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I. Sorption by Basic Polymer Sorbents

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ABSTRACT

An important aspect of recovery of product carboxylic acids from fermentation broths is the selectivity for the desired acid, as opposed to substrate sugars. In this work uptakes of glucose and competitive uptakes of lactic acid and glucose by three commercially available basic solid polymeric sorbents have been investigated. The results show a low capacity for glucose and a high selectivity for lactic acid over glucose. The main factor governing selectivity is the swelling tendency of the polymeric sorbent. Marked swelling of the sorbent in the solution reduces selectivity for acid over water and glucose. Because of high uptake capacity and relatively low swelling, Dowex MWA-1 gives better selectivity in the pH 5-6 range than do Amberlite IRA-35 and Reillex 425.

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Introduction

Carboxylic acids are readily made by fermentation and are among the most attractive substances that can be manufactured from biomass (Ng, et al, 1983; Jain, et al., 1989). Recovery of carboxylic acids from fermentation broths presents a challenging separation problem. The dilute, complex nature of the fermentation broth makes recovery methods, such as adsorption, that are potentially selective for carboxylic acids highly attractive (King, 1987; Tung and King, 1994). The key to successful application of adsorption to the recovery of carboxylic acids lies in the selection and availability of a sorbent[1] with suitable characteristics. Important characteristics are high sorbent capacity for the acid, high selectivity of sorption, regenerability and, depending upon the process configuration, biocompatibility with microorganisms.

Many fermentations to produce carboxylic acids operate most effectively at pH above pK_{a1} of the acid product. For example, lactic acid ($pK_a = 3.86$), is typically produced at pH 5 to 6 (Vickroy, 1985; Jain, et al, 1989). One approach for recovering carboxylic acids from such solutions is to use solid sorbents or extractants that are sufficiently basic to retain substantial capacity several pH units above the pK_{a1} of the carboxylic acid. Tung and King (1994) investigated the sorption of lactic acid and succinic acid using several commercially available basic polymeric sorbents. The results for recovery of lactic acid show that the uptake in the pH 5 - 6 range varies substantially among sorbents and is strongly dependent upon the basicity, as well as the capacity, of the resin. Reillex 425 (see Table 1)

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[11] -- The terms "sorbent" and "sorption" are used to connote situations where a polymeric solid can take up solute by either or both surface (adsorption) attachment or bulk infusion (absorption).

has virtually no selective uptake of lactic acid in this pH range. Dowex MWA-1 and Amberlite IRA-35 (see also Table 1) are candidates for use for product recovery in a fermentation process at pH 5 - 6. Furthermore, many fermentations, such as that for lactic acid production, are subject to end-product inhibition (Yabannavar and Wang, 1991; Davison and Thompson, 1992). If a solid sorbent can be used *in-situ* or in an external recycle loop, higher overall yields can be achieved.

In order to separate the desired acid efficiently from water and other species, a selective process is needed. Sorbents to be used in fermentation processes should provide high selectivity between the product carboxylic acid and substrate sugars. In addition to conservation of substrate, one reason why very high selectivities are sought is the tendency for small amounts of sugars in a product such as lactic acid to cause discoloration. Relatively few measurements have been reported for uptake capacities for sugars and/or for selectivity between carboxylic acids and sugars with synthetic sorbents. Kaufman et al (1994) screened a series of solid sorbents preliminarily for possible utilization in biparticle fluidized-bed fermentation to produce lactic acid from immobilized *Lactobacillus delbreuckii*, measuring selectivity between acid and sugar as well as other properties.

In this work, adsorption isotherms for uptake of glucose by a number of basic polymeric sorbents were examined so as to ascertain and compare the characteristics of the different sorbents. To identify selectivities between a carboxylic acid and the sugar, other batch sorption experiments were performed over a wide pH range with aqueous solutions containing lactic acid and glucose. It was necessary to devise a method of analysis which would measure small differences in sugar concentration in aqueous solutions with sufficient precision.

Materials and Methods

Materials. The solid sorbents used and their manufacturers are listed in Table 1. Dowex MWA-1, Reillex 425 and Amberlite IRA-35 were used as solid sorbents. All three sorbents were washed successively with water, methanol, aqueous NaOH and aqueous HCl, and then were dried to constant weight in a vacuum oven at 60°C and 60 KPa. Reillex 425 was pre-wet by stirring in methanol and then displacing the methanol with water, because it is difficult to wet that sorbent directly with water. The other two sorbents were initially in the dry form.

D(+)-glucose monohydrate, USP (Fluka Chemie AG, Buchs), was used as received. Lactic acid (Aldrich, 85% in water, A.C.S. reagent grade) was diluted with water to approximately 15% (w/w) and boiled under total reflux for 12 hours to hydrolyze dimers or multimers present in the concentrated solution. All aqueous solutions were prepared from distilled water that had been further purified by passage through a Milli-Q water filtration system (Millipore Corp.).

Composite Sorption Isotherms. Sorption isotherms for glucose onto various sorbents were generated by contacting known weights of sorbents (typically 1.0 g, dry basis) and glucose solutions of known concentration (typically 10 g) in 20 ml scintillation vials sealed with foil-lined caps. The vials were placed in a temperature-controlled shaker bath at an oscillation rate of 120 min^{-1} for 24 hours, which preliminary tests demonstrated to be more than sufficient for equilibration. Equilibration temperatures were 25, 40 and 60°C for Dowex MWA-1 and Reillex 425, and 25 and 40°C for

Amberlite IRA-35, for which the highest allowable operating temperature was found to be less than 60°C. The pH of the solution was not adjusted, and buffering agents were not used.

Initial and final concentrations of glucose were determined by high-performance liquid chromatography, HPLC, (Perkin Elmer Series 10), using a Bio-Rad Fast Acid Analysis Column with a differential refractometer (Waters Model 401) detector. A mobile phase of 0.01 N H_2SO_4 was used.

The decrease of glucose concentration in aqueous solution was used to compute the composite uptake of glucose by the sorbents, i.e., the degree of surface or site enrichment (Kipling, 1965). Points for the composite adsorption isotherm were calculated as:

$$Q_{cg} = \frac{W_o \; (C_{g,i} - C_{g,f})}{m} \tag{1}$$

Any water and glucose initially adhering to or absorbed into the sorbent must be included in W_0 and $C_{g,i}$.

Since depletions of glucose in the bulk solution are small, it was important to gain very high precision in the analysis by HPLC. Typical reproducibilities of analysis were within 1%.

Uptake vs. pH Curves. In these experiments, 10 g of aqueous solution containing 4.0% (w/w) lactic acid and 1.0% glucose were contacted with 1 g of sorbent (dry basis) in a sealed vial, as in the sorption isotherm experiments. For measurements of the effect of pH upon sorbent capacity, the aqueous solutions were adjusted to various pH values using aqueous NaOH. After equilibration, the pH of the solution was measured with an Orion Model 601A pH meter equipped with an Orion Ross pH electrode. The acid and glucose concentrations of the aqueous phase were determined by HPLC.

The composite uptake of glucose, Q_{cg}, is calculated from Equation (1), and that of lactic acid, Q_{ca}, by an analogous expression:

$$Q_{ca} = \frac{W_o (C_{a,i} - C_{a,f})}{m} \qquad (2)$$

Individual Uptake. The total uptakes of solutes and water cannot be determined by simply measuring the changes of solute concentration in the supernatant solution during equilibration. The individual uptakes of lactic acid (Q_{ia}), glucose(Q_{ig}), and water(Q_{iw}) are defined as:

$$Q_{ia} = \frac{W_o C_{a,i} - W_f C_{a,f}}{m} \qquad (3)$$

$$Q_{ig} = \frac{W_o C_{g,i} - W_f C_{g,f}}{m} \qquad (4)$$

$$Q_{iw} = \frac{W_o (1 - C_{a,i} - C_{g,i}) - W_f (1-C_{a,f} - C_{g,f})}{m} \qquad (5)$$

The individual uptakes give the total amounts of solute or water taken up by the sorbent, including selective uptake at the surface and/or on reactive sites and non-selective uptake due to swelling and pore filling (Kipling, 1965). Calculation of the individual isotherms requires an assumption about the boundary between sorbed and bulk solution. In this work, the sorbed solution is defined as that solution which is retained by the sorbent after centrifugation for 10 minutes at 2000 rpm in a IEC HN-S2 (Damon/IEC Division) Centrifuge.

Equations (6) and (7) describe the relationships between the composite and individual uptakes:

$$\frac{W_o\ (C_{a,i} - C_{a,f})}{m} = Q_{ia} - (Q_{ia} + Q_{ig} + Q_{iw})\ C_{a,f} \tag{6}$$

$$\frac{W_o\ (C_{g,i} - C_{g,f})}{m} = Q_{ig} - (Q_{ia} + Q_{ig} + Q_{iw})\ C_{g,f} \tag{7}$$

It is obvious that the individual uptakes of solutes must always be greater than the composite uptakes, and the composite uptake approaches the individual uptake at very low solute concentration and/or when there is very little water uptake.

In this work, composite uptakes were computed directly. After centrifugation, the total solution uptake ($Q_{ig} + Q_{iw}$) or ($Q_{ia} + Q_{ig} + Q_{iw}$) was measured, and individual uptakes were then computed from Equations (6) and (7).

Results and Discussion

Composite Isotherms. Figures 1, 2 and 3 show composite isotherms for adsorption of glucose, measured for various polymeric sorbents at 25, 40 and 60°C. All three sorbents provide rather low capacities for the sugar. Also, the binding is weak, as is evidenced by the continual rises of the curves. Glucose exhibits *negative* deviations from ideality in aqueous solution, i.e., activity coefficients less than 1 (Miyajima et al, 1983). Correspondingly, addition of glucose serves to *increase* the surface tension of water. Hence there should be little or negative surface enrichment of glucose if there is no preferential chemical interaction of the sugar with the polymeric sorbent surface.

Glucose capacities provided by the three different adsorbents are similar to each other. That for Reillex 425 is higher, which may relate to its higher surface area and/or weak Van der Waals interaction of the sugar with the polyvinylpyridine matrix.

Glucose capacities decrease with increasing temperature. The relatively small change with temperature implies a low enthalpy of adsorption for glucose.

Effect of pH on Competitive Adsorption. Figures 4, 5 and 6 show the measured surface excesses of lactic acid and glucose on the three different polymeric sorbents as a function of the pH of the aqueous solution, for a constant feed concentration of the solutes and the constant initial phase ratio (10g solution/g sorbent).

The effect of pH on adsorption of the weakly ionizable acid is well known and corresponds to previous results (Getzen et al, 1969; Ward and Getzen, 1970; Müller et al, 1980; Kuo et al, 1987; Tung and King, 1994).

For overall bioprocess optimization, the effect of pH on the separation should be considered together with the effect of pH on the fermentation itself. For lactic acid fermentation, the sorbent should demonstrate substantial uptake in the pH 5-6 range (Tung and King 1994; Dai and King, 1995). The results in Figures 4 - 6 show that the uptake in this range is strongly dependent upon the basicity of the sorbent. As is shown in Table 1, the order of the apparent pK_a values for these weak-base resins is Amberlite IRA-35 > Dowex MWA-1 > Reillex 425. Reillex 425 gives virtually no selective uptake of lactic acid in the pH 5-6 range over the range of temperatures. In the same pH range, uptakes are 0.17-0.28 g lactic acid/g sorbent for Dowex MWA-1 and 0.29-0.35 g lactic acid/g sorbent for Amberlite IRA-35.

The uptake data for lactic acid with all three sorbents are well described by a 1:1 complexation equilibrium, which gives a functional form equivalent to the Langmuir Equation:

$$\frac{Q_{ca}}{Q_m} = \frac{K\ C_{a,f}}{1 + K\ C_{a,f}} \tag{8}$$

The solid curves shown in Figure 4, 5 and 6 are calculated by means of Equation 8. These results are similar to those of Tung and King (1994), although there are two competing solutes (lactic acid and glucose) in this work. Weakly basic sorbents, such as Dowex MWA-1 and Amberlite IRA-35, provide a complexing mechanism for uptake of the carboxylic acid and limit additional mechanisms which might result in the indiscriminate binding of competing compounds.

It is of interest to note that all the three sorbents give small negative surface enrichments of glucose at all values of pH, as shown in Table 2 and Figures 4, 5 and 6. Thus the presence of lactic acid on the sorbents appears to displace glucose that is sorbed in the absence of lactic acid. (Compare Figures 1 - 3 with Figures 4 - 6.) As a result of the non-enrichment of glucose by adsorptive mechanisms, the uptake of glucose is determined by the amount of uptake of bulk solution, e.g., by swelling and/or interstitial entrainment.

Water Uptake and Swelling. Figures 7, 8 and 9 show measured individual uptakes of water from glucose solutions by the polymeric sorbents. There are three points that are worth discussing. First, the polymeric sorbents used all have substantial water capacities because of their polarity, combined with chain relaxation and consequent swelling. Second, it should be noted that the water capacities of the three sorbents decrease slightly as the concentration of glucose in the equilibrium solution increases. This is probably the result of competitive uptake between glucose and water and the decrease in the activity of water as the glucose concentration increases. Third, the water uptake increases with increasing operating temperature, reflecting greater relaxation of the polymer chains. The water uptake by Amberlite IRA-35 is substantially higher, and the water uptake of Reillex 425 is somewhat higher than that of Dowex MWA-1.

Figures 10 and 11 present water uptakes measured during competitive adsorption between lactic acid and glucose at 25 and 40°C. The water uptakes increase with increasing uptakes of lactic acid. This behavior must result from increased swelling of these weak basic sorbents, attributable to solvation of the amine-carboxylic acid complex.

As shown in Figure 12, there is a direct correlation between uptakes of glucose and water. For all three polymeric sorbents, higher water uptake is accompanied by higher uptake of glucose. It thereby appears that water brings glucose into the sorbent.

Selectivity of Competitive Adsorption. Figures 13 and 14 show selectivities obtained between lactic acid and glucose at 25 and 40°C. Figures 15 and 16 show selectivities between lactic acid and water at 25 and 40°C, reported as "inverse selectivities" -- the weight ratio of water to lactic acid taken up. In Figures 13 through 16, the abscissa is the pH value of the equilibrium aqueous phase.

It is clear that, among the basic sorbents studied, Dowex MWA-1 gives the best selectivities for uptake of lactic acid, as opposed to water and glucose, in the pH 5-6 range. Although Amberlite IRA-

35 gives higher uptakes of lactic acid in the middle pH range, the marked swelling of that sorbent leads to substantial uptakes of water and glucose, and decreases the selectivities for lactic acid over water and glucose. The uptake and selectivity for lactic acid with Reillex 425 are much lower than for Dowex MWA-1 or Amberlite IRA-35 in the pH 5-6 range.

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Nomenclature

$C_{a,f}$ weight fraction lactic acid in final solution (%)

$C_{a,i}$ weight fraction lactic acid in initial solution (%)

$C_{g,f}$ weight fraction glucose acid in final solution (%)

$C_{g,i}$ weight fraction glucose in initial solution (%)

K complexation constant for sorption (g resin/g lactic acid)

m mass of dry sorbent (g)

Q_{ca} composite uptake of lactic acid (g lactic acid/g sorbent)

Q_{cg} composite uptake of glucose (g glucose/g sorbent)

Q_{ia} individual uptake of lactic acid (g lactic acid/g sorbent)

Q_{ig} individual uptake of glucose (g glucose acid/g sorbent)

Q_{iw} individual uptake of water (g water/g sorbent)

Q_m maximum value of sorbed lactic acid at high concentration (g lactic acid/g sorbent)

W_0 initial mass of bulk solution (g)

W_f final mass of bulk solution (g)

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Table 1. Properties of Basic Sorbents Used[a]

Sorbent	Dowex MWA-1	Reillex 425	Amberlite IRA-35
Manufacturer	Dow Chemical Co.	Reilly Tar & Chemical Co.	Rohm & Haas Corp.
Matrix	Polystyrene-divinylbenzene	Poly(4-vinyl pyridine)	Acrylic
Functional Group	3° Amine	Pyridine	3° Amine
Maximum Temperature(°C)	100.0	100.0	60.0
Apparent pK_a	3.92[b]	6.70[b]	8.32[b]
N_2 BET Surface Area (m^2/g)	23.0	90.0	20 - 30

[a] Sources: Dow Chemical Company, 1983; Reilly Industries, 1989; Rohm & Haas Company, 1981. [b] Gustafson et al, 1970.

Table 2. Surface Depletion of Glucose during

Simultaneous Sorption of Lactic Acid and Glucose (25 and 40 °C)

Temperature (°C)	Dowex MWA-1 pH	Dowex MWA-1 Q_{cg} (mg/g)	Reillex 425 pH	Reillex 425 Q_{cg} (mg/g)	Amberlite IRA-35 pH	Amberlite IRA-35 Q_{cg} (mg/g)
25	2.78	-8.1	2.15	-3.6	4.38	-13.1
	4.88	-8.1	2.62	-3.2	4.98	-12.9
	6.07	-7.4	3.16	-2.8	6.08	-13.1
	7.00	-5.3	3.76	-2.2	6.48	-12.5
	7.47	-4.5	4.25	-2.1	7.22	-12.4
	8.05	-4.0	5.09	-1.4	7.65	-11.8
	8.69	-3.6	6.04	-1.4	8.09	-11.4
	8.79	-3.4	6.48	-1.4	8.29	-10.3
40	2.75	-7.4	2.09	-3.7	3.49	-15.4
	3.71	-7.2	2.79	-3.3	4.78	-14.8
	4.64	-8.1	3.31	-3.3	5.44	-14.3
	5.36	-6.7	3.99	-3.1	5.80	-14.7
	6.19	-5.5	4.68	-2.4	6.33	-11.9
	6.73	-4.9	5.29	-2.8	6.68	-11.0
	7.26	-4.4	5.86	-3.4	7.29	-9.3
	8.01	-4.3	6.14	-2.7	8.20	-9.3

List of Figure Captions

Figure 1. Composite Sorption Isotherms for Glucose onto Dowex MWA-1 at Different Temperatures.

Figure 2. Composite Sorption Isotherms for Glucose onto Reillex 425 at Different Temperatures.

Figure 3. Composite Sorption Isotherms for Glucose onto Amberlite IRA-35 at Different Temperatures.

Figure 4. Effect of pH on Composite Uptakes of Glucose and Lactic Acid By Dowex MWA-1. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 5. Effect of pH on Composite Uptakes of Glucose and Lactic Acid By Reillex 425. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 6. Effect of pH on Composite Uptakes of Glucose and Lactic Acid By Amberlite IRA-35. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 7. Individual Uptake of Water from Glucose Solution by Dowex MWA-1.

Figure 8. Individual Uptake of Water from Glucose Solution by Reillex 425.

Figure 9. Individual Uptake of Water from Glucose Solution by Amberlite IRA-35.

Figure 10. Individual Sorption of Water by Polymeric Sorbents at 25°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 11. Individual Sorption of Water by Polymeric Sorbents at 40°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 12. Relationship of Glucose and Water Uptakes by the Three Polymeric Sorbents at 25 and 40°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 13. Selectivity (Proportion of Lactic Acid to Glucose in Sorbate) at 25°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 14. Selectivity (Proportion of Lactic Acid to Glucose in Sorbate) at 40°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 15. Inverse Selectivity (Proportion of Water to Lactic Acid in Sorbate) at 25°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

Figure 16. Inverse Selectivity (Proportion of Water to Lactic Acid in Sorbate) at 40°C. $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 10$.

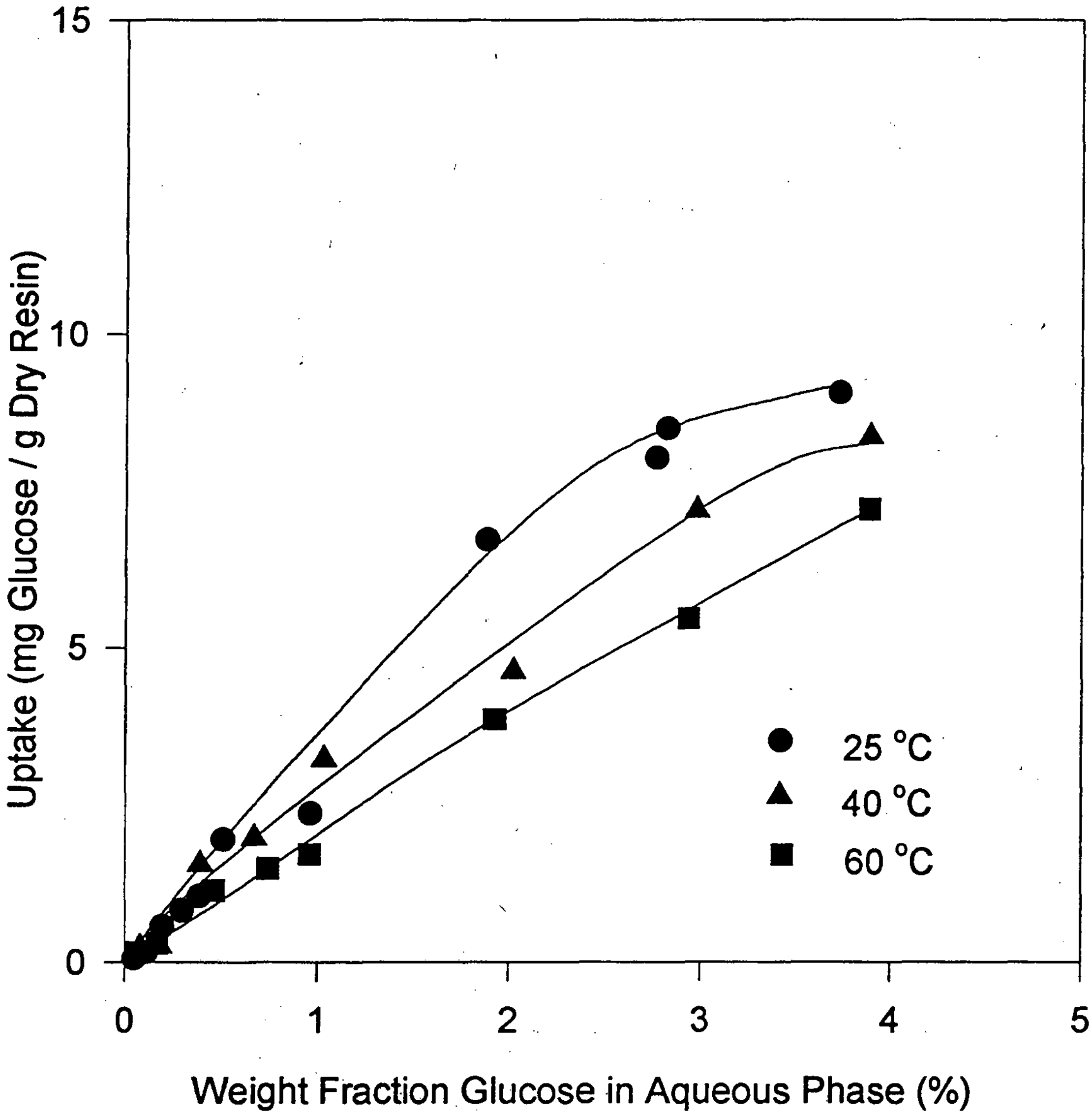


Figure 1 Composite Sorption Isotherms for Glucose onto Dowex MWA-1 at Different Temperatures

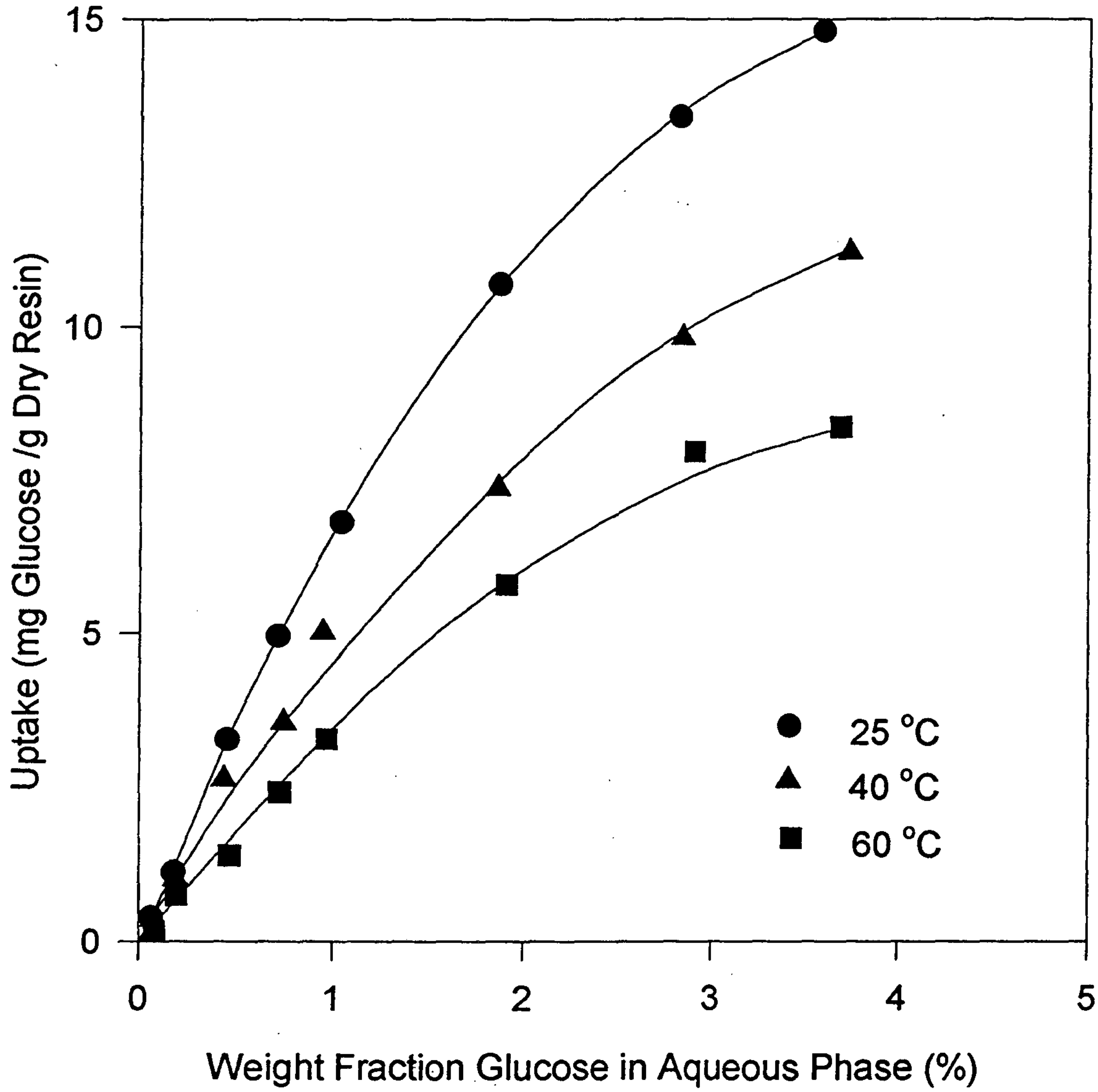


Figure 2 Composite Sorption Isotherms for Glucose onto Reillex 425 at Different Temperatures

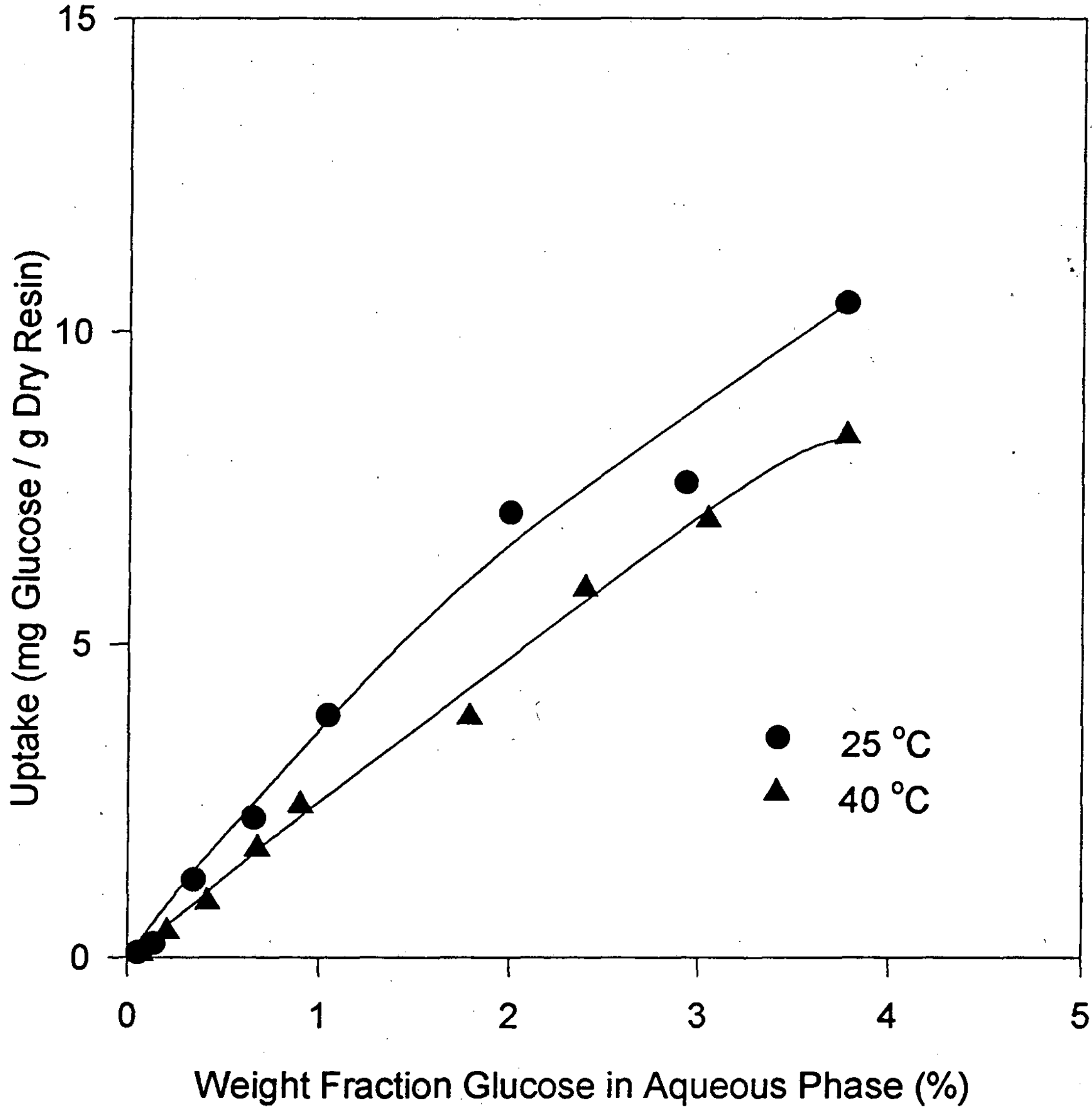


Figure 3 Composite Sorption Isotherms for Glucose onto Amberlite IRA-35 at Different Temperatures

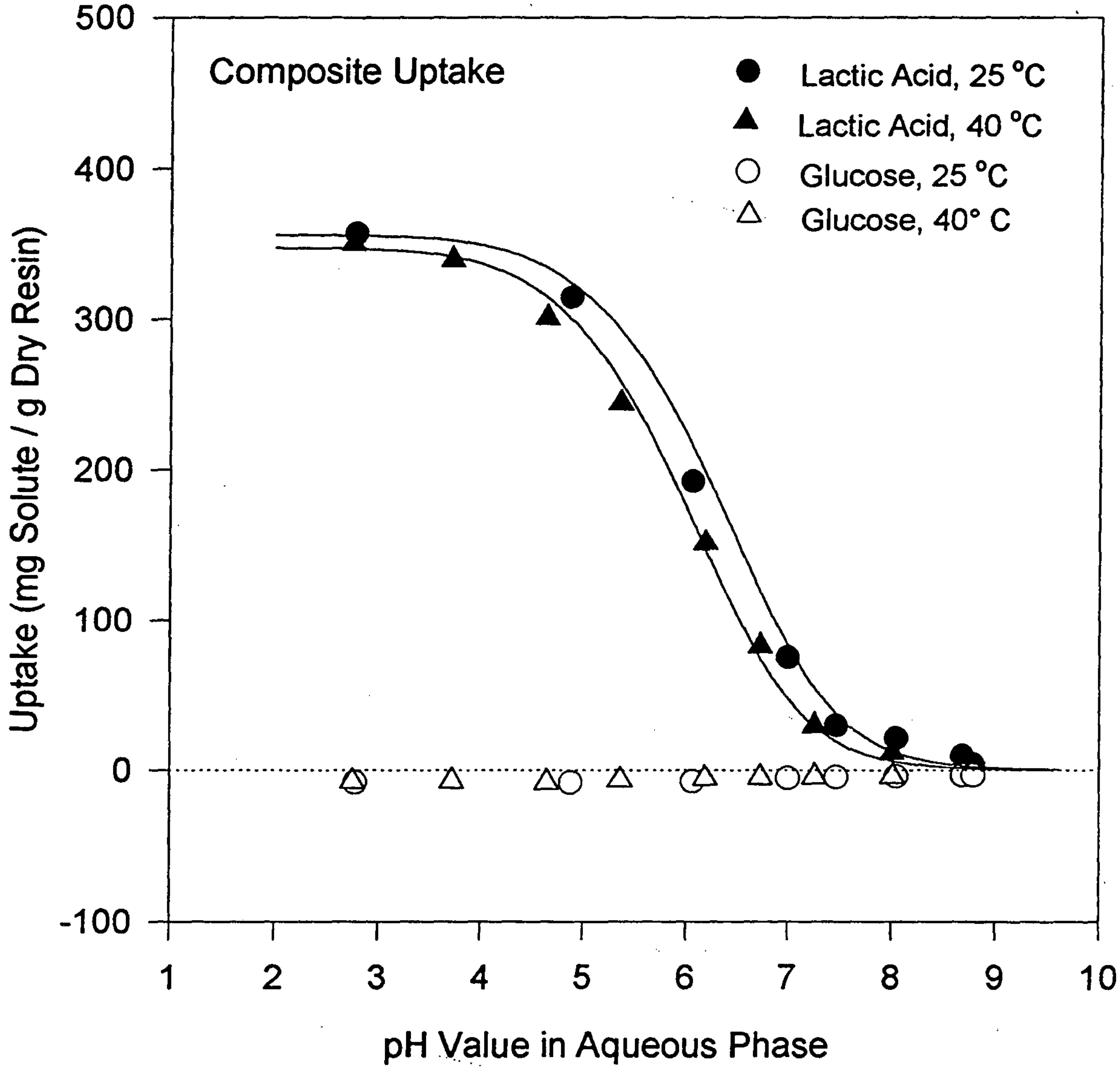


Figure 4 Effect of pH on Composite Uptakes of Lactic Acid and Glucose by Dowex MWA-1, $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 1.0$

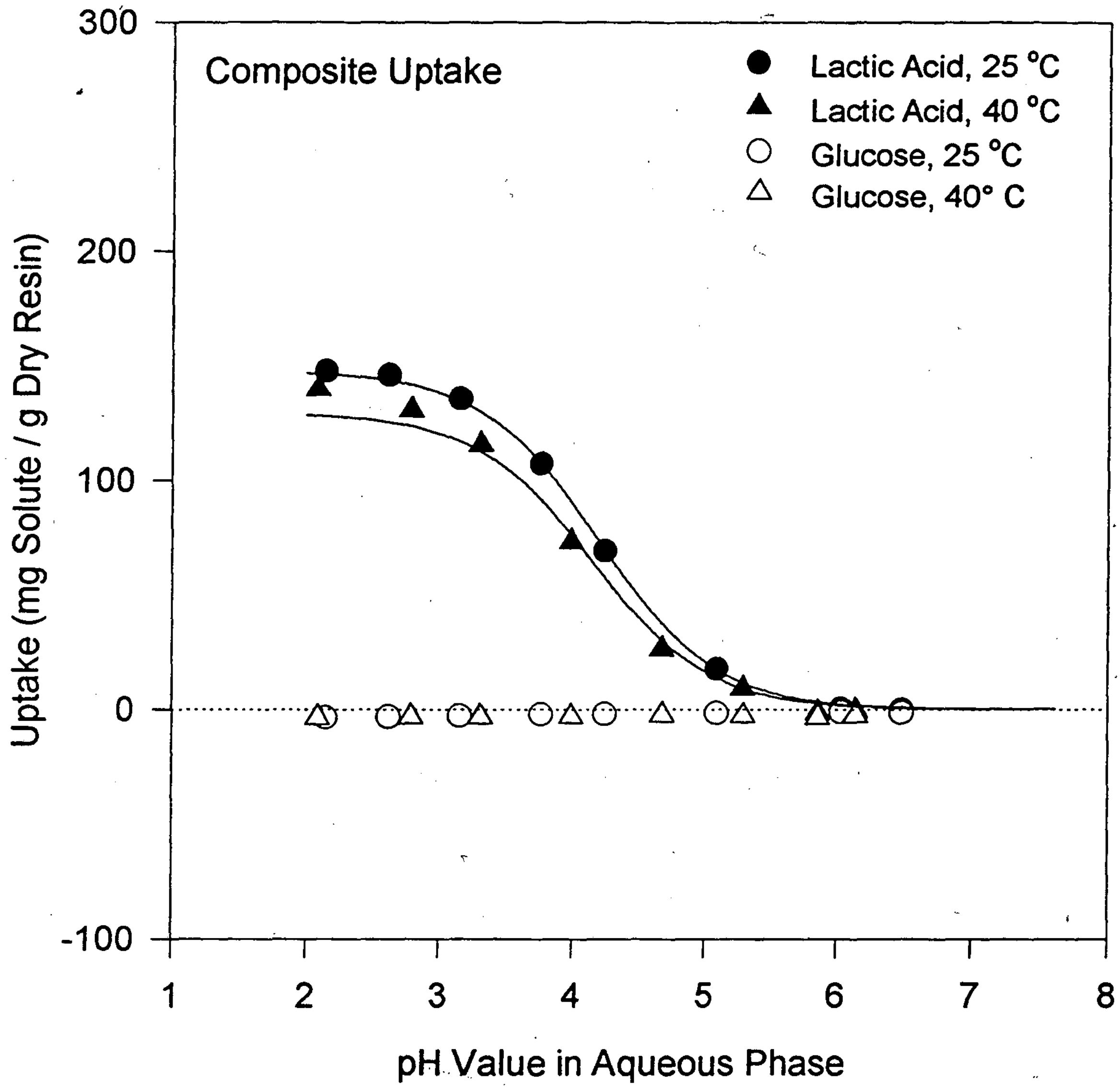


Figure 5 Effect of pH on Composite Uptakes of Lactic Acid and Glucose by Reillex 425, $C_{a,i} = 4.0\%$, $C_{g,i} = 1.0\%$, $W_0/m = 1.0$

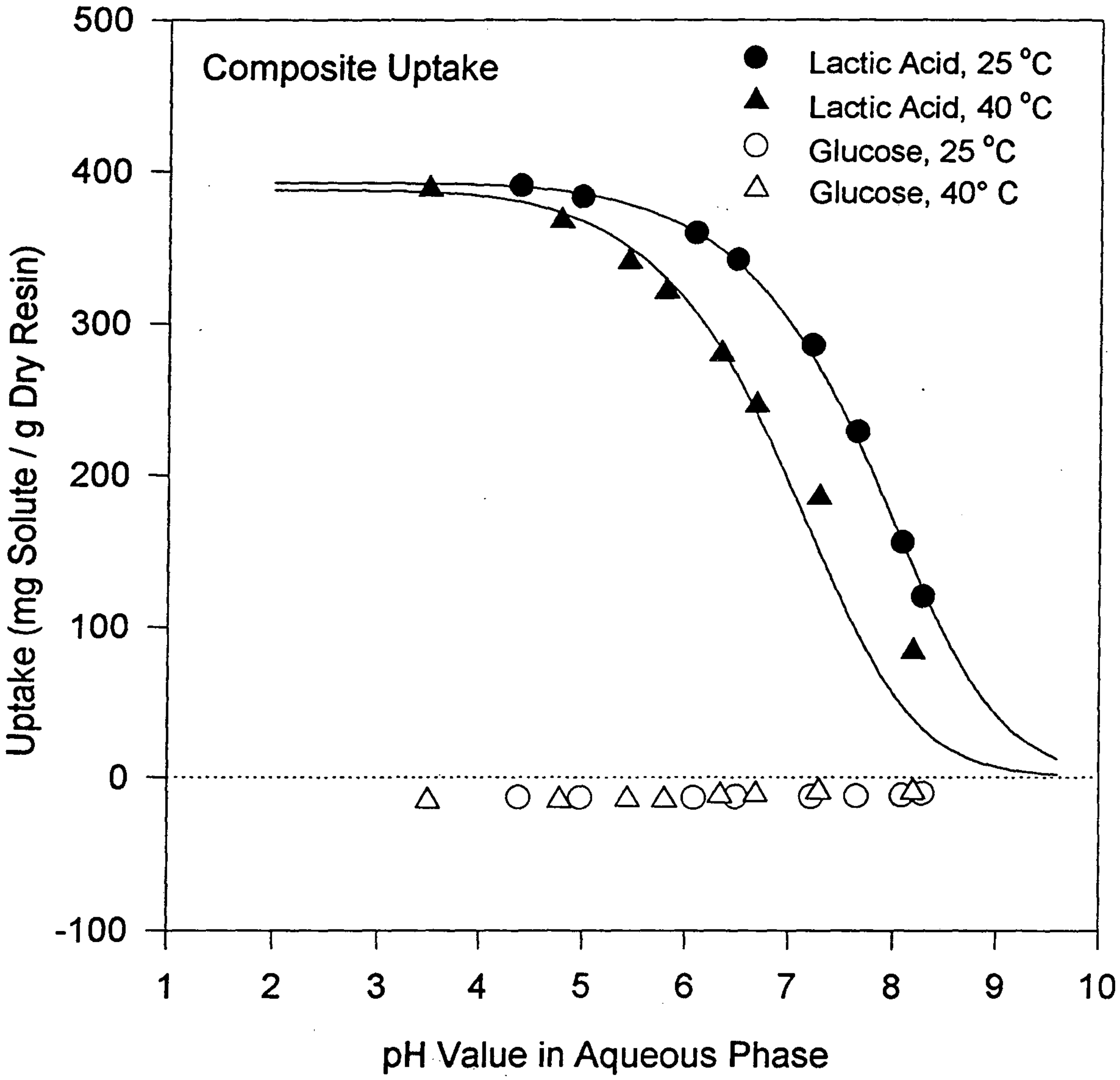


Figure 6 Effect of pH on Composite Uptakes of Lactic Acid and Glucose by Amberlite IRA-35, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

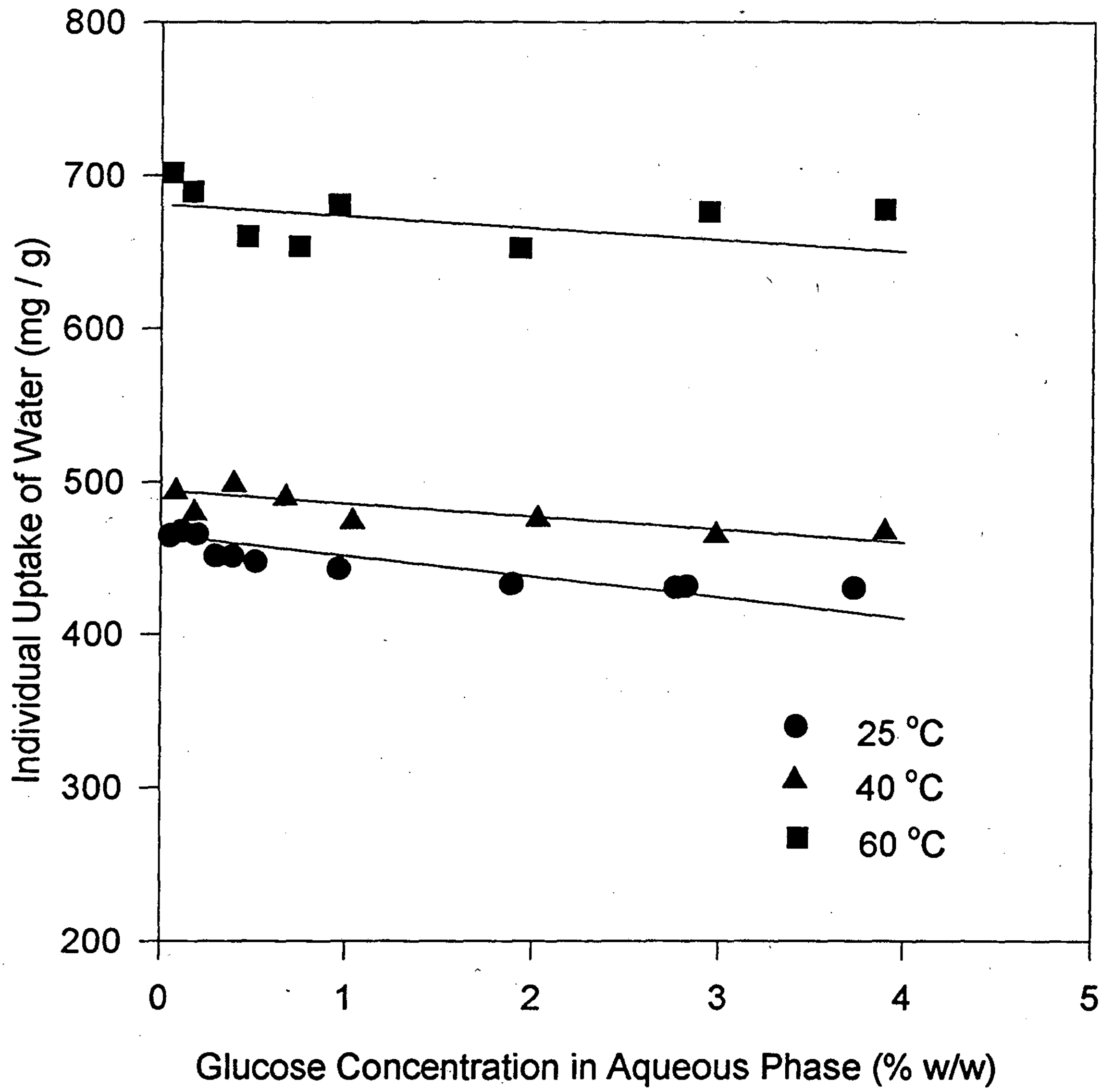


Figure 7 Individual Uptake of Water from Glucose Solution by Dowex MWA-1 at Different Temperatures

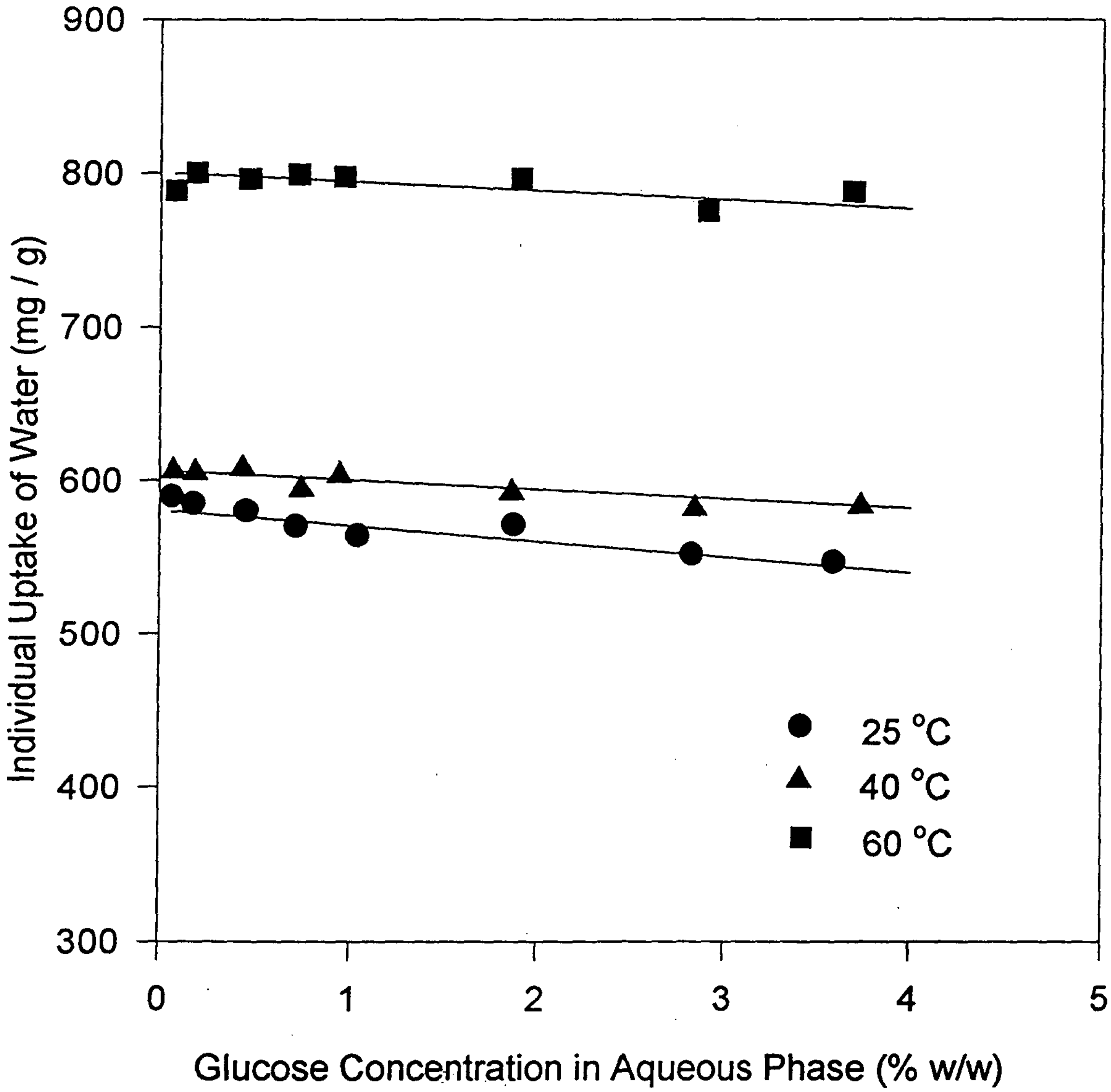


Figure 8 Individual Uptake of Water from Glucose Solution by Reillex 425 at Different Temperatures

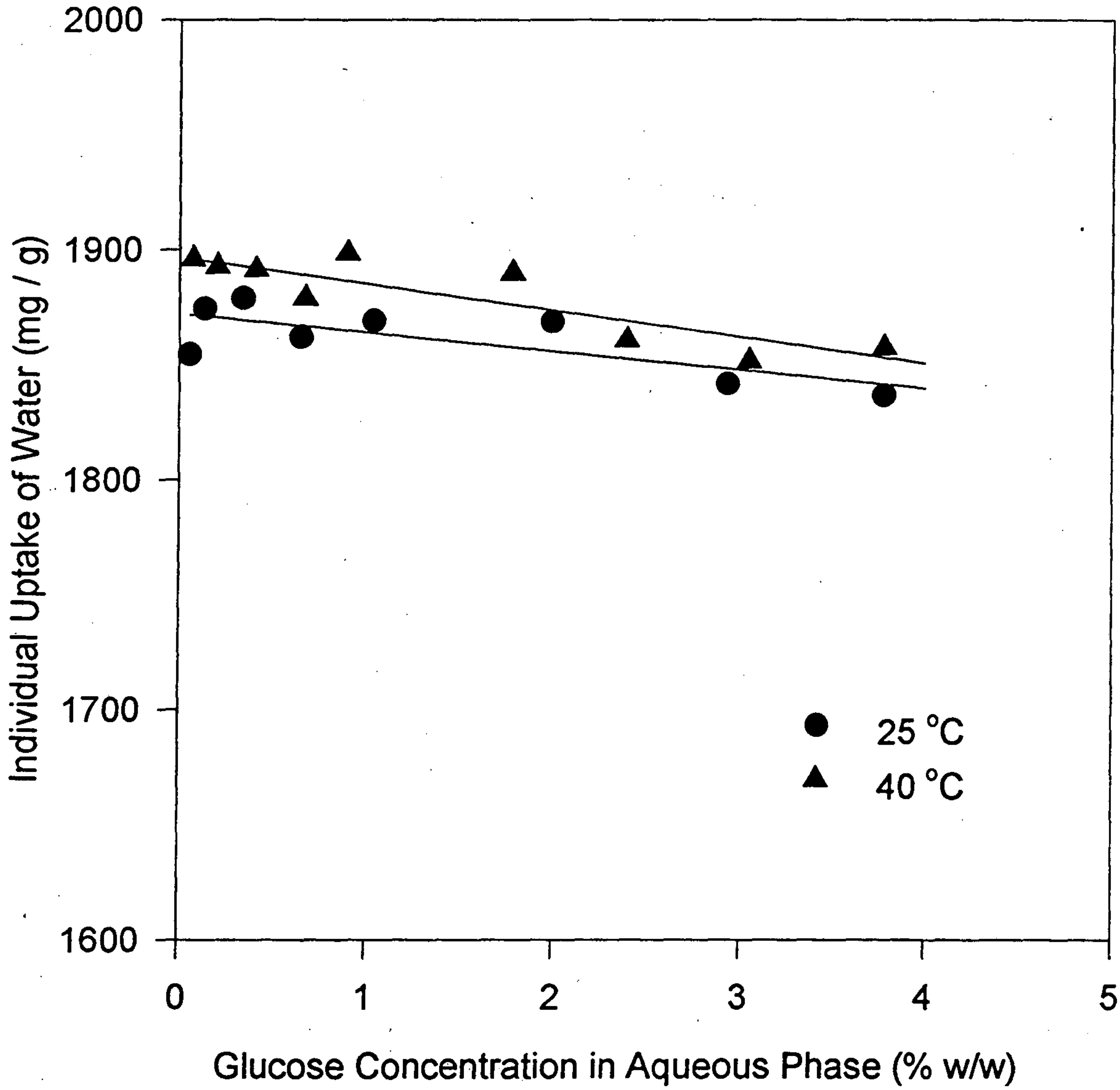


Figure 9 Individual Uptake of Water from Glucose Solution by Amberlite IRA-35 at Different Temperatures

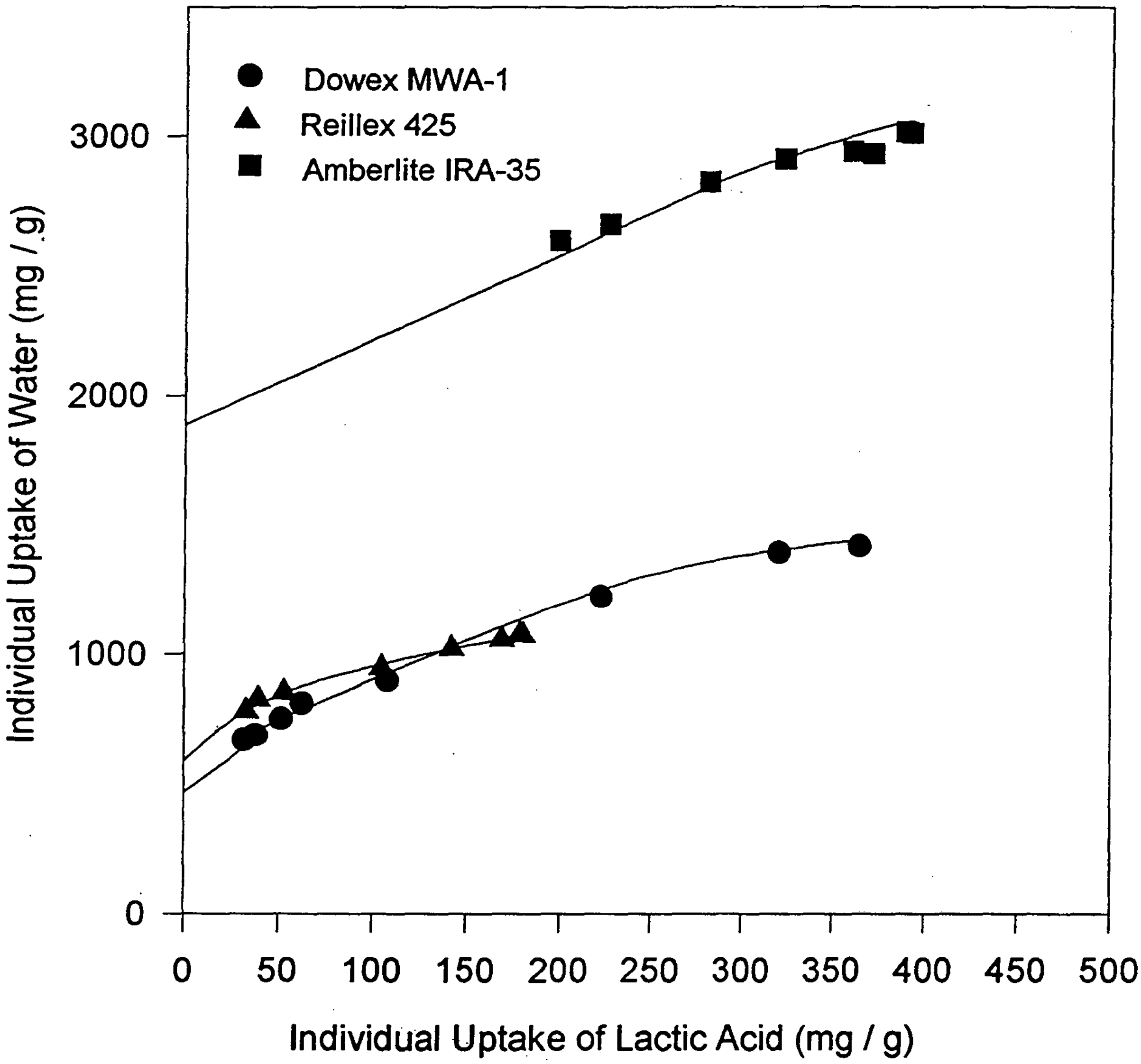


Figure 10 Individual Sorption of Water by Polymeric Sorbents at 25 °C, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

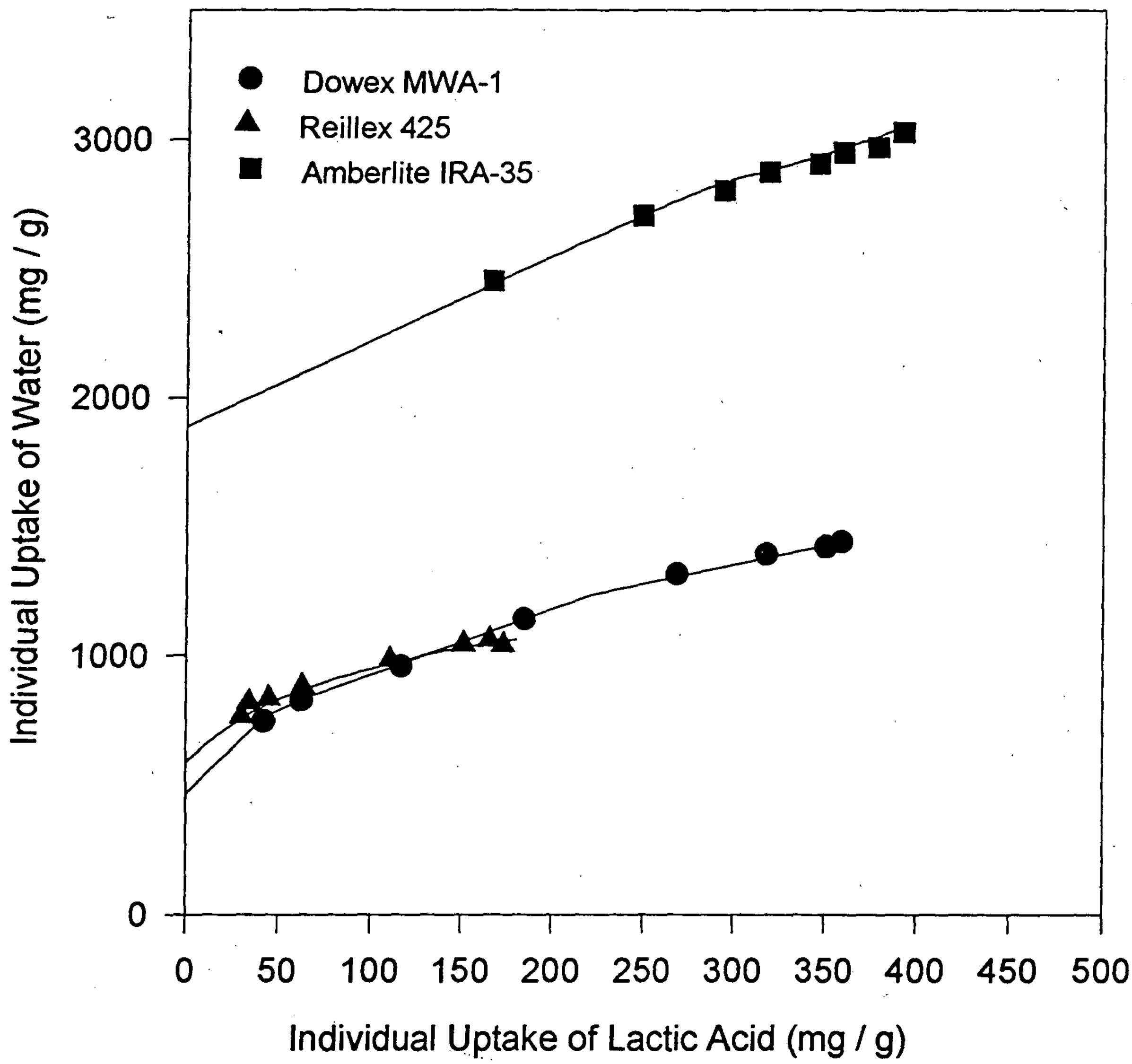


Figure 11 Individual Sorption of Water by Polymeric Sorbents at 40 °C, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

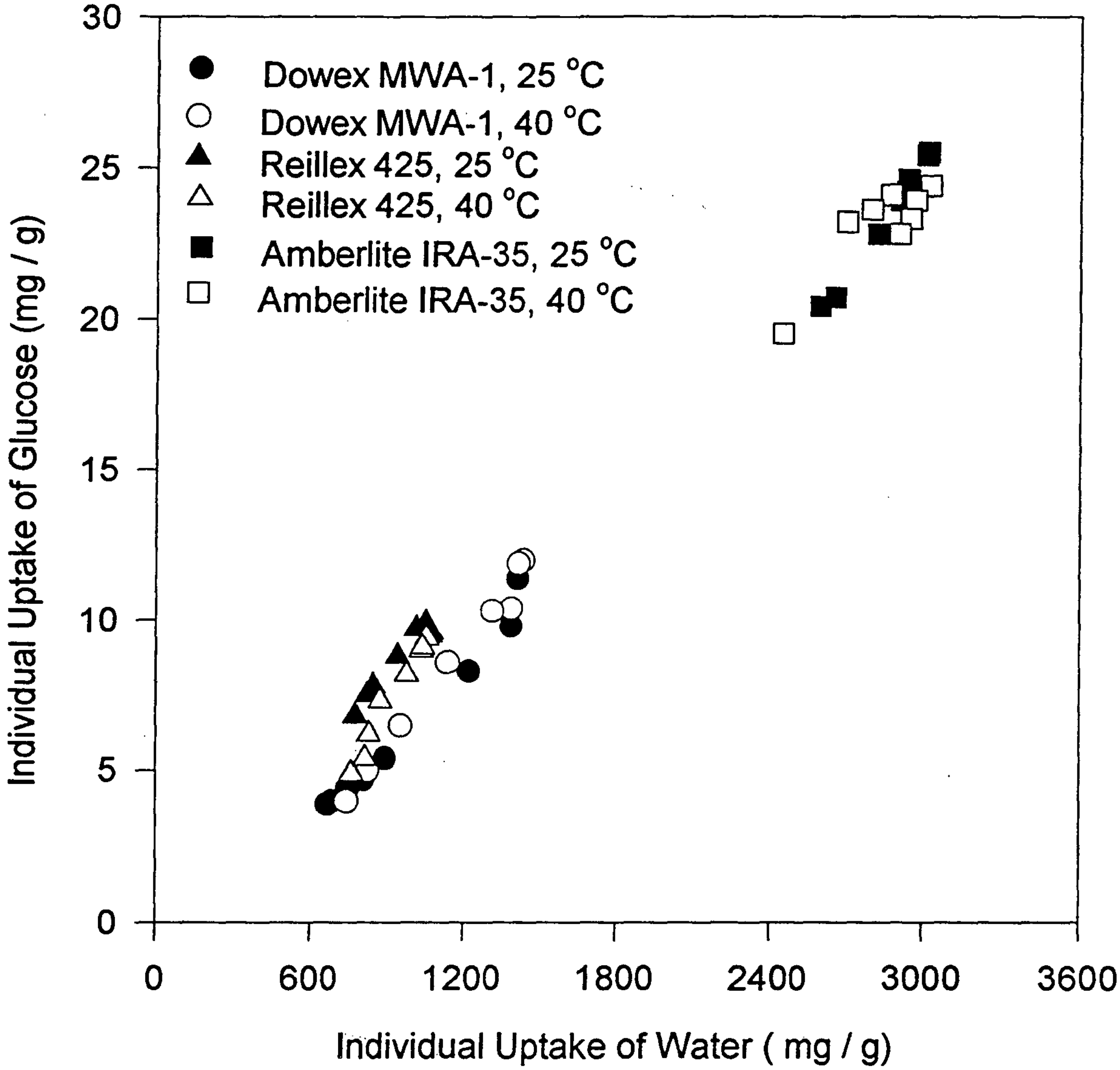


Figure 12 Relationship of Glucose and Water Uptakes by Three Polymeric Sorbents at 25 and 40 °C $C_{a,i}$ = 4.0 %, $C_{g,i}$ =1.0 %, W_0 / m =10

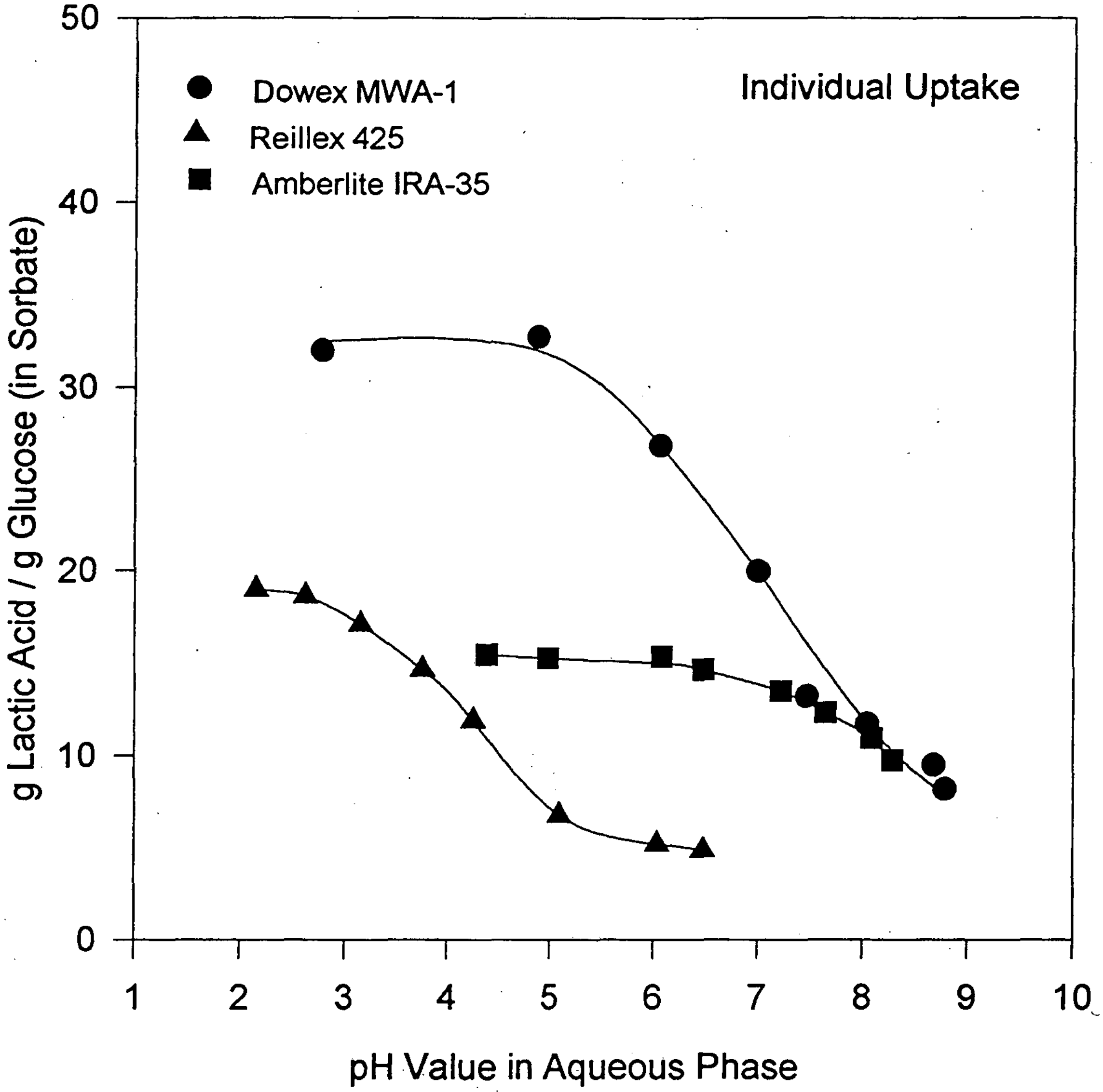


Figure 13 Selectivity (Proportion of Lactic Acid to Glucose in Sorbate) at 25 °C, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

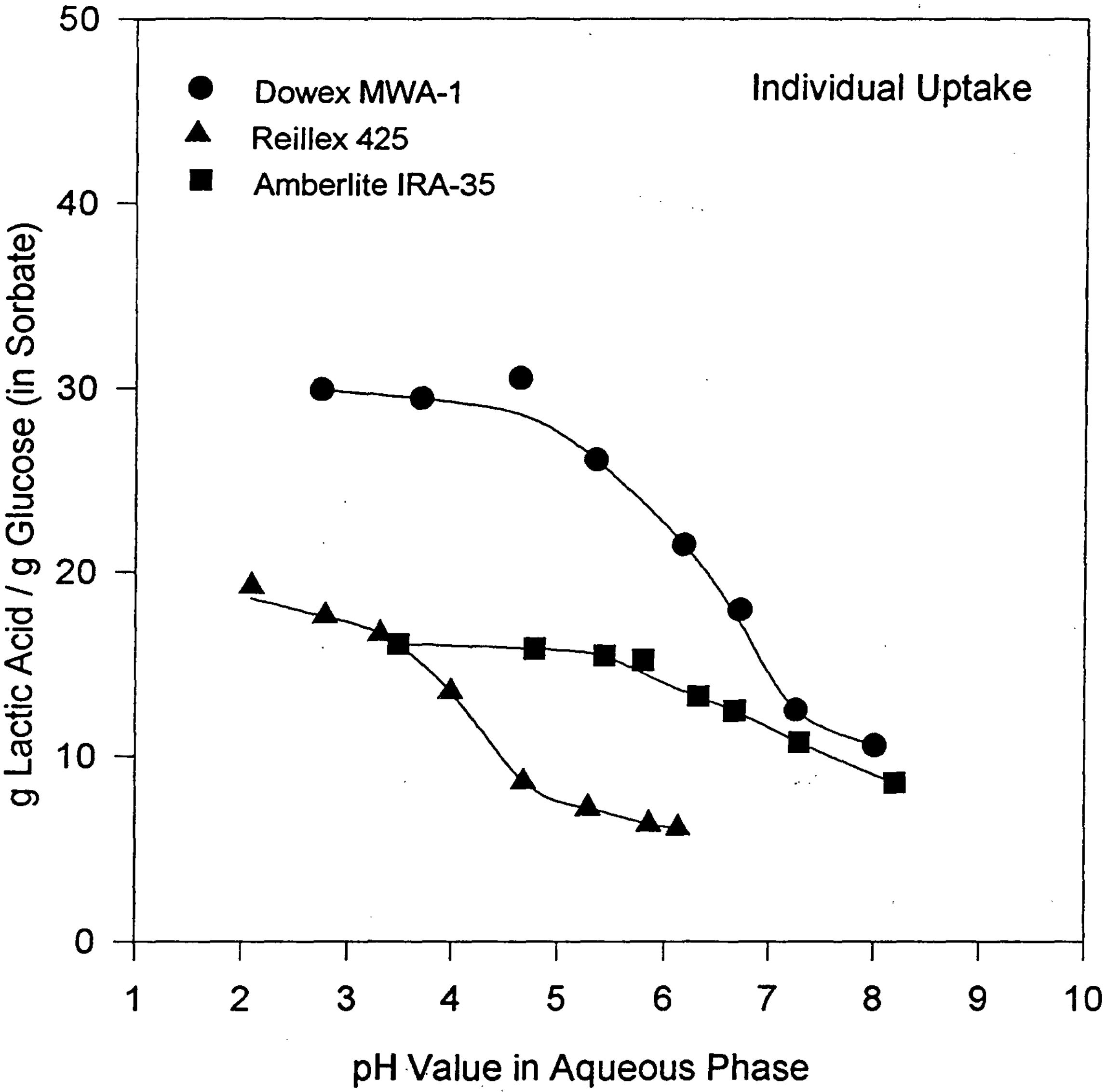


Figure 14 Selectivity (Proportion of Lactic Acid to Glucose in Sorbate) at 40 °C, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

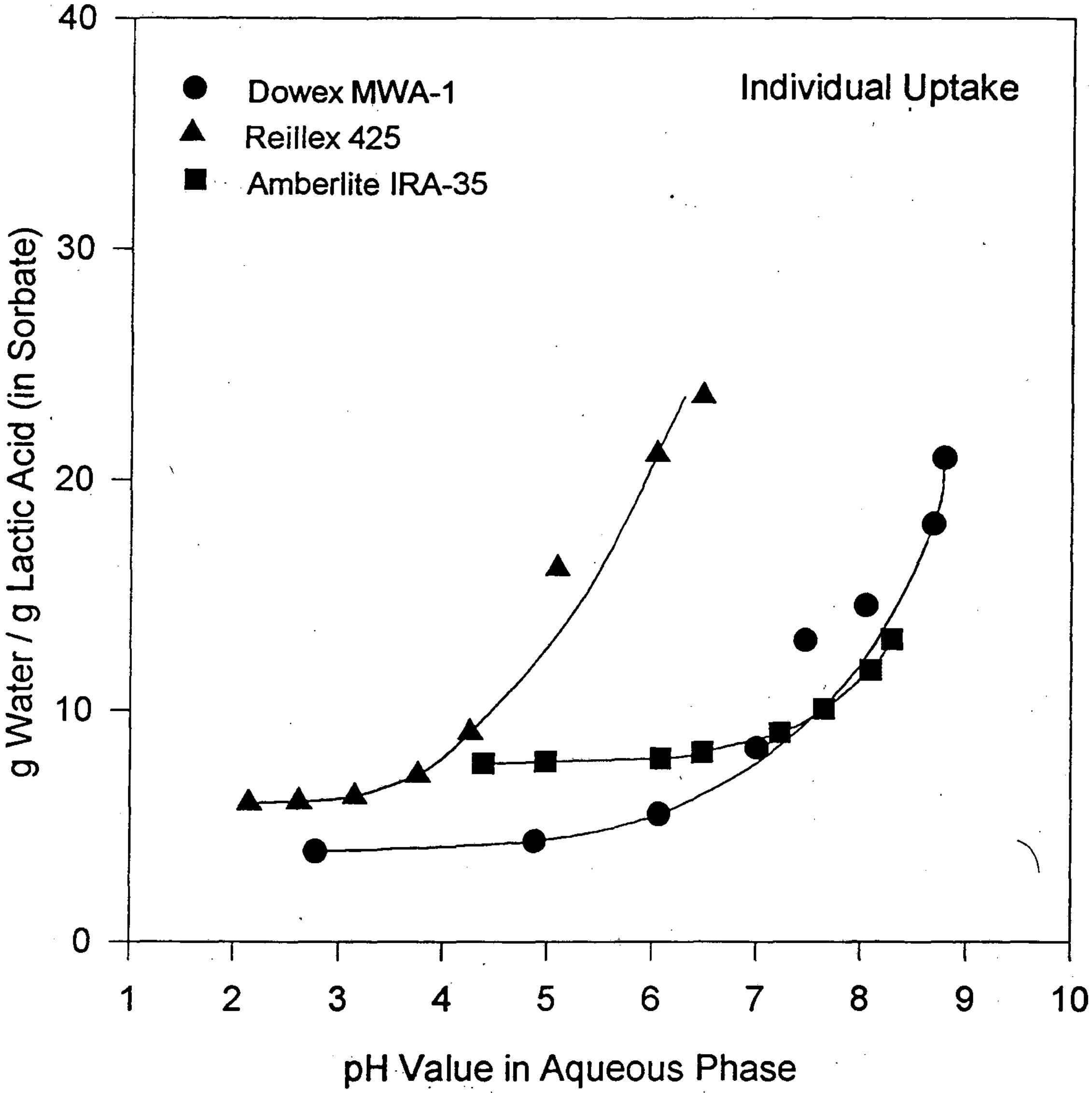


Figure 15 Inverse Selectivity (Proportion of Water to Lactic Acid in Sorbate) at 25 °C, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

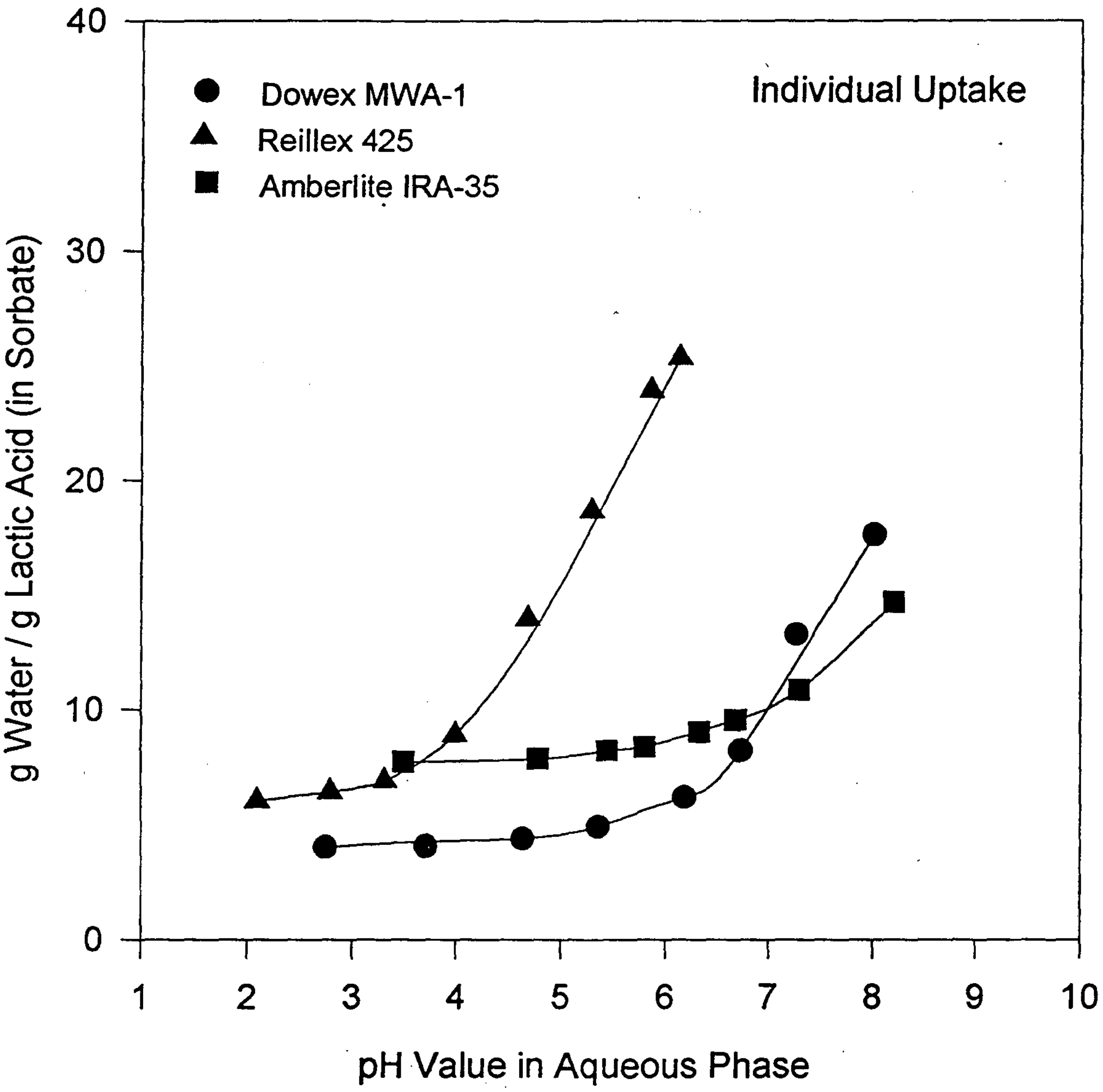


Figure 16 Inverse Selectivity (Proportion of Water to Lactic Acid in Sorbate) at 40 °C, $C_{a,i}$ = 4.0%, $C_{g,i}$ = 1.0%, W_0/m = 1.0

APPENDIX A: EXPERIMENTAL DATA

The experimentally measured quantities are listed below.

m	mass of sorbent (g)
W	mass of solution (g)
W_T	total mass of sorbent and sorbate (g)
pH_i	pH value in initial aqueous solution
pH_f	pH value in final aqueous solution
$C_{g,i}$	weight fraction glucose in initial solution (%)
$C_{g,f}$	weight fraction glucose in final solution (%)
$C_{a,i}$	weight fraction lactic acid in initial solution (%)
$C_{a,f}$	weight fraction lactic acid in final solution (%)
Q_{cg}	composite uptake of glucose (mg/g)
Q_{ca}	composite uptake of lactic acid (mg/g)
Q_{ig}	Individual uptake of glucose (mg/g)
Q_{ia}	Individual uptake of lactic acid (mg/g)
Q_{iw}	Individual uptake of water (mg/g)

A.1 Sorption Isotherms

The results of the sorption isotherm experiments are shown in Table A-1.

Table A-1. Data for Uptake of Glucose and Water

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
Sorbent: Dowex MWA-1 (25°C)							
1.0129	10.1252	3.8214	3.7308	9.059	1.4749	26.076	430.0
1.0036	10.0823	2.9116	2.8271	8.491	1.4575	21.277	431.0
1.0049	10.3096	2.8466	2.7693	8.023	1.4582	20.515	430.6
1.0072	10.0561	1.9569	1.8895	6.725	1.4586	15.193	433.0
1.0055	10.0179	0.9848	0.9612	2.347	1.4578	6.671	443.2
1.0017	9.9977	0.5277	0.5083	1.941	1.4545	4.239	447.8
1.0109	9.9999	0.3969	0.3863	1.050	1.4703	2.806	451.6
1.0043	9.9862	0.3056	0.2973	0.825	1.4602	2.175	451.8
1.0051	9.9909	0.2037	0.1980	0.567	1.4750	1.493	466.0
1.0038	9.9825	0.1131	0.1115	0.162	1.4742	0.685	467.9
1.0074	9.9840	0.0502	0.0495	0.071	1.4761	0.301	465.0

Sorbent: Dowex MWA-1 (40°C)

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
1.0026	10.4401	3.9760	3.8958	8.358	1.4987	27.635	467.2
1.0004	10.3298	3.0512	2.9816	7.182	1.4873	21.694	465.0
1.0038	10.2083	2.0714	2.0260	4.622	1.4959	14.554	475.7
1.0050	10.0994	1.0658	1.0338	3.213	1.4899	8.201	474.3
1.0009	10.0592	0.6890	0.6695	1.962	1.4964	5.276	489.8
1.0008	10.0327	0.4074	0.3919	1.550	1.5032	3.517	498.5
1.0012	10.0075	0.1843	0.1818	0.265	1.4828	1.139	479.9
1.0024	9.9961	0.0818	0.0795	0.234	1.4979	0.627	493.7

Sorbent: Dowex MWA-1 (60°C)

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
1.0007	10.4315	3.9566	3.8876	7.201	1.7140	34.912	677.9
1.0025	10.3157	2.9902	2.9372	5.466	1.7065	26.092	676.2
1.0023	10.1993	1.9646	1.9267	3.855	1.6748	16.782	652.6
1.0009	10.0897	0.9768	0.9599	1.704	1.6908	8.320	681.0
1.0008	10.0651	0.7571	0.7424	1.479	1.6615	6.380	653.8
1.0004	10.0373	0.4715	0.4602	1.140	1.6653	4.199	660.4
1.0013	9.9930	0.1709	0.1679	0.299	1.6946	1.459	689.3
1.0001	9.9904	0.0600	0.0584	0.160	1.7026	0.570	701.9

Amberlite IRA-35 (25°C)

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
1.0002	10.4314	3.8783	3.7780	10.460	2.9206	82.998	1837.0
1.0007	10.3262	3.0074	2.9339	7.582	2.9075	63.486	1842.0
1.0139	10.2206	2.0716	2.0006	7.102	2.9550	45.403	1869.1
1.0089	10.1126	1.0895	1.0460	3.856	2.9188	23.657	1869.4
1.0037	10.0597	0.6781	0.6560	2.222	2.8876	14.535	1862.4
1.0055	10.0290	0.3568	0.3445	1.228	2.9028	7.728	1879.2
1.0011	10.0066	0.1398	0.1376	0.214	2.8806	2.797	1874.6
1.0035	9.9943	0.0573	0.0565	0.081	2.8660	1.130	1854.9

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
Amberlite IRA-35 (40°C)							
1.0017	10.4255	3.8587	3.7787	8.326	2.9443	81.606	1857.7
1.0024	10.3358	3.1154	3.0477	6.981	2.9243	65.415	1851.9
1.0146	10.2629	2.4587	2.4006	5.884	2.9554	51.804	1861.1
1.0060	10.1891	1.8257	1.7879	3.828	2.9459	38.305	1890.0
1.0029	10.0910	0.9253	0.9014	2.410	2.9266	19.700	1898.4
1.0081	10.0619	0.6933	0.6760	1.722	2.9169	14.521	1878.9
1.0046	10.0309	0.4238	0.4150	0.879	2.9136	8.765	1891.5
1.0089	10.0094	0.2089	0.2045	0.411	2.9230	4.291	1892.9
1.0061	9.9978	0.0768	0.0730	0.065	2.9152	1.450	1896.1

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
Amberlite IRA-35 (60°C)*							
1.0034	10.3606	3.2543	3.1350	12.318			
1.0014	10.2635	2.4231	2.3141	11.171			
1.0017	10.1754	1.7389	1.6564	8.380			
1.0074	10.0886	0.8958	0.8265	6.940			
1.0044	10.0884	0.6770	0.6114	6.589			
1.0006	10.0342	0.4381	0.3910	4.723			
1.0015	10.0073	0.1942	0.1706	2.358			
1.0005	9.9921	0.0927	0.0825	1.019			

* In this case glucose gives an equilibrium mixture.

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
Sorbent: Reillex 425 (25°C)							
1.0052	10.4201	3.7396	3.5967	14.813	1.5911	35.777	547.1
1.0028	10.3248	2.9559	2.8255	13.426	1.5869	29.884	552.6
1.0021	10.2183	1.9814	1.8765	10.696	1.5968	21.832	571.6
1.0348	10.1135	1.1137	1.0438	6.832	1.6320	12.856	564.3
1.0083	10.0733	0.7619	0.7123	4.955	1.5925	9.082	570.3
1.0009	10.0409	0.4876	0.4549	3.280	1.5878	5.947	580.4
1.0063	10.0079	0.1924	0.1810	1.139	1.5975	2.202	585.3
1.0022	9.9946	0.0718	0.0678	0.402	1.5942	0.802	589.9

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
			Sorbent: Reillex 425 (40°C)				
1.0076	10.4250	3.8476	3.7392	11.220	1.6297	34.306	583.1
1.0077	10.3221	2.9390	2.8431	9.831	1.6212	27.140	581.7
1.0067	10.2024	1.9391	1.8663	7.383	1.6217	18.784	592.1
1.0021	10.0954	0.9951	0.9453	5.022	1.6175	10.827	603.3
1.0107	10.0669	0.7769	0.7413	3.551	1.6195	8.016	594.3
1.0028	10.0344	0.4626	0.4363	2.632	1.6174	5.306	607.6
1.0031	10.0071	0.1988	0.1885	1.028	1.6122	2.173	605.1
1.0049	9.9861	0.0773	0.0737	0.358	1.6153	0.806	606.2

m	W	$C_{g,i}$	$C_{g,f}$	Q_{cg}	W_T	Q_{ig}	Q_{iw}
			Sorbent: Reillex 425 (60°C)				
1.0000	10.4157	3.7743	3.6939	8.371	1.8267	38.908	787.8
1.0017	10.3174	2.9871	2.9097	7.972	1.8098	31.445	775.3
1.0037	10.2014	1.9686	1.9115	5.804	1.8247	21.440	796.5
1.0042	10.0961	1.0013	0.9685	3.282	1.8164	11.115	797.7
1.0025	10.0666	0.7462	0.7221	2.420	1.8121	8.252	799.3
1.0035	10.0357	0.4806	0.4666	1.401	1.8075	5.139	796.1
1.0059	10.0036	0.1980	0.1905	0.751	1.8132	2.280	800.3
1.0043	9.9896	0.0819	0.0802	0.169	1.7971	0.802	788.6

A.2 Sorbent pH Experiments

The results of the sorbent uptake-pH experiments are given in Tables A-2-1, A-2-2 and A-2-3.

Table A-2-1. Data from Sorbent Uptake-pH Experiments (only glucose to be sorbed)

m	W	pH	$C_{g,i}$	$C_{g,f}$	$W(C_{g,i}-C_{g,f})/m$
		Sorbent: Dowex MWA-1 (25°C)			
1.0055	11.9565	4.84	1.0548	1.0170	4.458
1.0019	11.7076	5.17	1.0878	1.0580	3.346
1.0021	12.8681	6.03	1.0470	1.0166	3.898
1.0008	14.3546	6.40	1.0426	1.0091	4.821
1.0036	10.5214	7.06	1.0429	0.9982	4.780
1.0047	10.0055	8.17	1.0795	1.0412	3.836
1.0022	10.0692	9.26	1.0439	1.0090	3.510

Table A-2-2. Data from Sorbent Uptake-pH Experiments (lactic acid and glucose to be sorbed)

m	W	pH_i	pH_f	$C_{g,i}$	$C_{a,i}$	$C_{g,f}$	$C_{a,f}$	Q_{cg}	Q_{ca}
Sorbent: Dowex MWA-1 (25°C)									
1.0007	10.0045	1.99	2.78	0.9998	4.0056	1.0809	0.4362	-8.06	356.9
1.0008	10.4028	3.00	4.88	0.9613	3.8515	1.0394	0.9189	-8.12	304.8
1.0010	10.0013	3.50	6.07	1.0005	4.0084	1.0744	2.0834	-7.38	192.3
1.0045	10.0019	4.09	7.00	0.9997	4.0054	1.0527	3.2539	-5.28	74.8
1.0019	10.0142	4.44	7.47	0.9990	4.0025	1.0439	3.7067	-4.49	29.6
1.0042	10.0039	4.92	8.05	0.9994	4.0039	1.0397	3.7933	-4.02	21.0
1.0028	10.0019	5.63	8.69	0.9998	4.0056	1.0359	3.9106	-3.60	9.5
1.0029	10.0019	5.90	8.79	1.0000	4.0065	1.0342	3.9669	-3.41	4.0

m	W	pH_i	pH_f	$C_{g,i}$	$C_{a,i}$	$C_{g,f}$	$C_{a,f}$	Q_{cg}	Q_{ca}
Sorbent: Dowex MWA-1 (40°C)									
1.0050	10.0143	1.99	2.75	0.9988	3.9975	1.0730	0.4821	-7.39	350.3
1.0005	10.0023	2.50	3.71	1.0000	4.0023	1.0720	0.6037	-7.20	339.8
1.0017	10.0160	3.02	4.64	0.9987	3.9971	1.0800	0.9888	-8.11	300.8
1.0034	10.0075	3.36	5.36	0.9996	4.0004	1.0671	1.5526	-6.73	244.1
1.0018	10.0014	3.78	6.19	1.0005	4.0041	1.0551	2.4865	-5.45	151.5
1.0062	10.0044	4.18	6.73	0.9999	4.0016	1.0489	3.1724	-4.87	82.5
1.0025	10.0090	4.65	7.26	0.9995	4.0002	1.0437	3.7074	-4.41	29.2
1.0004	10.0140	5.34	8.01	0.9990	3.9981	1.0415	3.8824	-4.25	11.6

m	W	pH_i	pH_f	$C_{g,i}$	$C_{a,i}$	$C_{g,f}$	$C_{a,f}$	Q_{cg}	Q_{ca}
Sorbent: Amberlite IRA-35 (25°C)									
1.0116	10.0006	1.99	4.38	0.9901	4.0032	1.1226	0.0529	-13.1	390.5
1.0012	10.0021	2.21	4.98	0.9901	4.0032	1.1195	0.1641	-12.9	383.5
1.0169	10.0440	2.49	6.08	0.9858	3.9859	1.1182	0.3448	-13.1	359.6
1.0128	10.0064	2.70	6.48	0.9895	4.0010	1.1159	0.5354	-12.5	342.4
1.0039	10.0056	3.09	7.22	0.9900	4.0028	1.1141	1.1356	-12.4	285.8
1.0148	10.0265	3.32	7.65	0.9879	3.9944	1.1079	1.6815	-11.8	228.5
1.0034	10.0021	3.59	8.09	0.9902	4.0035	1.1046	2.4422	-11.4	155.6
1.0035	10.0117	3.73	8.29	0.9891	3.9993	1.0927	2.7945	-10.3	120.2

m	W	pH_i	pH_f	$C_{g,i}$	$C_{a,i}$	$C_{g,f}$	$C_{a,f}$	Q_{cg}	Q_{ca}
Sorbent: Amberlite IRA-35 (40°C)									
1.0051	10.0049	1.99	3.49	1.0010	4.0071	1.1555	0.1076	-15.4	388.2
1.0032	10.0145	2.37	4.78	0.9994	4.0007	1.1471	0.3214	-14.8	367.3
1.0090	10.1721	2.61	5.44	0.9843	3.9402	1.1261	0.5600	-14.3	340.8
1.0073	10.0054	2.76	5.80	1.0005	4.0051	1.1493	0.7729	-14.7	321.1
1.0024	10.0045	3.03	6.33	1.0010	4.0068	1.1204	1.2017	-11.9	280.0
1.0041	10.0043	3.18	6.68	1.0009	4.0067	1.1115	1.5384	-11.0	245.9
1.0022	10.0062	3.44	7.29	1.0006	4.0053	1.0937	2.1523	-9.3	185.0
1.0013	10.0135	3.81	8.20	0.9996	4.0012	1.0926	3.1676	-9.3	83.4

m	W	pH_i	pH_f	$C_{g,i}$	$C_{a,i}$	$C_{g,f}$	$C_{a,f}$	Q_{cg}	Q_{ca}
Sorbent: Reillex 425 (25°C)									
1.0006	10.0011	1.99	2.15	1.0000	4.0461	1.0360	2.5676	-3.60	147.8
1.0015	10.1011	2.39	2.62	0.9827	4.0062	1.0145	2.5554	-3.21	146.3
1.0025	10.0001	2.90	3.16	1.0001	4.0465	1.0282	2.6831	-2.80	136.0
1.0013	10.0054	3.46	3.76	0.9994	4.0439	1.0216	2.9715	-2.22	107.2
1.0008	10.0009	3.91	4.25	0.9998	4.0453	1.0204	3.3515	-2.06	69.3
1.0009	10.0622	4.62	5.09	0.9938	4.0210	1.0078	3.8445	-1.41	17.7
1.0013	10.0243	5.30	6.04	0.9976	4.0363	1.0111	3.9931	-1.35	4.3
1.0063	10.0004	5.72	6.48	0.9999	4.0458	1.0148	4.0466	-1.47	-0.1

m	W	pH_i	pH_f	$C_{g,i}$	$C_{a,i}$	$C_{g,f}$	$C_{a,f}$	Q_{cg}	Q_{ca}
Sorbent: Reillex 425 (40°C)									
1.0043	10.0060	1.99	2.09	0.9985	4.1100	1.0356	2.7040	-3.70	140.1
1.0029	10.0000	2.64	2.79	0.9994	4.1135	1.0327	2.8020	-3.32	130.9
1.0050	10.0029	3.14	3.31	0.9988	4.1112	1.0324	2.9470	-3.34	115.8
1.0055	10.0029	3.76	3.99	0.9988	4.1112	1.0304	3.3734	-3.14	73.4
1.0000	10.0116	4.39	4.68	0.9980	4.1078	1.0224	3.8439	-2.44	26.4
1.0039	10.0285	4.96	5.29	0.9964	4.1014	1.0251	4.0089	-2.87	9.2
1.0021	10.0008	5.45	5.86	1.0014	4.1222	1.0360	4.1357	-3.45	-1.3
1.0030	10.8543	6.01	6.14	0.9206	3.8352	0.9452	3.8409	-2.67	-0.6

Table A-2-3. Data of Individual Uptakes (lactic acid and glucose to be sorbed)

m	W_T	pH_i	pH_f	Q_{cg}	Q_{ca}	Q_{ig}	Q_{ia}	Q_{iw}
Sorbent: Dowex MWA-1 (25°C)								
1.0007	2.7967	1.99	2.78	-8.06	356.9	11.4	364.7	1418.6
1.0008	2.7250	3.00	4.88	-8.12	304.8	9.8	320.6	1392.4
1.0010	2.4551	3.50	6.07	-7.38	192.3	8.3	222.6	1221.7
1.0045	2.0213	4.09	7.00	-5.28	74.8	5.4	107.7	899.1
1.0019	1.8803	4.44	7.47	-4.49	29.6	4.7	62.1	809.9
1.0042	1.8132	4.92	8.05	-4.02	21.0	4.4	51.6	749.6
1.0028	1.7330	5.63	8.69	-3.60	9.5	4.0	38.0	686.3
1.0029	1.7080	5.90	8.79	-3.41	4.0	3.9	31.9	667.3

m	W_T	pH_i	pH_f	Q_{cg}	Q_{ca}	Q_{ig}	Q_{ia}	Q_{iw}
Sorbent: Dowex MWA-1 (40°C)								
1.0050	2.8252	1.99	2.75	-7.39	350.3	12.0	359.0	1440.1
1.0005	2.7853	2.50	3.71	-7.20	339.8	11.9	350.6	1421.4
1.0017	2.7240	3.02	4.64	-8.11	300.8	10.4	317.8	1391.2
1.0034	2.6039	3.36	5.36	-6.73	244.1	10.3	268.9	1315.9
1.0018	2.3384	3.78	6.19	-5.45	151.5	8.6	184.7	1140.9
1.0062	2.0948	4.18	6.73	-4.87	82.5	6.5	116.8	958.6
1.0025	1.8997	4.65	7.26	-4.41	29.2	5.0	62.4	827.6
1.0004	1.7933	5.34	8.01	-4.25	11.6	4.0	42.3	746.3

m	W_T	pH_i	pH_f	Q_{cg}	Q_{ca}	Q_{ig}	Q_{ia}	Q_{iw}
Sorbent: Amberlite IRA-35 (25°C)								
1.0116	4.4815	1.99	4.38	-13.1	390.5	25.4	392.4	3012.3
1.0012	4.4378	2.21	4.98	-12.9	383.5	25.5	389.1	3017.9
1.0169	4.4028	2.49	6.08	-13.1	359.6	24.2	371.1	2934.3
1.0128	4.3828	2.70	6.48	-12.5	342.4	24.6	360.2	2942.6
1.0039	4.2750	3.09	7.22	-12.4	285.8	23.9	322.8	2911.7
1.0148	4.1892	3.32	7.65	-11.8	228.5	22.8	281.1	2824.2
1.0034	3.9200	3.59	8.09	-11.4	155.6	20.7	226.6	2659.4
1.0035	3.8306	3.73	8.29	-10.3	120.2	20.4	198.9	2597.9

m	W_T	pH_i	pH_f	Q_{cg}	Q_{ca}	Q_{ig}	Q_{ia}	Q_{iw}
Sorbent: Amberlite IRA-35 (40°C)								
1.0051	4.4658	1.99	3.49	-15.4	388.2	24.4	391.9	3026.8
1.0032	4.3842	2.37	4.78	-14.8	367.3	23.9	378.1	2968.2
1.0090	4.3704	2.61	5.44	-14.3	340.8	23.3	359.4	2948.7
1.0073	4.3060	2.76	5.80	-14.7	321.1	22.8	346.4	2905.6
1.0024	4.2258	3.03	6.33	-11.9	280.0	24.1	318.6	2873.0
1.0041	4.1345	3.18	6.68	-11.0	245.9	23.6	293.9	2800.1
1.0022	3.9848	3.44	7.29	-9.3	185.0	23.2	249.1	2703.7
1.0013	3.6408	3.81	8.20	-9.3	83.4	19.5	166.9	2449.6

m	W_T	pH_i	pH_f	Q_{cg}	Q_{ca}	Q_{ig}	Q_{ia}	Q_{iw}
Sorbent: Reillex 425 (25°C)								
1.0006	2.2645	1.99	2.15	-3.60	147.8	9.5	180.2	1073.4
1.0015	2.2686	2.39	2.62	-3.21	146.3	9.6	178.6	1077.0
1.0025	2.2408	2.90	3.16	-2.80	136.0	9.9	169.1	1056.2
1.0013	2.1754	3.46	3.76	-2.22	107.2	9.7	142.0	1020.9
1.0008	2.0620	3.91	4.25	-2.06	69.3	8.8	104.8	946.8
1.0009	1.9140	4.62	5.09	-1.41	17.7	7.8	52.8	851.7
1.0013	1.8741	5.30	6.04	-1.35	4.3	7.5	39.1	825.1
1.0063	1.8298	5.72	6.48	-1.47	-0.1	6.8	33.0	778.5

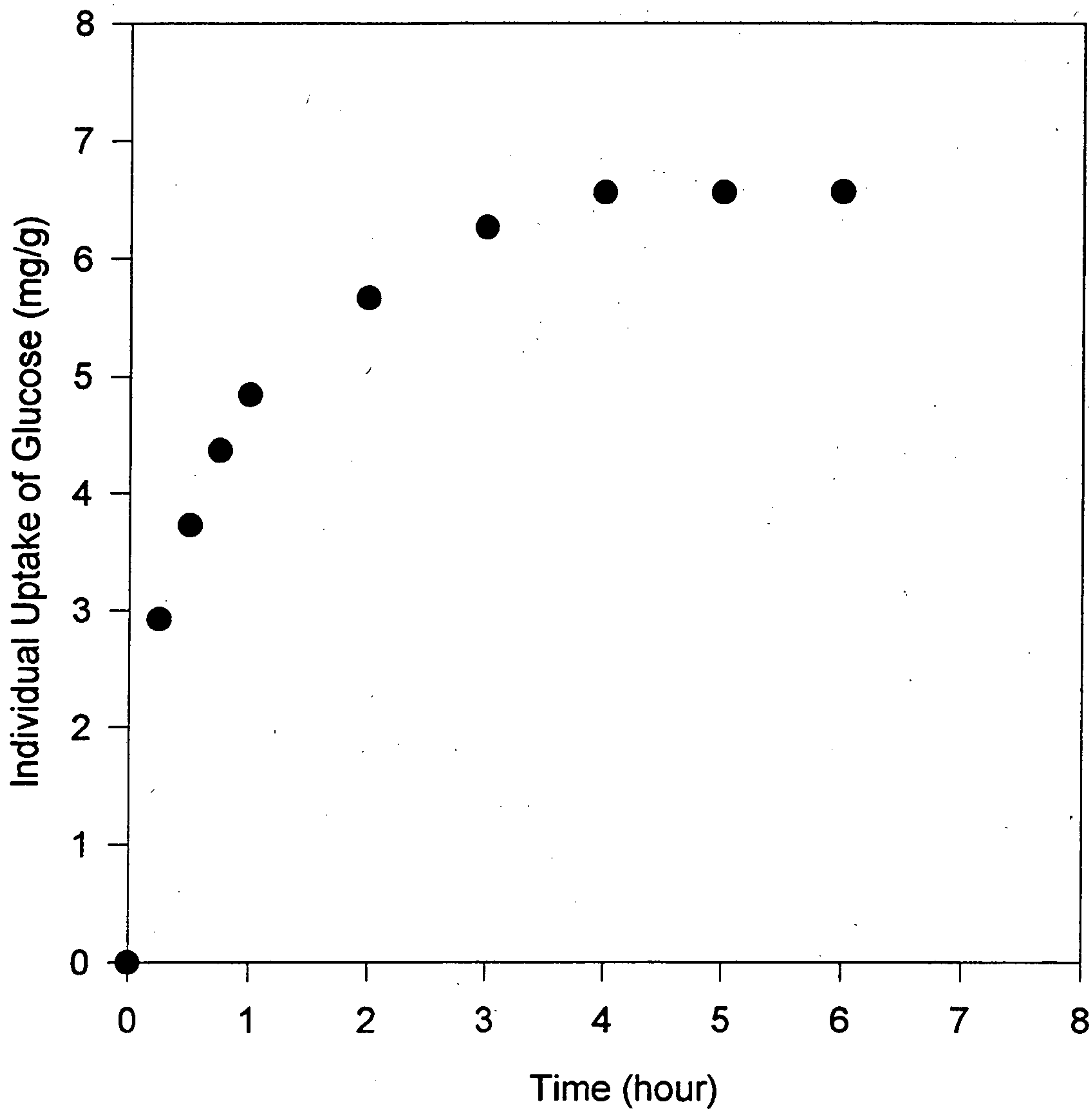
m	W_T	pH_i	pH_f	Q_{cg}	Q_{ca}	Q_{ig}	Q_{ia}	Q_{iw}
Sorbent: Reillex 425 (40°C)								
1.0043	2.2313	1.99	2.09	-3.70	140.1	9.0	173.1	1039.6
1.0029	2.2415	2.64	2.79	-3.32	130.9	9.4	165.5	1060.1
1.0050	2.2144	3.14	3.31	-3.34	115.8	9.1	151.3	1043.0
1.0055	2.1133	3.76	3.99	-3.14	73.4	8.2	110.6	982.9
1.0000	1.9491	4.39	4.68	-2.44	26.4	7.3	62.9	878.9
1.0039	1.8920	4.96	5.29	-2.87	9.2	6.2	44.7	833.7
1.0021	1.8614	5.45	5.86	-3.45	-1.3	5.4	34.2	817.9
1.0030	1.8043	6.01	6.14	-2.67	-0.6	4.9	30.1	763.9

A.3 Sorption Kinetics

The results of the sorption kinetics experiment are shown in Table A-3.

Table A-3. Data of Sorption Kinetics of Glucose

t(hr)	m	W	$C_{g,i}$	$C_{g,f}$	W_T	Q_{ig}	Q_{iw}
			Sorbent: Dowex MWA-1 (25°C)				
0.25	1.0022	9.9992	0.9980	0.9685	1.0102	2.992	5.0
0.50	1.0000	10.0310	0.9980	0.9622	1.0175	3.724	13.8
0.75	1.0006	10.0108	0.9980	0.9640	1.1051	4.366	100.1
1.00	1.0005	10.0048	0.9980	0.9792	1.3078	4.842	302.5
2.00	1.0034	10.0109	0.9980	0.9724	1.3290	5.665	319.9
3.00	1.0001	10.0099	0.9980	0.9779	1.4416	6.268	435.2
4.00	1.0007	10.0080	0.9980	0.9750	1.4447	6.565	437.4
5.00	1.0036	10.0014	0.9980	0.9750	1.4481	6.562	437.9
6.00	1.0012	10.0000	0.9980	0.9750	1.4455	6.565	437.7



Kinetics for Sorption of Glucose by Dowex MWA-1 at 25 °C, $C_{g,i}$ = 1.0%, W_0 / m =10

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