

The Desalting Property of Ion-Exchange Resins in Organic Solvent

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Abstract The desalting property of ion-exchange resins in organic solvent is reported by using potassium acetate as a model compound. The experimental results show that the solvability of the solvent, stirring speed, and temperature are the factors which influence the ion-exchange rate. The increase of solvability, stirring speed and temperature will speed up the ion-exchange process.

Keywords desalination, ion-exchange, ion-exchange resins, organic solvent

1 INTRODUCTION

Ion-exchange resins are widely used in separation^[1,2], enrichment^[3,4], wastewater treatment^[5], organic synthesis^[6], pharmacy^[7], and desalination of aqueous solutions^[8,9]. The properties of ion-exchange resins in the aqueous solution were intensively studied in the past decades. A vast amount of thermodynamics and kinetics data on using different ion-exchange resins in aqueous solutions were obtained and were found applications in industries. Contrast to the above mentioned, the property of the ion-exchange resins in organic solvents was seldom reported^[10--14]. The properties of the organic solvents may be varied from one to another, including their dipolar property, and protophilic/protophobic properties. In order to obtain a suitable purified product, many kinds of organic solvents are used as reaction media and the product obtained in these media must be purified. Otherwise, the impurities coexisting in the solvent or product will degrade the product, make an inaccuracy in reaction components, and shorten the life of the commercial product. Organic compounds are usually purified by distillation or recrystallization method. However, distillation and recrystallization, in many instances, are not economical (even impossible) to be adopted when removing trace inorganic impurities from the organic media or high viscosity media such as polyether used for polyurethane. In these cases, ion-exchange process could be a suitable alternative method for removing the impurities. After ion-exchange process, resins can be separated simply from the mixture by filtration.

2 REAGENTS AND EXPERIMENTAL

Both cation-exchange resin (001×7) and anion-exchange resin (201×7) are obtained from the chemicals factory of Nankai University. The resins were pretreated with alcohol with concentrations of 95%, 75%, 50% and 25% successively, and then immersed in water. The treated cation-exchange resin was

regenerated with hydrochloric acid of concentration 1.0 mol·L⁻¹ while the anion-exchange resin regenerated with sodium hydroxide of concentration 1.0 mol·L⁻¹. Then resins were thoroughly washed with pure water until the solution obtained is neutral. The regenerated resins were dried at 40°C under vacuum. Other reagents of analytical grade without further purification were obtained from Tianjin Chemical Reagents Company. The ion-exchange process was monitored by determining the pH of the solution with an acidity-meter of high accuracy (Shanghai Precision and Scientific Instruments Co., Ltd).

The experiments were conducted in a sealed glass beaker. 100 ml 2% potassium acetate in solvents was used as the experimental solution. 10.0 g cation-exchange resin or 12.0 g anion-exchange resin was added into the solution alternatively or simultaneously at experimental temperature. Acidity change was monitored and recorded during the ion-exchange process.

3 RESULTS AND DISCUSSION

3.1 Effect of temperature on ion-exchange process

The exchange of ions between the solution and resin might be thought as a chemical reaction in two phases. The ions in the solution must diffuse into the resin and react with the ions adsorbed in resins. At higher temperature, the time required for exchange will be shorter due to higher diffusivity. The second pH sharp decline points appeared in Fig. 1 clearly show that the total exchange time of potassium ions becomes shorter from 15°C to 45°C. The relationship of $\ln t$ vs. $1/T$, in which t refers to the time for potassium ions to be totally exchanged and T is the temperature of the solution, is shown in Fig. 2. R in Fig. 2 is the linearly dependent coefficient of the curve. The curve as shown in Fig. 2 probably indicates that the ion-exchange process is a chemical reaction and the ion-exchange rate can be speeded up in expo-

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nenial form. The curve also indicates that temperature is a key factor affecting the ion-exchange process. The part of curves with pH increasing in Fig. 1 shows that temperature has less influence on anion-exchange than on cation-exchange process. The results may come from the higher swelling capacity of the anion-exchange resins in organic solvent than that of cation-exchange resins. The results can also be explained from the lower solvability of potassium ions in ethanol than that of acetate anions.

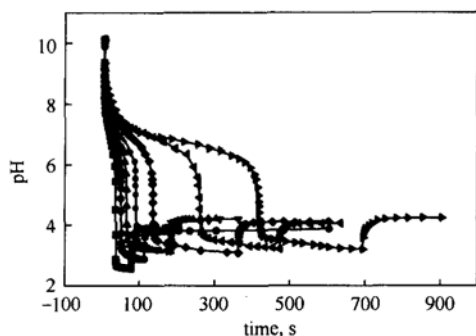


Figure 1 The effect of temperature on the ion-exchange behavior

(10.0 g cation ion-exchange resin was added into 100 ml ethanol containing 2.0 g potassium acetate, and then 12.0 g anion ion-exchange resin added after potassium ion was totally exchanged under different temperatures)

temperature, °C: ■—45; ●—40; ▲—35; ▼—30;
◆—25; ◀—20; ▶—15;

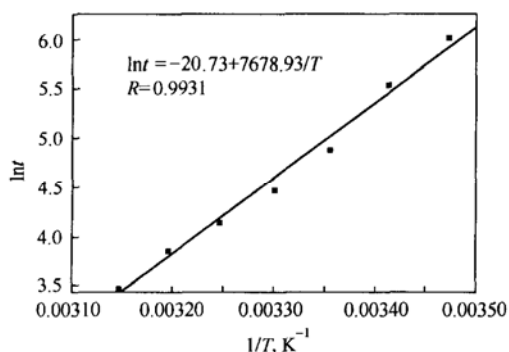


Figure 2 Relationship of $\ln(t)$ vs. $(1/T)$

(10.0 g cation ion-exchange resin was added into 100 ml ethanol containing 2.0 g potassium acetate, and then 12.0 g anion ion-exchange resin added after potassium ion was totally exchanged under different temperatures)

R =correlation coefficient

3.2 Effect of rate of stirring on the ion-exchange process

Ion-exchange is a complex process which relates to the diffusion of ions into resins and reaction with ions adsorbed in resins. Because of low solvability of the organic solvent to the inorganic salts, inorganic salts can not be dissolved in organic solvent easily, and the driving force caused by the concentration difference is not as high as in an aqueous solution. The reaction rate is mainly determined by the rates of diffusion of ions both in solution and in resin. In order to enhance the mass transfer, stirring is a simple and effective way. The sharp pH increase after anion-exchange resin has

been added into the solution as shown in Fig. 3 indicates that anion-exchange between anions in solution and anions on the resin surface is a fast process. The pH is higher for a stirring system in comparison with no agitation. It shows that the rate of ion-exchange is faster for the former in comparison with the latter. Even after 33 hours, the anion-exchange was not completed. Upon cation-exchange resin added, the pH decreases sharply and ion-exchange continues until ions in solution exchanged totally. Fig. 3 demonstrates that the higher the stirring speed, the shorter the total ion-exchange time needed.

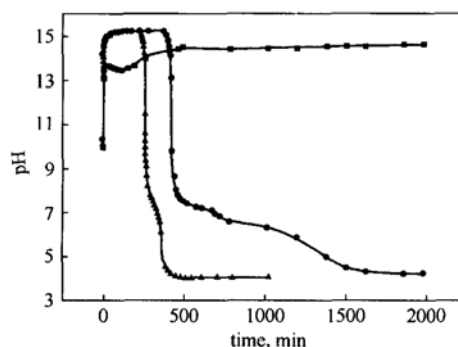


Figure 3 Effect of rate of stirring on the ion-exchange process

(12.0 g anion ion-exchange resin was added into 100 ml ethanol containing 2.0 g potassium acetate, and then 10.0 g cation ion-exchange resin added after acetate ion was totally exchanged under different stirring rate at room temperature)

stirring rate, $r \cdot \text{min}^{-1}$: ■—still; ●—150; ▲—300

3.3 Effect of solvent used on the ion-exchange process

Different solvents have different solubility towards a certain compound and ions. The solvability of a solvent to certain salt is determined by its dipolar property and protophilic/protophobic properties. Potassium ion has one positive charge and it is highly solvated in a protonated solvent. The solubility of the acetate ion is not as high as potassium ion in the solvent. 2.0 g potassium acetate can totally be dissolved in ethanol and can not be totally dissolved in acetone and tetrahydrofuran. After resins added into the solution, potassium ion will exchange with proton adsorbed in cation-exchange resin, and acetate ion will exchange with hydroxide ion adsorbed in anion-exchange resin. The combination of proton with hydroxide ion in resins produces water. With the ion exchange going on, the potassium acetate will be adsorbed in resins and the solution will become clear. Consequently, the solution is desalted. Fig. 4 indicates that ion-exchange is much easier to take place in ethanol than in acetone and tetrahydrofuran. 2.0 g potassium acetate will be totally adsorbed onto resins in about 50 minutes in ethanol, and the same process will take 12 hours in acetone, and still longer time required by using tetrahydrofuran. The results clearly show that the solubility of salt used in solvent has significant influence on the ion exchange process.

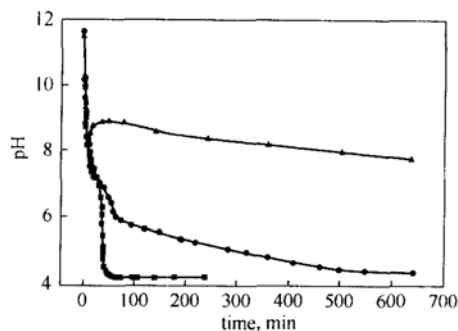


Figure 4 Effect of types of solvent used on the ion-exchange process

(10.0 g cation ion-exchange resin was added into 100 ml ethanol, acetone and tetrahydrofuran containing 2.0 g potassium acetate, respectively, at room temperature)

solvent: —■— ethanol; —●— acetone; —▲— tetrahydrofuran

3.4 Effect of the order of addition of resins

The ion-exchange is a process in which the salt dissolves in a solvent and the ions are adsorbed onto resins. The driving force is the affinity of resins to the ions. When the proton form of cation-exchange resin is added into the solution, only cation-exchange occurs and acidic solution forms. With the ion-exchange going on, the concentration of proton increases in solution, and potassium ion concentration has the same tendency to increase. The final concentration of the ion in the solution is determined by the ion exchange equilibrium. When hydroxide form of anion-exchange resin is added, the same phenomenon is observed. In order to minimize the ion concentration, proton and hydroxide ions must be removed. Simultaneously by adding the proton form of cation-exchange resin and hydroxide form of anion-exchange resin into the solution is the optimal method. Fig. 5 shows that 2.0 g potassium acetate was totally removed in about 37 minutes by adding two types of resins simultaneously, while cation-exchange resin added first and then the anion-exchange resin added afterward will take about 90 minutes, and when anion-exchange resin added first and then cation-exchange resin added will only take about 56 minutes. The results demonstrate that the order of addition of resins has a significant effect on the ion-exchange process. From the results, we may conclude that cation-exchange is the key ion exchange step.

4 CONCLUSIONS

Ion-exchange process can occur in organic solvents. The ion-exchange property of resins are strongly affected by operating temperature, stirring rate, solvent used, and the order of addition of resins. The increase of the temperature and stirring rate can increase the rate of ion exchange. The selection of a higher solubility solvent and by addition both types of resins simultaneously into the solution are the optimum operating procedure. The experiments show that trace amount of salts can be removed by ion-exchange process effectively.

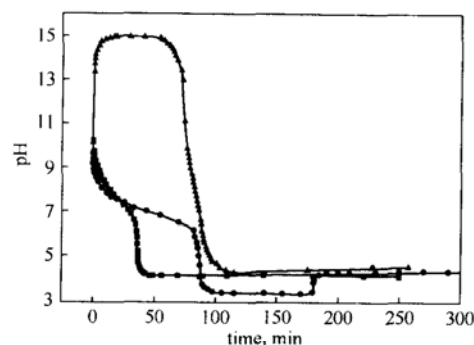


Figure 5 Effect of orders of addition of resins on the ion-exchange process

—■— cation-exchange resin and anion-exchange resin added simultaneously; —●— cation-exchange resin added and then anion-exchange resin added; —▲— anion-exchange resin added and then cation-exchange resin added

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