

STRUCTURAL FEATURE AND EXCHANGE KINETICS OF CARBOXYLATED POLYPROPYLENE ION EXCHANGE RESIN

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ABSTRACT

The present article deals with the exchange process of bivalent metal ions, such as Zn^{2+} , Cd^{2+} and Hg^{2+} , etc., taken up by non-crosslinked carboxylated polypropylene (CPP) resin. The control factor of the exchange rate deduced from the kinetic data is governed basically by the chemical reaction rather than the mass transfer effect particle diffusion and/or liquid film diffusion. In solution, all the graft chains in the outer shell of a CPP resin could form a "quasi-macromolecular solution" domain. This opinion further demonstrates the structural pattern of CPP resin proposed in earlier paper^[1].

INTRODUCTION

Three-dimensional structure is a general character of the conventional ion exchange resin. They are prepared by copolymerization of the bifunctional monomers and at least one kind of the polyfunctional monomer. Although the crosslink density is differed from each other, but the mass transfer effect is presented in all of them throughout the course of the exchange process.

In contrast, CPP resin is obtained by grafting the unsaturated carboxylic acid onto the polypropylene particles, the graft chains are all attached onto the surface of polymeric matrix via the covalent bonds. It is a non-crosslinked ion exchange resin. In aqueous solution, the CPP resin presents in either of the two possible forms: (1) Besides one linking on the matrix, all segments of each branched chain will extend freely. Among them, the bulky hydrated ions can penetrate easily. Finally they are adsorbed on the active sites and exchanged with the bound ions. The less mass transfer resistance leads to the higher exchange rate(2). The graft chains twist with each other to form a random coil structure. In this case, all of the entering ions and the bound ions must overcome the considerable resistance and penetrate into the crosslinked resin networks to complete the exchange course.

The structural pattern of the CPP resin is proposed based on the higher exchange rate and efficiency of the beads which have been proved by the authors^[1]. In the present article, we attempt to further demonstrate the morphological structure, that we have measured the exchange rate of the bivalent cations, such as Zn^{2+} , Cd^{2+} and Hg^{2+} , etc., taken up by CPP resin and made a preliminary approach to the controlling step of the exchange rate according to the behavior of its exchange kinetics.

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EXPERIMENTAL

The graft procedure was reported previously^[2].

In order to measure the amount of metal ion uptake, the CPP-Na resin (100mg) was suspended in the 0.02M salting liquid (50.00ml). The suspension was stirred with the magnetic stirrer at 21.0°C. for a given time. The clear liquid (10.00ml) was titrated with 0.01M EDTA solution^[3-4].

RESULTS AND DISCUSSION

In normal case, the ion exchange process is going on in the order of five steps as follows:

1. Entering ions move towards the resin in solution. Finally, they transport across the stagnant film of solution surrounding the resin particles—film diffusion.
2. Within the resin beads, the entering ions diffuse to reach the vacant exchange sites—particle diffusion.
3. Exchange reaction takes place at the active sites—chemical reaction.
4. The bound ions replaced by the entering ions penetrate outward—particle diffusion.
5. The bound ions leave the resin particle, across the liquid film, and enter into the solution—film diffusion.

It can thus be seen that the rate of ion exchange is governed by film diffusion, particle diffusion and chemical reaction.

Exchange kinetics is built up from one of the principal processes.

As mentioned above, the main body of CPP resin is the graft polymer. Its graft chains have not been crosslinked by chemical or physical process, the solvation thus reaches easily. They are highly extended in solution if repel one another. The tentative idea is expressed as the model depicted in Figure 1.

All the exchange sites of the bead are distributed onto the graft chains, none of them within the matrix. The entering ions move merely among the branched chains. They are unnecessary to penetrate into the polymeric matrix. For this reason, the particle diffusion of the ions within the bead have not been considered (Fig.2).

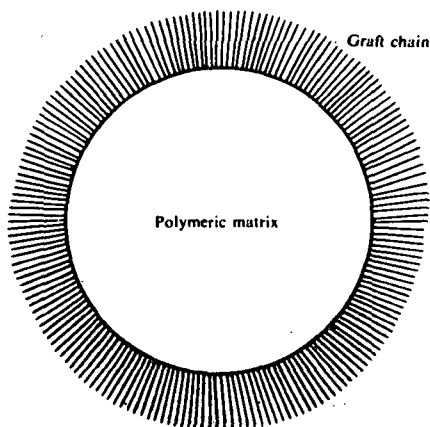


Fig.1 Model of the solvate CPP resin

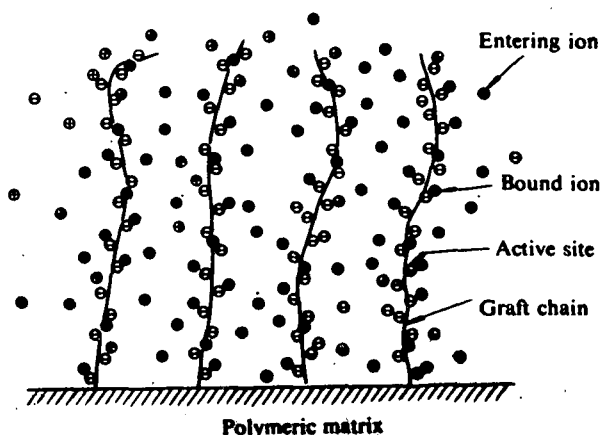


Fig.2 Schematic representation of entering ions taken up by CPP resin

Though the particle diffusion will not present in the polymeric matrix, but it could take place within the part of the graft chains. If the solvate CPP resin became a random coil structure by the graft chains twist with each other, the considerable mass transfer resistance certainly arise in the exchange process. Thus, the particle diffusion among the graft chains should be an important step of the rate control.

If the intra-particle transport of the metal ions were the rate controlling, it could be characterized by an almost constant diffusion coefficient throughout the exchange process. Thus the effect of particle diffusion control on the exchange kinetics is governed by [5]

$$\frac{Q_t}{Q} \equiv F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2 Bt)}{n^2} \quad (1)$$

Where

$$B \equiv \pi^2 D / r^2 \quad (2)$$

Here r is the average radius of the beads and D is the diffusion coefficient of the entering ions in the beads.

The results of exchange rate of Zn^{2+} , Cd^{2+} and Hg^{2+} ions taken place by CPP-Na resin are summarized in Table 1 and plotted according to the relations of Bt against t [6] in Figure 3. It shows that the particle diffusion is not the principal factor to affect the exchange process.

Tab. 1 The relations of F and Bt vs. t in the exchange process of $\text{Me}^{2+}/\text{CPP-Na}^*$

Time	Zn^{2+}		Cd^{2+}		Hg^{2+}	
(min.)	F^{**}	Bt	F^{**}	Bt	F^{**}	Bt
10	53.8	0.36	53.8	0.36	29.7	0.09
20	79.8	1.11	72.8	0.83	42.7	0.21
30	86.3	1.49	86.9	1.54	52.4	0.34
40	88.8	1.69	92.3	2.07	61.8	0.52
50	91.6	1.98	98.7	3.09	64.2	0.57
60	95.8	2.68	100	—	65.8	0.62
1440	100(94.6)***		100(82.7)***		100(87.5)***	

*Resin (total exchange capacity 3.77meq/g-R): 0.1g; volume of 0.02M metal ion solution: 50.00mL; temp.: 21.0 $\pm$ 0.6°C.; stirred with magnetic stirrer.

** $F = Q_t/Q_{\infty}$ (Q_t and Q_{∞} being the amounts uptake at time t and 24 hours, respectively.)

***Values for the exchange efficiency (in %) in parenthesis.

As the rate is governed by liquid film diffusion, the exchange process is of first order according to [5]

$$\log(1 - F) = -\frac{R}{2.303} t \quad (3)$$

Where R is a parameter of the system given by

$$R \equiv 3D_0/r\delta\chi \quad (4)$$

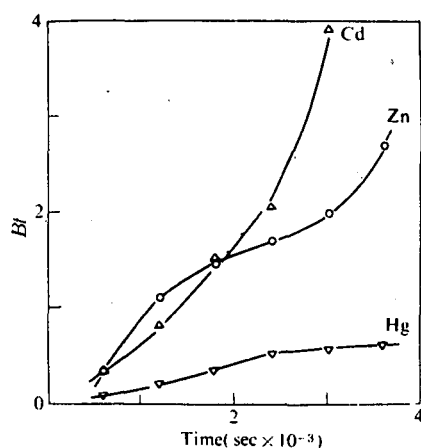


Fig. 3 The relations of Bt vs. t in the exchange process of $\text{Me}^{2+}/\text{CPP-Na}$

Here D_0 is the diffusion coefficient of the ions in solution, r is the average radius of the beads, δ the thickness of the stagnant solution film and χ the distribution coefficient between the solution and resin of the entering ions.

Figure 4 is plotted according to Eq. (3) and it can be seen that the graphs are noticeably curved. Obviously, this is not the case for liquid film diffusion control.

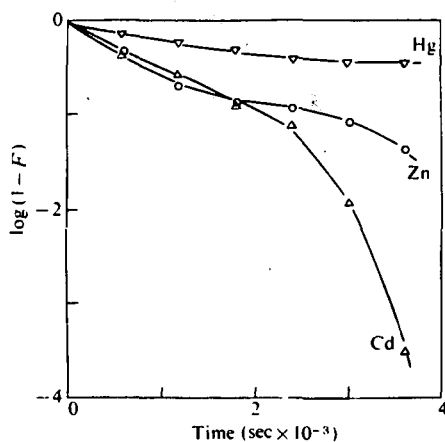
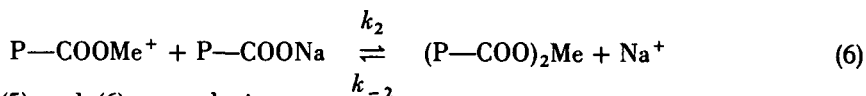
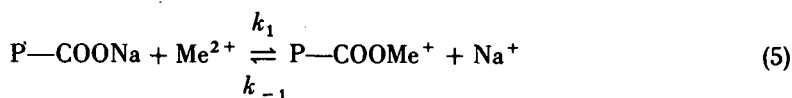


Fig. 4 Relations between $\log(1-F)$ and t in the exchange process of $\text{Me}^{2+}/\text{CPP-Na}$ resin

Where the controlling step is the exchange equilibrium between the bound ion and the entering ion at the exchange site, the exchange reaction may be considered here is a succession of two bimolecular steps.



From Eqs. (5) and (6), one obtains

$$\begin{aligned}
 \frac{dx}{dt} &= k_2[\text{P-COOMe}^+], [\text{P-COONa}]_t \\
 &= k_2(k_1[\text{P-COONa}]_t, [\text{Me}^{2+}]_t)[\text{P-COONa}]_t \\
 &= k(a-2x)^2(b-x)
 \end{aligned}$$

Here a and b are the initial concentrations of exchange centres of CPP-Na resin and Me^{2+} ion in mole, respectively; x being the amount of $(\text{P-COO})_2\text{Me}$ formed at time t ; k_1 and k_2 are the rate constants; and $k = k_1 \times k_2$.

Integrates the Eq. (7), the obtained relation of material concentration against reaction time is

$$\frac{1}{2b-a} \left(\frac{1}{a-2x} - \frac{1}{2b-a} \log \frac{b-x}{a-2x} \right) = kt \quad (9)$$

Plot of $\frac{1}{2b-a} \left(\frac{1}{a-2x} - \frac{1}{2b-a} \log \frac{b-x}{a-2x} \right)$ vs. t are finely linear (Fig. 5).

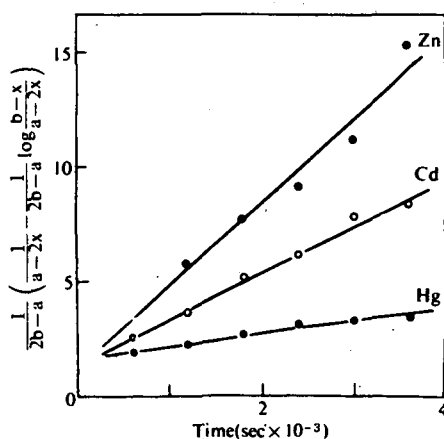


Fig. 5 $\frac{1}{2b-a} \left(\frac{1}{a-2x} - \frac{1}{2b-a} \log \frac{b-x}{a-2x} \right)$ vs. t ,
according to Eq. (9), for exchange process of Me^{2+} /CPP-Na resin

The results presented in Figures 3—5 draw a preliminary conclusion that the reaction rate is governed basically by the exchange equilibrium rather than particle diffusion or liquid film diffusion. This conclusion fully proves that the solvate CPP resin display really the structural feature presented in Figures 1—2.

In order to clarify whether the method of exchange kinetics used for studying the morphology of solvate resin is suitable or not, the crosslinked carboxylic acid ion exchanger, E. Merck IV, has been selected as contrast. The experimental conditions are all the same with CPP resin.

The exchange rate of Zn^{2+} , Cd^{2+} and Hg^{2+} ions taken up by E. Merck IV resin are summarized in Table 2.

Plot of Bt against t is expected to be linear (Fig. 6). The value B and diffusion coefficient D

of Zn^{2+} , Cd^{2+} and Hg^{2+} ions taken up by E. Merck IV resin thus obtained are 12.7, 4.83, 3.64 $\times 10^{-5}\text{sec}^{-1}$ and 8.04, 3.06, 2.30 $\times 10^{-9}\text{cm}^2\text{sec}^{-1}$, respectively.

Tab. 2 Relations between F and Bt vs. t in the exchange process of Me^{2+} /E. Merck IV resin (Na form)*

Time (min.)	Zn^{2+}		Cd^{2+}		Hg^{2+}	
	F	Bt	F	Bt	F	Bt
10	54.0	0.37	47.8	0.27	37.9	0.16
20	78.9	1.07	62.7	0.54	50.2	0.30
30	92.8	2.12	71.4	0.78	64.5	0.58
40	93.0	2.16	75.7	0.93	72.1	0.80
50	97.7	3.33	88.6	1.68	77.3	1.00
60	99.0	4.11	87.5	1.60	80.3	1.14
1440	100(71.1)**		100(70.9)**		100(65.3)**	
$B \times 10^5$ (sec^{-1})	12.7		4.83		3.64	
$D \times 10^9$ ($\text{cm}^2 \times \text{sec}^{-1}$)	8.04		3.06		2.30	

* Resin (total exchange capacity 10.4meq/g-R, $r = 0.25\text{mm}$): 0.1g; volume of 0.02M metal ion solution: 50.00mL; temp.: $21.0 \pm 0.6^\circ\text{C}$. stirred with magnetic stirrer.
** Values for the exchange efficiency (in %), in parenthesis.

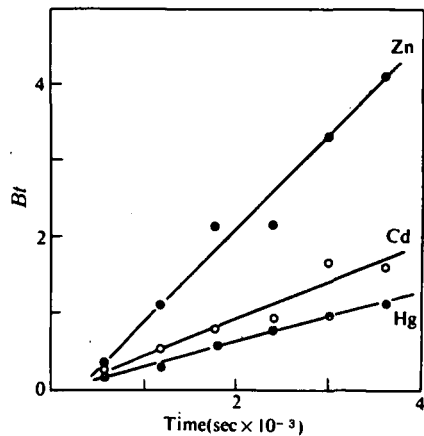


Fig. 6 t - Bt curves for exchange process of Me^{2+} /E. Merck IV resin (Na form)

If the exchange process of entering ions with the crosslinked resin not only governed by particle diffusion but also controlled by chemical reaction, the function $\frac{1}{2b-a}\left(\frac{1}{a-2x} - \frac{1}{2b-a}\log\frac{b-x}{a-2x}\right)$ versus t will appear a linear relation.

Clearly, this is not the case (Fig. 7), which indicates that the effect of ions reaction on exchange rate is smaller than that of particle diffusion in the case of the crosslinked exchanger. It forms a sharp contrast with non-crosslinked CPP resin.

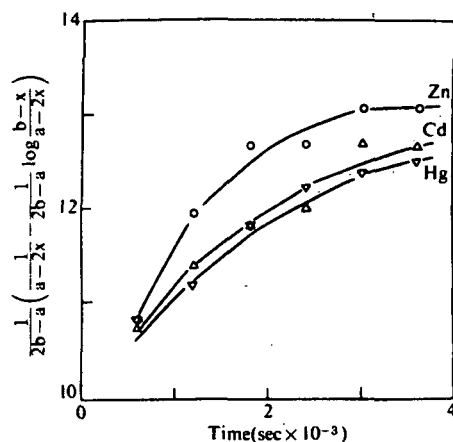


Fig. 7 Plot of $\frac{1}{2b-a} \left(\frac{1}{a-2x} - \frac{1}{2b-a} \log \frac{b-x}{a-2x} \right)$ vs. t ,
for exchange process of Me^{2+} /E. Merck IV resin (Na form)

Analysis and synthesis of exchange kinetic data expounds that the graft chains of CPP resin have the freedom similar to the free macromolecules in solution, the "quasi-macromolecular solution" domain thus is formed and covers the bead. As a consequence, the mass transfer resistance has not exerted a great influence upon the process of chemical reaction. Now that is the basic reason why the exchange rate of the CPP resin is so high (Fig. 8).

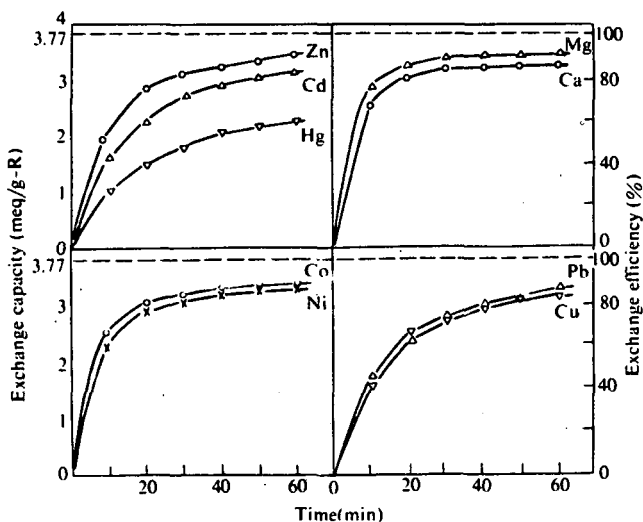


Fig. 8 Exchange rate of the bivalent ions taken up by CPP-Na resin

Keywords:

CPP resin; exchange kinetics; Ion exchanger; Mechanism; Structural feature

REFERENCES

- [1] 吴锦远、杨超雄, 高分子通讯 (*Polymer Communications*) **1982**, (5), 368.
- [2] 吴锦远、杨超雄, 合成纤维 (*Synthetic Fiber*) **1984**, (1), 9.
- [3] Welcher, F. J., The Analytical Use of EDTA, Von Nostrand, Princeton **1958**.
- [4] Flaschka, H. A., EDTA Titration, Pergamon Press, New York, **1959**.
- [5] Heitner-Wirguin, C. and Markovits, G., *J. Phys. Chem.*, **1963** 67(11) 2263.
- [6] Reichenberg, D., *J. Am. Chem. Soc.*, **1953**, 75, 589.