand the K_d value for acetic acid decreases from 0. 8 in a very dilute solution to 0. 6 in a 25% aqueous solution. Obviously, no predetermined rule can be stated which will describe the behavior of all solutes (14).

Nature of the Resin

Effect of Crosslinkage

To understand the effect of crosslinkage, it is necessary to know the structure of the resin (18):



Chemical structure of styrene divinylbenzene resin

The degree of crosslinkage in a styrene divinylbenzene bead refers to the fraction of divinylbenzene it contains. Thus a resin of 4% crosslinkage is made with beads composed of 4% divinylbenzene and 96% styrene and other monovinyl monomers. (The percent crosslinkage is indicated by an 'X' number following the name of a particular Dow resin. Thus Dowex 50 W X 8 is made from a copolymer containing 8% divinylbenzene.) The divinylbenzene contributes the third dimension to the polymer network and makes it insoluble (6).

The fraction of divinylbenzene in the bead determines to what extent the ion exchange resin is free to swell and shrink. While an ion exchange resin containing only a small fraction of a percent of divinylbenzene is insoluble, it will take up many times its own

weight of water and swell into a jelly like mass. As the amount of crosslinkage increases, the wet volume capacity increases, and the dry weight capacity decreases.

Several other physical-chemical properties of the resin are affected by the amount of crosslinkage. As the crosslinkage decreases and the resin swells, diffusion of ions within the resin becomes faster. This can give materially faster equilibration rates, especially where large ions are concerned. As the crosslinkage is increased the diffusion path becomes small enough to bar the entrance of large ions or molecules. By control of the size of these diffusion paths it then becomes possible to separate by size. If the crosslinkage of the resin is controlled to the right degree, the sugar molecule will enter the bead, but larger molecules such as color bodies, etc. will be excluded or screened out. At the same time ionizable compounds such as sodium and potassium salts, amino acids, etc. are excluded because of the Donnan membrane effect (15).

Effect of Particle Size

Decreasing the size of the resin particles materially decreases the time required for the resin to reach equilibrium with a contacting solution (6). As the time required to attain equilibrium is decreased, the efficiency of a given volume of resin increases, or conversely, the volume of the resin required to do a specific operation decreases.

However, as the particle size of a resin in a column becomes smaller, the frictional loss or pressure drop of a liquid flowing through the column increases. So a compromise has to be made; usually a 50-100 mesh resin is preferred.

Wheaton and Bauman (25) reviewed the importance of these effects as applied to the principle of ion exclusion. They conclude it is necessary that the fixed ionic concentration inside the resin particles be great, that water content of the resin be high enough to give appreciable capacity, and that equilibrium be rapidly attained, i. e., that diffusion rates be as high as possible. The first requirement favors a high crosslinked resin, the second favors a low crosslinked resin, and the third implies either low crosslinkage or small particle size or both. Thus, a compromise must be made depending on the requirement of a particular job. No one combination has been found which is most suitable in every case.

Operating Variables

Temperature

At higher temperature the diffusion velocity is more rapid than at room temperature, and therefore all steps may be performed more easily and more rapidly. When an elevated temperature is employed the resistance to flow is lowered. Because of the decrease in

viscosity it is possible to decrease the particle size, in which case equilibrium is attained earlier. Experiments at room temperature give little or no separation of sucrose from ionic impurities (18).

Flow Rate

It is better to have a lower flow rate, thus providing more contact time. If the flow rate is increased more solution must be passed through the resin to reach equilibrium and the total contact time remains the same.

EXPERIMENTAL APPARATUS

Equilibrium Determinations

The experimental apparatus for equilibrium determinations consisted of a reservoir, preheater and equilibrium cell as shown in Figure 1. Hot water at 90° C was circulated from a constant temperature bath through the jackets of the cell and preheater during an experiment.

The equilibrium cell is shown in detail in Figure 2. Basically, the cell consisted of a 6-inch length of 1/2-inch i. d. plexiglass tubing surrounded by a water jacket through which hot water could be circulated. The inner tube of the equilibrium cell was made of two pieces so that a 20 x 150 mesh stainless steel wire screen could be inserted 1-inch from the lower end. A small piece of glass wool placed upon this screen prevented the resin from leaving the cell during an experiment.

The water jacket consisted of a 3 1/2-inch length of 2-inch pyrex glass pipe with a rubber stopper at each end. The stoppers were bored to accomodate the equilibrium tube; the top stopper was also bored to accomodate the inlet and outlet tubes for hot water circulation. The water jacket was made of pyrex to facilitate visual observation of the resin in the equilibrium cell so that the formation of air bubbles in the resin bed, which cause incomplete

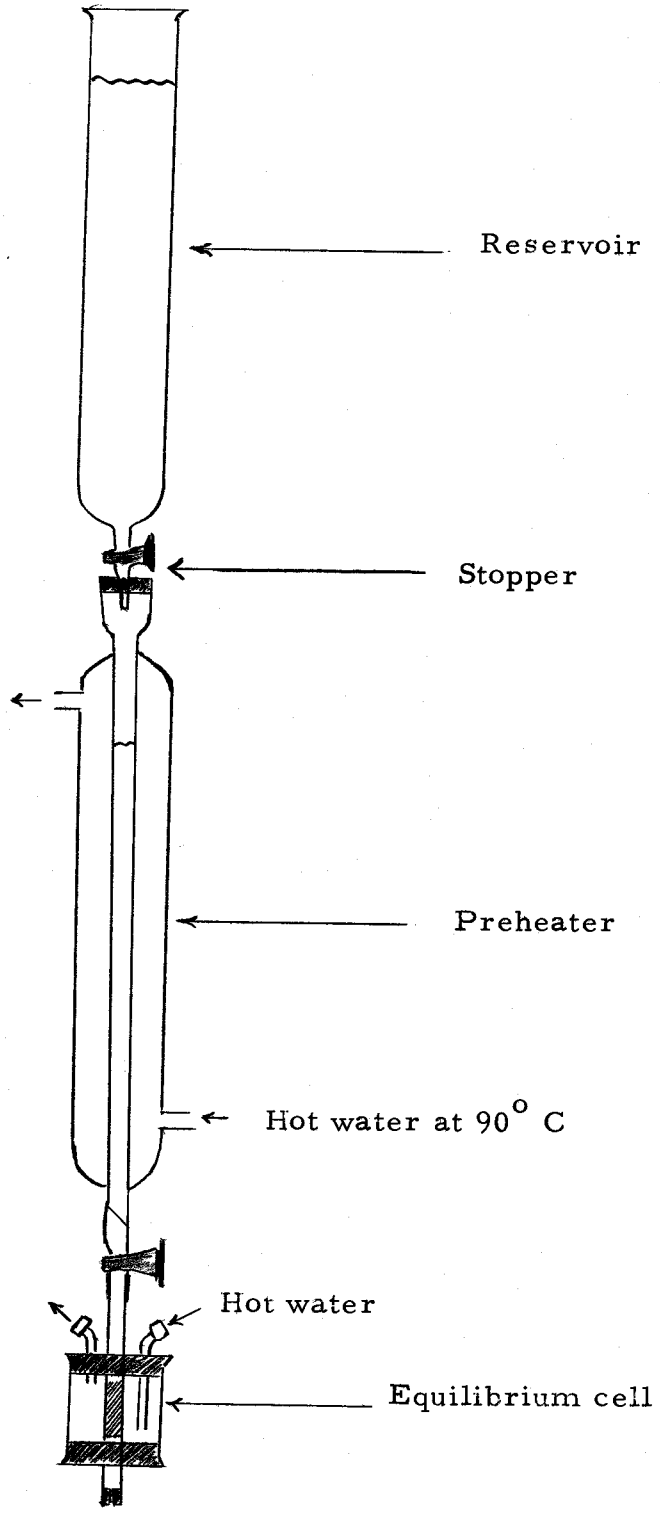


Figure 1. Equilibrium measurement apparatus.

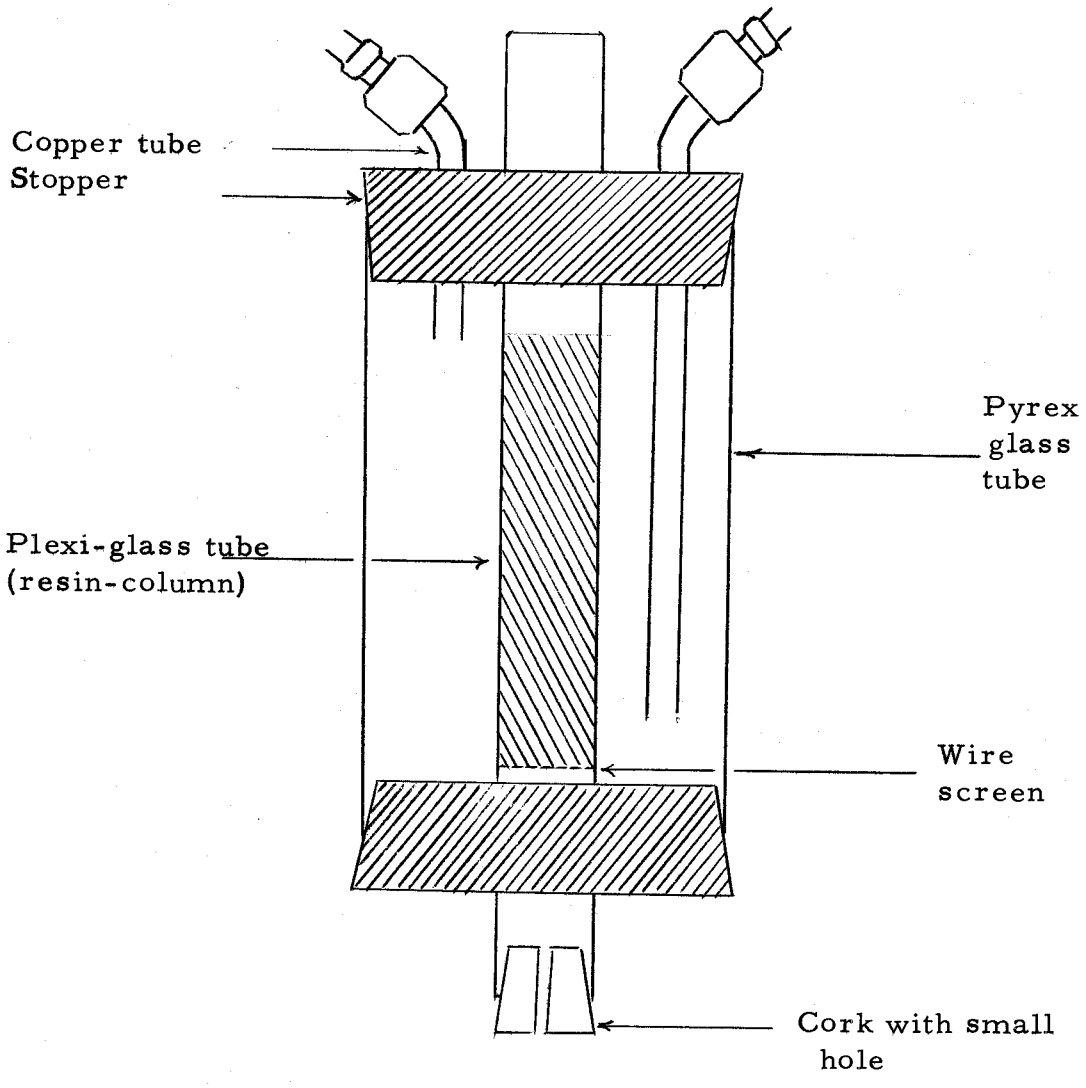


Figure 2. Equilibrium cell.

absorption and channeling, could be avoided. It was necessary to use pyrex since a white film forms on plexiglass after some use at 90° C. Visual observation was found possible with one plexiglass tube, but not with two.

The equilibrium cell was connected to the preheater by a pyrex glass valve as shown in Figure 1. The preheater was connected to the reservoir (500 ml. burette) by a rubber stopper. The valve on the reservoir was kept completely open and the valve of the preheater was regulated during operation to keep the level of liquid in the preheater, and thus the flow rate, nearly constant. A cork with a small hole was placed at the bottom of the cell to prevent air from entering the resin bed.

The cell and preheater were lagged with Tygon tubing to decrease heat losses as it was necessary to keep the temperature constant at 90° C. Tygon tubing (transparent) was used so that level of the liquid in the preheater and the resin in the cell could be observed.

Ten units, each consisting of an equilibrium cell, preheater and reservoir, were used. Six units were used for loading the resin and four units were used for eluting. The hot water for these units was provided from two constant temperature baths, each of which contained a heating unit (stirrer, heater and pump combined; Techne, Ltd.) and two knife heaters (total of 900 watts).

Volume Measurement

Volume changes were measured by using jacketed burettes as shown in Figure 3. A small amount of glass wool was kept above the valve of the burette so that no resin would escape when the valve was opened. Fifty mesh glass beads were placed above the glass wool so that the lower level of the resin could be measured accurately. Hot water was circulated through the heat exchanger as in the case of the equilibrium cell. As shown in Figure 3 a reservoir was also provided in order that the resin could be brought to equilibrium with solutions of various concentrations and the volume of a known amount of resin saturated with a given solution could then be measured.

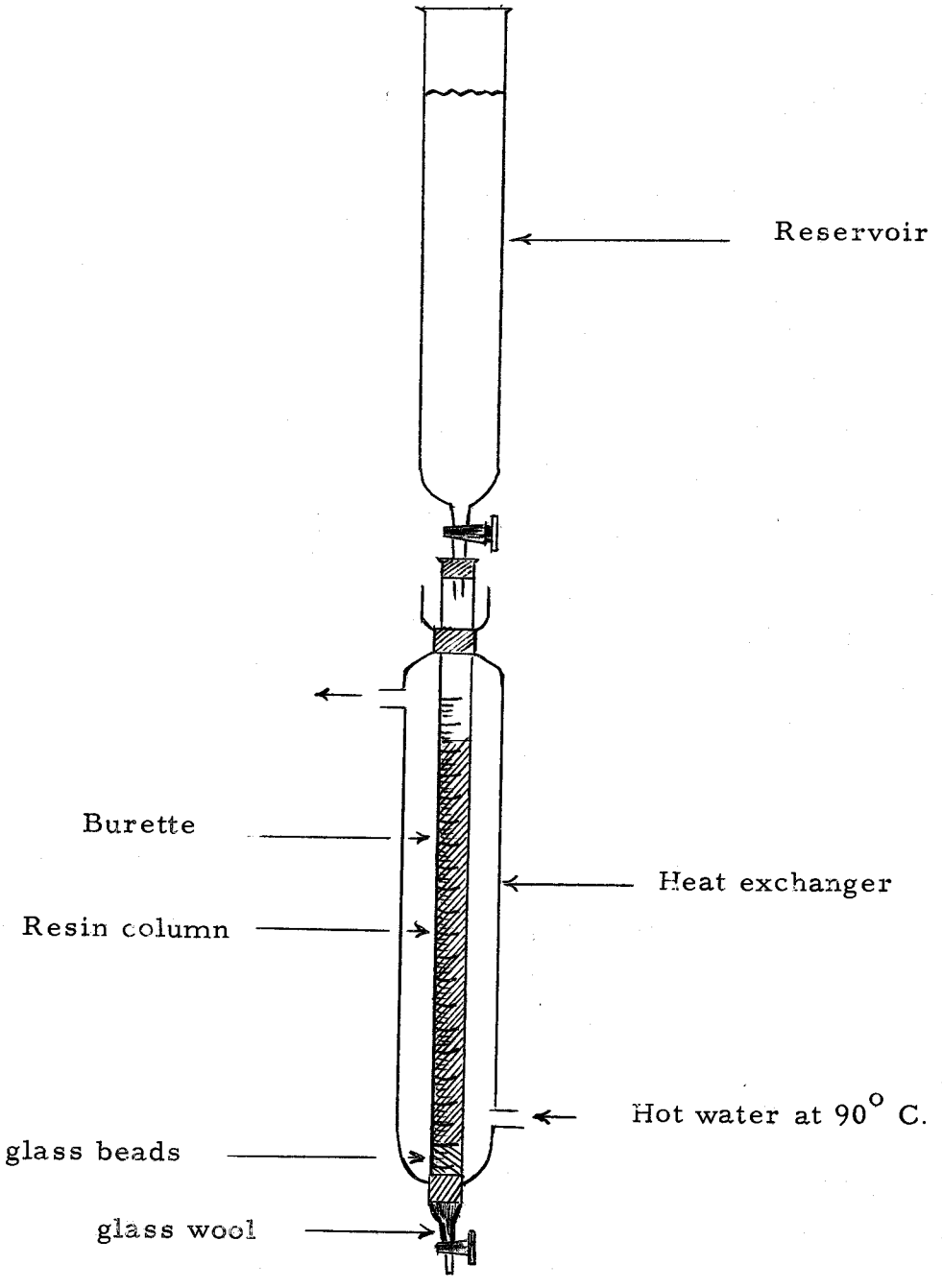


Figure 3. Volume measurement apparatus.

EXPERIMENTAL PROCEDURE

The experimental procedures consisted of preparation of the resin, measurement of bulk volume, determination of the equilibrium data, and measurement of changes in the volume of the resin. These procedures will be presented separately.

Preparation of the Resin

The original Dowex 50 W X 4, 50 to 100 mesh resin was received in the wet potassium form. To prepare the resin for the equilibrium experiments the resin was first rinsed with distilled water and then placed in a burette. The resin was contacted with a stream of 5% potassium chloride which was slowly passed through the burette for 5 to 6 hours. At the end of this time it was assumed that the resin was completely in the potassium form.

The resin should be in the same ionic form as the ionic portion of the materials to be separated. In actual practice this will, of course, adjust itself after the required number of cycles, as the resin is converted and comes to equilibrium with surrounding solution (25). The resin was again rinsed with distilled water to make it free of chloride. Silver nitrate solution was used to check for traces of chloride.

Measurement of Bulk Volume

The bulk volume of the resin is defined as follows:

$$\text{Bulk Volume} = \frac{\text{Volume of wet resin}}{\text{1 gm. of dry resin}}$$

In order to determine this quantity, three samples of the chloride-free resin were placed in 100 ml measuring cylinders. After the resin had settled, three different readings of the resin volume were taken for each sample at an interval of 30 minutes. The values were then averaged. Each sample of resin was then poured into a separate 1, 000 ml beaker. After settling, most of the water could be removed and care was taken so that no resin should be lost. Each beaker was covered with paper to prevent dirt from contaminating the sample and was then kept overnight on top of an oven. The resin was then dried in a vacuum oven at 90° C until a constant weight was obtained. From the wet volume and the dry weight, the bulk volume was calculated.

Experimental Measurement of Equilibrium

Three to four grams of accurately weighed dry resin was treated with a saturated solution of potassium chloride. (The use of a saturated salt solution in the rewetting process prevented shattering of the resin by rapid swelling.) The treated resin was then completely

transferred to the cell and made free of chloride by washing with distilled water. The resin was then considered ready for the equilibrium measurements.

The cell was attached to the preheater as shown in Figure 1. After the resin was back washed to fluidize the resin bed to remove any air bubbles, it was heated for some time before the solution was passed through. Because plexiglass is a poor conductor of heat, it was worthwhile to heat the resin before loading to bring it to the proper temperature. The temperature was measured by inserting a thermometer into the resin bed. A constant temperature was very important as the absorption is temperature dependent.

A solution of sucrose and potassium chloride was heated to the temperature of the experiment and was then slowly passed through the equilibrium cell which was maintained at the same temperature. A sufficient volume of solution was passed through the cell to bring the resin and solution into equilibrium. The approximate solution volume required to attain equilibrium was determined in several initial experiments as that volume beyond which no further increase in solution volume would increase the amount of sucrose on the resin. In later experiments, this volume plus a suitable volume (about 100 ml) increment to insure an equilibrium state was used.

After equilibration the resin cell was disconnected from the controlled temperature bath and the preheater, and was quickly placed in

a centrifuge (International Centrifuge Type SB No. W6875, International Equipment Co., Boston) so that centrifuging could be done nearly at the same temperature. The resin was centrifuged at 2000 R. P. M. for 4 minutes. It was found that this time and force were sufficient to remove the interstitial sucrose-potassium chloride solution from the resin bed (7, 16). After centrifuging the outside of the cell was completely cleaned so that there was no danger of contaminating the effluent solution during the eluting stage.

After centrifuging the resin was unloaded with distilled water at the same conditions (90° C) as before. After collecting about 50 ml of the eluting solution the resin was back washed to fluidize the bed and thus remove any gas bubbles. The resin was unloaded until the exit solution was pure water. This was checked at 20° C with a refractometer (Precision Refractometer, Bausch & Lomb Optical Co.) and using the conversion tables (sugar chart, series 794) (2), provided with the instrument.

About 250-300 ml of solution was collected. The beaker with solution was weighed and the refractive index of the eluted product was found at 20° C. Duplicate readings were taken for each concentration. If the resin was loaded with sugar-salt solution, the salt content was determined by using Mohr's method (9). Mohr's method determines the chloride content by titrating against a standard silver nitrate solution using potassium chromate as the internal indicator.

Measurements showed that no significant sugar inversion occurred and that the presence of potassium chloride in low concentrations did not interfere with the refractometer measurement, and, at these concentrations, the refractometer readings for sucrose and potassium chloride were found to be additive.

Attempts to use a polarimeter for sucrose determination in the presence of potassium chloride failed due to salt interference. Salt can be removed for polarimeter analysis but the procedure is laborious, and the results obtained with the polarimeter were not considered accurate enough to warrant its use (3).

Measurement of Volume Changes

About 11 grams of accurately weighed dry resin was treated with a saturated potassium chloride solution and was then transferred to the burette used for volume measurement. The resin was heated for some time by passing hot water through the heat exchanger to bring it to 90° C. The solution was then passed slowly through the resin. After equilibrium was attained, or the level of the resin had become constant, the top and bottom levels were noted. Then the resin was unloaded and the experiment was repeated with another solution. For each concentration two readings were noted in two such assemblies.

PRESENTATION AND DISCUSSION OF RESULTS

The effect of temperature on the absorption of sucrose from 60% by weight sucrose -- 0% by weight potassium chloride solution is shown in Figure 4. It is obvious from Figure 4 that with increasing temperature the amount of sucrose absorbed increases. According to Asher (1), at a higher temperature a better separation is to be expected because viscosities are lower and conditions are nearer equilibrium because of faster diffusion rates. Also operation of the columns at 90°C lowers the possibility of fermentation taking place during purification. Fermentation is not desirable since microorganisms are produced which are adsorbed on the resin, and thus the efficiency of column separation is decreased.

As stated by Helfferich (8) and Calmon (4) the heat effect in ion exchange is less than two kilocalories per gram mole exchanged. It is probable that the forces involved in ion exclusion are less specific or weaker than in ion exchange, and therefore the heat effect will be even smaller. From Le Chatelier's principle, if the heat effect is small, the temperature effect will also be small. On the other hand, an increase in temperature causes an increase in the flexibility and volume of the resin matrix, thus permitting a greater number of sucrose molecules to squeeze into the resin structure.

Based on the data of Figure 4 and the fact that ion exclusion

column kinetics will improve with increasing temperature, it was decided to measure further equilibrium data and make the ion exclusion column runs at 90° C. A higher temperature might lead to vapor formation at points of low solute concentration or pressure in the ion exclusion column or associated apparatus. An introduction of gas bubbles into the resin bed would seriously impair uniform flow in the column.

The sucrose absorption isotherms at 90° C for potassium chloride solution concentrations of 0%, 1%, 3% and 6% by weight are shown in Figure 5 and presented in Table 1. From the curves it is apparent that as the amount of sucrose in the feed increases the absorption is increased. Thus the distribution coefficient based upon the volume of the wet resin increases with increased concentration as shown in Figure 6; this agrees qualitatively with the statement of Nachod and Schubert (14) that K_d of most nonionic materials increases with increased concentration. Also it is evident from Figure 5 that as the concentration of salt increases the absorption of sucrose decreases.

The decrease in the resin sucrose capacity with increasing potassium chloride solution concentration can be explained by two phenomena. The first is a decrease in resin volume with increasing salt concentration causing a reduction of resin water content. Due to the higher concentration of solute in the outer phase the water inside the

resin diffuses out. Therefore there is a decrease in the volume of the resin.

To examine the effect of resin swelling on sucrose absorption the volume of the resin as a function of the sucrose and potassium chloride concentrations was determined. These data are shown in Figure 7. These data were extrapolated and used in conjunction with the information presented in Figure 5 to redetermine the results to eliminate the swelling effect. Although a closer grouping of the data was obtained, the data at the four potassium chloride concentrations still fell on four distinct curves as shown in Figure 8. Thus some factor other than resin swelling was present.

The second factor which decreases sucrose absorption might be an increase in sucrose solubility with the addition of potassium chloride to the solution phase. This increase in solubility is reported by Rorabaugh (17) and Jose Ramon (5) and might reduce the driving force for sucrose diffusion and absorption in the resin. Also it is evident from the data presented in Table 4 that the absorption of salt in the resin increases with an increase in salt concentration. This agrees with the statement of Helfferich (8) that as the salt concentration increases the Donnan potential decreases and the exclusion is decreased.

The relative ratios of sugar to salt in the resin and in the solution are shown in Figure 9. It can be seen that the ratio of sugar to salt

is higher in the resin than in the solution. Thus, simple batch elution of the equilibrium resin contents would lead to an increase of the sucrose purity. It is also evident from Figure 9 that the mere presence of salt markedly affects sucrose absorption.

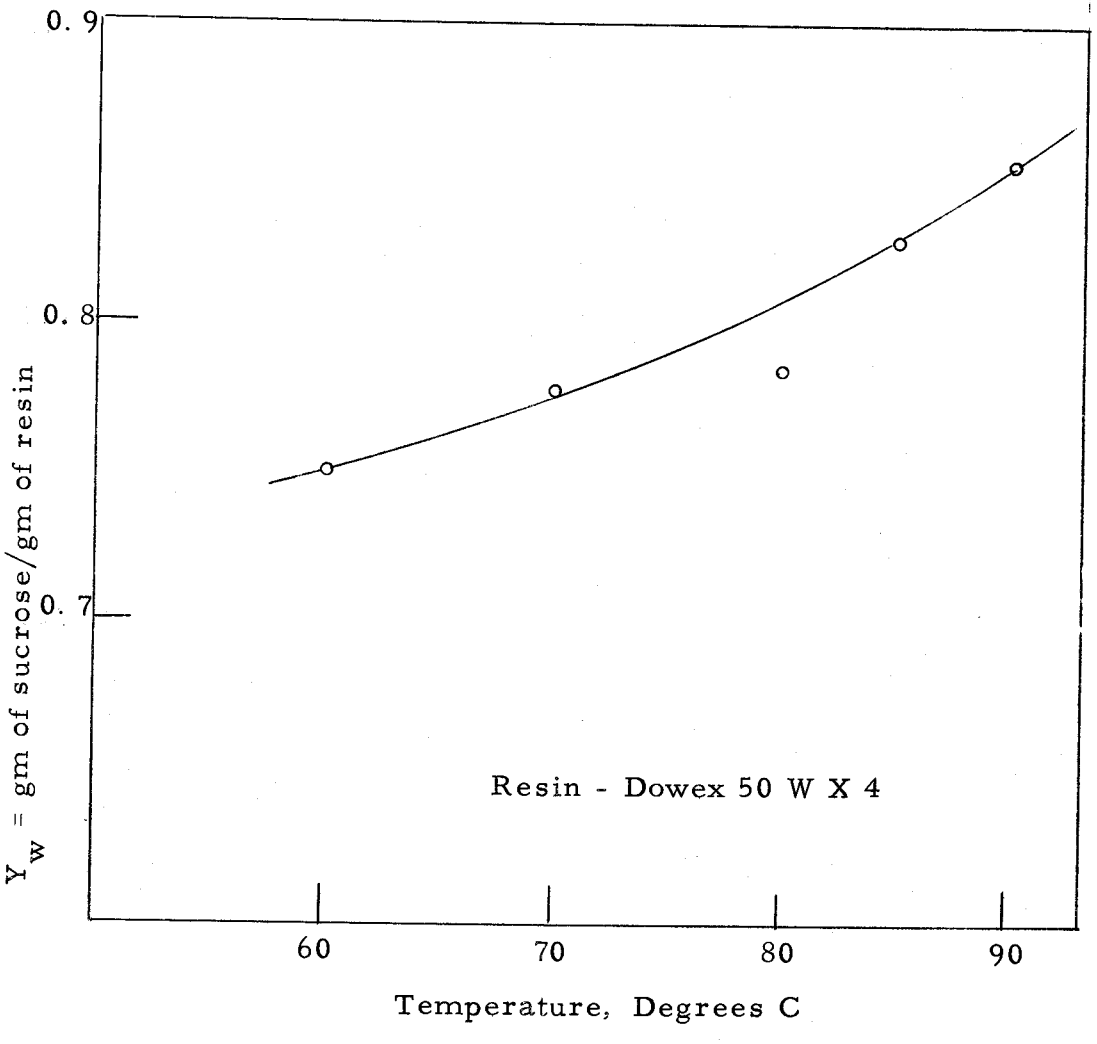


Figure 4. Resin loading as a function of temperature for 60% (wt.) sucrose solutions.

Table 1. Equilibrium sucrose concentrations (weight basis) for the sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C.

Solution			X	Yw
			gm of sucrose	gm of sucrose
Salt	% Wt.	Sucrose % Wt.	gm of water	gm of dry resin
A	0	10	0.11	0.07461
		20	0.25	0.1720
		30	0.43	0.3286
		40	0.665	0.5004
		50	1.0	0.6567
		60	1.5	0.8535
B	1	10	0.112	0.053
		20	0.253	0.155
		30	0.435	0.262
		40	0.678	0.368
		50	1.02	0.536
		60	1.54	0.724
C	3	10	0.115	0.048
		20	0.26	0.144
		30	0.448	0.246
		40	0.702	0.346
		50	1.06	0.528
		60	1.62	0.70
D	6	10	0.119	0.036
		20	0.27	0.142
		30	0.47	0.235
		40	0.74	0.328
		50	1.14	0.489
		60	1.77	0.677

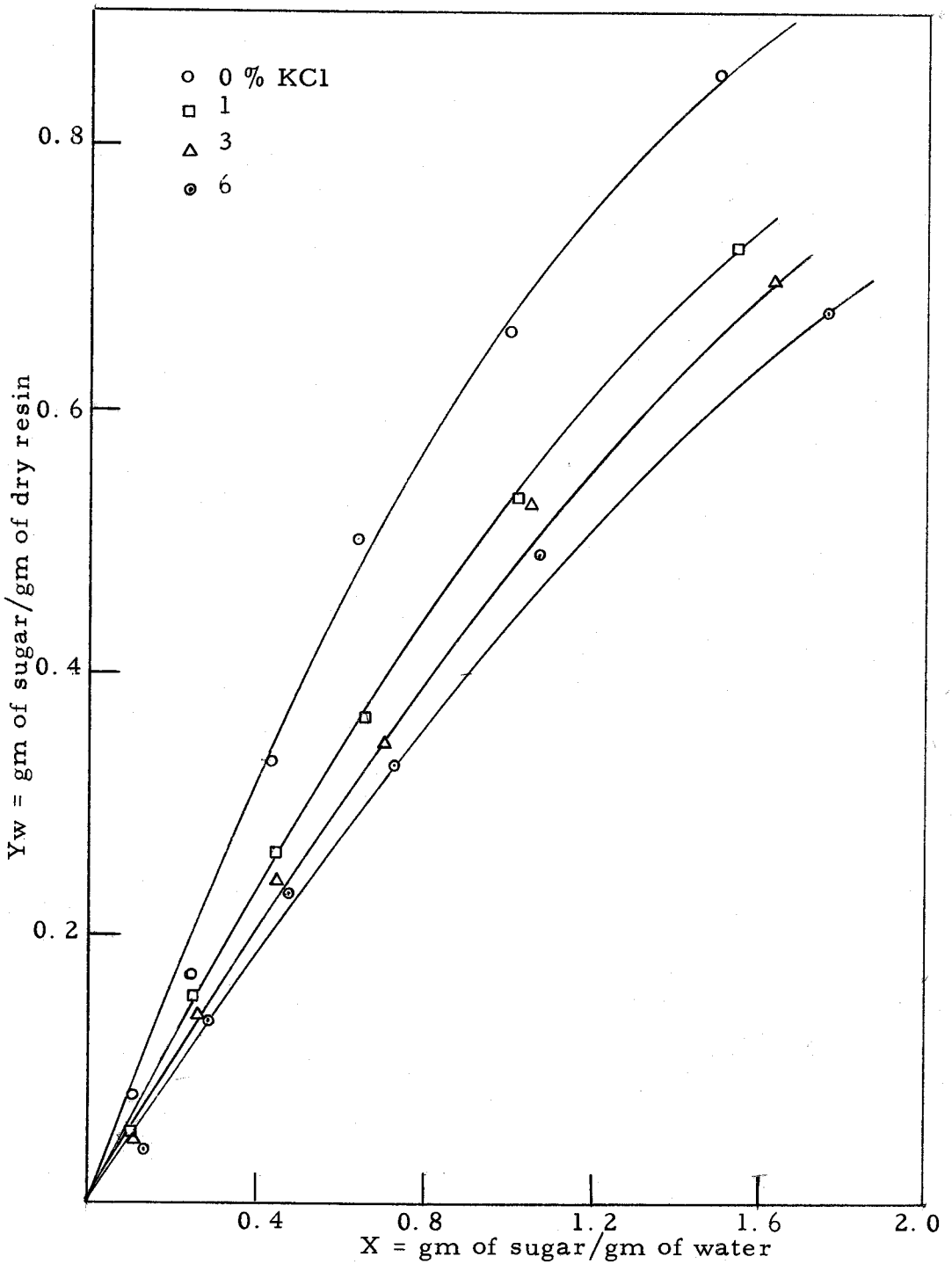


Figure 5. Equilibrium isotherms (weight basis) for sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C.

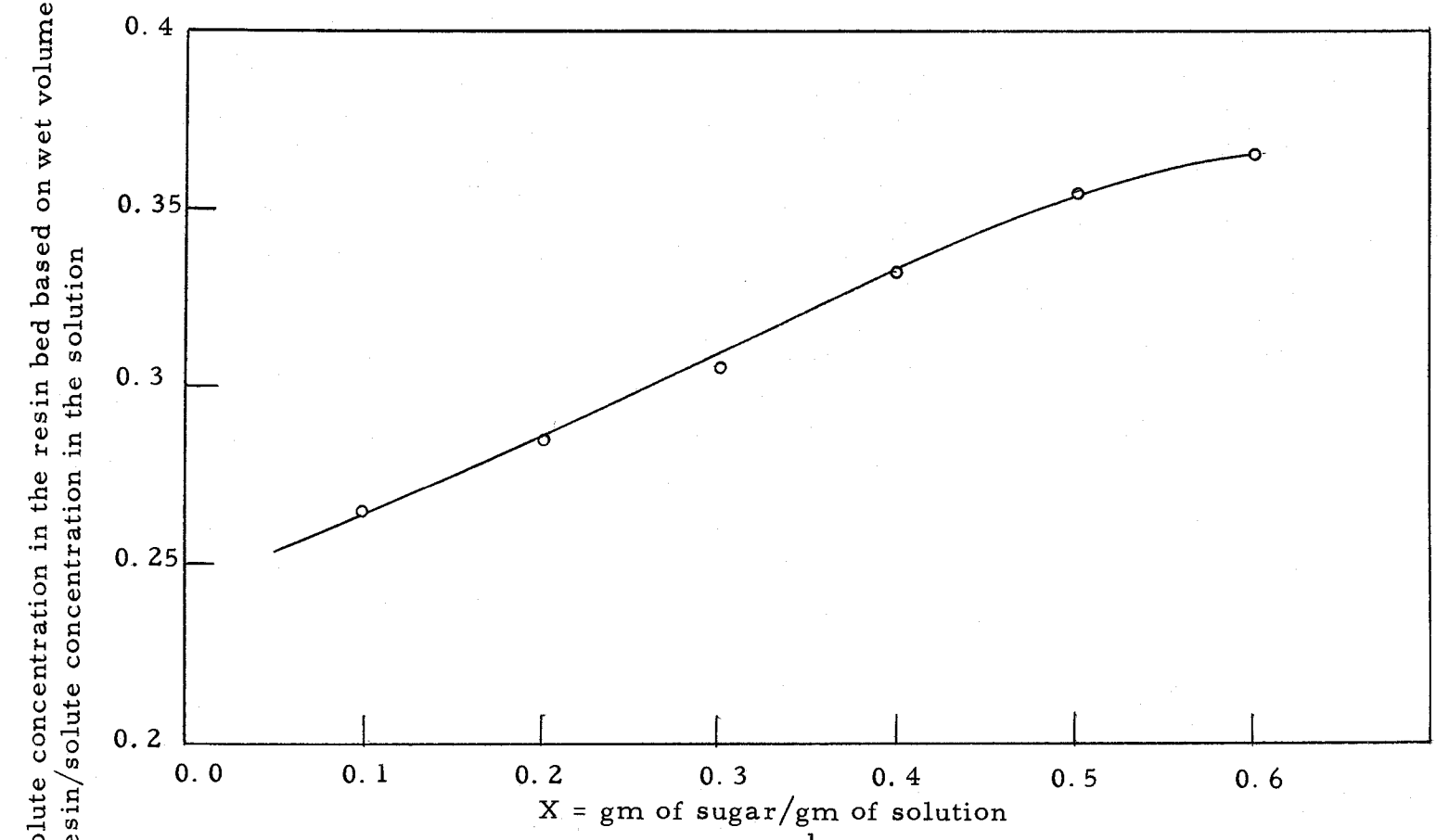


Figure 6. Modified distribution coefficient (K_d^1) as a function of sugar concentration for the sucrose-water system on Dowex 50 W X 4 resin at 90° C.

Table 2. Bulk volume of the resin as a function of solution concentration at 90° C.

Solution		Bulk - Volume ml. of wet resin / gm. of dry resin
Salt % (wt)	Sucrose % (wt)	
0	0	3.20
	10	3.20
	30	3.13
	40	3.16
1	0	3.13
	10	3.10
	30	3.09
	40	3.04
3	0	2.97
	10	2.93
	30	2.91
	40	2.90
6	0	2.83
	10	2.82
	30	2.79
	40	2.67

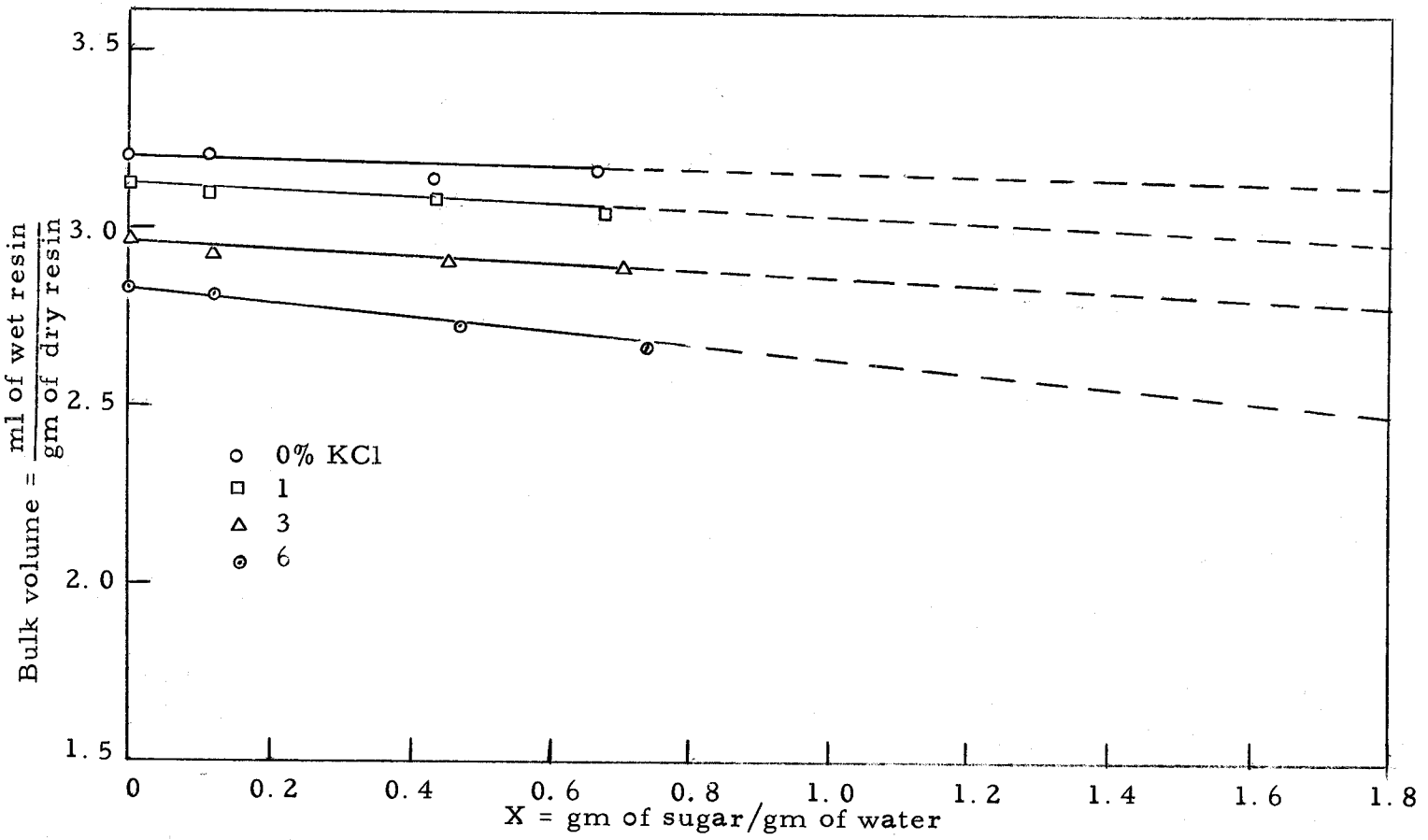


Figure 7. Resin bulk volume as a function of solution solute concentration at 90° C.

Table 3. Equilibrium sucrose concentrations (volume basis) for the sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C.

Solution		Yw	Bulk volume	Yv sugar
				gm of sugar
Salt % (wt)	Sucrose % (wt)	(smoothed value)	(smoothed values)	ml of wet resin (smoothed value)
0	10	0.085	3.19	0.02666
	20	0.19	3.18	0.0597
	30	0.32	3.18	0.1005
	40	0.48	3.16	0.152
	50	0.665	3.15	0.211
	60	0.85	3.13	0.272
1	10	0.065	3.11	0.0209
	20	0.15	3.10	0.0484
	30	0.25	3.08	0.0812
	40	0.384	3.06	0.1255
	50	0.55	3.03	0.1815
	60	0.725	2.98	0.244
3	10	0.06	2.96	0.0203
	20	0.135	2.94	0.046
	30	0.234	2.92	0.08
	40	0.36	2.90	0.124
	50	0.52	2.86	0.182
	60	0.695	2.81	0.247
6	10	0.055	2.81	0.01955
	20	0.13	2.78	0.0468
	30	0.225	2.74	0.0822
	40	0.35	2.68	0.1305
	50	0.512	2.61	0.196
	60	0.674	2.50	0.269

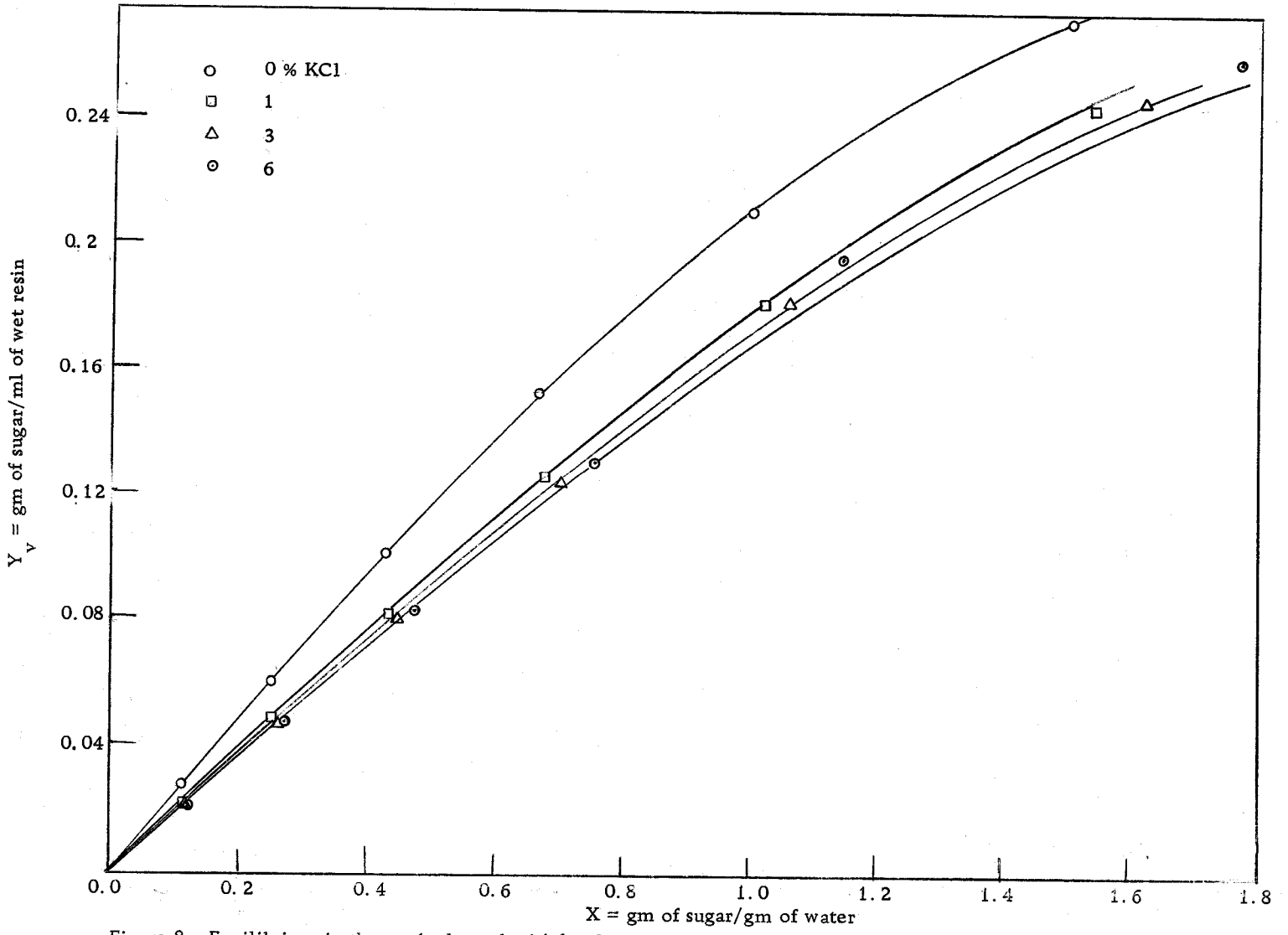


Figure 8. Equilibrium isotherms (volume basis) for the sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C.

Table 4. Equilibrium salt concentrations (weight basis) for the sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C.

Solution		Yw salt gm of salt / gm. of dry resin
Salt % (wt)	Sucrose % (wt)	
1	10	0.0026
	20	0.00331
	30	0.0036
	40	0.0037
	50	0.003764
	60	0.0042
3	10	0.0123
	20	0.0127
	30	0.01354
	40	0.0139
	50	0.016
	60	0.0176
6	10	0.03123
	20	0.03323
	30	0.03634
	40	0 03736
	50	0 0375
	60	0.03913

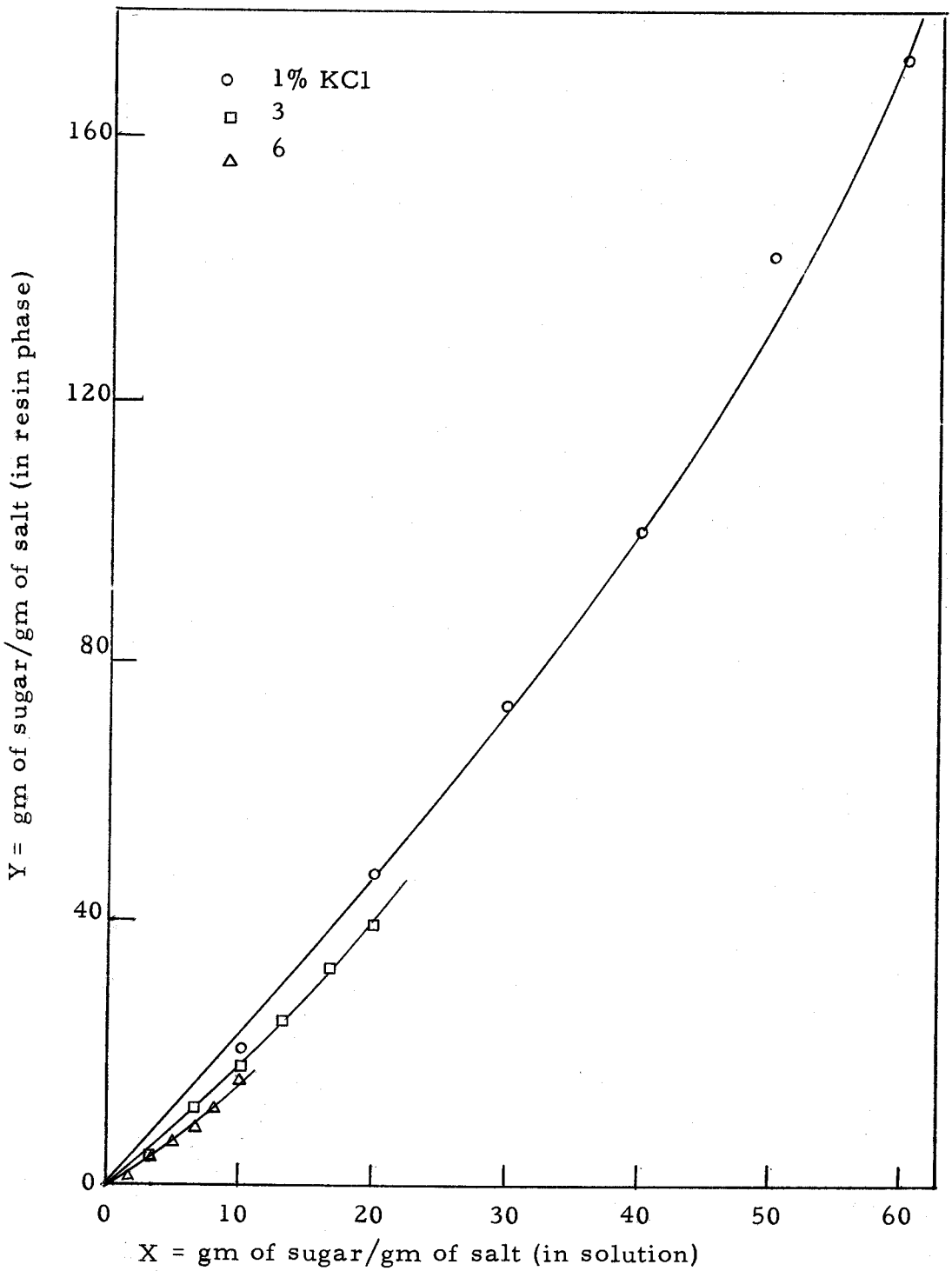


Figure 9. A comparison of the ratio of sucrose to potassium chloride in the resin and in the solution.

SUMMARY

Equilibrium data were determined for the sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C. To obtain a better separation a resin with a higher capacity, lower cross-linkage, and smaller particle size was desirable, and Dowex 50 W X 4, 50-100 mesh resin was selected to meet these criteria.

From this work the following results were obtained:

1. More sucrose was absorbed at higher temperatures, and a temperature of 90° C was selected as desirable.
2. The absorption of sucrose in the resin increased with increasing sucrose concentration in the contacting solution.
3. The modified distribution coefficient, K_d' (the ratio of solute concentration in the resin based on the wet volume of the resin to that in the solution), for sucrose-water solutions increased with increasing sucrose concentration.
4. The presence of salt in the solution decreased the capacity of the resin for sucrose and increased the absorption of salt in the resin.
5. The ratio of sugar to salt was higher in the resin than in the solution; thus, simple batch elution of the equilibrium resin contents could lead to an increase of the sucrose purity.

SUGGESTION FOR FURTHER WORK

It was evident from our results that a good separation was possible, and equilibrium data were obtained. Therefore, a continuous counter-current ion exclusion column should be designed and built so that economic feasibility may be evaluated.

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APPENDICES

APPENDIX A

Sample Calculations

a. Sample calculation for equilibrium in the sucrose-water system

Data from entry (2) in Table 6

Weight of dry resin: 3.8347 gm

Total weight of solution eluted: 332.2 gm

Refractometer readings of eluted solution at 20° C. 21.21

The sugar concentrations at equilibrium conditions were calculated from the above data as follows:

1. Percent sugar (by weight) in solution = 0.898 (from conversion table) (2)

2. Thus, weight of sugar = 0.00898 (332.2)
   = 2.98 gm

3. Therefore $Yw = \frac{\text{gm of sugar absorbed}}{\text{gm of dry resin}} = \frac{2.98}{3.8347}$

   = 0.778

The results are shown in Table 6 for each concentration.

b. Sample calculation for Equilibrium of sucrose-potassium chloride-water system.

Data from entry (6) in Table 7

Weight of dry resin 3.8333

Total weight of solution eluted 275.2 gm

Total weight of solution titrated 269.1 gm

Normality of silver-nitrate solution 0.04936

Volume of titrating solution used 41.3 ml

Refractometer reading of eluted solution at 20° C 21.21

The total solids concentrations at equilibrium conditions was calculated from the above data as follows:

1. Percent total solids (by weight) in solution from conversion table (2) = 1.012

2. Thus, weight of total solids = 0.01012 (275.2)

   = 2.784 gm.

3. Therefore Yw (total solids) = $\frac{\text{gm of total solids absorbed}}{\text{gm of dry resin}}$

   = $\frac{2.784}{3.833}$ = 0.7264

The salt concentration at the equilibrium conditions was calculated from the above data as follows:

1. Amount of salt in the solution = $\frac{(0.04963)(74.55)(41.3)}{1000}$

   = 0.1529 gm.

2. Therefore Yw (total salt) = $\frac{\text{amount of salt absorbed}}{\text{gm of dry resin}}$

   = $\frac{0.1529}{3.833}$ = 0.03988

Yw Total solid = 0.72640

Yw Total salt = 0.03988

Yw Total sugar = 0.68652

The results are shown in Table 7 for each concentration.

c. Sample calculation for modified distribution coefficient (K_d^1) data for the sucrose-potassium chloride-water system on Dowex 50 W X 4 at 90° C.

Data from entry (1) Table 8.

$$\frac{\text{gm of sugar}}{\text{gm of solution}} = 0.1$$

Density of the solution at 90° C. = 1.00698
(Ref. 10)

$$A = \frac{\text{gm of sugar}}{\text{ml of solution}} = 0.1\ (1.00698) = 0.1007 = A$$

$B = Yv = 0.02666$ (Ref: Table 3. Salt 0% Sugar 10%)

$$\text{Modified Distribution Coefficient} = \frac{B}{A} = \frac{0.02666}{0.1007}$$

$$= \underline{0.265}$$

APPENDIX B

Table 5. Bulk volume of the resin for the water-Dowex 50 W X 4 system at room temperature.

Wet volume in ml A	Weight of dry resin, gm B	Bulk volume = wet volume in ml / gm. of dry resin A/B	Average of three readings Bulk - Volume
59.8	19.923	3.0	
73.5	23.721	3.1	3.05
92.0	30.198	3.05	

Table 6. Equilibrium sucrose concentrations as a function of temperature for the sucrose-water-Dowex 50 W X 4 system.

Sucrose (%) wt.	Temperature °C.	Yw sugar gm. of sugar / gm. of dry resin A	B	Average of A & B
1) 60	60	0.755	0.75	0.75
2)	70	0.78	0.778	0.778
3)	80	0.792	0.776	0.784
4)	85	0.8269	0.8299	0.8284
5)	90	0.8515	0.8555	0.8535

Table 7. Equilibrium data (weight basis) for the sucrose-potassium chloride-water system on Dowex 50 W X 4 resin at 90° C.

Solution				gm of sugar			gm of salt
Salt	Sugar	Yw sugar		gm of dry resin	Yw salt		gm of dry resin
% wt.	% wt.	A	B	Average of A & B	A	B	Average of A & B
0	10	0.07329	0.07593	0.07461			
	20	0.1641	0.1798	0.1720			
	30	0.3278	0.3294	0.3286			
	40	0.5014	0.4993	0.5004			
	50	0.6488	0.6645	0.6567			
	60	0.8379	0.8732	0.8535			
1	10	0.0544	0.0528	0.0531	0.002316	0.002956	0.0026
	20	0.184	0.126	0.155	0.003173	0.00343	0.00331
	30	0.2581	0.2675	0.262	0.00361	0.0036	0.0036
	40	0.372	0.364	0.368	0.00381	0.0036	0.0037
	50	0.5212	0.5504	0.5358	0.003689	0.003839	0.003764
	60	0.720	0.727	0.724	0.004202	0.004196	0.0042
3	10	0.0497	0.0473	0.048	0.0134	0.0114	0.01229
	20	0.146	0.145	0.144	0.01203	0.01329	0.01266
	30	0.256	0.123	0.246	0.01457	0.01251	0.01354
	40	0.354	0.332	0.346	0.01344	0.01439	0.01389
	50	0.537	0.509	0.528	0.01728	0.01468	0.01598
	60	0.727	0.686	0.70	0.0181	0.0173	0.0176

Table 7 Continued.

Solution				gm of sugar			gm of salt
Salt	Sugar	Yw sugar		gm of dry resin	Yw salt		gm of dry resin
% wt.	% wt.	A	B	Average of A & B	A	B	Average of A & B
6	10	0.03737	0.03452	0.03595	0.03039	0.03213	0.03123
	20	0.1342	0.1503	0.1422	0.03369	0.03276	0.03323
	30	0.2244	0.2447	0.2346	0.03958	0.0331	0.03634
	40	0.3246	0.3310	0.3278	0.03823	0.03649	0.03736
	50	0.4998	0.4778	0.4888	0.03749	0.03728	0.03739
	60	0.6865	0.6676	0.6770	0.03988	0.03837	0.03913

Table 8. Modified distribution coefficient (K_d^1) for the sucrose-water system on Dowex 50 W X 4 resin at 90° C.

Run no.	gms of sugar / gms of soln.	gms of sugar / ml of soln. (A)	Yv sugar (smooth value) gm of sugar / ml of wet resin (B)	K_d^1 B/A
1)	0.1	0.1007	0.02666	0.265
2)	0.2	0.2098	0.0597	0.285
3)	0.3	0.3282	0.1005	0.306
4)	0.4	0.4568	0.152	0.333
5)	0.5	0.597	0.211	0.354
6)	0.6	0.750	0.272	0.363

Table 9. Resin volume as a function of solution solute concentration for the sucrose-potassium chloride-water system on Dowex 50 W X 4 at 90° C.

Solution			Bulk - Volume ml of wet resin / gm of dry resin		
Salt % wt.	Sucrose % wt.	X = gm of sugar / gm of water	A	B	Average of A & B
0	0	0	3.24	3.15	3.20
	10	0.11	3.26	3.14	3.20
	30	0.43	3.17	3.09	3.13
	40	0.665	3.22	3.1	3.16
1	0	0	3.17	3.08	3.13
	10	0.112	3.14	3.05	3.10
	30	0.435	3.13	3.06	3.09
	40	0.678	3.08	2.99	3.04
3	0	0	3.0	2.93	2.97
	10	0.115	2.95	2.90	2.93
	30	0.448	2.96	2.86	2.91
	40	0.702	2.89	----	2.90
			2.91		
6	0	0	2.86	2.79	2.83
	10	0.119	2.86	2.78	2.82
	30	0.47	2.82	2.76	2.79
	40	0.74	2.72	2.62	2.67

Table 10. The ratio of sugar to salt in the resin and in the solution.

Solution		(X)		In solution	Yw sugar	Yw salt	In resin
		gm of sugar	gm of salt	gm of sugar / gm of salt	gm of sugar	gm of salt	gm of sugar / gm of salt
Salt % wt.	Sugar % wt.	gm of water A	gm of water B	in solution A/B	gm of resin (C)	gm of resin (D)	in resin (C/D)
1	10	0.112	0.0112	10	0.053	0.0026	20.4
	20	0.253	0.01265	20	0.155	0.00331	46.7
	30	0.435	0.0145	30	0.262	0.0036	72.8
	40	0.678	0.01695	40	0.368	0.0037	99.5
	50	1.02	0.0204	50	0.536	0.003764	142.5
	60	1.54	0.0256	60	0.724	0.0042	172.5
3	10	0.115	0.0345	3.33	0.048	0.0123	3.9
	20	0.26	0.039	6.67	0.144	0.0127	11.4
	30	0.448	0.0448	10.00	0.246	0.01354	18.18
	40	0.702	0.0526	13.28	0.346	0.0139	24.9
	50	1.06	0.0638	16.6	0.526	0.016	33.1
	60	1.62	0.081	20.0	0.70	0.0176	39.8
6	10	0.119	0.0715	1.665	0.036	0.03123	1.15
	20	0.27	0.081	3.34	0.142	0.03323	4.28
	30	0.47	0.0937	5.01	0.235	0.03634	6.46
	40	0.74	9.11	6.73	0.328	0.03736	8.78
	50	1.14	0.136	8.38	0.489	0.0375	13.0
	60	1.77	0.1765	10.04	0.677	0.03913	17.3

APPENDIX C

Table 11. Typical analysis of beet molasses. (12)

	%	Inorganic Constituents	%
Water	16.5	Silica	0.1
Total Solids	83.5	Potassium	3.9
Organic Constituents		Sodium	1.3
Sucrose	51	Iron oxide	0.02
Raffinose	1	Aluminum oxide	0.01
Invert sugar	1	Calcium	0.26
Glutamic acid	3.5	Magnesium	0.16
Other protein	5.5	Sulfate	0.55
Other organic	10.0	Phosphate	0.06
		Chloride	1.6
		Carbonate	3.5 (22)
Total	72.0	Total	11.5