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REGENERATION OF BASIC SORBENTS USED IN THE RECOVERY OF ACETIC ACID FROM DILUTE AQUEOUS SOLUTION

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Regeneration of Basic Sorbents Used in the Recovery of Acetic Acid from Dilute Aqueous Solution

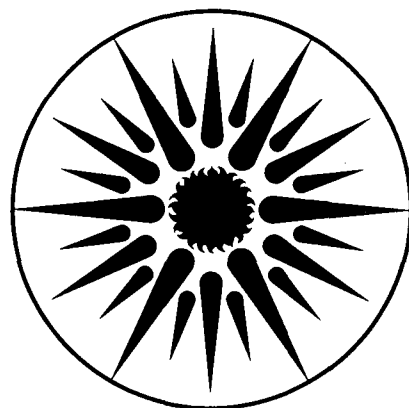M. Ng* and C.J. King
*(M.S. Thesis)

October 1988

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REGENERATION OF BASIC SORBENTS USED IN THE RECOVERY OF

ACETIC ACID FROM DILUTE AQUEOUS SOLUTION

MINDY NG

and

C. JUDSON KING

OCTOBER 1988

APPLIED SCIENCES DIVISION

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REGENERATION OF BASIC SORBENTS USED IN THE RECOVERY OF

ACETIC ACID FROM DILUTE AQUEOUS SOLUTION

MINDY NG

ABSTRACT

The regeneration of basic sorbents used in the recovery of dilute aqueous acetic acid was explored. The regeneration methods studied were solvent leaching and vaporization. The resins used were weak base anion exchange resins, Dow Chemical Company's Dowex MWA-1 (tertiary amine resin) and Celanese Corporation's Aurorez (polybenzimidazole resin).

The equilibrium between the aqueous acetic acid solution and the resins was measured in batch experiments. The composite isotherms calculated from these data were comparable to those of other researchers.

Methanol was used as the solvent to leach acetic acid from the resin. The equilibrium data from the batch experiments were used in the local-equilibrium theory of fixed-bed devices to model the desorption behavior of acetic acid in methanol. Both sorption and desorption equilibrium data were used in chemical complexation models to obtain sorption affinities and capacities of the resin for acetic acid. However, the amount of methanol needed to achieve a high degree of regeneration was too large to be economical.

Thermal regeneration of the resins at 100 C was also studied. For Dowex MWA-1, both batch and fixed-bed behavior were studied. The effects of the air temperature and flow rate on the rate of vaporization of acetic acid in the fixed bed were investigated. For Aurorez, the interesting phenomenon of pore closing, which occurs during vaporization of polar solvents from the sorbent, led to a study of the displacement of the polar solvents by increasingly nonpolar solvents before vaporization. Several alcohols were investigated in batch experiments as the initial displacer used, followed by toluene as the second displacer. The alcohols studied were methanol, ethanol, n-propanol, isopropanol and tert-butanol. Thermal regeneration at 100 C for two hours was then carried out to vaporize the toluene and return the resin to its original state. Sorption isotherms measured after thermal regeneration were found comparable to those measured initially for both resins.

DEDICATION

To my mother:

whose example and sacrifices

enabled all her children

to be what they are.

ACKNOWLEDGEMENTS

Because no man is an island, no work is completed without the guidance and inspiration of those around us. I would like to thank Professor C.J. King for all the invaluable help he has given me in the past two years. My thanks also goes to Dr. Hanson and Dr. Porter for their time and advice in producing this thesis.

I am especially grateful to the members of my research group and my friends for their friendship and assistance in my research. Without Dan Arenson, Bob Fields, Tony Garcia, Terry Grant, Baishen Liang, Loree Poole, Bill Rixey, Mark Smith, Jack Starr, Janet Tamada, Dave Wallack, Judith Bourzutschky and Michael Mead, my stay at Berkeley would not have been as educational, pleasant and short as it was.

And above all, I am indebted to my family whose constant love and support have always and will always help me to reach my goals.

Mindy Ng

Berkeley, CA

September, 1988

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1 INTRODUCTION

When the cost of petroleum rises, as it inexorably must over the next few decades, biological processes will become increasingly attractive for the production of organic chemicals such as carboxylic acids. The major cost involved in many biological processes is the recovery and purification of the product. The high cost results from the relatively dilute and complex solutions produced and from the sensitivity of biological systems to chemical and heat contamination.

Acetic acid is one of the carboxylic acids which can be produced by fermentation. An aqueous fermentation exit solution generally has a concentration of 1-5 weight percent product[1]. Since the relative volatility of water to acetic acid is close to one at these concentrations, conventional distillation is not a preferred recovery scheme[2]. Current commercialized alternative recovery methods include azeotropic distillation and solvent extraction followed by azeotropic distillation[2]. One of the many recovery schemes currently being investigated is the use of solid sorbents with basic chemical functional groups which will preferentially complex with carboxylic acids. Sorption has a potential advantage over solvent extraction because recovery is possible without chemical contamination of recycle streams. It should be possible to accomplish regeneration and product recovery without chemically changing the product.

To keep the cost of any recovery scheme low, the separating agents used should be regenerable. The focus of this work is the regeneration of

basic sorbents used in the recovery of acetic acid from dilute aqueous solution. Solvent leaching and vaporization of acetic acid are the two methods explored. The two resins used are weak base anion exchange resins, Dow Chemical Company's Dowex MWA-1 (tertiary amine) and Celanese Corporation's Aurorez (polybenzimidazole). Previous work on other tertiary amine resins indicates that elution of carboxylic acids by methanol is slow and incomplete[3,4,5]. Therefore other methods of regeneration, such as vaporization, are of interest for tertiary amine resins such as Dowex MWA-1. Aurorez is of interest for thermal regeneration because it has a higher maximum operating temperature (588 C) than most other resins (100 C or less). By extension, this work should be applicable to recovery of other carboxylic acids as well.

2.2 RESIN PRETREATMENT

Both sorbents were pretreated to remove any impurities. The resins were washed with water, methanol, 0.05 N hydrochloric acid and 0.05 N sodium hydroxide successively. After the sodium hydroxide wash, the resins were extracted for at least 24 hours in a soxhlet device with methanol and were dried in a 100 C vacuum oven for at least 48 hours. The dried resins were stored in sealed bottles. All chemicals used and their properties are listed in Appendix A.

3 SORPTION AND SOLVENT REGENERATION OF ACETIC ACID

3.1 EXPERIMENTAL EQUIPMENT AND PROCEDURE

For the sorption part of the experiment, the dry resin was equilibrated with aqueous acetic acid solution in a 10 to 1 weight ratio of solution to dry resin. Equilibration took place in a shaker bath (Precision Corporation) at room temperature for at least 48 hours at the natural pH of the solution. Equilibrium for both sorbents should be approached closely after 20 hours[5].

The total solution uptake at equilibrium was determined by weighing the acid-loaded resin after centrifugation (Damien/International Equipment Company) at 2000 rpm for 10 minutes in a fine grade 15 ml fritted glass funnel enclosed in a plastic centrifuge tube. Most of the removable interstitial fluid comes off under these conditions[9].

Colorimetric titration with aqueous sodium hydroxide and with phenolphthalein as the indicator was used to determine the equilibrium solution concentration of acetic acid. The acid-loaded resin was then put into a clean vessel, and methanol was added in various weight ratios. Equilibration and analysis were done as described above for sorption of acetic acid. Equilibrium should be approached closely after 24 hours[5]. A potentiometric Karl Fischer titrator (Quintel Corporation) was used to determine the equilibrium concentration of water in the solvent.

3.2 ISOTHERMS FOR THE SORPTION AND SOLVENT REGENERATION
OF ACETIC ACID

Two types of isotherms, composite and individual, are generally used in the analysis of solid-liquid equilibrium data.

The composite uptake is defined as:

$$\frac{W_o (C_i - C_f)}{m} \qquad (1)$$

where W_o : initial weight of the liquid (g)

C_i : initial weight fraction of solute in

solution (g solute/g solution)

C_f : final weight fraction of solute in solution

(g solute/g solution)

m : weight of dry resin (g)

The composite isotherm is a measure of the preferential uptake of the solute over the solvent by the sorbent.

The individual uptake is defined as:

$$\frac{W_o C_i - W_f C_f}{m} \qquad (2)$$

where W_f : final weight of the liquid (g)

(as determined after centrifugation)

The above definition of the individual isotherm assumes that the adsorbate is any liquid retained by the resin after centrifugation in

the form of interstitial fluid, as well as selectively and nonselectively imbibed liquid. Other possible assumptions of the boundaries of the adsorbed material are discussed by Kipling[10].

The weight of the bulk liquid changes due to pore filling and sorption of acetic acid and wat_r by the resin. This change is reflected in the difference between the individual and composite isotherm. The individual uptake is always greater than the composite uptake.

Measured isotherms are presented in Figures 2 and 3 for sorption of acetic acid from aqueous solution. For the two resins investigated, the difference between the individual and composite isotherm increased as the solution concentration of acetic acid increased in the concentration range studied. This increase resulted from greater solution uptake by the swelling polymers. The difference in the two isotherms was greater for Aurorez than for Dowex MWA-1, indicating that Aurorez imbibed more liquid in its pores. Although Aurorez imbibed more liquid in the pores, it adsorbed less acetic acid per gram of resin than Dowex MWA-1. The isotherms measured for both resins were comparable to results obtained by other researchers. The differences within each type of isotherm were probably due to the different batches of resins used. In Figure 2, 1 and 2 refer to the different batches of Dowex MWA-1 used in this work.

Measured isotherms for regeneration by methanol are shown in Figures 4 and 5. Leaching of sorbed acetic acid by methanol was found to be more effective for Aurorez than for Dowex MWA-1. A comparison of Figures 4

FIGURE 2. ISOTHERMS FOR SORPTION OF ACETIC ACID FROM WATER BY DOWEX MWA-1

LEGEND
■ This work, 1-individual
+ This work, 1-composite
◇ This work, 2-individual
△ This work, 2-composite
× Garcia-individual (11)
▽ Garcia-composite (11)

UPTAKE (g acetic acid/g resin)

EQUILIBRIUM SOLUTION CONCENTRATION (wt% acetic acid)
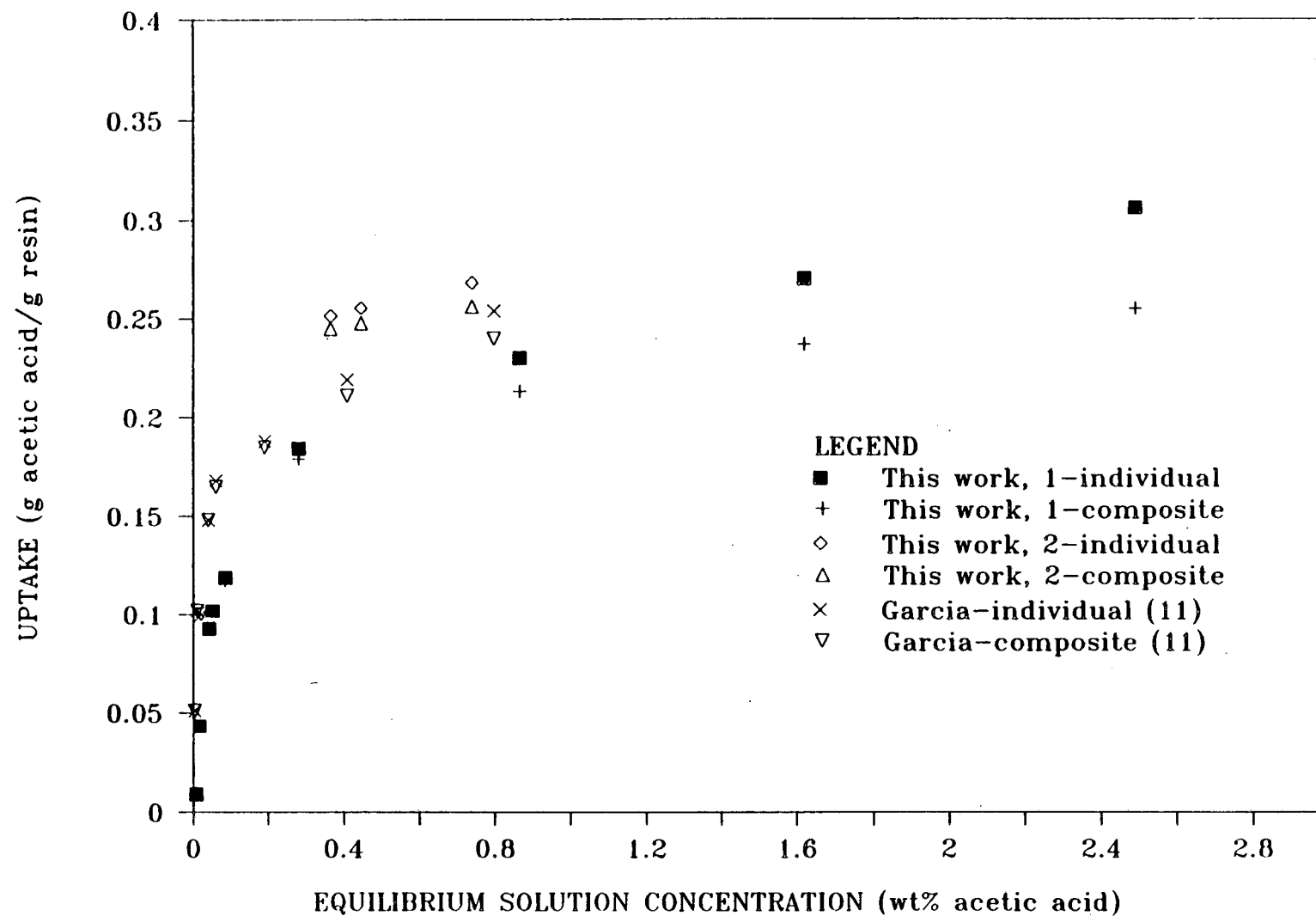
FIGURE 3. ISOTHERMS FOR SORPTION OF ACETIC ACID FROM WATER BY AUROREZ

LEGEND
■   This work—individual
+   This work—composite
◇   Garcia—individual (11)
△   Garcia—composite (11)
×   Chanda, O'Driscoll and Rempel (8)

UPTAKE (g acetic acid/g resin)

EQUILIBRIUM SOLUTION CONCENTRATION (wt% acetic acid)
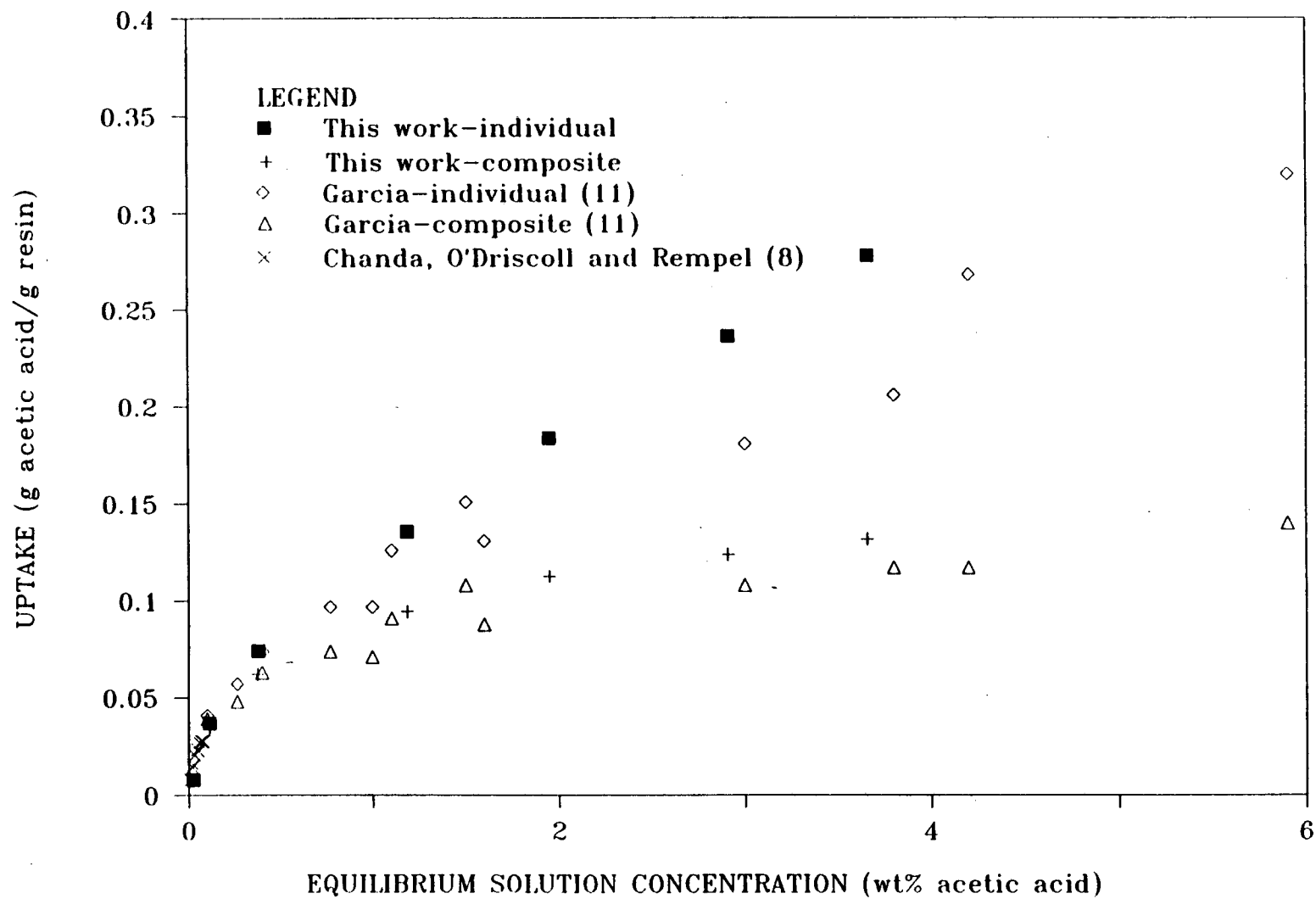
FIGURE 4. COMPOSITE ISOTHERM FOR METHANOL REGENERATION
OF ACETIC ACID FROM DOWEX MWA−1
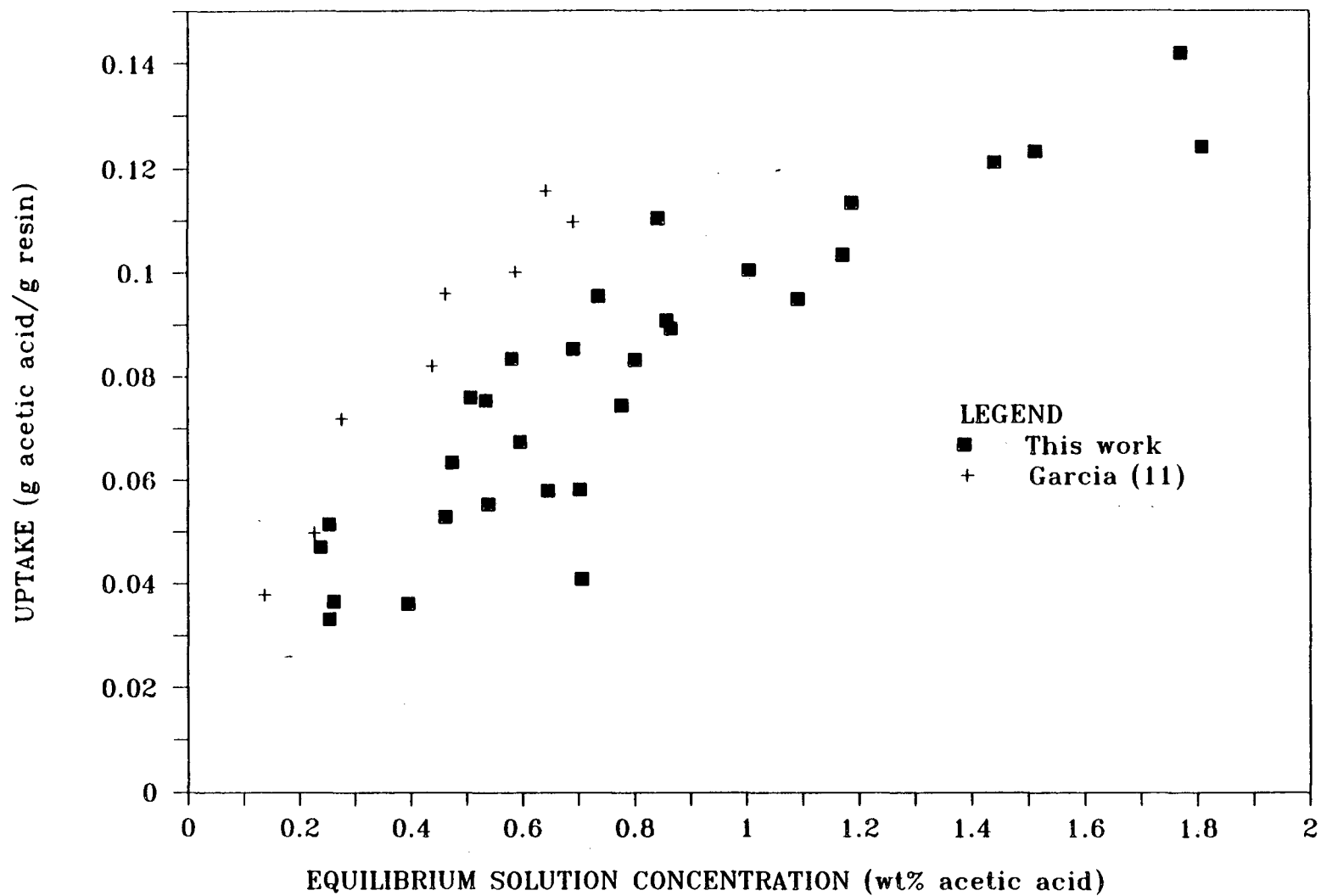
FIGURE 5. COMPOSITE ISOTHERM FOR METHANOL REGENERATION
OF ACETIC ACID FROM AUROREZ
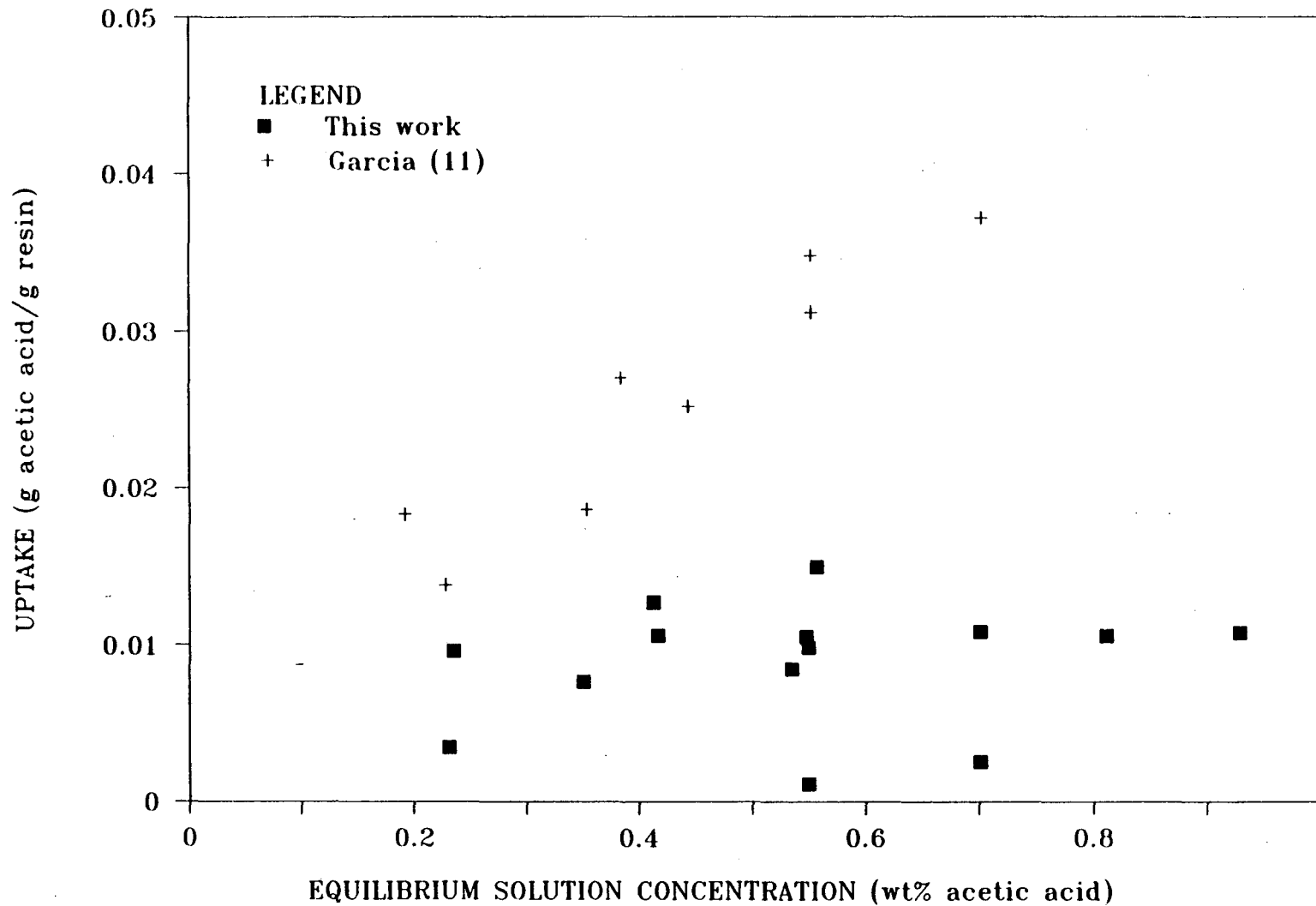
and 5 shows a greater partitioning of the acetic acid to the Dowex MWA-1 resin phase than to the Aurorez resin phase at the same equilibrium acetic acid concentration in the solvent. The greater amount of easily leached liquid in the pores and the weaker interaction with the functional group both contribute to the more effective regeneration of Aurorez. Because the degree of regeneration of acetic acid by methanol from Aurorez was relatively high, some of the difference between the composite isotherms measured by different researchers for methanol regeneration of Aurorez may be the result of taking the difference between two numbers that were relatively close in value. For both resins, the regeneration of water was greater than 80% and apparently independent of the amount of acetic acid present for the concentration range studied.

For both resins, batch methanol regeneration was found to be an unattractive recovery scheme. The amount of methanol needed to achieve a high degree of regeneration is too large. To achieve 70% regeneration of acetic acid from Dowex MWA-1 that had been at equilibrium with a 2.5 weight percent aqueous acetic acid solution, a 35:1 weight ratio of methanol to resin was needed. For Aurorez that had been at equilibrium with a 3 weight percent aqueous acetic acid solution, a 30:1 weight ratio of methanol to resin was needed to achieve 75% regeneration of the acetic acid.

Previous work on other tertiary amine resins such as Dow Chemical Company's Dowex WGR[3] and Rohm and Haas Company's Amberlite IRA-45[4], indicates that methanol elution of carboxylic acids from these resins

in a fixed bed is slow and incomplete. The high basicity of amine resins makes reversing the acetic acid-amine complex difficult[3]. Given the amount of methanol needed to achieve a high degree of regeneration in the batch studies and the results from fixed-bed studies of solvent leaching of other tertiary amine resins[3,4], fixed-bed elution of acetic acid by methanol is not expected to be an effective regeneration method for Dowex MWA-1.

Chanda, et al. also investigated the sorption of carboxylic acids from dilute aqueous solution by Aurorez, as well as regeneration[8]. One of the carboxylic acids studied was acetic acid at equilibrium solution concentrations of less than 0.08 weight percent. The regeneration method studied by Chanda, et al. was stripping of carboxylic acid from the resin with 0.1M aqueous sodium hydroxide solution at 25. C. They found that within one minute, the regeneration of the resin was over 95% complete for all carboxylic acids studied. Although this regeneration process is rapid and complete, the end product of acetic acid regeneration, sodium acetate, is generally not the desired product.

3.3 THE IDEAL EXCHANGE MODEL

A simple model, the ideal exchange model, can be used to calculate the sorption affinities of acetic acid and the capacity of the resin[5].

The model assumes that a 1:1 complex is formed between the acetic acid and the basic functional group and is described by the pseudo-chemical reactions:

$$HOAc_{(1)} + H_2O_n\text{-}B \dashrightarrow nH_2O_{(1)} + HOAc\text{-}B \qquad (3)$$
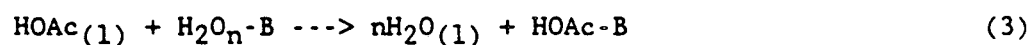
    for sorption of acetic acid from water

and

$$HOAc\text{-}B + mS_{(1)} \dashrightarrow S_m\text{-}B + HOAc_{(1)} \qquad (4)$$
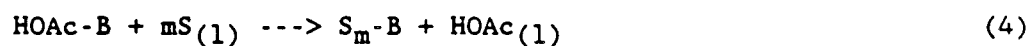
    for desorption of acetic acid by a solvent

where HOAc : acetic acid

    H_2O : water

    B   : basic functional group

    S   : solvent

    l   : liquid (bulk) phase

    n   : number of water molecules needed for complexation with the basic site

    m   : number of solvent molecules needed for complexation with the basic site

In this model, the "bond" is a representation of a complexation interaction and not of a covalent bond. In the second reaction, effects due to the simultaneous presence of water are ignored.

By assuming 1) solvent activity is constant over the range of interest,

2) ratio of remaining activity coefficients is constant,

3) all basic sites are uniform (i.e. equally accessible and basic),

4) number of accessible basic sites remains constant,

5) effect of water on the desorption is negligible, and

6) acid-base complex is reversible in the desorption,

then the equilibrium constants are

$$K_1 = \frac{[HOAc\text{-}B]\ [H_2O_{(1)}]^n}{[HOAc_{(1)}]\ [H_2O_n\text{-}B]} \tag{5}$$

and

$$K_2 = \frac{[HOAc_{(1)}]\ [S_m\text{-}B]}{[HOAc\text{-}B]\ [S_{(1)}]^m} \tag{6}$$

leading to

$$\frac{q}{q_m} = \frac{K_s\ C_{HOAc}}{1 + K_s\ C_{HOAc}} \tag{7}$$

where

$$K_s = \frac{K_1}{[H_2O]^n} \tag{8}$$

or

$$\frac{C_{HOAc}}{q} = \frac{C_{HOAc}}{q_m} + \frac{1}{q_m\ K_s} \tag{9}$$

and

$$\frac{q_r}{q_{mr}} = \frac{C_{HOAc}}{K_r + C_{HOAc}} \tag{10}$$

where

$$K_r = [S]^m K_2 \tag{11}$$

or

$$\frac{C_{HOAc}}{q_r} = \frac{C_{HOAc}}{q_{mr}} + \frac{K_r}{q_{mr}} \tag{12}$$

where K_1 : equilibrium constant for exchange between acetic acid and

water [(meq water/g solution)^n/(meq acetic acid/g

solution)]

K_2 : equilibrium constant for exchange between acetic acid and

methanol [(meq acetic acid/g solution)/(meq solvent/g

solution)^m]

K_s : sorption affinity for acetic acid in water

(g solution/meq acetic acid)

K_r : sorption affinity of acetic acid in methanol

(meq acetic acid/g solution)

C_{HOAc} : concentration of acetic acid in the bulk solution phase

(meq acetic acid/g solution)

q : composite uptake of acetic acid in sorption

(meq acetic acid/g resin)

q_r : composite uptake of acetic acid in desorption

(meq acetic acid/ g resin)

q_m : number of basic sites available on resin for acetic

acid in the sorption process

(meq of sites/g resin)

q_{mr} : number of basic sites available on resin for acetic

acid in the desorption process

(meq sites/g resin)

The affinities and capacities calculated from the model are listed in

Table II.

TABLE II. IDEAL EXCHANGE MODEL-SORPTION AFFINITIES AND RESIN CAPACITIES

	Dowex MWA-1		Aurorez	
	q	K	q	K
Theoretical*	4.3	----	5.7/2.7	----
Model-Sorption				
Garcia[5]	4.9	64	2.2	15
This work	4.4	50	2.1	13
Model-Regeneration				
Garcia[11]	3.8	----	1.0	----
This Work	4.2	0.27	0.4	0.09

*For Aurorez, the capacity as measured by the uptake of HCl is 2.7 meq acetic acid/g resin[5] and the theoretical value is 5.7 meq acetic acid/g resin[8].

A test of any model is how well the calculated values agree with the

expected values. The sorption affinity and capacities calculated for

Dowex MWA-1 agreed well with the theoretical capacity and the values

calculated by Garcia for both sorption and regeneration. For sorption

of acetic acid from water by Aurorez, there is good agreement between

the values calculated by Garcia and this work. Both capacities were

much lower than the theoretical value but close to the measured value.

The lowered capacity was the result of pore closing which occured in

the drying of polar solvents from Aurorez[12]. In the pretreatment, the

resin was dried extensively after extraction with methanol. The drying

history of the resin would affect its capacity.

For the methanol regeneration data, the capacity calculated in this work for Aurorez did not agree well with either the theoretical value or the value calculated by Garcia. The calculated capacity was expected to be lower than the theoretical capacity because water, which was ignored in the model, did occupy some of the basic sites. Because water does take up some of the basic sites, the value of the calculated capacity for acetic acid can change depending on the range of water concentration being modelled. The value of the resin capacity cannot be calculated with confidence for the data for methanol regeneration of Aurorez, because the data used in the model did not include the saturation portion of the isotherm. If the data include only the initial, linear portion of the isotherm, equation 12 reduces to a one parameter equation with the resin capacity fixed[5]. Because of the scatter in the sorption and regeneration data, there was also a substantial potential error in the calculated values of the capacity and affinities (Appendix B).

The model agrees more closely with the theoretical resin capacity for Dowex MWA-1 than for Aurorez. For Dowex MWA-1, the drying history of the resin had no effect on the capacity. Because the number of sites occupied by water at the beginning of the regeneration process was smaller for Dowex MWA-1 than for Aurorez, the effect of neglecting the water in the model was probably smaller.

3.4 THE LOCAL-EQUILIBRIUM THEORY OF FIXED-BED DEVICES

Given that most industrial processes are continuous rather than batch, the predicted breakthrough curve for elution of acetic acid from a fixed bed of sorbent by methanol was of interest. Because previous work on other terciary amine resins indicates that elution of carboxylic acids by methanol in a fixed bed is slow and incomplete, elution of acetic acid by methanol from Dowex MWA-1 was not expected to be an efficient regeneration method. A theoretical prediction of the behavior would help to decide whether or not the process is likely to be efficient.

The affinities calculated using the ideal exchange model were used in the local-equilibrium theory[13] to predict the fixed bed behavior for the desorption of acetic acid by methanol.

By assuming 1) all basic functional groups are uniform,

2) ideal behavior in both phases,

3) concentration of acetic acid is the same in the bulk phase and the fluid phase in the pores, and

4) local equilibrium exists at all times at all points between the resin and the adjacent fluid,

then for desorption:

$$\frac{dq}{dc} = \frac{\epsilon}{\rho} \left(\frac{vt}{x} - 1 \right) \tag{13}$$

where q : concentration of acetic acid on the resin

(meq acetic acid/g resin)

c : concentration of acetic acid in the bulk solution

(meq acetic acid/g solution)

ϵ : void fraction of the bed, assumed to be 0.4

ρ : bulk density of the resin (g/cc)

v : interstitial fluid velocity (cm/s)

t : time (s)

x : axial length along the bed (cm)

Recall from the ideal exchange model that:

$$q = \frac{q_m\, c}{K_r + c} \qquad (14)$$

where q_m : capacity of the resin (meq of sites/g resin)

K_r : sorption affinity of acetic acid in methanol

(meq acetic acid/g solution)

then

$$B = \frac{vt}{x} = \frac{\rho}{\epsilon} \cdot \frac{q_m \left(1 - \dfrac{c}{K_r + c} \right)}{K_r + c} + 1 \qquad (15)$$

where B : bed volumes of methanol

The capacity of the resin, q_m, is taken to be the initial concentration of acetic acid on the resin because the effect of water is neglected. It was assumed that only the sites occupied by acetic acid were involved in the interaction with methanol. The sorption affinity for

acetic acid in methanol and resin capacity (for acetic acid in water) calculated from the ideal exchange model were used in applying equation 15.

Table III lists the predicted number of bed volumes of methanol needed for 80%, 90%, and 99.9% regeneration of the resins that had been equilibrated with 1, 3 and 5 weight percent aqueous acetic acid solution (Appendix C).

TABLE III. LOCAL-EQUILIBRIUM THEORY OF FIXED BED DEVICES-BED VOLUMES

Resin	Concentration of aqueous acetic acid solution (weight %)	q_m	$c_{initial}$	% regeneration	B
Aurorez	1	1.43	0.192	80	6.9
				90	7.9
				99.9	8.9
	3	1.82	0.585	80	7.9
				90	9.4
				99.9	11.1
	5	1.92	0.960	80	8.1
				90	9.8
				99.9	11.7
Dowex MWA-1	1	3.93	2.26	80	16.7
				90	20.3
				99.9	24.3
	3	4.23	6.71	80	17.4
				90	21.5
				99.9	26.1
	5	4.30	11.6	80	17.5
				90	21.7
				99.9	26.5

The number of bed volumes of methanol needed for complete regeneration of Dowex MWA-1 is quite large, indicating that fixed bed regeneration

of the resin by methanol is economically unfeasible. Fixed-bed regeneration of Aurorez by methanol appears to be more nearly feasible. However, the capacity for acetic acid of Dowex MWA-1 is twice that of Aurorez. Thus, the amount of methanol needed for fixed-bed regeneration of the same amount of acetic acid from either resin is approximately the same.

The local-equilibrium model sets a lower limit on the number of bed volumes of regenerant required. The methanol must be introduced at a very slow rate in order for local equilibrium to exist throughout the bed. It would be more practical to increase the flow of methanol to increase the driving force for the desorption of acetic acid, which means more methanol will be used. Also as the acetic acid in the resin is removed, the resin shrinks. This may decrease the accessibility of some of the acetic acid/base sites and thus decrease the efficiency of mass transfer between the two phases. Again, either more time or more methanol would be needed to accomplish the regeneration of the resin.

4 THERMAL REGENERATION - BATCH EXPERIMENTS

4.1 VAPORIZATION

4.1.1 EXPERIMENTAL EQUIPMENT AND PROCEDURES

The procedure for the sorption of an initial 3 weight percent aqueous acetic acid solution onto the resin was as described in section 3.1. Batch thermal regeneration was carried out in a vacuum oven (VWR Scientific) at 100 C and 22-24 in. Hg vacuum for various times. There was an ambient air sweep of 250-280 ml/min (Omega Engineering Incorporated rotameter), measured at ambient pressure and temperature.

Analysis of the acetic acid remaining on the resin consisted of titration of the resin with sodium hydroxide and measuring the pH after 48 hours equilibration in the shaker bath (Precision Corporation). The amount of sodium hydroxide added at the inflection point of the pH curve was assumed to be equivalent to the amount of acetic acid remaining on the resin. Runs made using this method with known concentrations of acetic acid on the resins had an error margin of 5%. The amount of water regenerated was assumed to be the difference between the total weight lost and the weight of acetic acid lost. No weight loss was expected due to sources other than acetic acid and water as the resin pretreatment included drying of the resin at the same conditions as the thermal regeneration, for at least 48 hours. Sorption of aqueous acetic acid by the regenerated resin was carried out as described in section 3.1 for the sorption of aqueous acetic acid by the dry resin.

4.1.2 VAPORIZATION OF ACETIC ACID

Batch experiments were carried out for vaporization of acetic acid from Dowex MWA-1 and Aurorez. Results are shown in Figures 6 to 10. Since each point corresponds to a different initial sorbent loading, points marked "initial" are shown as well in Figures 6 and 7. For both resins, there was no significant vaporization of the acetic acid until most of the water had been vaporized (Figures 8 and 9). Since the acid/base complex is stronger for acetic acid than for water, this result was not unexpected. Also, as the water in the pores vaporized, the concentration of acetic acid in the remaining bulk liquid should increase. This could increase the tendency toward formation of acetic acid/base complexes. For Dowex MWA-1, there appeared to be an induction period of two hours during which no acetic acid was vaporized at all. The induction period was probably related to heating up the resin and the liquid in the pores. For Aurorez, there was probably also a similiar induction period of less than two hours.

For Dowex MWA-1, the greatest rate of vaporization appeared to occur between the 4th and 8th hour, and approximately 80% of the acetic acid was vaporized within 24 hours. Sorption of aqueous acetic acid by the regenerated resin showed no change in the composite isotherm, indicating that the resin capacity was not affected by the process (Figure 10). Previous work by Frierman et al[3] showed that complete regeneration was possible at 66 C and 25 mmHg for Dowex MWA-1 equilibrated with a 5 weight percent aqueous acetic acid solution. The capacity of the regenerated resin also showed no change.

FIGURE 6. VAPORIZATION OF ACETIC ACID FROM DOWEX MWA-1
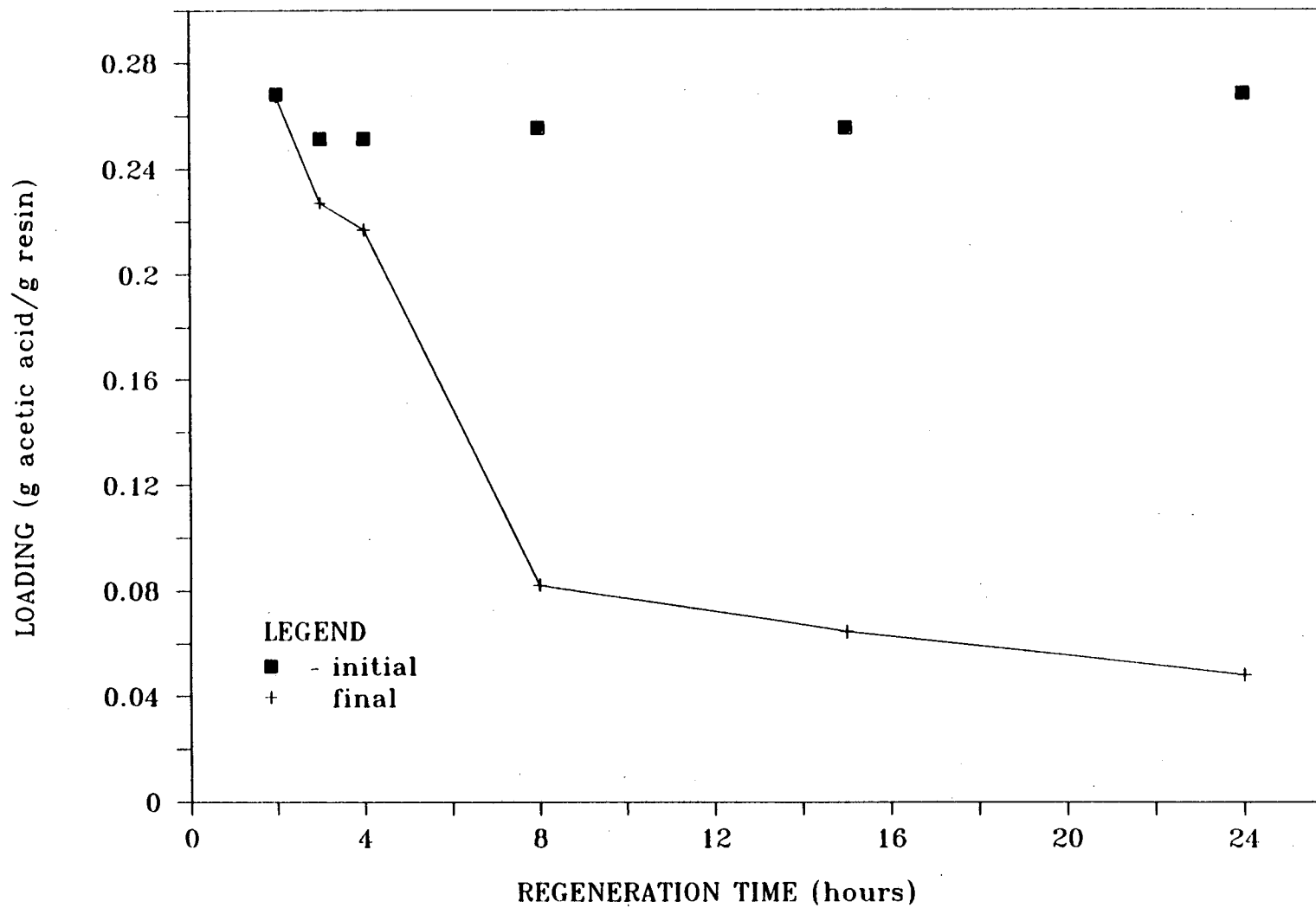
FIGURE 7. VAPORIZATION OF ACETIC ACID FROM AUROREZ
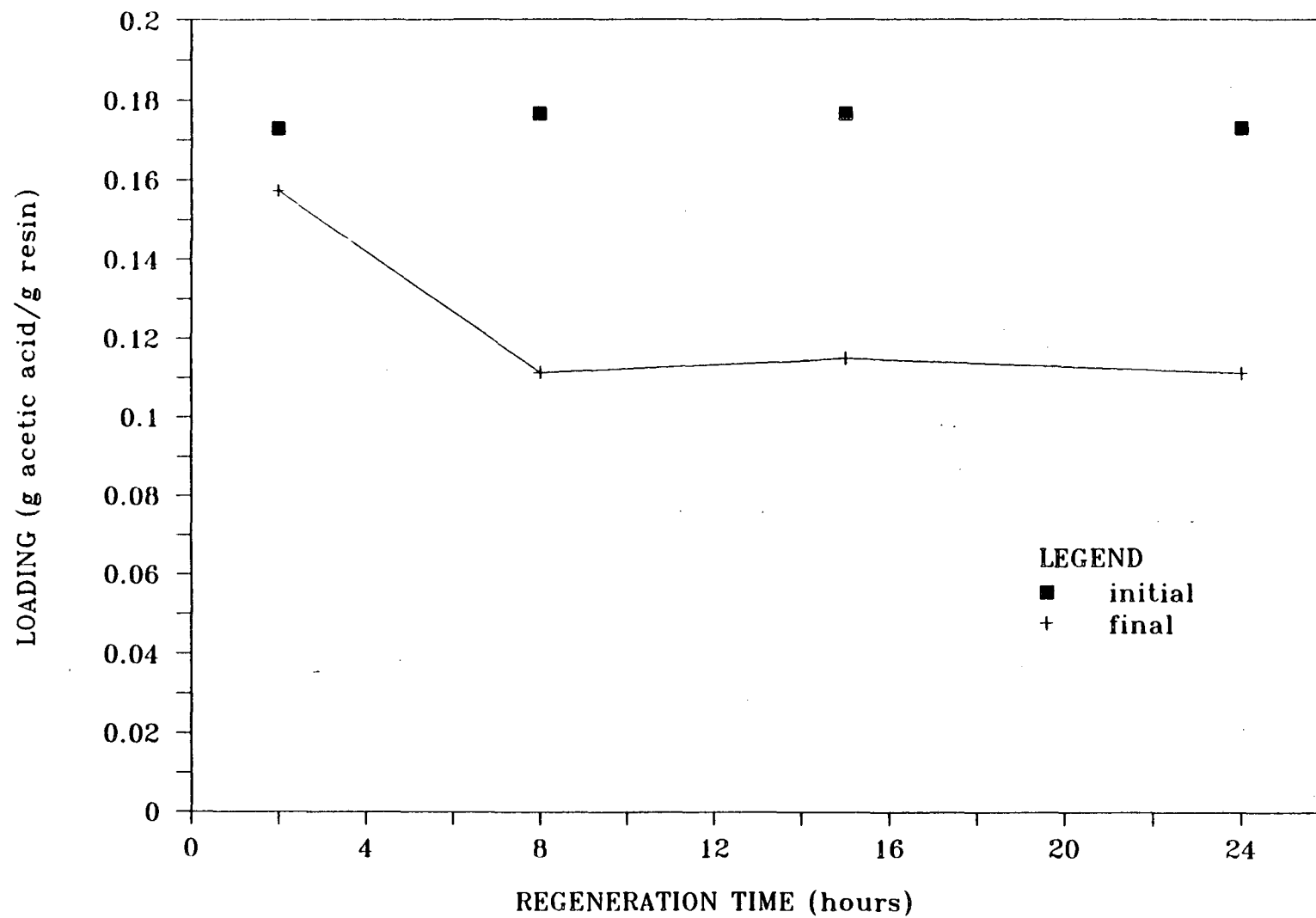
FIGURE 8. VAPORIZATION OF ACETIC ACID AND WATER FROM DOWEX MWA-1
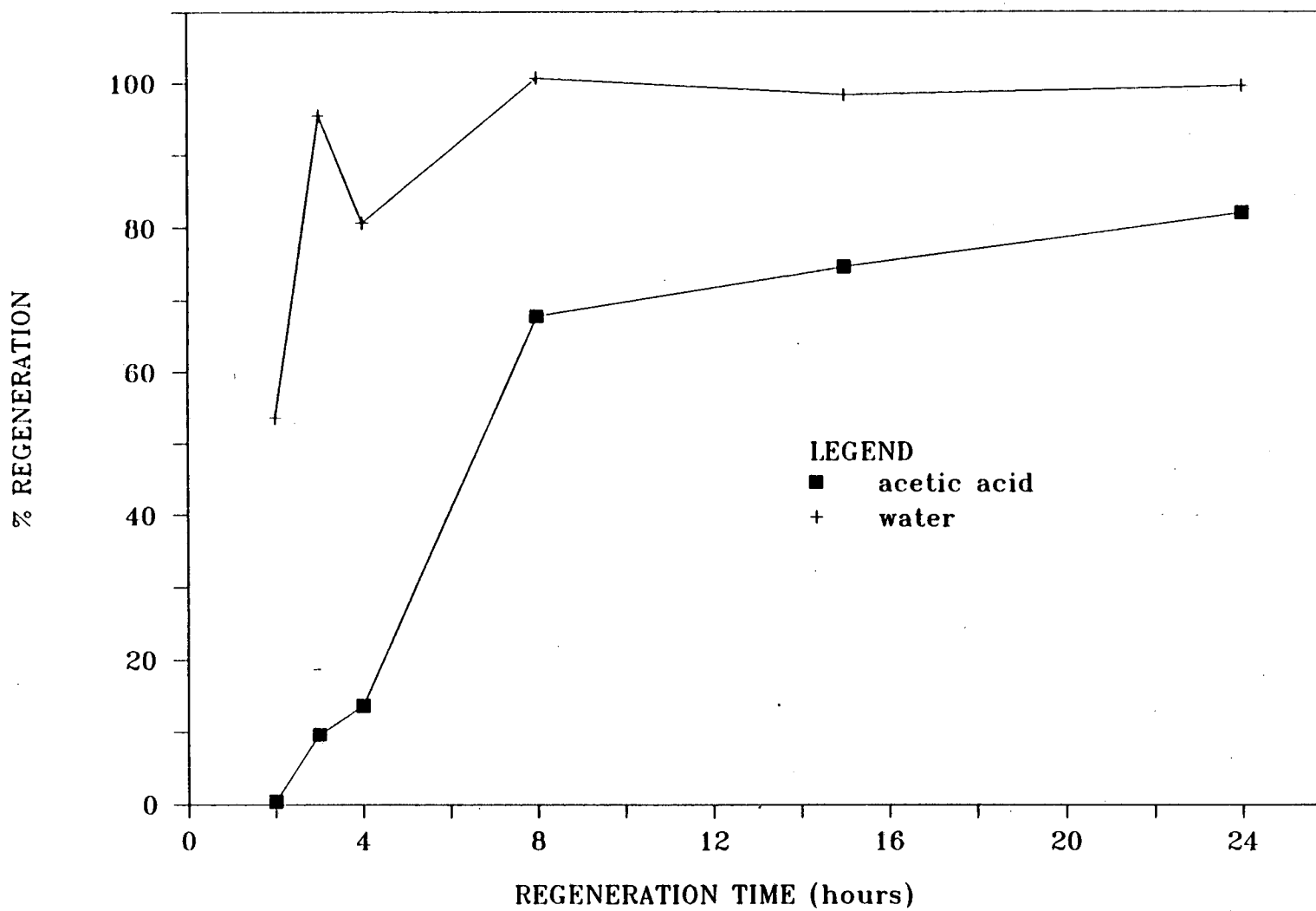
FIGURE 9. VAPORIZATION OF ACETIC ACID AND WATER FROM AUROREZ
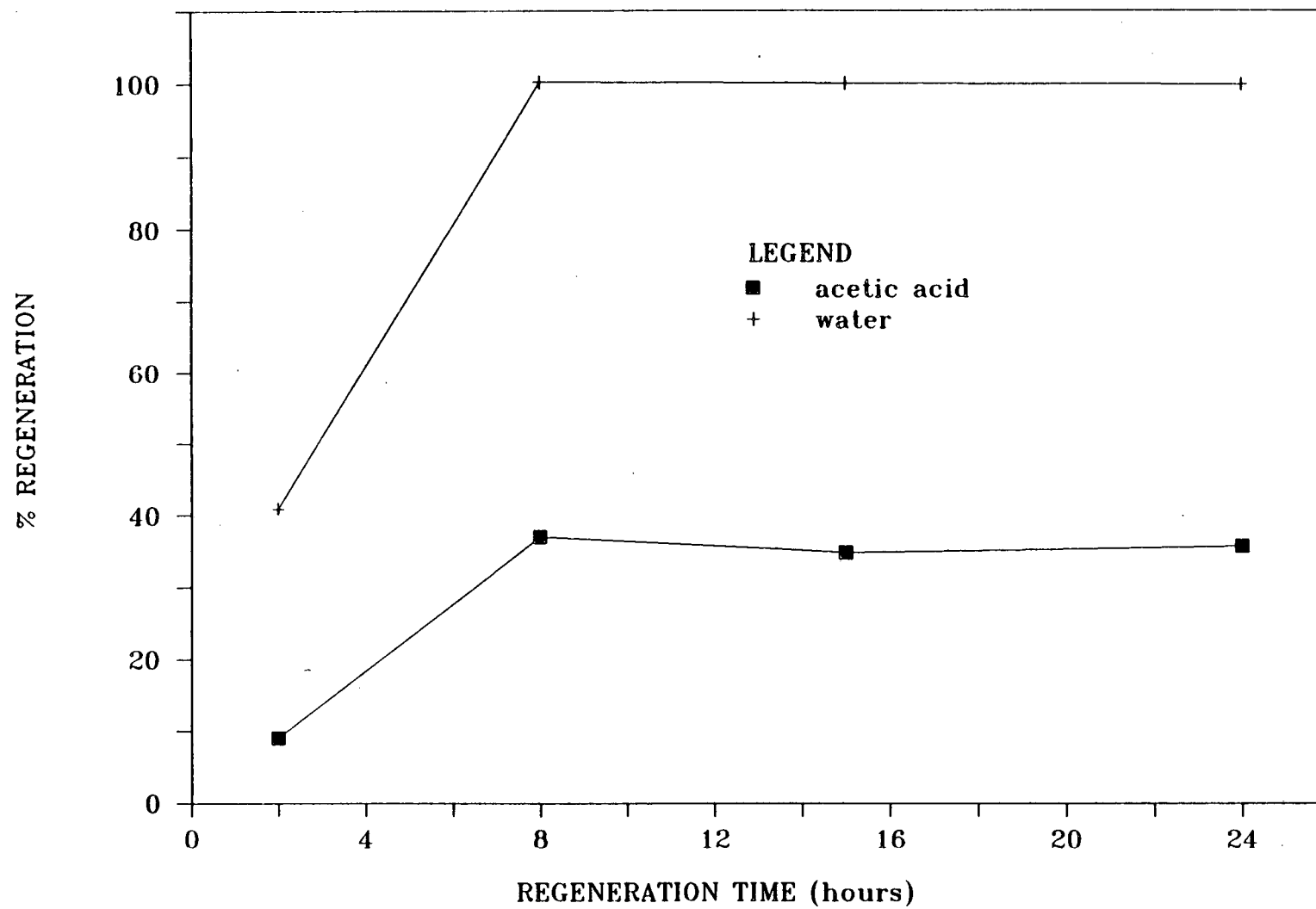
FIGURE 10. COMPOSITE ISOTHERM FOR SORPTION OF ACETIC ACID
FROM WATER BY DOWEX MWA-1 AFTER THERMAL REGENERATION

LEGEND
■   first sorption, batch 1
+   first sorption, batch 2
◇   sorption after thermal regeneration,
      batch 2

LOADING (g acetic acid/g resin)

EQUILIBRIUM SOLUTION CONCENTRATION (wt% acetic acid)
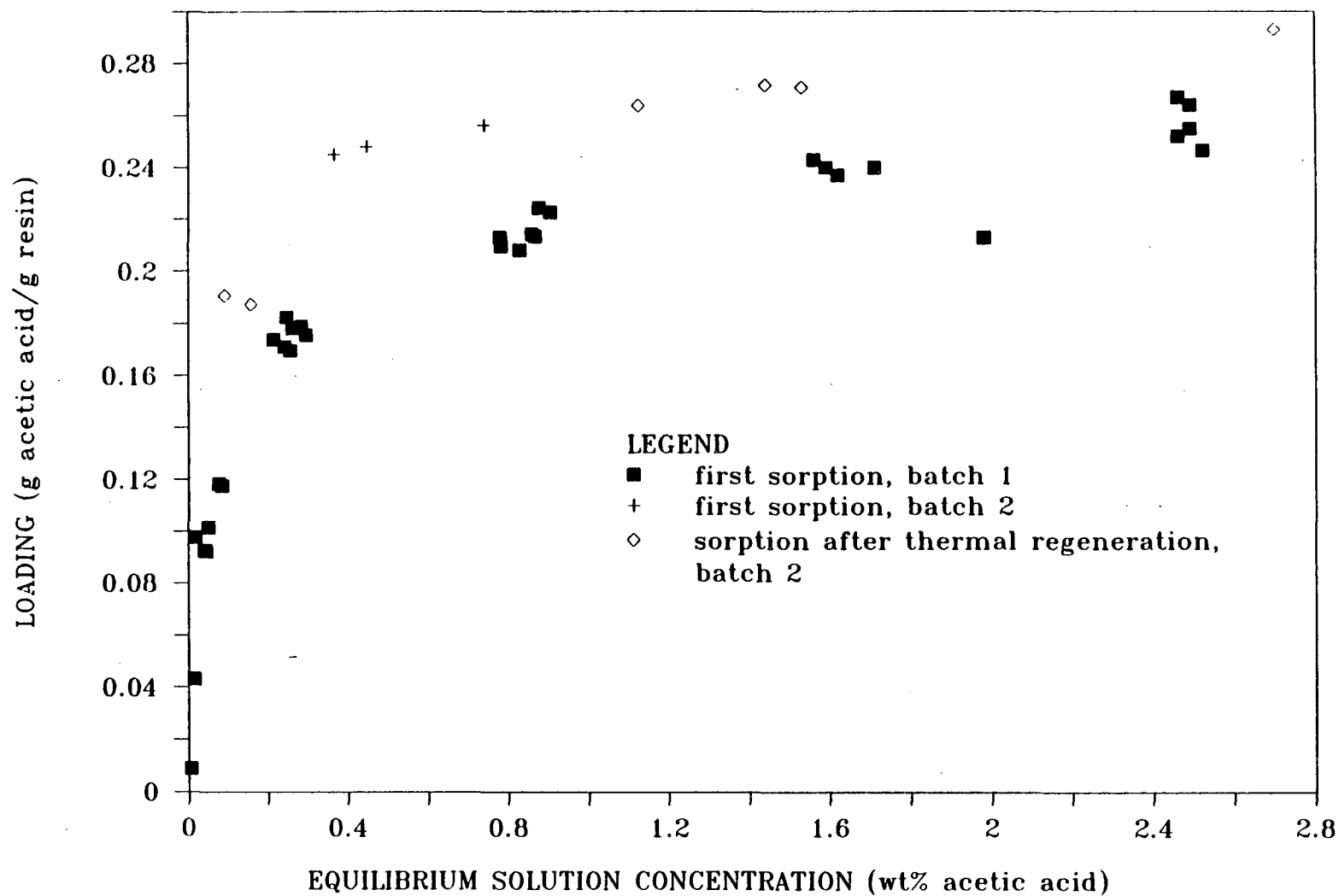
For Aurorez, the greatest rate of vaporization appeared to occur between the 2nd and 8th hour with a limit of 0.115 g of unrecoverable acetic acid/g resin (65% of the initial sorbed acid). Communications with a Celanese representative revealed that vaporization of polar solvents sorbed by Aurorez, such as water, seals the pore openings[12]. This could then trap any acetic acid left in the pores. A sequential displacement of the sorbed polar solvent by less polar solvents before drying was recommended by the manufacturer as a means to help the resin maintain its capacity.

Sorption of aqueous acetic acid by the regenerated Aurorez showed no change in the composite isotherm. However, while the resin capacity remains essentially the same, the actual sorption of acetic acid from water is small as most of the sites were already occupied by the unregenerated acetic acid.

4.2 SEQUENTIAL SOLVENT REGENERATION

4.2.1 EXPERIMENTAL EQUIPMENT AND PROCEDURES

Regeneration with sequential solvents was explored for Celanese Aurorez, in an effort to overcome the pore-sealing problem. The procedure for the sorption of acetic acid from an initial 3 weight percent aqueous solution and for the initial solvent leaching by various alcohols was as outlined in section 3.1 for the sorption and methanol regeneration of acetic acid. Displacement of the alcohol by toluene was done in a similar manner as for the displacement of water by an alcohol.

Analysis of the toluene solution consisted of (1) two-phase colorimetric titration with aqueous sodium hydroxide and with phenolphthalein as the·indicator for acetic acid, (2) Karl Fischer potentiometric titration (Quintel Corporation) for water, and (3) gas chromatography (Varian Model 3700) for the alcohols. See Appendix D for gas chromatography conditions.

Toluene was vaporized from the sorbent in a vacuum oven (VWR Scientific) at 100 C and 22-24 in. Hg vacuum. There was an ambient air sweep of 250-280 ml/min (Omega Engineering Incorporated rotameter) measured at ambient pressure and temperature. Vaporization time was 2 hours. Sorption of aqueous acetic acid by the regenerated resin was carried out as described in section 3.1 for sorption of aqueous acetic acid by the dry resin.

4.2.2 ALCOHOL-TOLUENE REGENERATION

The five alcohols investigated as the initial displacer were methanol, ethanol, n-propanol, isopropanol and tert-butanol. These alcohols were chosen since they are fully miscible with water. The effectiveness of acetic acid regeneration decreased with increasing number of carbons in the alcohol molecule (Figure 11). Regeneration of the resin by n-propanol was only slightly greater than that by isopropanol. The order of the ranking suggests that polarity determines the ability of the alcohol to reach and solvate the acetic acid in the resin. The effectiveness of water regeneration followed the same trend as the acetic acid regeneration (Figure 12).

For the systems with t-butanol and isopropanol, there is much scatter in the composite uptake of acetic acid (Figure 13). For each of the three separate resin samples used in the study, the results were consistent. The composite uptake of acetic acid for each resin sample was approximately the same regardless of the equilibrium solution concentration, indicating perhaps a saturation limit. The limit may vary for each resin sample, since the drying history and thus the extent of surface sealing of each sample would be slightly different. The apparent equilibria for the three samples in the systems with n-propanol, ethanol and methanol were more similar. The surface-sealing phenomena may have less effect on the smaller alcohols which may still be able to pass through most pore openings to solvate the acetic acid.

The individual uptake of water also showed substantial scatter but again was consistent for each resin sample (Figure 14). The higher the

FIGURE 11. ALCOHOL REGENERATION OF ACETIC ACID FROM AUROREZ

LEGEND
■ tertbutanol
+ isopropanol
◇ propanol
△ ethanol
× methanol

WEIGH RATIO OF ALCOHOL TO RESIN
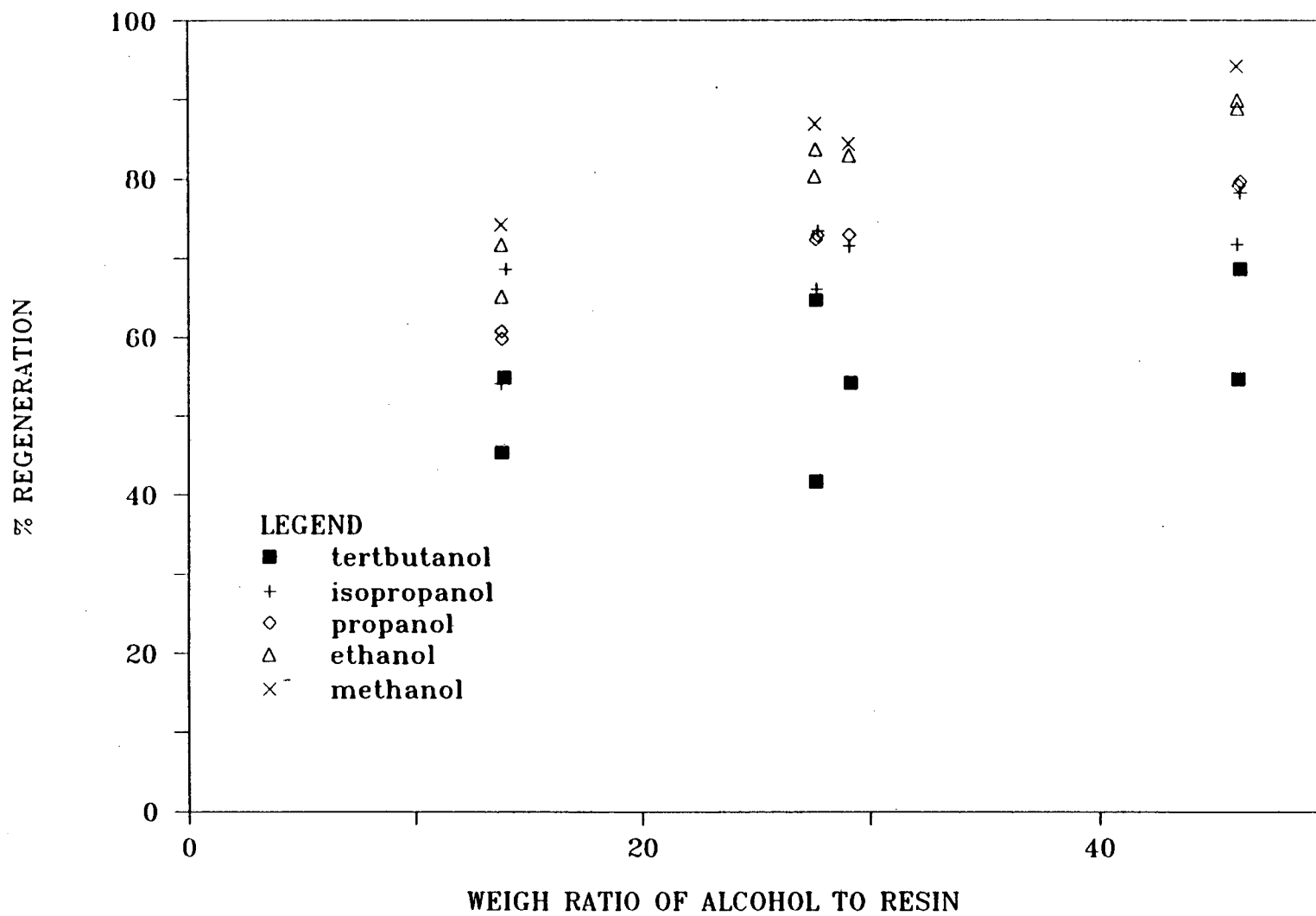
% REGENERATION

FIGURE 12. ALCOHOL REGENERATION OF WATER FROM AUROREZ

LEGEND
■ tertbutanol
+ isopropanol
◇ propanol
△ ethanol
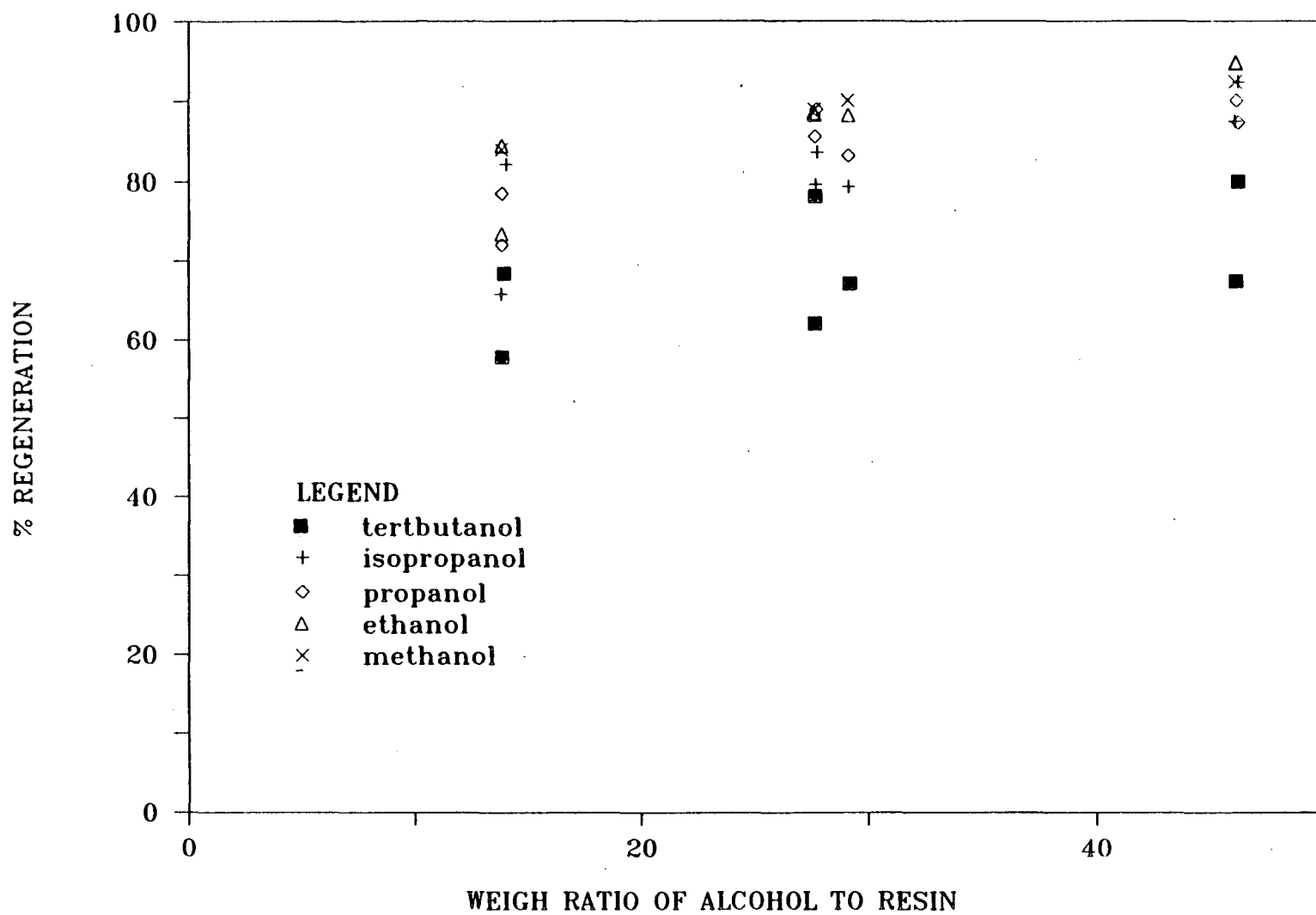✕ methanol

% REGENERATION

WEIGH RATIO OF ALCOHOL TO RESIN

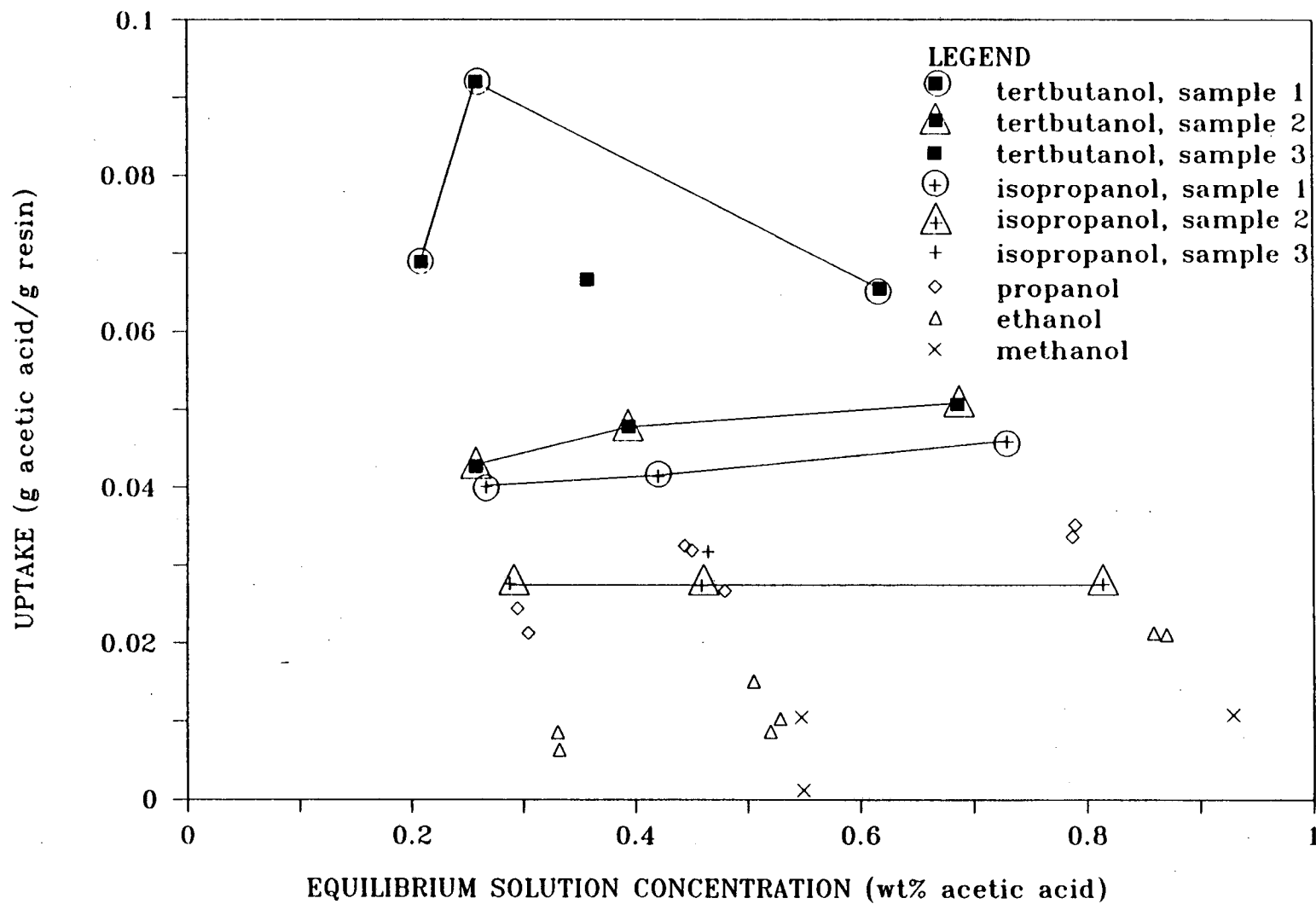FIGURE 13. COMPOSITE ISOTHERM FOR ALCOHOL REGENERATION OF ACETIC ACID FROM AUROREZ

FIGURE 14. INDIVIDUAL ISOTHERM FOR ALCOHOL REGENERATION OF WATER FROM AUROREZ
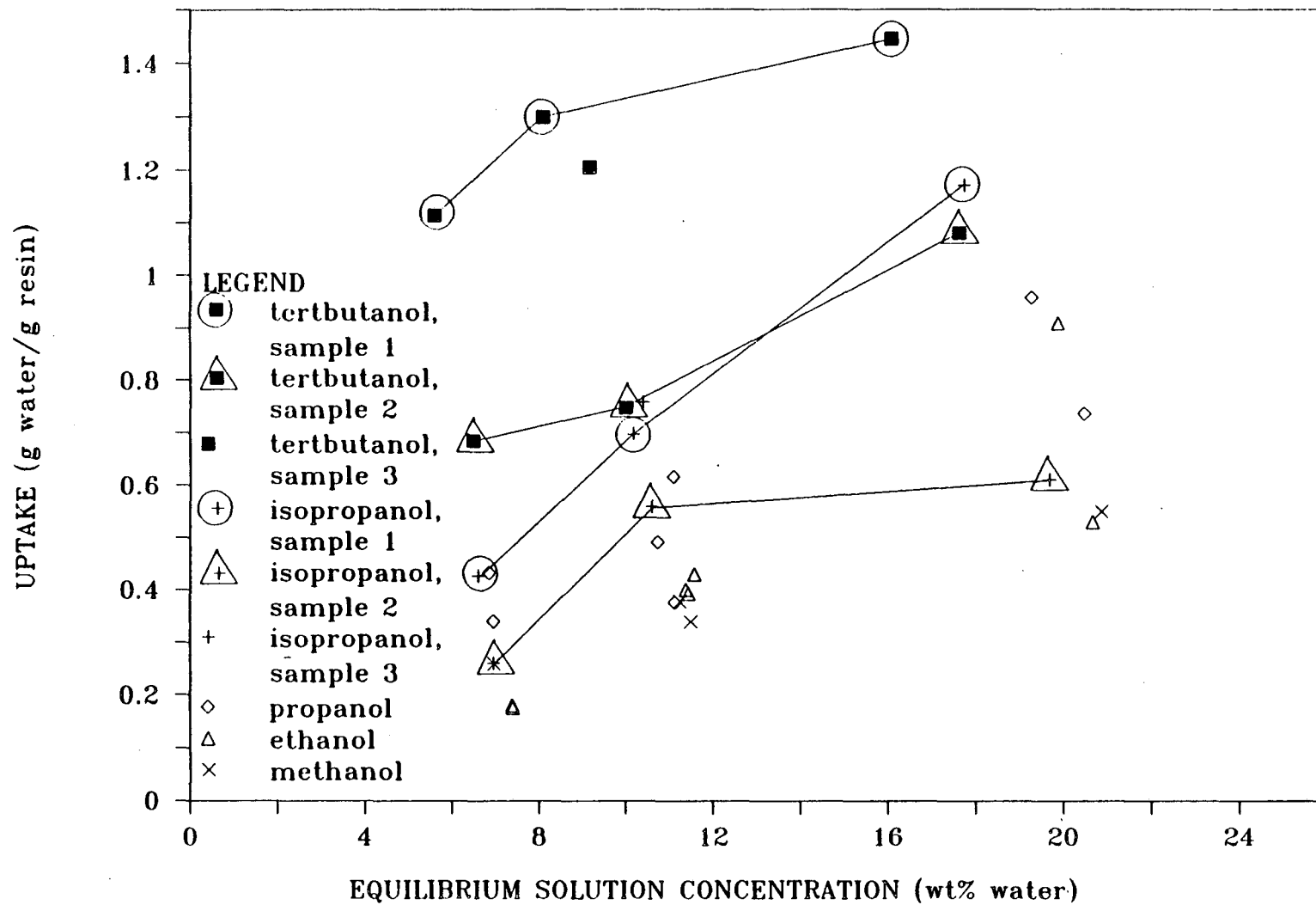
composite uptake of acetic acid, the higher the individual uptake of water. This link between the effectiveness of the acetic acid regeneration and the water regeneration indicates that the surface sealing phenomena may be mostly responsible for the scatter in the data.

The measured composite isotherm is presented in Figure 15 for regeneration of acetic acid by toluene. Displacement of the alcohol by toluene resulted in very little additional regeneration of acetic acid or water by toluene. Little water was expected to be recovered as it was mostly leached by the alcohol, and water is relatively insoluble in toluene. The equilibrium concentration of water in toluene was between 0.3 and 0.7 weight percent for most samples regardless of the amount of toluene added. This probably relates to the solubility of water in toluene. The effectiveness of the regeneration of acetic acid and water by the various alcohol-toluene solvent combinations followed the same trend as the regeneration of acetic acid by various alcohols (Figures 16 and 17). However, there was not much difference in the effectiveness of regeneration between the methanol-toluene and the ethanol-toluene combination or between the propanol-toluene and the isopropanol-toluene combination.

Vaporization of the toluene, residual alcohol, water and acetic acid was essentially complete after two hours. Sorption of aqueous acetic acid by the regenerated resin was comparable to that by the dry resin, indicating that full regeneration and reuse of the resin is possible using this method (Figure 18). The scatter in the composite isotherm

for sorption by the regenerated resin resulted from the small amount of resin left at that point.

FIGURE 15. COMPOSITE ISOTHERM FOR TOLUENE REGENERATION OF ACETIC ACID FROM AUROREZ

LEGEND
- ■ tertbutanol
- + isopropanol
- ◇ propanol
- △ ethanol
- ✕ methanol

UPTAKE (g acetic acid/g resin)

EQUILIBRIUM SOLUTION CONCENTRATION (wt% acetic acid)
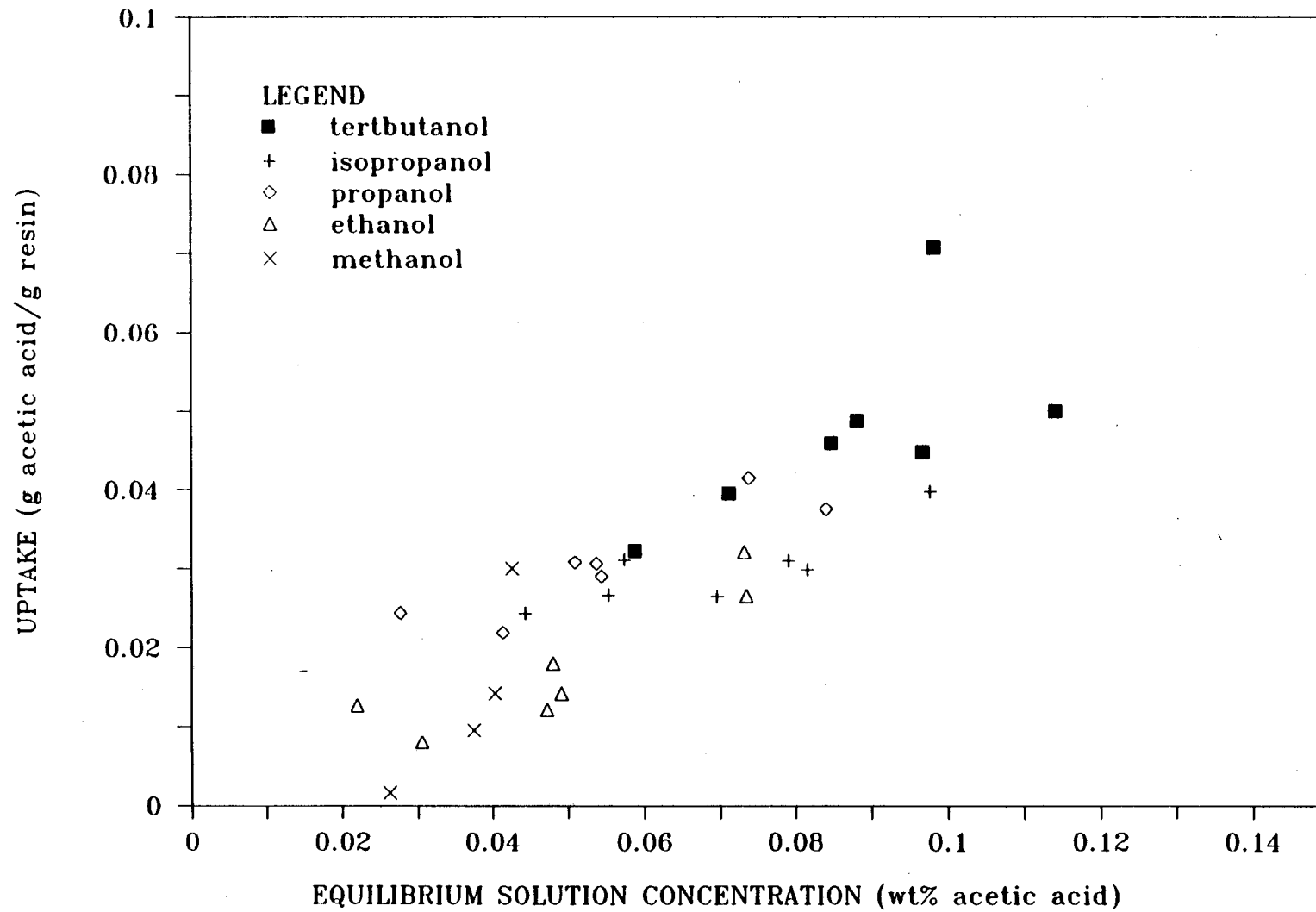
FIGURE 16. ALCOHOL—TOLUENE REGENERATION OF ACETIC ACID FROM AUROREZ

LEGEND
- ■   tertbutanol—toluene
- +   isopropanol—toluene
- ◇   propanol—toluene
- △   ethanol—toluene
- ×   methanol—toluene

% REGENERATION

WEIGHT RATIO OF ALCOHOL TO RESIN
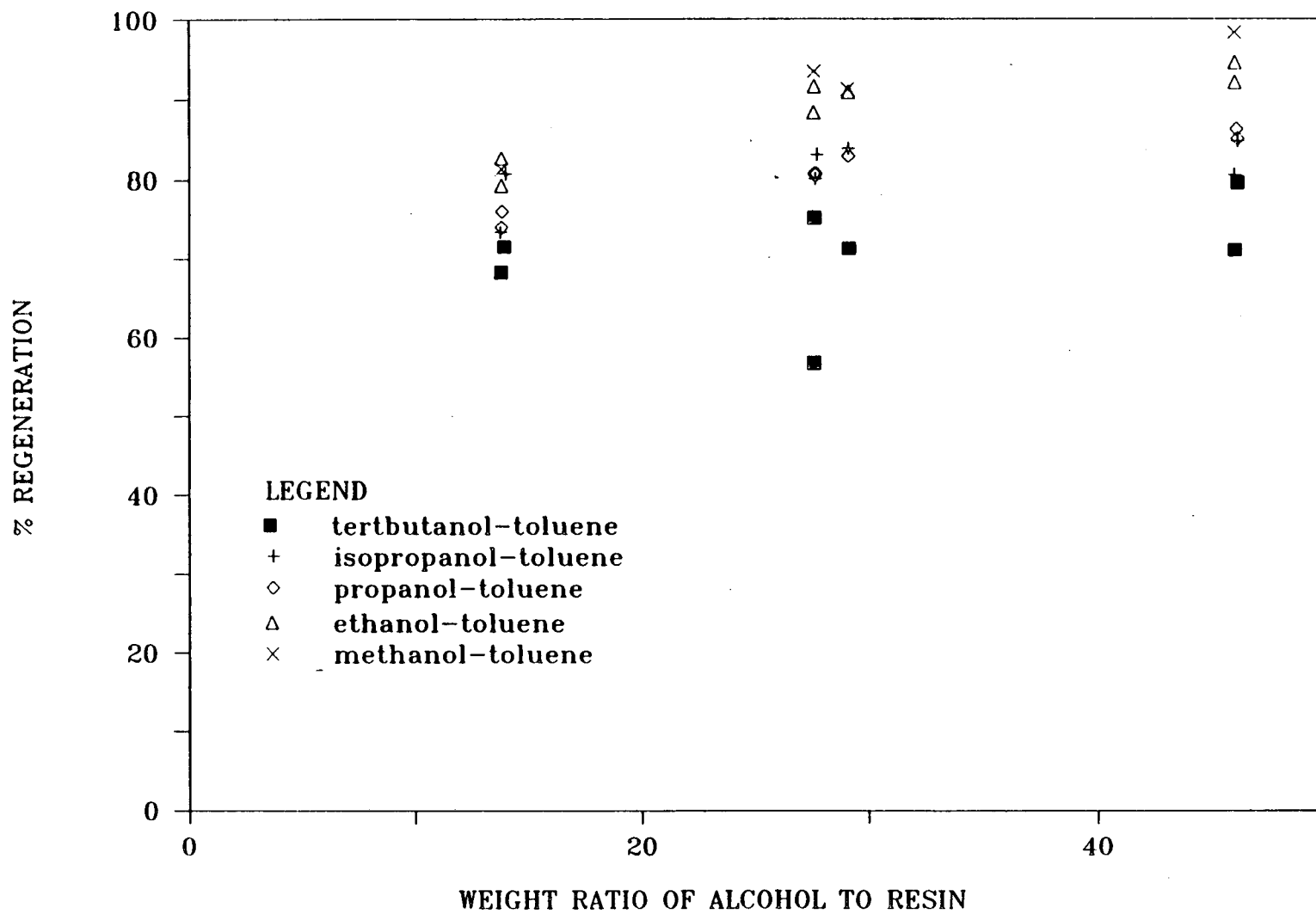
FIGURE 17. ALCOHOL-TOLUENE REGENERATION OF WATER FROM AUROREZ

LEGEND
■ tertbutanol
+ isopropanol
◇ propanol
△ ethanol
× methanol

% REGENERATION

WEIGH RATIO OF ALCOHOL TO RESIN

FIGURE 18. COMPOSITE ISOTHERM FOR SORPTION OF ACETIC ACID FROM WATER BY AUROREZ AFTER THERMAL REGENERATION

LEGEND
■   first sorption
+   sorption, after thermal regeneration
◇   sorption, after solvent and thermal regeneration
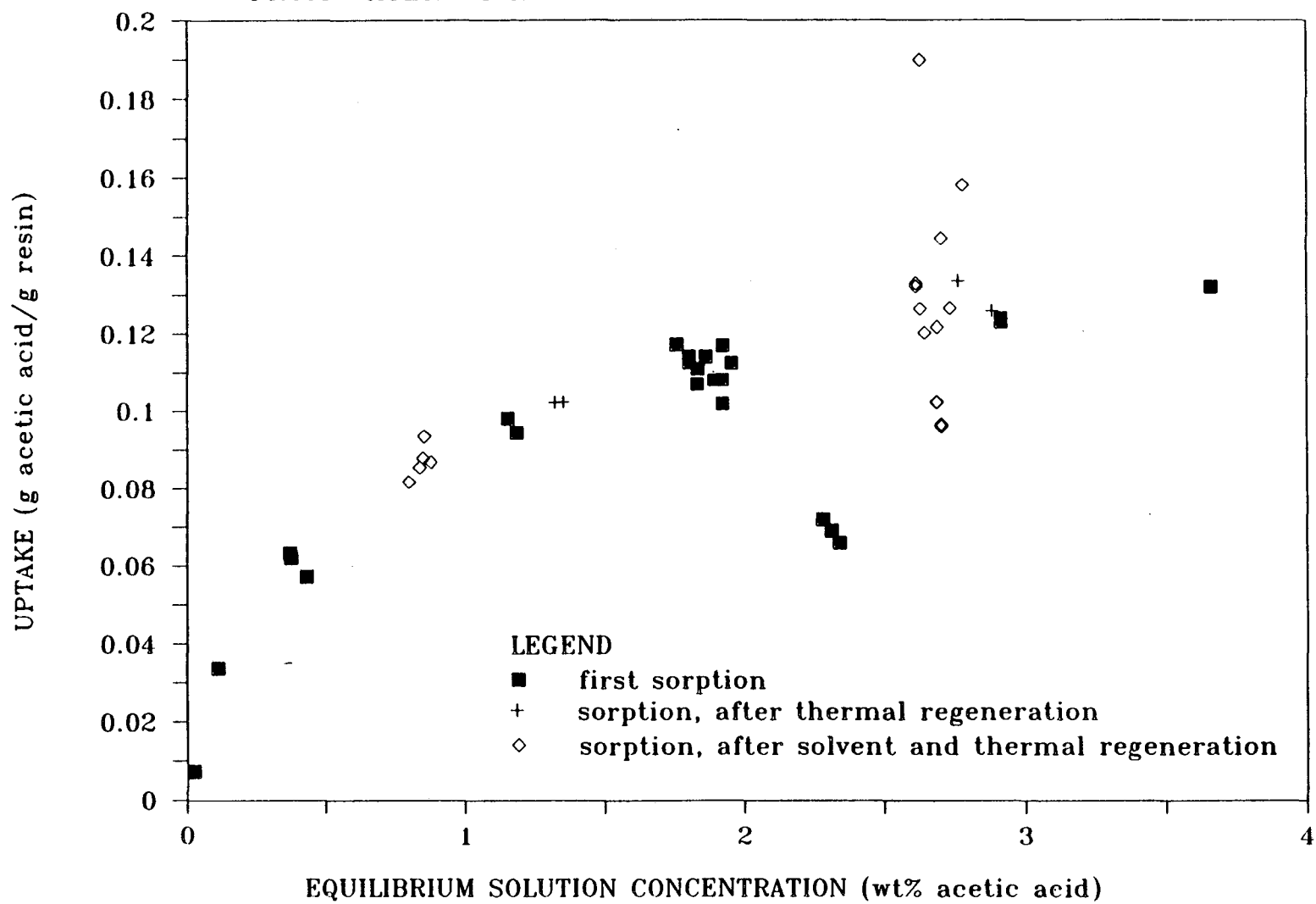
5 THERMAL REGENERATION - FIXED BED EXPERIMENTS

5.1 EXPERIMENTAL EQUIPMENT AND PROCEDURE

The apparatus for the fixed bed sorption of acetic acid from water by Dowex MWA-1 is shown in Figure 19. The resin was prewetted with a known amount of water. The 3 weight percent aqueous acetic acid solution was pumped (Microflow Pulsafeeder Metering Pump; Interspace Corporation, Lapp Insulator Division) to the top of the glass column (Bio-Rad Laboratories) from a stirred reservoir at a rate of 1 ml/min for 3 to 4 hours. The valve at the bottom of the column was opened when the pump was started. The column was 1.5 cm (diameter) by 20 cm (length) and jacketed. A glass fritted filter (coarse grade) at the bottom of the column kept the resin in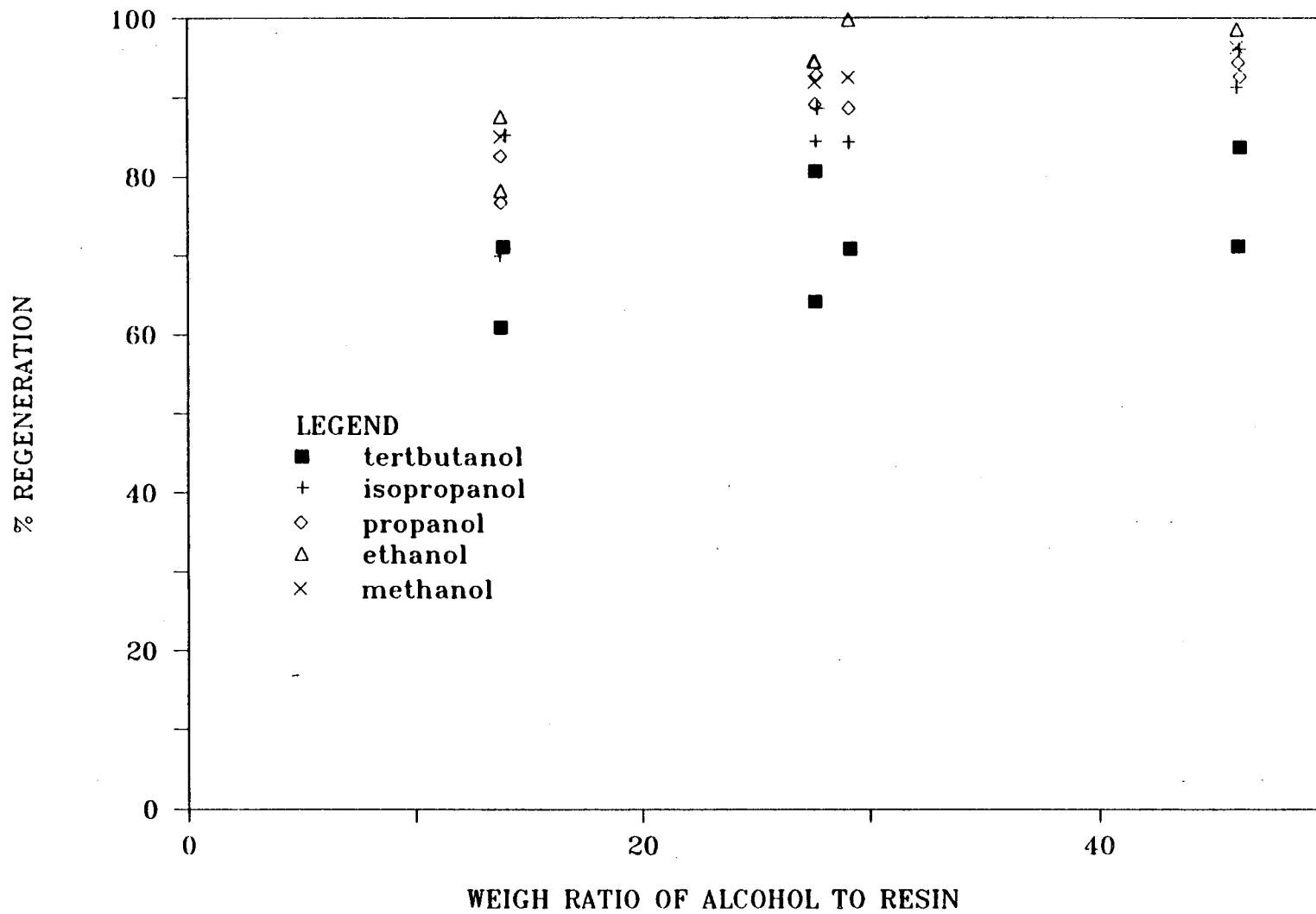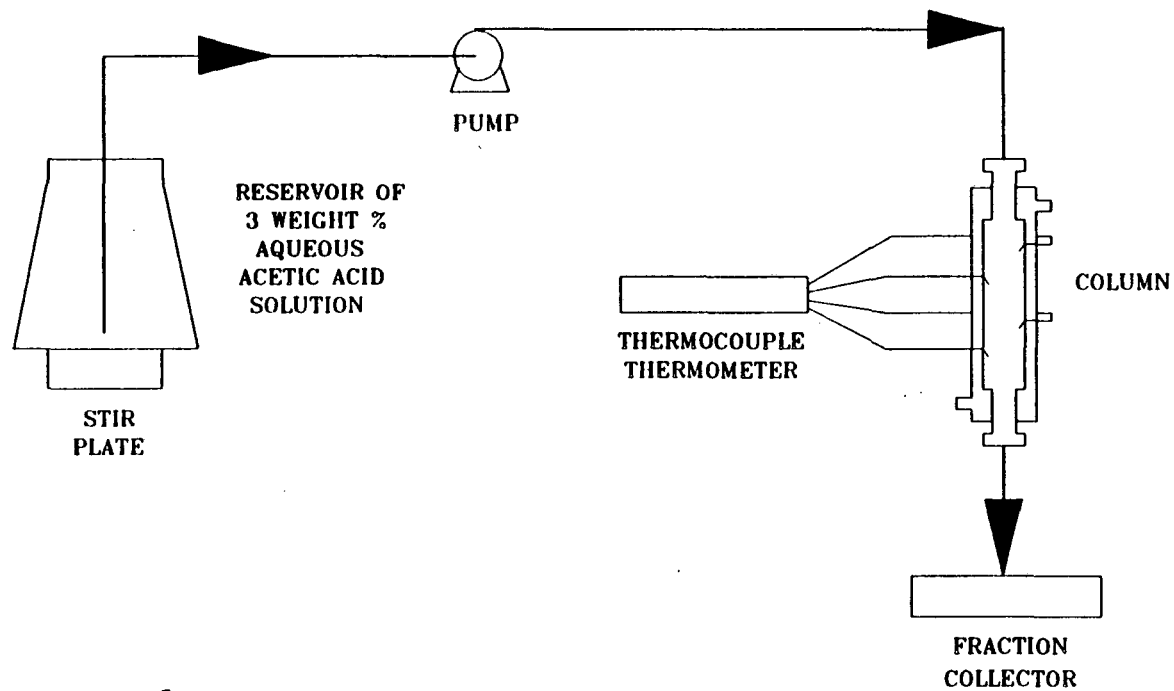 the column. The temperature along the centerline of the column was monitored using four type E thermocouples at 5.5, 8.5, 11.5, and 14.5 cm from the bottom of the column. The thermocouples were all connected to a digital multithermocouple thermometer (Omega Engineering Incorporated). Samples were collected from the outlet of the column over periods of 10 minutes in glass scintillation vials using a fraction collector (LBK-Produkter AB). The solution left in the column was blown out with air at the same flow rate as was used for the regeneration. All sorption runs were carried out at room temperature. Colorimetric titration with aqueous sodium hydroxide and with phenolphthalein indicator was used to determine the effluent concentration of acetic acid. Any acetic acid or water that entered the column but was not detected leaving, was considered sorbed by the resin.

FIGURE 19. FIXED-BED APPARATUS FOR SORPTION OF ACETIC ACID BY SORBENTS

PUMP

RESERVOIR OF
3 WEIGHT %
AQUEOUS
ACETIC ACID
SOLUTION

STIR
PLATE

THERMOCOUPLE
THERMOMETER

COLUMN

FRACTION
COLLECTOR

The apparatus for the fixed bed vaporization of acetic acid from Dowex MWA-1 is shown in Figure 20. A rotameter (Cole Parmer) was used to regulate the air flow. Heating tape was wrapped around the tubing preceding the column to preheat the air and around the tubing after the column to prevent condensation in the tubing. The oil bath temperature was regulated by a temperature controller (Hallikainen Model 1140) with a high temperature cutoff switch. Three heating blades and a heating plate were used to heat the oil and keep it at the desired temperature. A centrifugal pump was used to circulate the oil in the column jacket.

For analysis of scrubber liquid, 0.2 M aqueous sodium hydroxide solution was used to neutralize the regenerated acetic acid. Samples were collected from the scrubber every 10 minutes for 4 to 6 hours by pulling a slight vacuum in the glass sample vial and withdrawing the liquid from the scrubber by suction. Colorimetric titration with hydrochloric acid and phenolphthalein indicator was used to determine the amount of acetic acid regenerated. Dilution of the aqueous sodium hydroxide solution by the regenerated water was not taken into account as it would have made less than 3% difference.

FIGURE 20. FIXED–BED APPARATUS FOR VAPORIZATION OF ACETIC ACID FROM SORBENTS

VARIAC

MIXER

HEATING
TAPE

FLOWMETER

VARIAC

THERMOMETER

TEMPERATURE
CONTROLLER

COLUMN
WITH
JACKET

HEATING
BLADES (3)

THERMOCOUPLE
THERMOMETER

HIGH TEMPERATURE
CUTOFF SWITCH

PUMP

TEMPERATURE
SENSOR

COMPRESSED
AIR CYLINDER

RESERVOIR
OF OIL

VACUUM
LINE

SCRUBBER
WITH
AQUEOUS
SODIUM
HYDROXIDE

HEATING
PLATE

SAMPLE
VIAL

STIR
PLATE
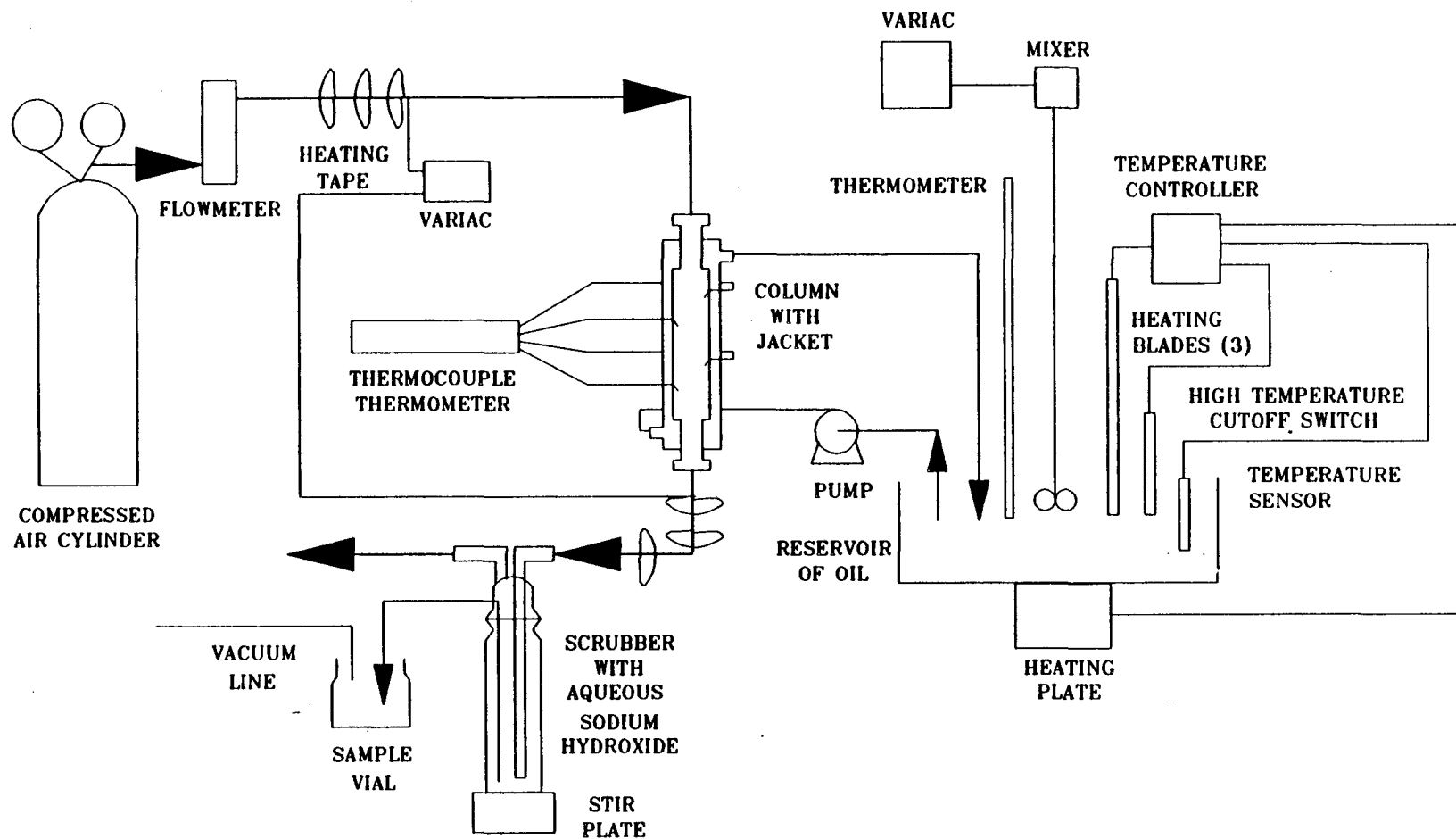
5.2 SORPTION AND VAPORIZATION OF ACETIC ACID

Fixed-bed sorption and vaporization experiments were carried out for Dowex MWA-1. The average amount of acetic acid sorbed by the 8.2 g of resin, 0.38 g acetic acid/g resin, was as expected from the batch studies done by Munson et al[14] but higher than the extrapolated value from the results of this work (0.32 g acetic acid/g resin). The average amount of water sorbed by the resin, 1.46 g water/g resin, was lower than expected from the batch studies done by Munson et al (1.8 g water/g resin)[14] but as expected from the extrapolated value from the results of this work.

There was some swelling of the resin when water was added to prewet the dry resin. The height of the resin in the bed increased from 9 cm to 10 cm. However, most of the swelling occurred when the resin sorbed acetic acid. The height of the resin in the bed increased from 10 cm to 13-14 cm in 1.5-2 hours. The breakthrough curves for the sorption of acetic acid from water by Dowex MWA-1 are shown in Figure 21. The data points are plotted at times corresponding to the middle of the sampling interval. The breakthrough of acetic acid in the effluent occurred after 80-90 minutes. The effluent acetic acid concentration was the same as the inlet solution acetic acid concentration after 2.5-3 hours. The effluent solution for the first 90 minutes was a light yellow and was clear thereafter. The color may be the result of a slight degradation of the resin from drying. However, the resin capacity appeared to be unaffected by the drying. The above results were observed for two samples of Dowex MWA-1.

FIGURE 21. FIXED-BED SORPTION OF ACETIC ACID FROM WATER BY DOWEX MWA-1
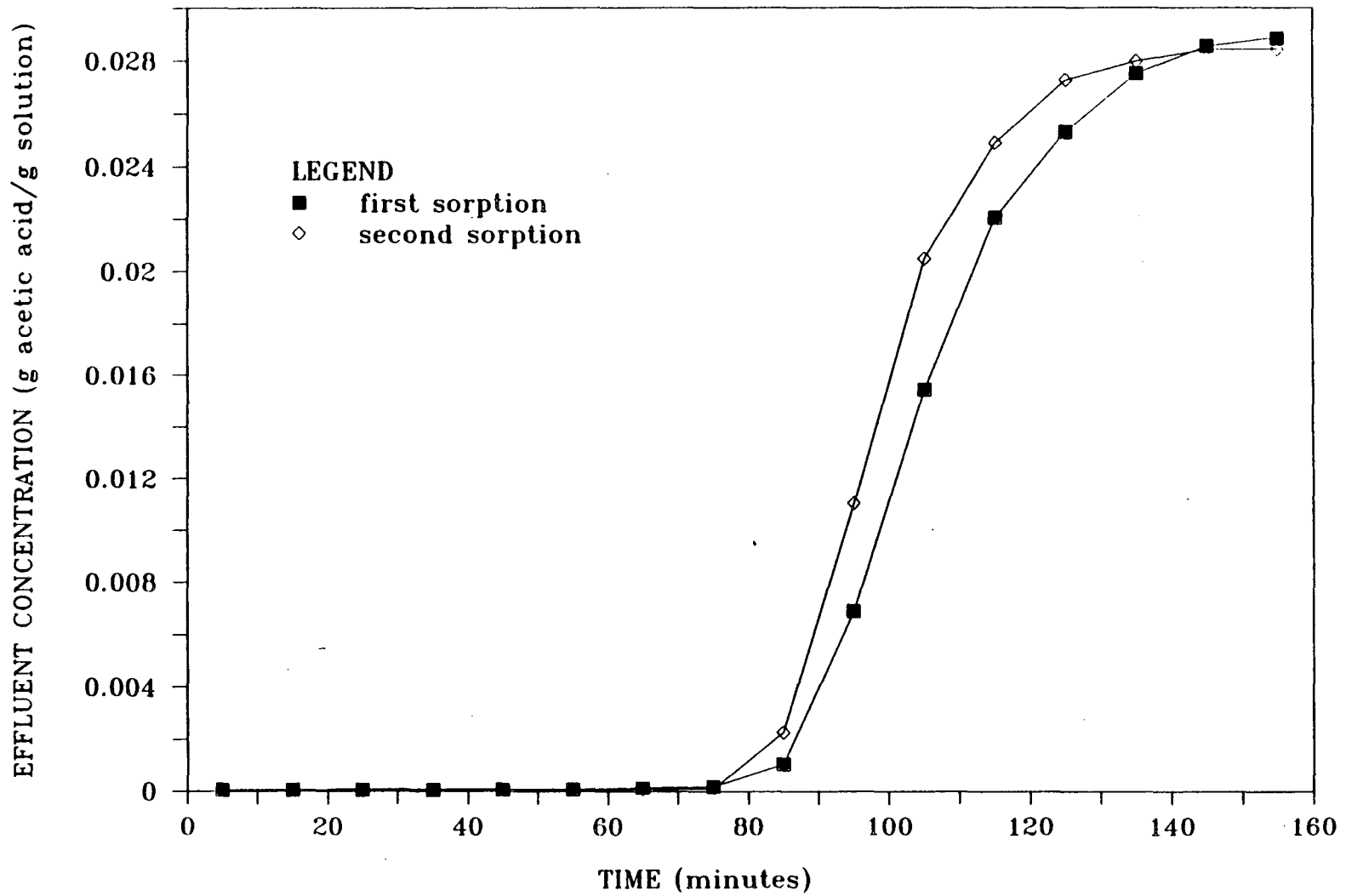
The results of the vaporization of acetic acid from the resin with an air flow rate of 2.6 1/min (ambient temperature and 4 psig) and a jacket temperature of 100 C, the stated maximum operating temperature for Dowex MWA-1[6], are shown in Figure 22. There was no significant vaporization of acetic acid from the resin before the first fifty minutes and after the second hour. The first fifty minutes was probably an induction period similar to that observed in the batch experiments, when the resin and the liquid in the pores were being heated up and the water was vaporized. It took 40 minutes for all the temperatures measured along the column to reached steady state (Figure 23). The temperature at 14.5 cm reached steady state relatively quickly as there was no heat sink involved, i.e. no resin to heat up or water to vaporize. The temperature at 11.5 cm should also reach steady state quickly because the resin shrinks as it is being regenerated and the level of the resin should fall below the thermowell. The temperature at 8.5 cm probably took longest to reach steady state because, at the beginning of the process, energy is needed both to vaporize the water and heat up the resin. By the time the air reached the thermocouple at 5.5 cm, it was probably nearly saturated with water and no energy was needed to vaporize the water, only to heat up the resin. Later in the process, when energy was needed to vaporize the water, energy was probably no longer needed to heat up the resin. Thus, the temperature at 5.5 cm may reach a steady state more quickly than at 8.5 cm because it does not simultaneously have to satisfy two heat sinks.

After four hours, the height of the resin decreased to the original

FIGURE 22. FIXED-BED VAPORIZATION OF ACETIC ACID FROM DOWEX MWA-1

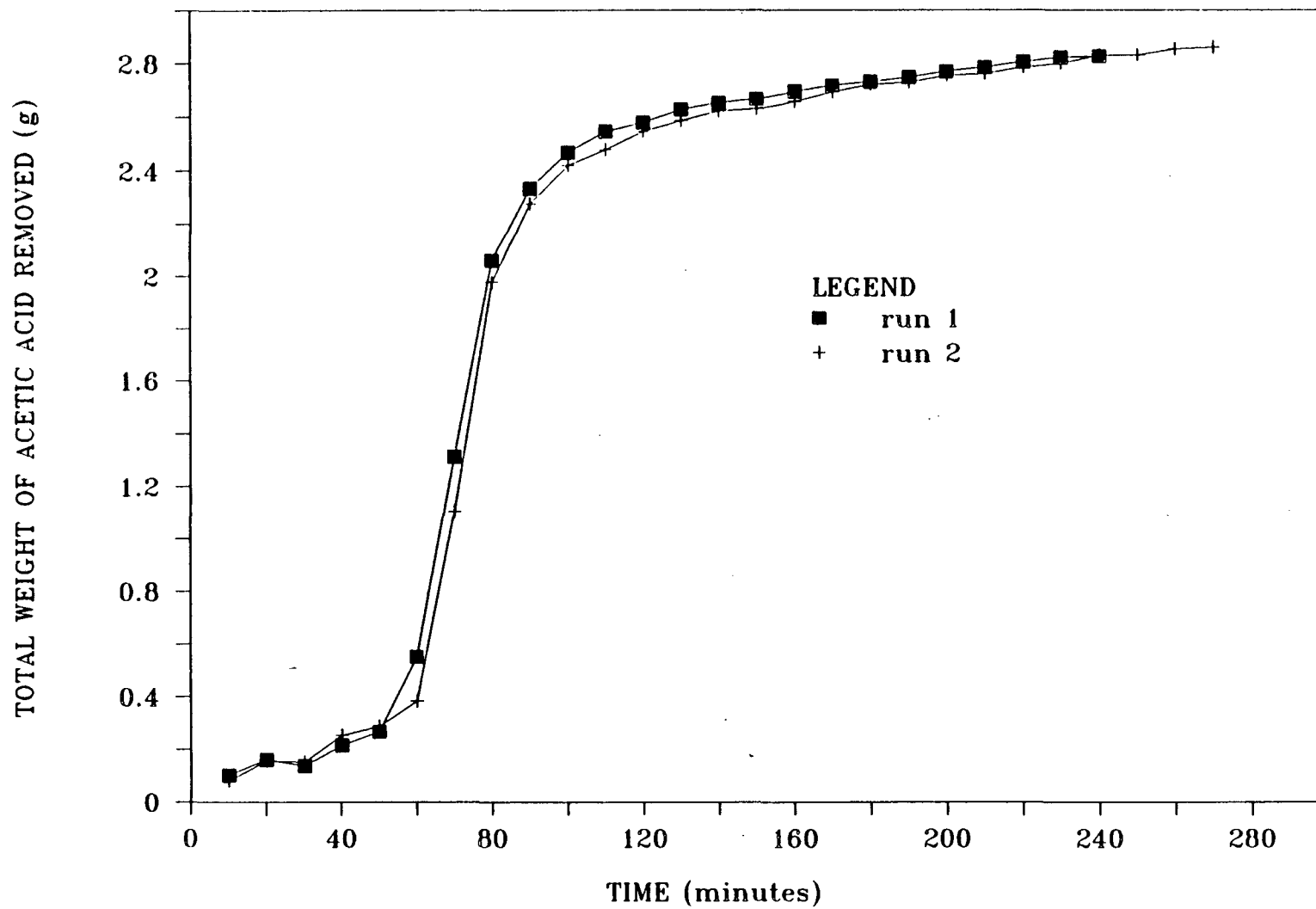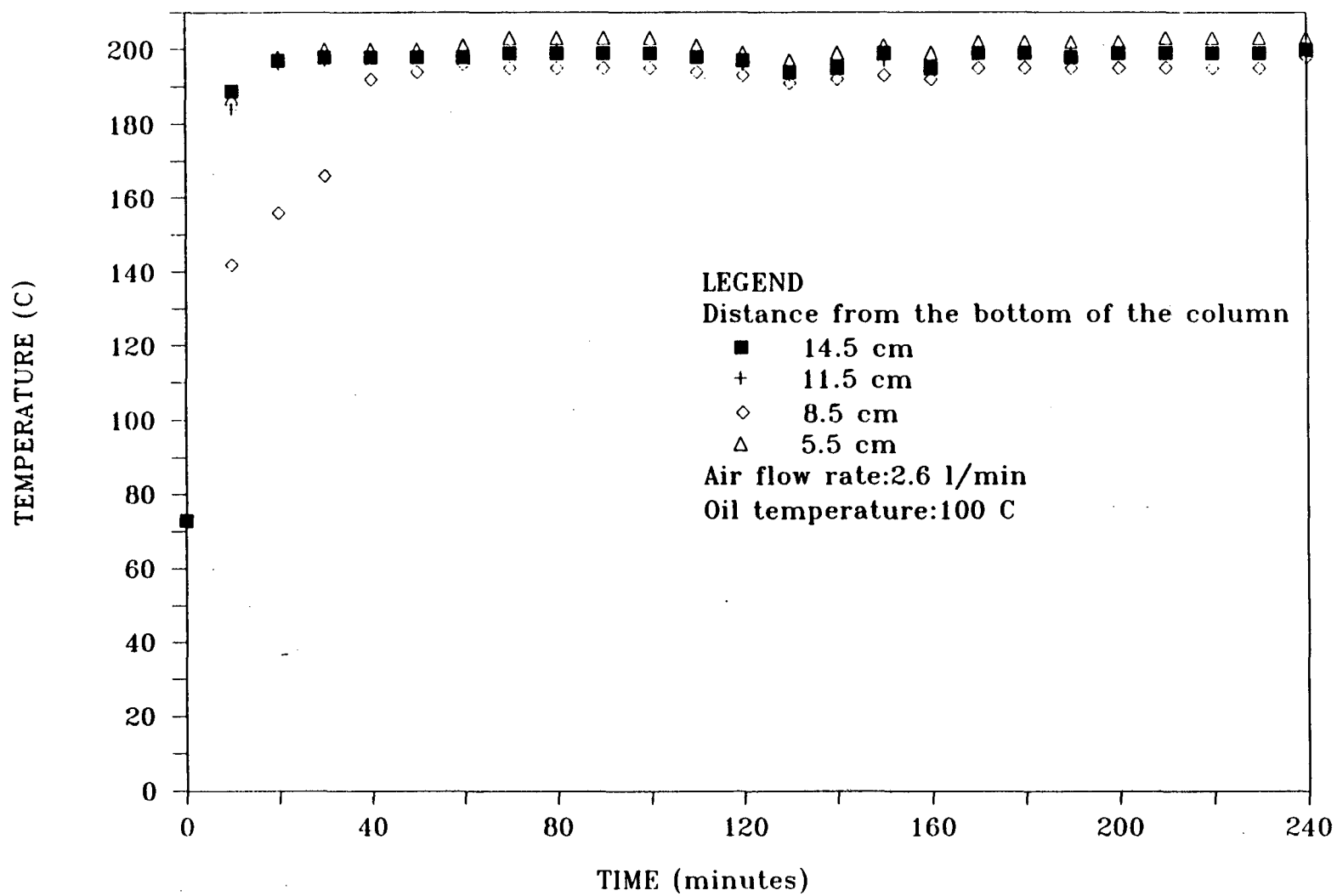# FIGURE 23. TEMPERATURE PROFILE IN COLUMN DURING VAPORIZATION
OF ACETIC ACID FROM DOWEX MWA-1

LEGEND
Distance from the bottom of the column
■   14.5 cm
+   11.5 cm
◇   8.5 cm
△   5.5 cm
Air flow rate:2.6 l/min
Oil temperature:100 C

TEMPERATURE (C)

TIME (minutes)

height of the dry resin, and the regeneration of the resin was 90%
complete. The incomplete regeneration was reflected in an upward shift
of the sorption breakthrough curve for the regenerated resin (Figure
21). The vaporization behavior of the regenerated resin appeared to be
unaffected by any previous regeneration of the resin.

Four cycles of sorption and vaporization at the above conditions were
carried out with one resin sample without any degradation of the resin
capacity. More runs were not possible because of the migration of fine
particles to the bottom of the column. The particles formed a plug,
making the passage of air and liquid impossible.

The effects of the air flow rate and the jacket temperature on the rate
of vaporization of acetic acid were also investigated. A run was
carried out at an air flow rate of 2.6 l/min and a jacket temperature
of 85 C (Figure 24). The induction period (1.5 hours) was longer at
this lower temperature. A potentially beneficial phenomenon observed
in the batch experiments was the lack of significant vaporization of
acetic acid until most of the water had been vaporized. Acetic acid
may be recovered at a higher concentration by collecting only a
fraction of the condensate. At the lower temperature, it would take
longer to regenerate the water. The rate of vaporization of acetic
acid was much lower at the lower jacket temperature. The resin was 95%
regenerated after 6 hours.

A run was also carried out at an air flow rate of 3.9 l/min and a
jacket temperature of 100 C (Figure 25). The induction period of

FIGURE 24. THE EFFECT OF TEMPERATURE ON VAPORIZATION OF ACETIC ACID FROM DOWEX MWA-1
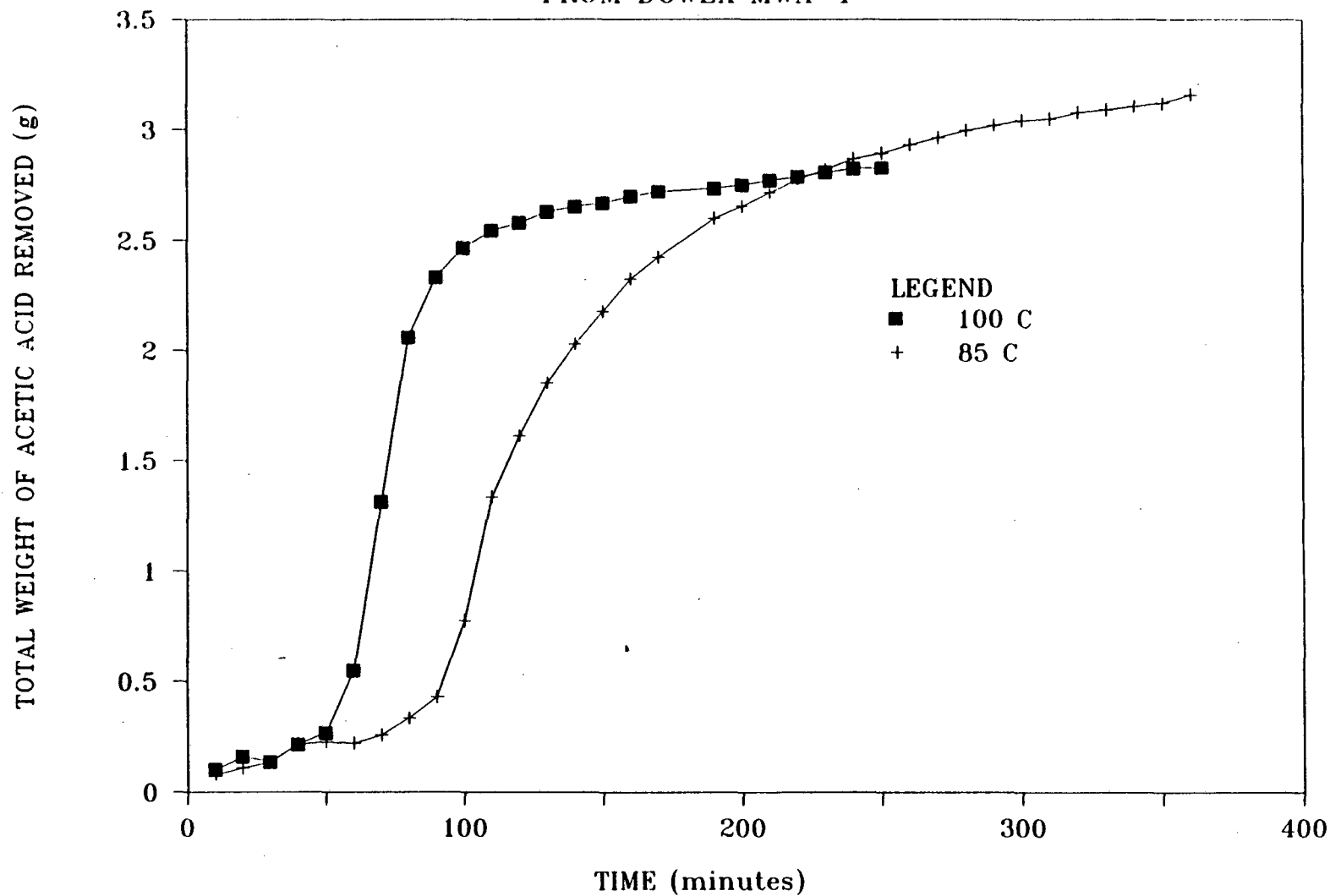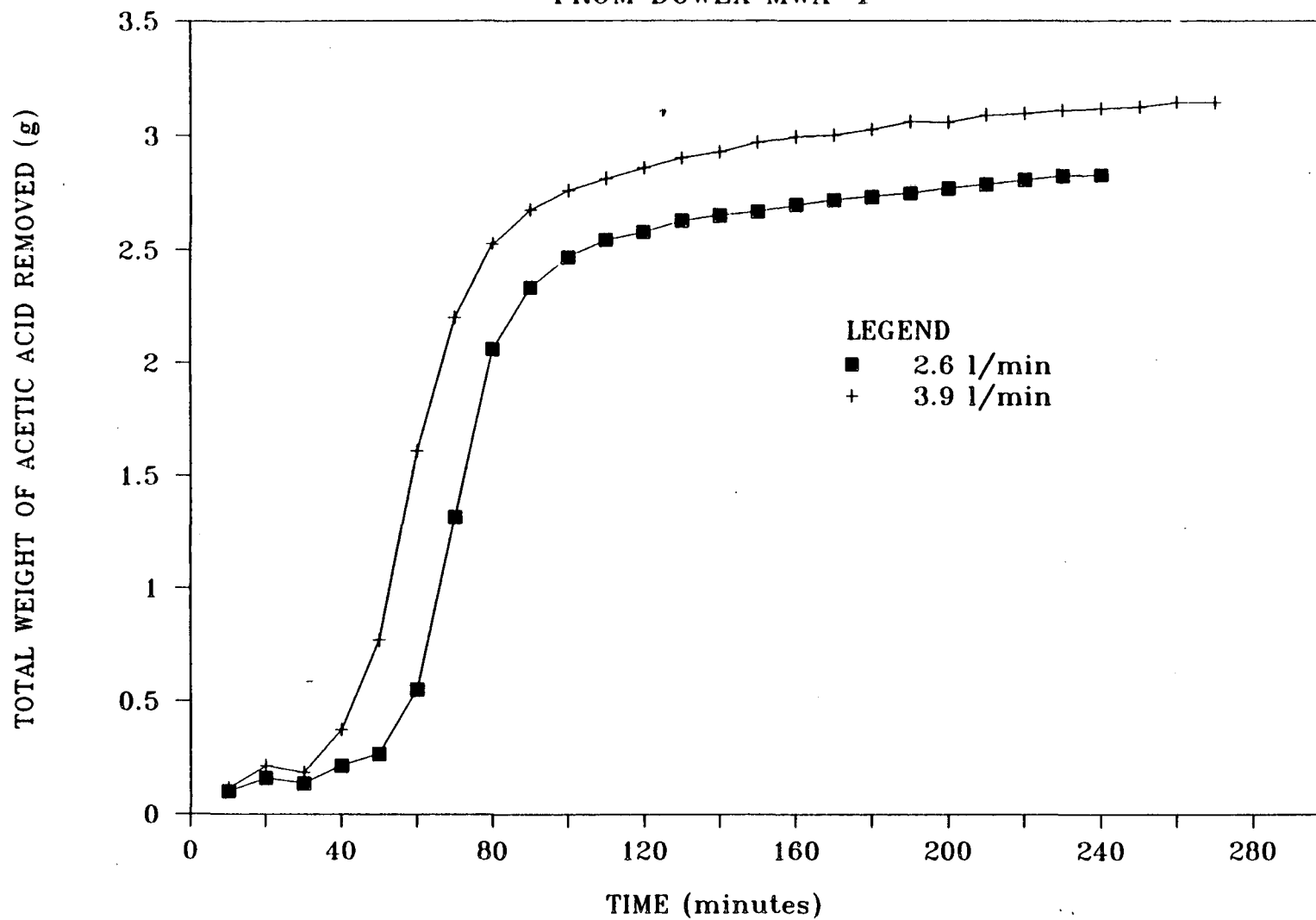
FIGURE 25. THE EFFECT OF AIR FLOW RATE ON VAPORIZATION OF ACETIC ACID FROM DOWEX MWA-1

thirty minutes was shorter than for the lower air flow rate, probably the result of more rapid heat-up and regeneration of water. The rate of vaporization of acetic acid was not significantly affected by the higher air flow rate. The upward shift of the regeneration curve was probably more the result of the greater amount of acetic acid on the resin than the greater air flow rate. The average temperature in the column was 5 C lower at the higher air flow rate and may have significantly reduced the expected increase in the rate of vaporization of acetic acid. The resin was 95% regenerated after 4 hours. The results showed that the effect of air flow rate on the vaporization of acetic acid from Dowex MWA-1 was less than the effect of the temperature. Thus, at the air flow rates studied, the regeneration rate was not limited by the carrying capacity of the air. It may be possible to achieve 95% regeneration at a lower air flow rate in four hours at a jacket temperature of 100 C.

While full regeneration seems possible with this method, the amount of air needed to achieve a high degree of regeneration is large. To achieve 80% regeneration at an air flow rate of 2.6 l/min and a jacket temperature of 100 C, over 100 liters of air was needed for each gram of acetic acid recovered. Further experiments directed toward identifying an optimum air flow rate may be worthwhile.

6 CONCLUSIONS

Both solvent and thermal regeneration have proven to be difficult for Dowex MWA-1 and Aurorez. The amount of methanol needed to achieve a high degree of regeneration in a batch process is large. The local-equilibrium theory of fixed-bed devices, which sets a lower limit on the number of bed volumes of methanol required, predicts that continuous solvent regeneration of Dowex MWA-1 would require about 25 bed volumes for full regeneration. Fixed-bed regeneration of Aurorez by methanol would require about half as much methanol. However, the capacity for acetic acid of Dowex MWA-1 is twice that of Aurorez. Thus, the amount of methanol needed for fixed-bed regeneration of the same amount of acetic acid is approximately the same for both resins.

Thermal regeneration of Dowex MWA-1 is also difficult. A large amount of air is required, and recovery of the product from the rather dilute air stream would be costly.

The sequential solvent approach to the regeneration of Aurorez is feasible and appears to overcome the surface sealing of pores which occurs upon vaporization of polar solvents.

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APPENDIX A:CHEMICAL PROPERTIES OF SOLVENTS

Various properties of the solvents used are shown in Table IV.

Table IV. CHEMICAL PROPERTIES OF SOLVENTS[15]

CHEMICAL	SOURCE	BP	ρ	MW	DC
Water	Distilled water further purified by a Millipore* system	100	1	18	78.54[b]
Acetic Acid	Fisher-glacial, reagent	118	1.05	80	6.15[a]
Methanol	Fisher-acetone free, absolute	65	0.79	32	32.63[b]
Ethanol	Fisher-absolute	78.5	0.79	46	24.30[b]
Propanol	Baker-reagent	97.4	0.80	60	20.1[b]
Isopropanol	Fisher-certified	82.4	0.79	60	18.3[b]
Tert-butanol	Mallinkrodt-analytical	82.3	0.79	74	10.9[c]
Toluene	Fisher-certified	110.6	0.87	92	2.38[b]

BP : boiling point at atmospheric pressure (C)

ρ : density (g/cc)

MW : molecular weight

DC : dielectric constant

[a] 20 C

[b] 25 C

[c] 30 C

*Millipore Corporation-Water Purification System

APPENDIX B:THE IDEAL EXCHANGE MODEL

Table V reports parameters fitted to the ideal exchange model. Figures
26 to 29 show the experimental data and the results of the model.

TABLE V. IDEAL EXCHANGE MODEL-LINEAR REGRESSION

Dowex MWA-1		Slope*	Intercept**
Sorption-	This work	0.226 ± 0.004	0.00452 ± 0.00323
	Garcia[5]	0.204	0.00319
Regeneration-	This work	0.241 ± 0.053	0.0643 ± 0.0205
	Garcia[11]	0.263	-------

Aurorez		Slope*	Intercept**
Sorption-	This work	0.481 ± 0.064	0.0368 ± 0.0517
	Garcia[5]	0.454	0.0303
	Chanda et al[8]	1.31	0.00994
Regeneration-	This work	2.81 ± 1.07	0.251 ± 0.151
	Garcia [11]	1.00	-------

* g resin/milliequivalents of sites

** [(milliequivalents of acetic acid)(g resin)]/[(g solution)

   (milliequivalents of sites)]

± standard error of estimate

FIGURE 26. IDEAL EXCHANGE MODEL FOR SORPTION OF ACETIC ACID FROM WATER
BY DOWEX MWA-1
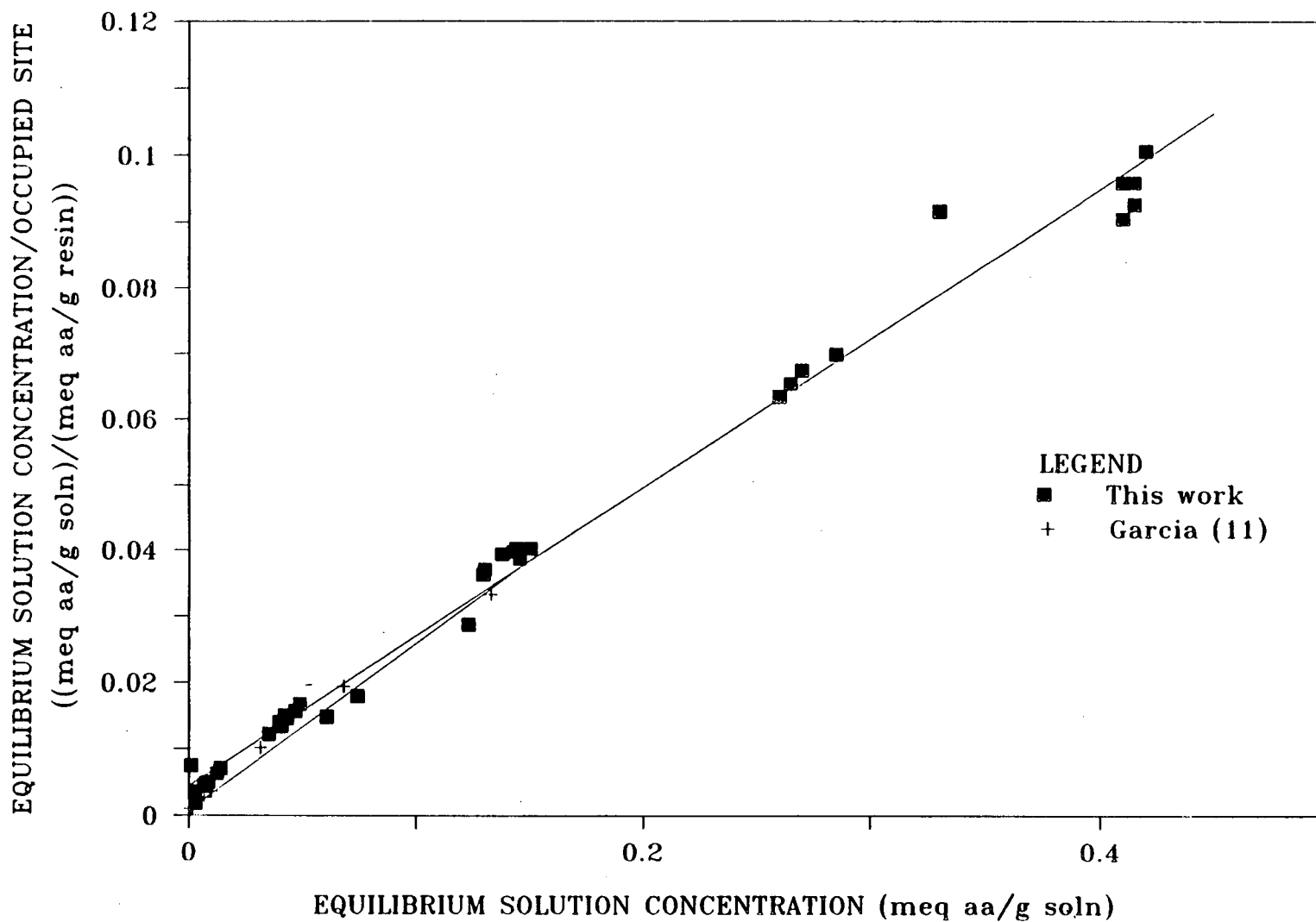

LEGEND
■   This work
+   Garcia (11)

FIGURE 27. IDEAL EXCHANGE MODEL FOR SORPTION OF ACETIC ACID FROM WATER BY AUROREZ
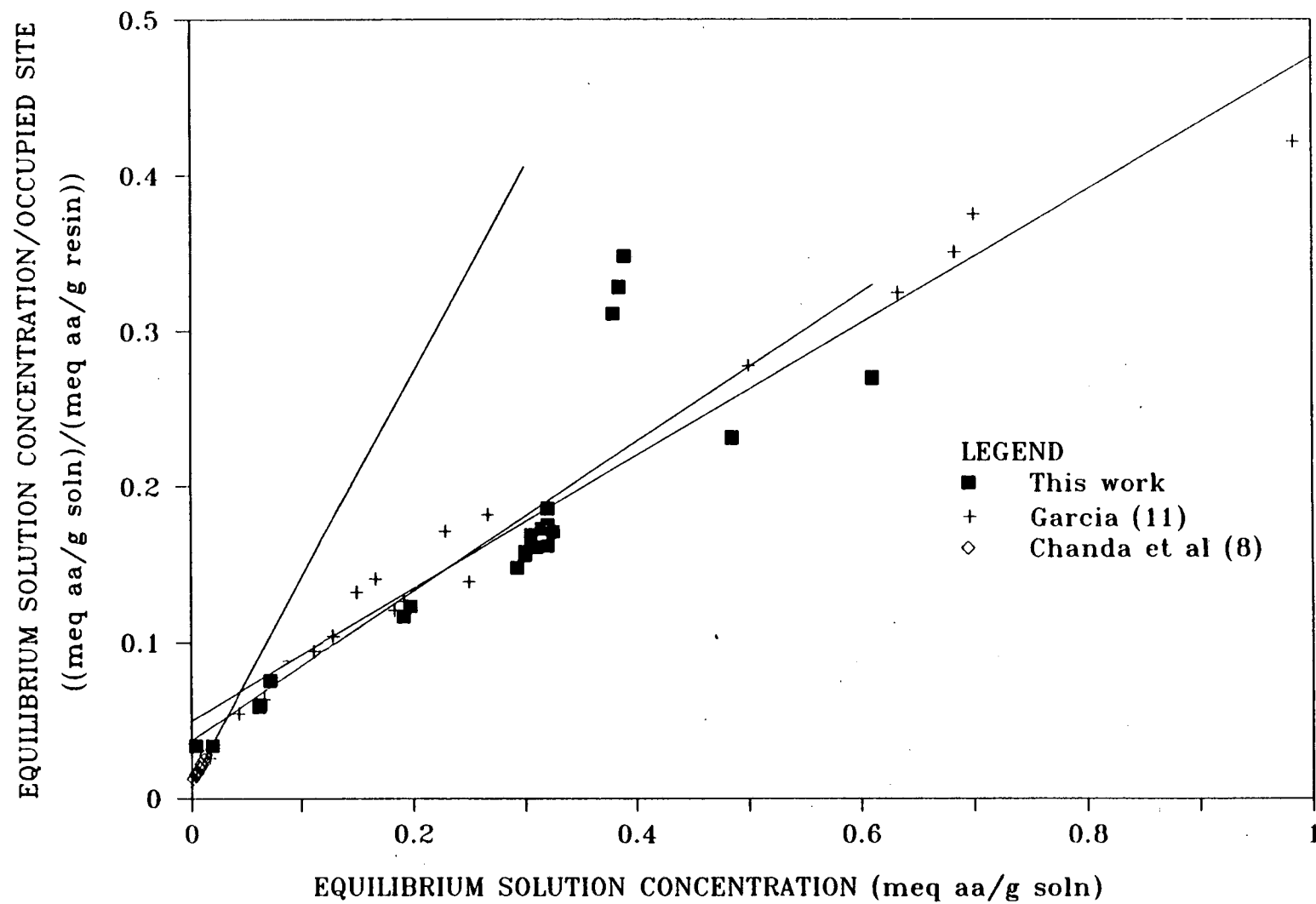
FIGURE 28. IDEAL EXCHANGE MODEL FOR METHANOL REGENERATION
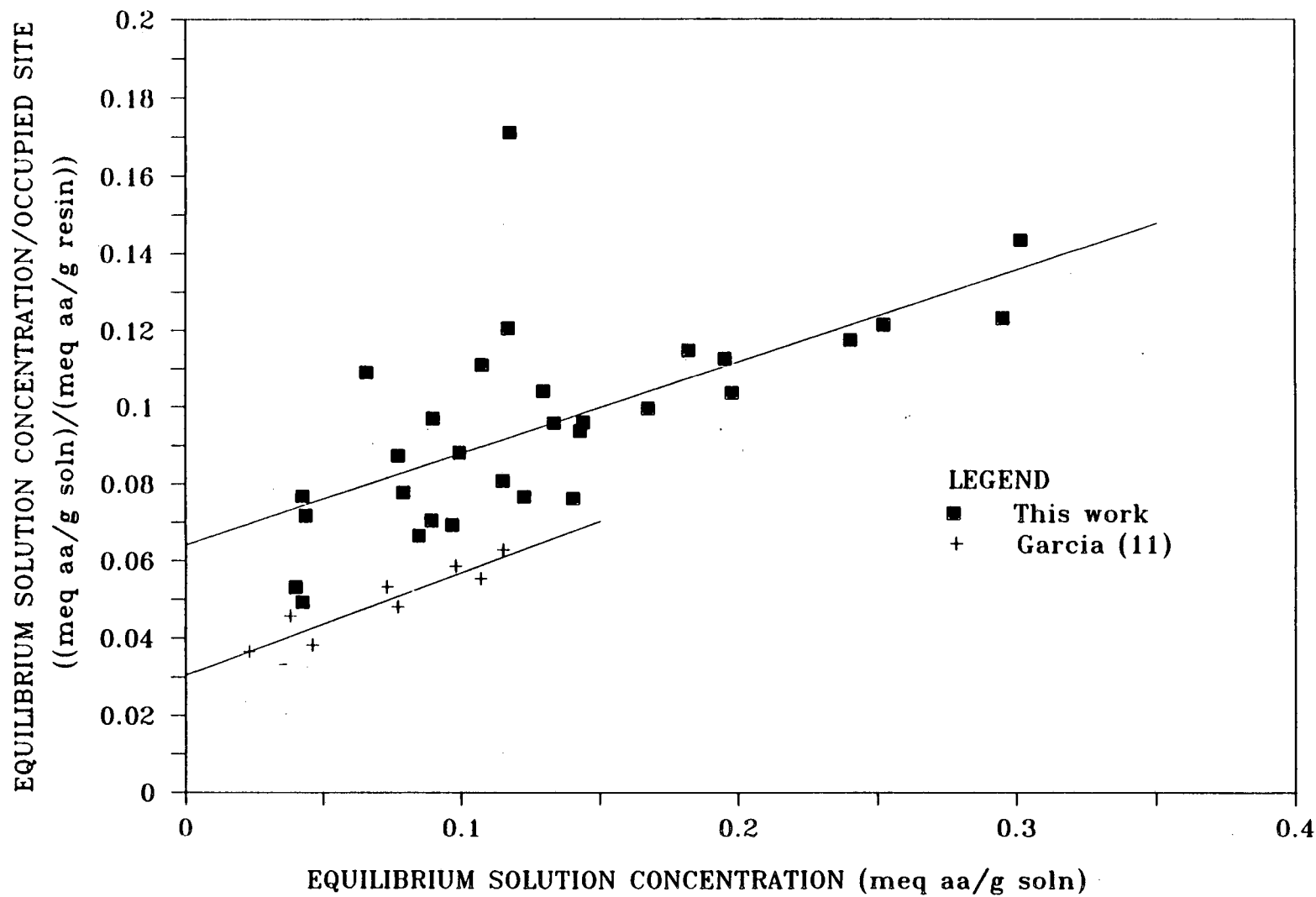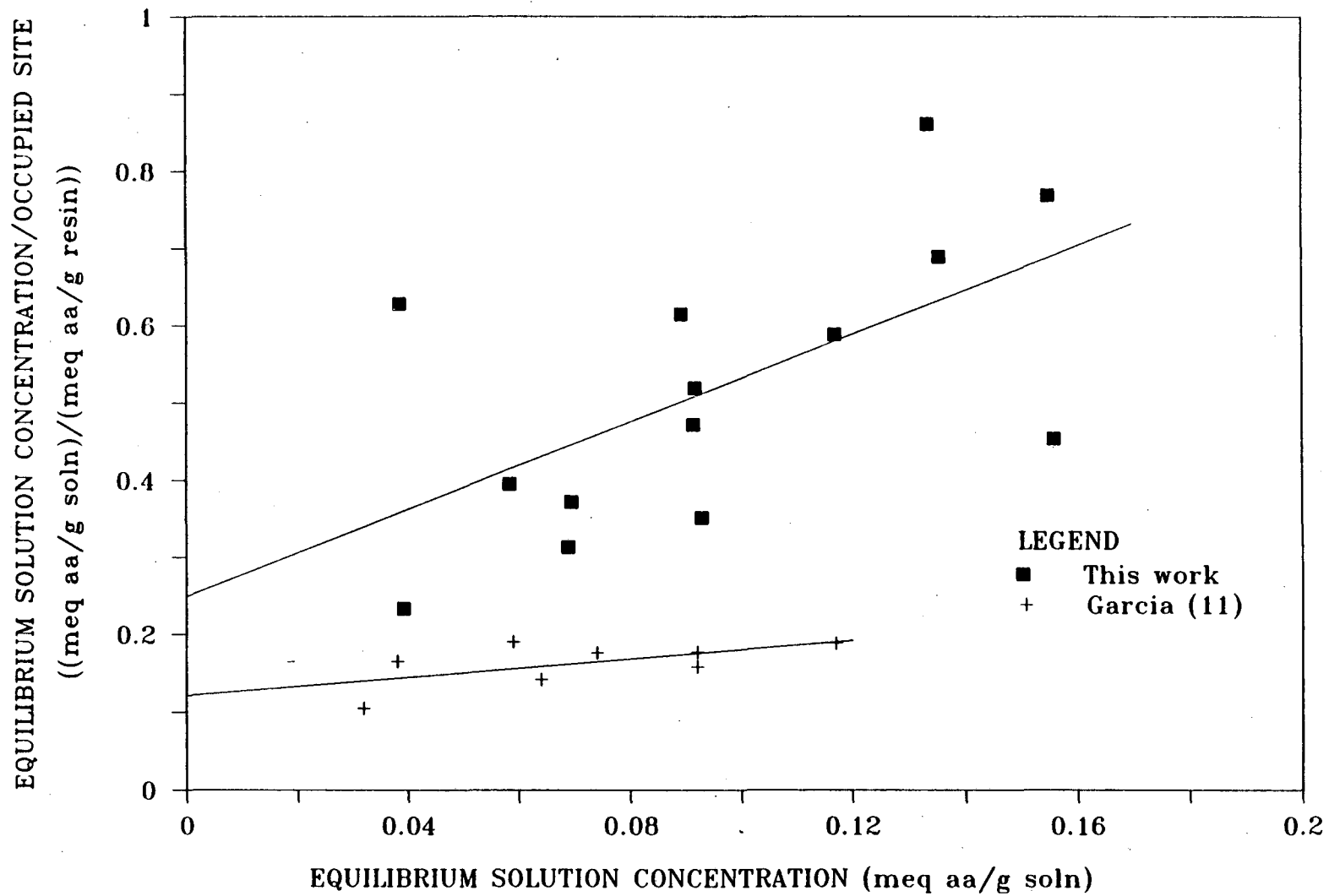OF ACETIC ACID FROM DOWEX MWA-1

FIGURE 29. IDEAL EXCHANGE MODEL FOR METHANOL REGENERATION
OF ACETIC ACID FROM AUROREZ

APPENDIX C:THE LOCAL-EQUILIBRIUM THEORY OF FIXED-BED DEVICES

Figures 30 and 31 show the prediction of the local-equilibrium theory of fixed-bed devices for the number of bed volumes of methanol needed for regeneration of acetic acid from Dowex MWA-1 and Aurorez. The resins were assumed to be equilibrated with 1, 3, and 5 weight percent aqueous acetic acid solution.

FIGURE 30. LOCAL-EQUILIBRIUM THEORY OF FIXED BED-DEVICES PREDICTION FOR METHANOL REGENERATION OF ACETIC ACID FROM DOWEX MWA-1

LEGEND
——— 1 wt% aqueous acetic acid solution
      3 wt% aqueous acetic acid solution
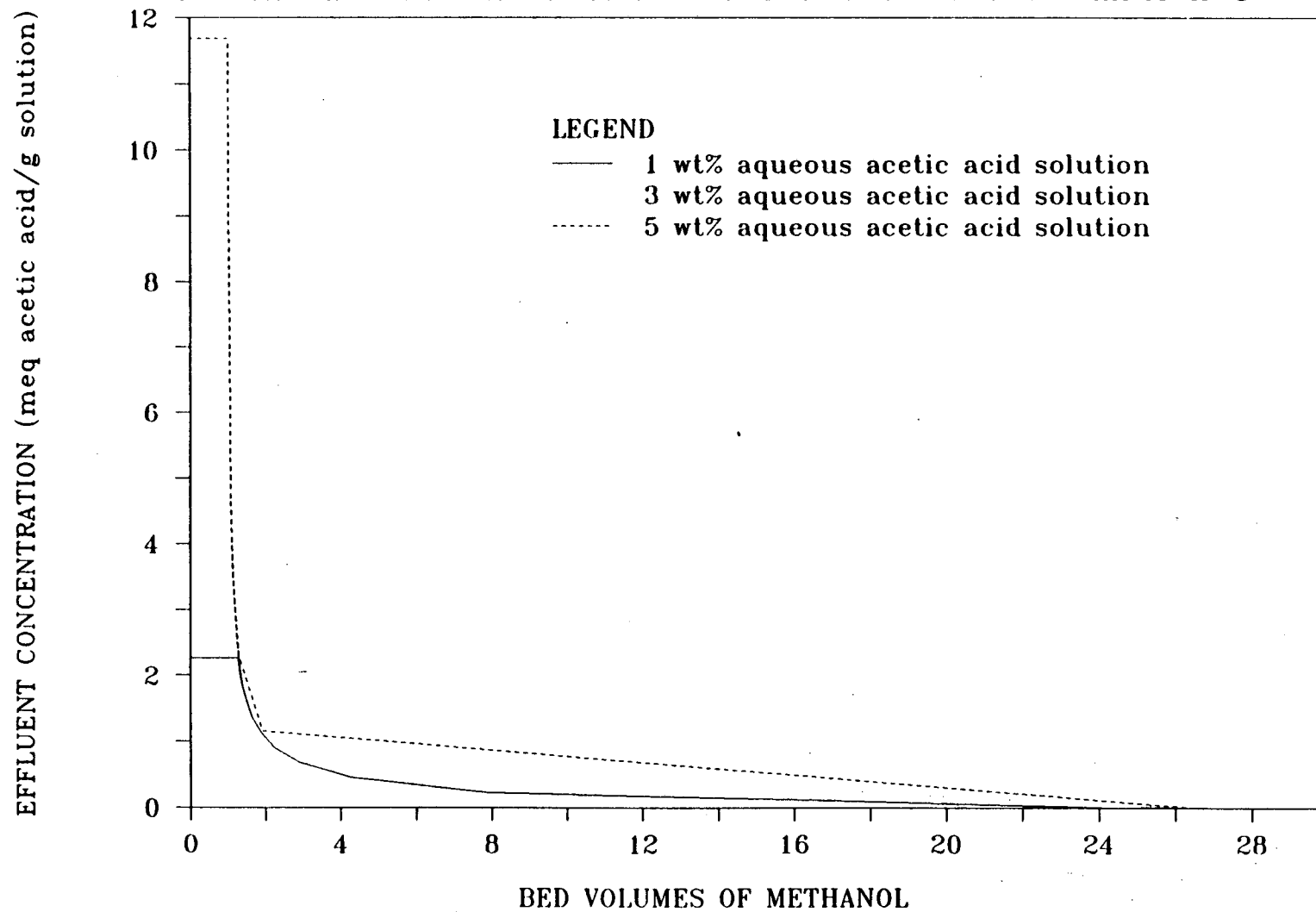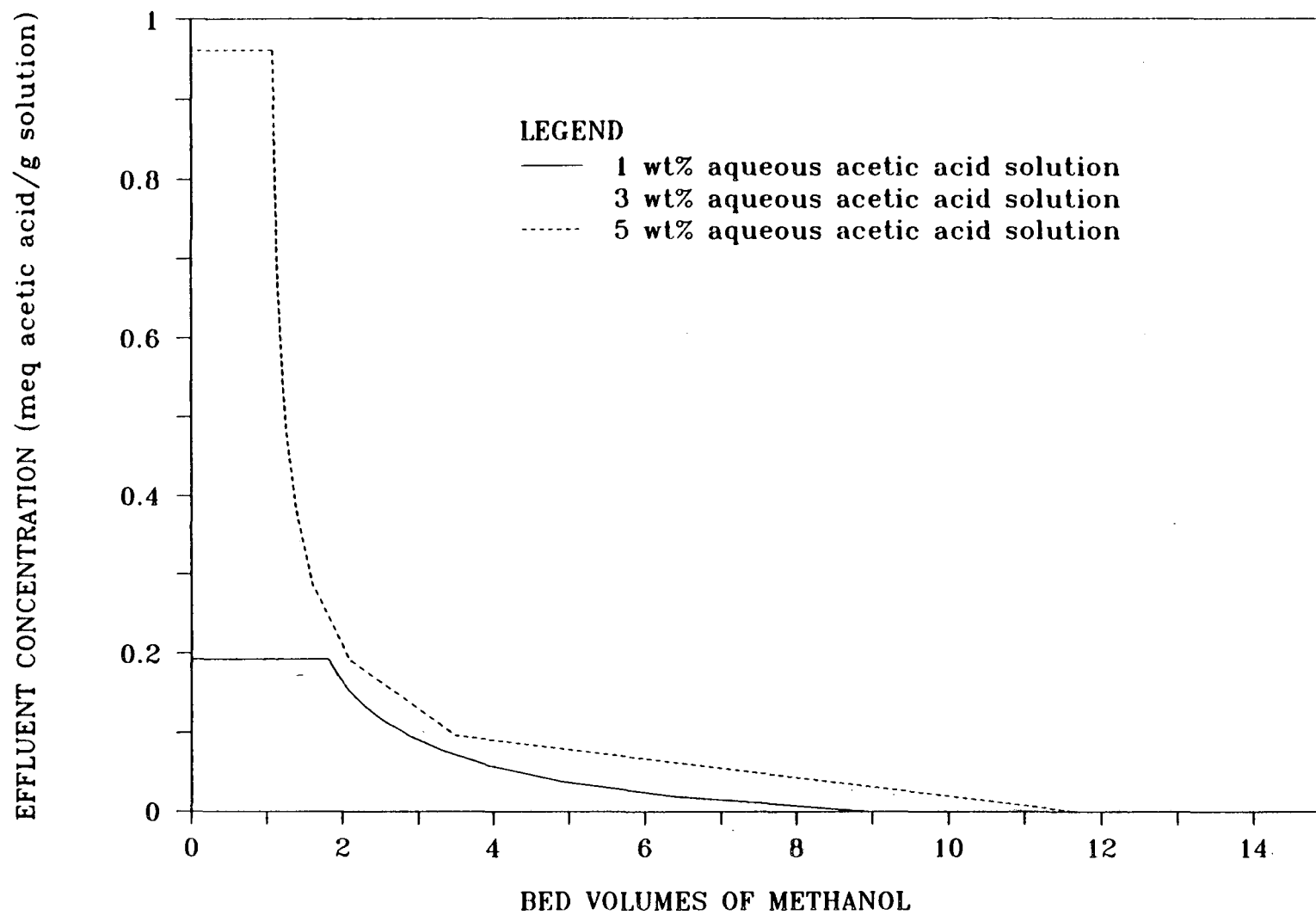------- 5 wt% aqueous acetic acid solution

FIGURE 31. LOCAL-EQUILIBRIUM THEORY OF FIXED-BED DEVICES PREDICTION FOR METHANOL REGENERATION OF ACETIC ACID FROM AUROREZ

APPENDIX D:GAS CHROMATOGRAPH

Gas Chromatograph : Varian Model 3700 with Thermal Conductivity

Detector

Column : 0.25 inches (I.D.) by 72 inches

Packing : Porapak Q

Detector Temperature : 270 C

Filament Temperature : 300 C

Table VI. TEMPERATURE PROGRAMMING FOR GAS CHROMATOGRAPH

Alcohol	Initial Temp (C)	Time (min)	Final Temp (C)	Time (min)
Methanol	80	5	135	10
Ethanol	100	10	135	10
Propanol	90	17	135	8
Isopropanol	110	7	135	8
Tert-butanol	90	15	135	8

Programming is for alcohol in toluene.

Programming rate for all alcohols is 20 C/min.