

KINETIC STUDY OF AN OLEOPHILIC CATION EXCHANGE RESIN IN NONAQUEOUS MEDIA

Part I. Ethanol

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A kinetic study of the newly synthesized cation exchange resin was carried out in pure ethanol. The rates of exchange of $K^+ - Na^+$, $(C_2H_5)_2 - NH^+$ and $Na^{+22} - Na^{+23}$ were carried out using atomic absorption, potentiometric and trace isotope techniques respectively. The data fitted and explained assuming the rate-determining step as the chemical exchange reaction. Two processes emerged, one is fast and the other one is slow. This was explained as due to the difference of the acidity sites of the SO_3^- groups in the benzene rings of the resin.

INTRODUCTION

Both equilibrium and kinetic studies have been made but, with few exceptions, those investigations have dealt with reactions taking place in aqueous media. Theories of varying complexity which describe the exchange process have been developed as a result of these studies.

It is only within the last few years that any investigations have been carried out for nonaqueous systems.

A variety of exchange reactions have been made in aqueous-organic solvents [1-5]. Gable and Strobel [6] studied the exchange of univalent cations exchange resin (Dowex 50) in absolute ethanol. There has been very little investigation of equilibria and kinetics in nonaqueous solvents of low dielectric constant.

Gregor, Nobel and Gottlieb [7] studied the equilibrium swelling and resin phase composition for Dowex 50 in mixtures of water containing either methanol, ethanol, dioxane or isopropanol. They found that the resin system absorbed water selectively from solvent mixtures. When the solvent mixtures contained low mole fractions of water, the selectivity was high. The selectivity also increased as the dielectric constant of the other solvent decreased.

Few attempts have been made to synthesize ion-exchange resin to be suitable for uses in nonaqueous media of low dielectric constants. Meyers [8] reported ion exchange in nonaqueous media including hydrocarbons. He studied the equilibrium of exchange reactions for fatty acids in various solvents with polyamine resin (IR-4) in both the wet and dry states. He found that the acids could

be removed from solution only when water or some other highly ionizing solvent was present. When the resin was in the dry form and the solvent was dry benzene, no absorption occurred, however, a water-wet resin did remove the acid.

Exchange of cation exchange resins and different kinds of bases have been reported in a variety of solvents. In almost all of the processes, the system was not completely anhydrous. The resins were air-dried containing a certain amount of moisture. New methods have been invented to synthesize the kind of resin to be used in nonaqueous solvents.

The first method is mechanical, macroreticular resin. Kunin and his coworkers [9,10] have reported a new polymerisation technique for the preparation of the macroporous structure similar to those of conventional absorbents such as alumina. Amberlyst ion-exchange resins (Amberlyst 15 and Amberlyst XN-1002) are of the same kind of resins. Gregor *et al.* [11] have prepared a new class of oil-swelling ion-exchange resins.

The oleophilic groups are present in the resin matrix, either as part of the backbone, as side-chain substituents, or as cage polymers or copolymers. These resins have a lower ion-exchange capacity than the conventional resins due to the presence of inert groups. They are usually prepared with a lower per cent of cross-linking agent (1-2% divinyl benzene) to allow for the degree of swelling found with conventional resins. The swelling properties of these resins [12] and their equilibria [13] in various solvents are studied. In this communication we investigate the kinetics of one of a lauroyl sulfonated polystyrene resin in both absolute ethanol and water.

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EXPERIMENTAL

Materials

Potassium and sodium acetates were (Fisher Certified Reagent) anhydrous and heated to 160°.

Ethanol was (American Industries) dried with magnesium according to the method given by Fieser.

Diethylamine (Fisher Certified Reagent) was used as received.

Sodium and potassium chlorides (Mallinckrodt) were A.R. grade.

Bromophenol (Fisher Reagent).

Standard HCl (Fisher Reagent).

Sodium²² chloride was supplied by Nucleonic Corp., New York (U.S.A.).

Dowex 50x4. Sulfonated polystyrene divinyl benzene copolymer was supplied by Dow Chemical Co. The oleophilic resin has the notation LS1-4 means 1% cross-linked DVB polystyrene was 80% laurylated and 47% of the aromatic rings were sulfonated. This resin was prepared by the method described elsewhere [13].

Capacity Measurements

A known amount of dry resin (one dried in vacuum oven at 1 mm Hg at 79°) in the hydrogen form was shaken with excess amount of 1N NaCl solution. It was filtered and the liberated acid was titrated with standardized sodium hydroxide using phenolphthalein as indicator. The capacities of LS1-4 and Dowex 50x4 resins were found to be 1.26 and 5.2 equivalent/g respectively.

Swelling Measurements

Swelling measurements were carried out using the method of centrifugation. The swelling of resin LS1-4 was measured in both ethanol and water in the hydrogen form. It amounts to 187 and 37% in ethanol and water respectively. For Dowex 50x4 the values are 41 and 156% in ethanol and water respectively.

Analytical Procedures

Na-K Exchange. An atomic absorption spectrophotometer (Perkin - Elmer model 303) was used for the determination of sodium. A working curve in ethanol and water was used in this determination.

Diethylamine Neutralization. The aliquots were analyzed for the amine by titration of the samples with standardized 0.221N HCl using a 1-ml microburette, bromophenol

was used as indicator.

Na²² - Na Exchange. Sodium²² has a half-life of 2.6 years and emits gamma-radiation. The activity of the various samples from the experiments employing Na²² as a tracer was measured by means of scintillation Geiger counter (Nuclear Chicago, model No. 1810). The instrument was calibrated using cesium 137.

Procedure of Experiment

When the experiment was performed in absolute ethanol solution, special precautions had to be taken to prevent the moisture from the surrounding atmosphere. A glove bag of polyethylene with integral gloves provided a relatively water-free nitrogen atmosphere. The apparatus necessary for the experiment was inserted in the glove bag and then purged of residual air using dry nitrogen.

A known amount of the resin in the proper form; Na²³⁺, H⁺ or Na²²; dried at 70° in vacuum oven at 2-mm Hg was put in the glove bag. The resin was then transferred to a 500-ml Erlenmeyer flask (dried in an oven at 120° for 24 hr), then N₂ was passed through it for 1 hr before use. Then 165 ml absolute ethanol was added to the resin and shaken for half to 1hr, long enough to swell the resin completely. To start the exchange experiment, 35 ml of the proper concentrated solution in ethanol was added to give the necessary concentration. The zero time for the reaction was taken as the moment after addition of the concentrated electrolyte. The flask was then covered with a soft rubber stopper suitable for syringe insertion, and shaken vigorously at constant temperature.

Aliquots were taken out at intervals with a calibrated 1- or 2- ml syringe. At the end of the reaction these aliquots were analyzed using the proper technique. When the same experiment was performed in distilled deionized-water, it was carried out without the glove bag and the batch reactor was a 3-neck flask (500-ml capacity) with a stirrer.

RESULTS AND DISCUSSION

Both ordinary resin (Dowex 50x4) and oleophilic resin (LS1-4) were used in the present kinetic investigation. Three different types of experiments were carried out.

First is the exchange of the resin in the sodium form with potassium acetate in pure ethanol and in water. Fig. 1 shows the Na-K exchange at 25° for LS1-4 in ethanol using 0.1 and 0.2M potassium acetate. Fig. 2 represents the Na-K exchange at 25° for LS1-4 in water using 0.01, 0.05 and 0.1M potassium acetate. It can be shown from the first figure that the half-life time ($t^{1/2}$) for 0.1M

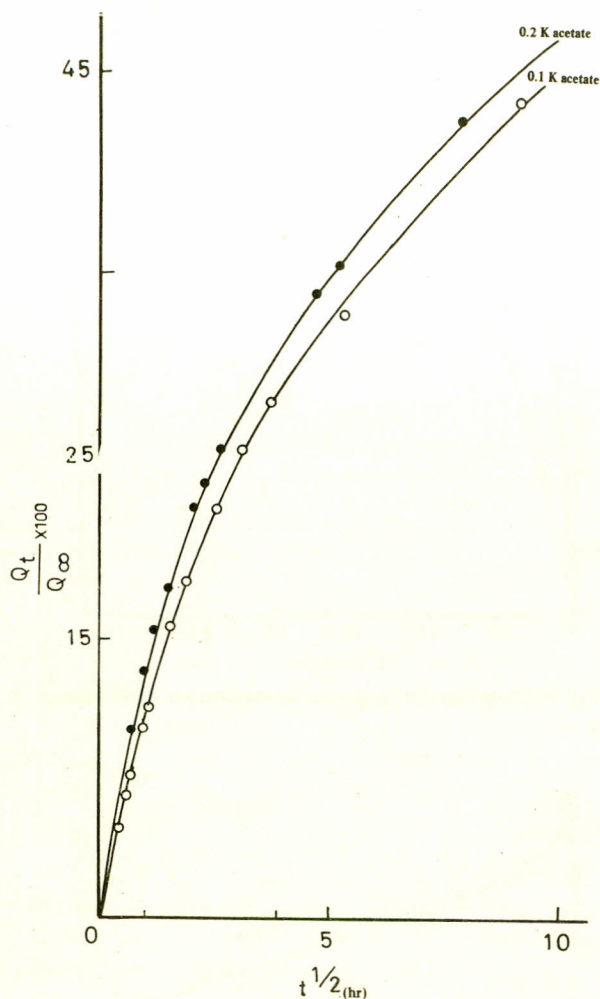


Fig. 1. Na - K exchange at 25°C for LS1-4 in ethanol (0.1 and 0.2M acetate).

potassium acetate is about 200 hr in ethanol and 30 sec in water. When the same experiment was carried out using Dowex 50x4 in ethanol, 10% exchange took place in more than 100 hr. Fig. 3 represents this latter result. The results in water seem to be consistent with the diffusion-controlled reaction. In ethanol the reaction is slowed down tremendously for both the oleophilic and the ordinary resin.

The second one includes an experiment which is expected to be diffusion controlled, with a molecule similar in size to that of potassium acetate. When diethylamine is neutralized with the hydrogen on the resin $t^{1/2}$ was indeed in the range of diffusion-controlled. $t^{1/2}$ is found to be 3 min in ethanol and 1 min in water. The results in ethanol and water are given in Fig. 4.

The third experiment was carried out to resolve this dilemma, namely whether our exchange reaction in ethanol is diffusion-controlled or chemical-controlled. Here a radiotracer technique was applied, i.e. self-diffusion between Na^{22+} - Na^{23+} . When sodium acetate concentrations

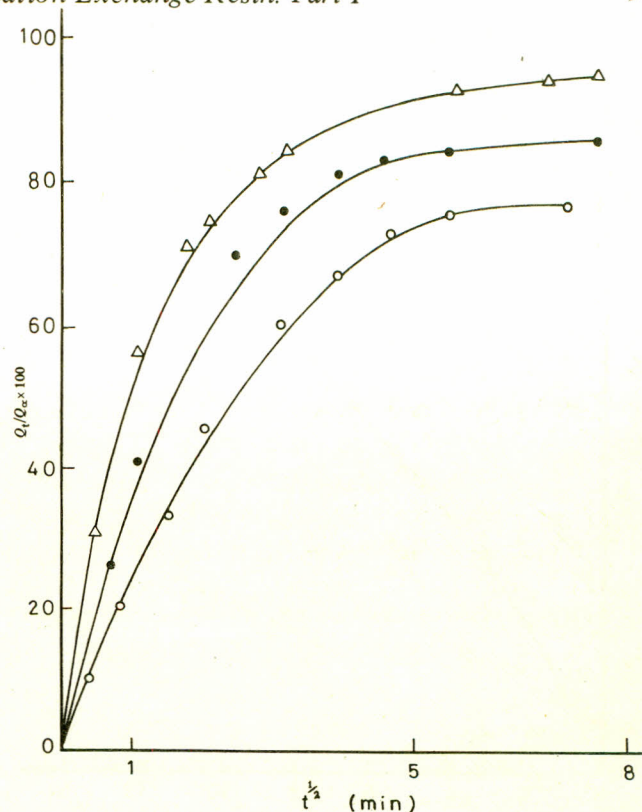
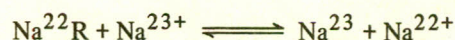


Fig. 2. Na - K exchange at 25°C for LS1-4 in water (0.01, 0.05 and 0.10M K acetate).

were 0.012 or 0.024M in ethanol, their $t^{1/2}$ values were 300 and 225 hr respectively at 25°C.

Calculations

In the radiotracer experiments resin in the Na^{22+} state was equilibrated with a solution containing a small amount of Na^{22}Cl and then the exchange reaction with Na^{23+} -acetate was studied in ethanol. In a typical experiment (0.024M sodium acetate) 0.929 g LS1-4 resin with a total capacity 1.17 meq was found to have a count rate (for all of its radioactivity) of 4×10^5 counts/min (cpm). For Na^{22} , $t^{1/2} = 2.6$ years or 1.37×10^6 min. Since for 1 meq of Na^{22} there are 6×10^{20} counts, and since $A = A_0 \exp(-0.693 t/t^{1/2})$, where A and A_0 are the amounts of activity at time t and $t = 0$, then the initial count rate would be 3.56×10^{14} cpm for this amount of resin if it was all in the Na^{22} form. Since the observed rate was 4×10^5 cpm, the mole fraction of Na^{22} in the resin amounted to 1.13×10^{-9} . Accordingly, the observed process is probably:



where $x \text{Na}^{23} = 1$, Na^{23+} = solution concentration. We assume that the concentration of Na^{23+} and Na^{22+} in the bulk solution phase is identical with the within the resin pore phase or that the diffusion process is very rapid com-

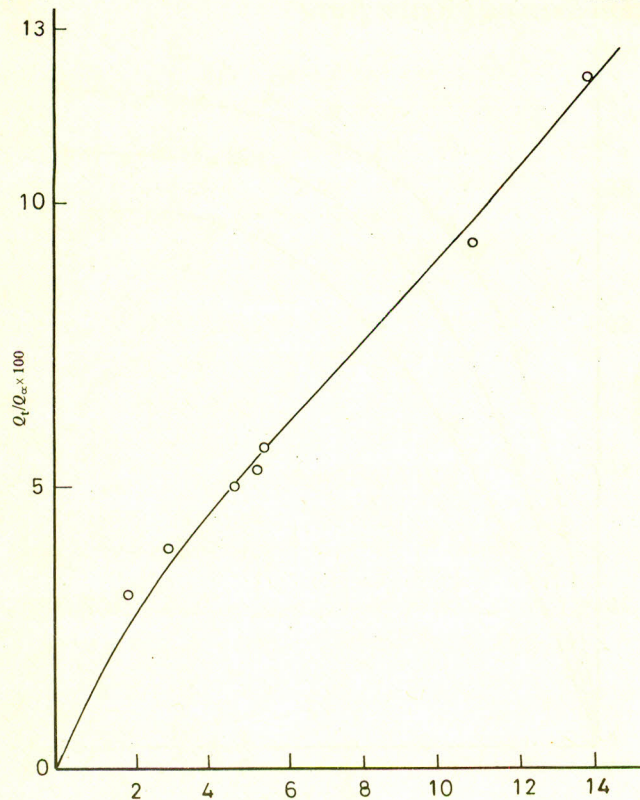


Fig. 3. Na - K exchange at 25°C for Dowex 50x4 0.1M K acetate.

pared to the exchange reaction. The half-time of the exchange reaction range from 5 to 200 hr, and $t_{1/2}$ for diffusion should be 1-4 min. Considering the reaction when $\text{Na}^{23+} = 0.024M$, the total amount of Na^{22+} withdrawn from the solution was in the order of 2-3% of that present initially, which is small enough to be ignored. Then, we can set the volume of the solution as constant at 200 ml= V and let the counting rate be a cpm in a 1.0-ml aliquot after t min, where the resin contained cpm at $t = 0$.

$$\text{then, } X_{\text{Na}^{22}\text{R}} = \frac{Q_0 - V_a}{Q_0} \times 1.13 \times 10^{-9}$$

from the half-time of the Na^{22} decay process, then

$$\frac{d(3.28 \times 10^{-15} a)}{dt} = k_1 \left(1 - \frac{V_a}{Q_0}\right) \times 1.13 \times 10^{-9} \times 2.4 \times 10^{-2} - a k_{-1} \times 3.28 \times 10^{-5}$$

Since $k_1 = k - 1 = k$ for the isotopic exchange reaction,

$$\frac{da}{dt} = k(8.26 \times 10^3 - 5.12 a) = 5.12 k(1.61 \times 10^3 - a)$$

$$da = (1.61 \times 10^3 - a) \times 5.12 k dt$$

Integrating,

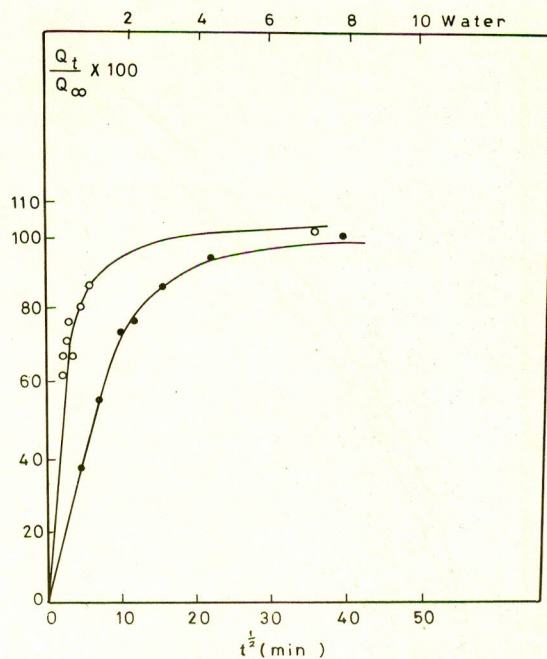


Fig. 4. Diethylamine hydrogen neutralization (O in ethanol, in water).

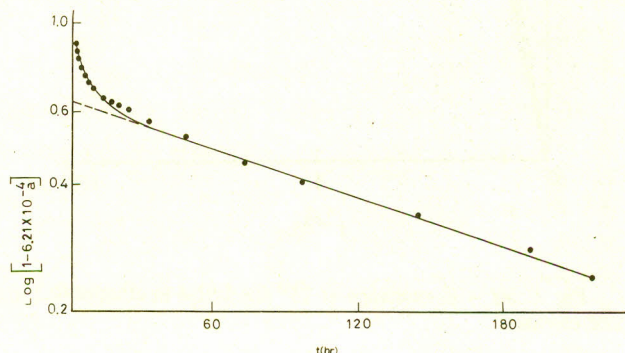


Fig. 5. $\text{Log}(1 - 6.21 \times 10^{-4} a)$ against time for $\text{RNa}^{22} - \text{Na}^{23}$ (0.024 m) at 25°C.

$$\ln(1 - 6.21 \times 10^{-4} a) = 5.12 kt$$

$$\log(1 - 6.21 \times 10^{-4} a) = 2.22 kt$$

when $\log(1 - 6.21 \times 10^{-4} a)$ is plotted versus time in hours (Fig. 5) the curve is not a straight-line. This is expected as the reaction does not follow a real first-order process but *pseudo* first order one. Also, from the plot one can observe that two reactions possibly occur, one is fast and the other is slow. The half-times may be calculated from the plots by defining the half-times as the time when half the activity has been displaced from the resin. The rate constants are calculated from the slopes of the plots taking, for example this particular reaction under investigation (Fig. 5). For the slow reaction the slope = -1.71×10^{-3} and $k = 7.5 \times$

Table 1. Analysis of the data at 25°

0.012M Na acetate		0.024M Na acetate	
$\log(1-10^{-3}a) = -1.69 kt$		$\log(1-6.21 \times 10^{-4}a) = -2.22 kt$	
<i>t</i> (hr)	<i>a</i> (cpm)	<i>t</i> (hr)	<i>a</i> (cpm)
0.15	78	0.45	140
0.30	86	1.30	234
1.00	113	2.00	282
2.00	144	4.20	362
4.00	188	6.15	420
6.00	216	7.50	445
7.00	275	13.30	551
12.40	189	17.00	570
16.10	301	20.00	581
19.10	307	24.00	598
23.30	331	33.00	672
33.10	384	48.00	754
48.00	424	72.00	884
72.00	482	96.00	956
96.00	514	144.00	1065
144.00	522	192.00	1159
168.00	545	216.00	1227
192.00	559		
216.00	612		

Table 2. Summary of K in Na²² - Na²³ exchange reaction at 25°.

Na ²³⁺ (M)	1/mole/hr	
	Slow	Fast
0.012	6.04×10^{-4}	8.5×10^{-3}
0.024	7.50×10^{-4}	12.0×10^{-3}

10^{-4} 1/mole/hr. For the fast reaction the slope = 2.67×10^{-2} and $k=12 \times 10^{-3}$ 1/mole/hr.

Analysis of the results are shown in Tables 1 and 2.

The presence of these two kinds of reactions can be explained as due to the difference in the acidity of the sulfonic groups when the benzene rings are lauroylated or hot. If one succeeds in obtaining a resin which has the same percentage of sulfonation and lauroylation, it is expected to get one kind of reaction, if the explanation given above is the plausible one.

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