Sorption of copper ions on templated poly (4-vinyl pyridine) resins

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Abstract

The equilibrium and kinetics sorption behaviour of copper ions at low solution concentration on Cu^{2+}-templated poly (4-vinyl pyridine) resins have been studied. The Langmuir isotherm equation fits the equilibrium sorption data well, while the kinetic data are in good agreement with a modified shrinking core model for fluid-solid chemical reactions. Pore diffusion controls the exchange rates at low solution concentration. Interestingly the diffusion coefficient which lies within the normal expected range for chelating resins is found to increase with increasing solution concentration, besides temperature. This phenomenon is discussed in the light of similar observations reported for ion exchange resins in the literature.

Key words: Sorption, equilibrium, kinetics, pore diffusion, templated poly (4-vinyl pyridine).

1. Introduction

In contrast to the conventional approach where the binding ability of chelating resins such as iminodiacetic resin, is changed by varying the pH, a preferred approach would be to modify the structure of the resin so as to make it selective for a particular metal ion, irrespective of pH. As an example of this approach a novel method was tried by Nishide et al[1] to obtain a metal ion-selective resin. A complex is first made between the chosen metal ion template and a polymeric ligand and it is then crosslinked by treating with a crosslinking agent. The metal ion is subsequently removed by leaching with acid. If the polymer chain conformation developed around the metal ion in the first step is maintained through the following two steps, the resulting resin should be selective for this metal ion and capable of removing this metal ion preferentially from a mixture of other metal ions. Since the stability of chain conformation depends on the density or degree of crosslinking, the aforesaid selectivity would also be dependent on the degree of crosslinking[2]. Nishide et al[2] used copper (II), cobalt (II), zinc (II) and cadmium (II) as template ions and poly (4-vinyl pyridine) (PVP) as polymeric ligand. Of these template ions, copper (II) gave the most promising results with regard to selectivity[2]. Nishide et al[3] studied the complex formation of copper (II)-templated quaternized PVP, in short QPVP with Cu^{2+} ion and sorption capacity of QPVP as a function of the degree of crosslinking.

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While copper (II)-templated QPVP resin showed promise as a selective resin for separation and recovery of Cu^{2+} from other ions, there has been no published report on the sorption kinetics of such templated resins. Such a study is reported in this paper. Unlike the method used by Nishide et al[3] for the preparation of templated QPVP resin, namely, complexing PVP of a relatively low degree of polymerisation with the template ion and quaternization of the resulting complex used in the form of solution in methanol, in the present work a relatively high molecular weight linear PVP was used as the starting resin to form an insoluble complex with copper (II) which was then used as a slurry in methanol for crosslinking quaternization. Also in place of 1,4-dibromobutane used by Nishide et al[1-3] dibromoethane was used since it was expected to produce tighter network by virtue of shorter crosslinks and hence greater stability of the templated resin, resulting in higher selectivity and stability constant.

2. Experimental

2.1 Preparation of templated resin

Poly (4-vinyl pyridine) (PVP) used in the work was made by bulk polymerisation of 4-vinyl pyridine obtained from Polysciences, Inc., Warrington, Pennsylvania, and purified by distillation under vacuum. To 400 ml of the distilled monomer was added 2.52 ml of 73% active cumene hydroperoxide, also obtained from Polysciences, Inc. The solution was purged with pure N_2 and transferred into 20 ml ampoules and sealed after purging with N_2. The ampoules were kept immersed in water bath at 60° C for 72 hours, and then kept in an air oven at 60° C for 48 hr. The glass ampoules were then broken and the polymer sticks were turned at a slow speed to obtain polymer turnings which would dissolve more easily in solvents. The average molecular weight of the polymer was determined by the viscosity method using Ubbelohde viscometer, and found to be 60,000.

2% PVP solution in methanol and an equal volume of $CuSO_4$ in methanol of concentration less than the theoretically required amount for complete chelation were mixed at equal rate with stirring by magnetic stirrer and stirred for about an hour to ensure uniform chelation throughout the polymer. Batches of polymer - Cu - chelate with copper contents of 4:6%, 6.5% and 7.3% based on the weight of the PVP were prepared.

The polymer chelate in the form of precipitate was taken in a flask; twice the theoretically required amount of dibromoethane was added stepwise, stirred and refluxed in methanol at 65° C using hot plate-cum-magnetic stirrer for 7 days to ensure complete crosslinking. The polymer, Cu-chelate, was blue in colour initially and became dark green at the end of the seventh day of crosslinking reaction. It was washed with methanol and dried in a vacuum oven.

The powdered crosslinked PVP resins were shaken in a mechanical shaker with 3N HCl for 6 hr to remove the uncrosslinked polymer and the metal ion used as template. They were then treated with 1N NaOH and stirred for 1 hr to neutralise the acid. The crosslinked resins derived from the resins having template copper ion contents of 4.6%, 6.5% and 7.3% are denoted as QPVP1, QPVP2 and QPVP3, respectively. The percentages of quaternization and crosslinking were calculated by using elemental analysis (EA) and IR spectra and are presented in Table I.

Table I

Elemental analysis of templated resins

Resin	C%	N%	Br% ion	Br% (Total)	% Quaterni-zation by IR	% Quaternization by EA	% Cross-linking
QPVP1	61.44	9.76	21.06	21.06	35.62	36.78	18.39
QPVP2	59.33	9.2	23.01	23.41	42.05	43.54	21.39
QPVP3	63.86	10.3	17.1	17.7	29.87	29.68	14.34

2.2 Metal ion selectivity

An equimolar (3 mM each) mixture of Cu, Ni, Co, Zn and Cd (as sulphate) was prepared. A measured quantity of each of the templated resins was shaken with a measured volume of solution on a mechanical shaker at ambient temperature (30°C) for 12 hr. After shaking, the supernatant solution was filtered and analysed for the metal ions using Perkin Elmer Atomic Absorption Spectrometer (Model 2380). The amount of metal ions sorbed by the resins was calculated by subtracting the amount in the supernatant solution from the amount initially present. The percentages of sorption of metals of QPVP resins are tabulated in Table II.

2.3 Equilibrium sorption measurements

A batch type equilibrium set-up was used to determine the metal ion uptake from solution by the templated resin. A weighed amount of the resin was shaken with a measured volume of the metal ion solution of known concentration on a mechanical shaker at ambient temperature (30°C) for 12 hr. The two phases were then separated and the supernatant solution was analysed for Cu^{2+} using Visible UV Spectrophotometer (Model UV 240, Shimadzu, Japan).

The equilibrium sorption on templated resins was measured for different equilibrium concentrations of the metal ion in solution. Since the solutions have pH in the range 5.1 - 5.5 and the sorption is also maximum in the same range, no pH adjustments of the solutions were made.

2.4 Kinetic measurements

Since sorption rate measurement necessitated continuous monitoring of the sorbate metal ion concentration in the supernatant solution during a sorption run, a conductivity meter

Table II

Selectivity of metal ions

% Sorption* of metal ions on templated resins

Resins	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}
QPVP1	46.850	2.700	0	0	1.859
QPVP2	35.630	1.351	0	0	1.367
QPVP3	60.630	5.093	2.016	0	1.258

connected to a strip chart recorder was found to be a convenient tool for kinetic studies. A precision conductivity meter (Century Instruments Private Ltd., Model CC 601) with multiple speed recorder was used in the present study. Calibration curves were first prepared by measuring the conductivity of metal ion solutions of known concentrations. Concentration profiles could then be constructed from the recorder output showing the conductivity *versus* time plots.

3. Results and discussion

3.1 Metal ion selectivity

According to Nishide *et al*[2], if the conformation of the polymer-ligand chain is maintained at its best for the template ion, the resin will preferentially form a complex with the template ion when the resin is dipped into a solution. It was established by Nishide *et al*[2] that untemplated resin does not sorb the metal ion selectivity.

From Table II, it is seen that selective sorption is more in the case of QPVP1 and QPVP2 which are relatively highly crosslinked. It becomes less and less as the degree of crosslinking decreases because the conformational structure of the polymer is distorted and is not rigid when the degree of crosslinking is decreased. The ionic radius of Cu^{2+} and stability of Cu^{2+} complex with four N-donor ligands possibly account for the high selectivity of copper ions.

3.2 Equilibrium sorption

The equilibrium data for Cu^{2+} sorption on QPVP1, QPVP2 and QPVP3 are plotted in fig. 3. The data were fitted to both Freundlich and Langmuir isotherm equations. The Freundlich isotherm did not fit well to the sorption data for any of the resins.
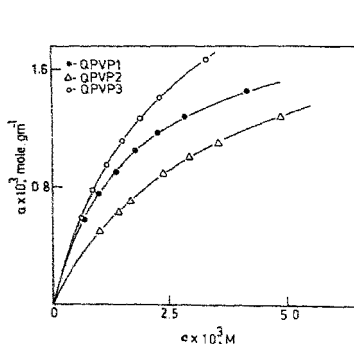

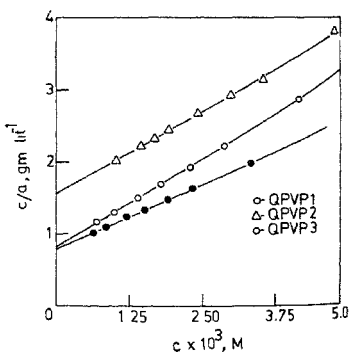FIG. 1. Sorption behaviour of Cu^{2+} on QPVP1, QPVP2 and QPVP3.

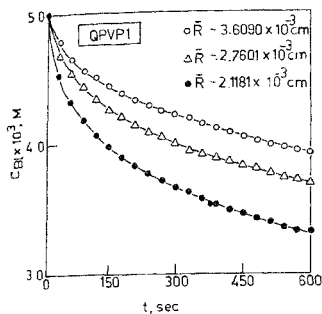FIG. 2. Langmuir isotherm of Cu^{2+} sorption on QPVP1, QPVP2 and QPVP3 resins.

FIG. 3. Variation of solution concentration [Cu^{2+}] with time: effect of particle size. $C_0 = 5.0 \times 10^{-3}$ M; T $= 30°$ C.
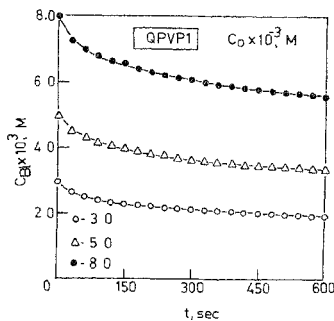

FIG. 4. Variation of solution concentration [Cu^{2+}] with time: effect of concentration. $\bar{R} = 2.1181 \times 10^{-3}$ cm; T $= 30°$ C.

The Langmuir isotherm fitted well to the sorption data (fig. 2). It can also be seen that the curve in fig. 1 resembles Langmuir-type isotherm. For the sorption of Cu^{2+} the Langmuir isotherm is written as

$$\frac{c}{a} = \frac{1}{KA_s} + \frac{c}{A_s}$$

where K is the binding constant (lit mole^{-1}) and A_s, the saturation constant (mole g^{-1}). By least squares fit, the values of K and A_s for sorption of Cu^{2+} on QPVP1, QPVP2 and QPVP3, were determined. These together with data for pyridine and PVP taken from literature are presented in Table III.

For comparison, it may be noted that Nishide et al[1-3] obtained K and A_s for Cu^{2+} complexes of QPVP in the range 97-2810 lit. mole^{-1} and 0.28-4.57 $\times 10^{-3}$ mole. g^{-1} respectively. The K value of Cu complex of PVP is about forty times as large as that of the monomeric copper complex of pyridine. Furthermore, K values are greater for the tem-

Table III

K and A_s values of Cu^{2+} complexes

	QPVP1	QPVP2	QPVP3	Py	PVP
K (lit. mole^{-1})	579.188	291.424	449.205	3.200	124.000
$A_s \times 10^3$ mole g^{-1}	2.066	2.184	2.783	—	4.286

plated resins than for the non-crosslinked PVP systems. This indicates that the copper complex of the templated resins is formed very readily. This phenomenon appears to be general with complexed polymer systems, and it can be explained by assuming that the concentration of the ligand is higher in the polymer domain, especially for the crosslinked and highly contracted resin systems; thus, once the metal ion is attached to one ligand group of the polymer chain, the other ligands coordinate more readily. Another reason for the larger values of K for the templated resins may be considered as follows. When the intrapolymer chelate is formed, the electrostatic repulsion of the polymeric chain of the ligand does not allow the chain to bend easily. In the case of crosslinked resins, however, the polymer chains are already contracted, so that energy is hardly required to give it a compact structure.

The decrease in K value is observed when the crosslinking content is increased. The reasons for this result are considered to be as follows: (1) The concentration of ligands in the polymeric system decreases with crosslinking, because the quaternized sites and dimethylene bridges occupy a large volume (ii) the complex formation is retarded by electrostatic repulsion between the coordinating copper ions and the pyridinium ions at the polymer chain in QPVP (iii) the structure of the copper complex is affected by crosslinking as discussed previously.

3.3 Diffusional effects

In order to study the effects of external diffusion on sorption, several conductometric runs were taken at various levels of stirring speed. The rpm of the stirrer was measured using stroboscope (Phillips (India), Model PR 9103). It is found that the stirring speed does not have any significant effect above 75 rpm. Since stirring speed used for all experimental conditions is around 250 rpm, it may be concluded that under the experimental conditions employed external diffusional effects on sorption are insignificant.
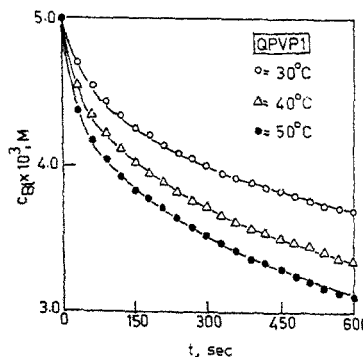

FIG. 5. Variation of solution concentration $[Cu^{2+}]$ with time: effect of temperature $\overline{R} = 2.760 \times 10^{-3}$ cm, $C_0 = 5.0 \times 10^{-3}$ M.

In the case of porous sorbate, internal diffusion, that is, diffusion in pores has significant influence on the rate of sorption. As in the case of catalysts, a convenient means of experimentally verifying the presence or absence of pore diffusional effects is to study the effect of the sorbent particle size. Thus, so long as there is pore diffusion, the sorption rate will increase with decreasing particle size. The results presented in fig. 3 for the resin QPVP1 are therefore indicative of pore diffusional control of sorption on the templated resin. Similar results were obtained with the other resins. The controlling mechanisms are further discussed later as a part of model development.

3.4 Sorption rate

The sorption of metal ions by the templated resins as a function of time with variations of concentration and temperature was measured conductometrically with a continuous recording facility. Representative results for the resin QPVP1 are presented in figs. 4 and 5. Similar curves were obtained for the other resins. As would be expected, the sorption rate is maximum in the beginning and drops off significantly with resin approaching saturation. The sorption rate is also seen to be influenced by the substrate concentration. These results are used for model selection.

3.5 Model development

The templated resins are used in the form of wet particles, having a range of particle sizes. For the purpose of modelling we may, however, consider the sorbent particle to be spherical with a diameter equal to the average of the size range. Since the binding constant of the templated resin for the metal ion is quite high, the surface layer of the resin particle which comes into contact with the solution first, would be expected to trap (complex) all the incoming metal ions till it is saturated. It may thus be postulated that the zone of resin-metal ion chelate moves into the resin particle leaving behind a completely chelated (saturated) resin layer.

For the sorption of metal ion on the templated resin one may visualise three steps occurring in succession:

(i) Diffusion of metal ion B through the aqueous film (surrounding the resin particle) to the surface of the particle.

(ii) Penetration and diffusion of B through the zone of chelated resin to the surface of the unchelated resin core.

(iii) Chelation of B at this chelation surface.

The physical picture is thus very similar to that discussed by Levenspiel[4].

Film-diffusion controls[5,6]

For film-diffusion control, the fractional conversion of resin, X, is given by

$$X = \frac{3K_1}{A_s \, \rho_p \, R} \int_0^t C_{Bl} \, dt \tag{1}$$

Diffusion through chelated layer control[5,6]

The fractional conversion, X, as a function of concentration-time integral is given by

$$1 - 3(1-X)^{2/3} + 2(1-X) = \frac{6D_e}{A_s \rho_p R^2} \int_0^t C_{Bl} \, dt \tag{2}$$

Chelating reaction controls[5,6]

In this case, the progress of the sorption is independent of the presence of any chelated layer. The fractional conversion X is given by

$$1 - (1-X)^{1/3} = \frac{K_s}{A_s \rho_p R} \int_0^t C_{Bl} \, dt \tag{3}$$

The above models were tested by plotting the L.H.S. of eqns. (1)-(3) against C_{Bl} dt. The best fit of the sorption rate data on each of the three resins was obtained with eqn. (2) for the shell diffusion model which predicts linearity of the plot of $1 - 3(1-X)^{2/3} + 2(1-X)$ *vs* $\int C_{Bl}$ dt. Figure 6 shows some typical plots. It is seen from fig. 7 that the stirring rate does not have any effect on the kinetics of sorption, implying that resistance offered by the stagnant solution film is practically nil. The fact that the rate of sorption is shell diffusion-controlled was further confimed by the 'interruption test' the results of which are shown in fig. 8. The slopes of these lines were used for the calculation of the diffusion coefficient, D_e. The values of D_e for Cu^{2+} diffusions in the resins are listed in Table IV.

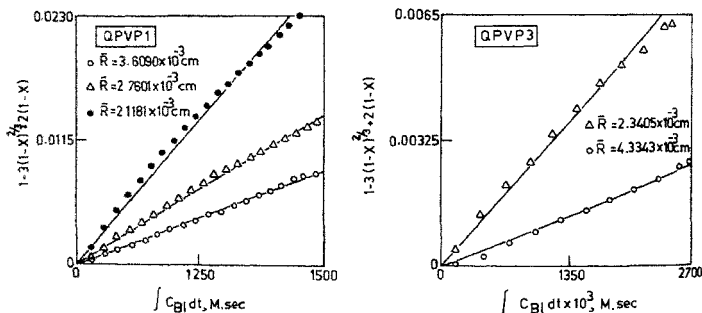FIG. 6. Correlation of kinetic data of copper sorption: shrinking core-shell diffusion model (effect of particle size); $C_0 = 5 \times 10^{-3}$ M; T = 30°C.
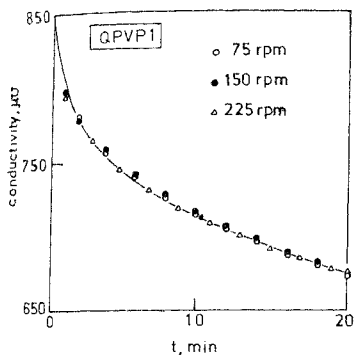
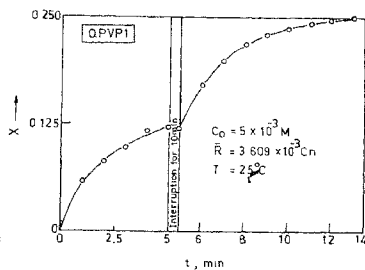FIG. 7. Bulk concentration measured in terms of conductivity vs time at different degrees of agitation.

FIG. 8. Interruption test.

Table IV

Results of the experiments

Expt. No.	Resin	$\bar{R} \times 10^3$ cm	C_o (mM/L)	T (°C)	$D_e \times 10^8$ cm^2/sec
1.	QPVP1	2.1181	5	30	1.961
2.		2.7601	5	30	1.755
3.		3.6090	5	30	1.866
4.		2.1181	3	30	1.335
5.		2.1181	8	30	2.650
6.		2.7601	5	40	3.087
7.		2.7601	5	50	4.343
8.	QPVP2	2.3334	3	30	1.563
9.		2.3334	5	30	1.766
10.		2.3334	8	30	3.027
11.	QPVP3	2.3405	5	30	0.941
12.		4.3343	5	30	1.147
13.		2.3405	3	30	1.004
14.		2.3405	8	30	1.755
15.		4.3343	5	40	2.002
16.		4.3343	5	50	3.264

As can be seen from Table IV, the D_e value increases with the increase in initial solution concentration, C_0 for all the three resins. Boyd[7] observed a similar trend for the diffusion of Na^+ ions into sulfonated polystyrene-divinyl benzene type cation exchangers. According to

him, diffusible anions from the external solution would enter the exchanger (Donnan distribution) and these might act to lower the activation energy and hence increase the diffusion. Ishibashi[8], Richman[9], Tetenbaum[10] and Meares[11,12] point out that this increase apparently occurs because of the increased Co-ion concentration in the pores. All of them found the explanation given by Schlögl[13,14] convincing. Schlogl pictures the interior of the resin as a field of potential energy troughs representing the fixed charges. In order to move from one trough to another, the counter-ions (exchangeable ions) have to pass the potential barrier in between. The Co-ions provide additional troughs of high mobility and thus facilitate the migration of the counter-ions. On this way, the average mobility of the counter-ions is increased when the Co-ion concentration is increased. The work of Clifford[15] on the diffusion of counter-ions in micellar solution containing added salt also supports this explanation.

Dickel[16, 17] studied the rate of Na^+-H^+ ion exchange of sulfonic polystyrene and found that the rate and thereby diffusion coefficient was dependent on concentration up to 1N NaCl. He considers that the kinetics of the ion exchange in resin exchangers is not adequately described by Fick's law with a concentration dependent diffusion coefficient.

According to Nikolaev's loose quasi-crystal model[18,19] freely moving ions, cations and gegenions present in the resin phase distort and diminish the depth of the potential well. The rate of diffusion of the ion which oscillates in a potential well near the functional group thus increases with an increase in the ionic strength. Fukazawa[20], in his study of the diffusion of Ce^{3+} and Pu^{4+} into Dowex A-1, also observed the increase in D_r with concentration. He found the above explanations of Nikolaev quite suitable to his observation.

The quaternized PVP resin having fixed ionic groups and their counter ions has an internal charge field similar to that in an ion-exchanger. Since complexation of metal ion by quaternised resins involves diffusion of the metal ion and its Co-ion through the charge field the observed concentration dependence on diffusivity—the diffusivity increasing with concentration—can also be related to the explanations given by Schlögl[13,14] and Nikolaev[18,19] as described above.

The D_r value increases with rise in temperature. It might be due to the fact that, with increasing temperature, the matrix becomes more flexible and the size of the solvated ions becomes smaller because solvation is reduced.

The activation energy, E_a, for diffusion of Cu^{2+} in the resins, QPVP1 and QPVP3 was estimated from an Arrhenius-type equation

Table V

E_a values of Cu^{2+} ions in QPVP1 and QPVP3

Resin	E_a (k cal. $mole^{-1}$)
QPVP1	10.514
QPVP2	10.302

$$D_e = A \exp(-E_a/RT)$$

and the values are presented in Table V.

E_a values in standard ion exchange resins are about 4 to 11 kcal. mole$^{-1,7,9,20-24}$. The E_a values of QPVP1 and QPVP3 are thus within the normal range.

4. Conclusions

Quaternised poly (4-vinyl pyridine) resins templated with Cu^{2+} show high degree of selectivity for Cu^{2+} for sorption from mixed ion solutions. The selectivity increases with the degree of crosslinking. The sorption process of copper in the resins follows shell diffusion controlled shrinking core model for all crosslinking contents, particle sizes for the resins, initial solution concentrations and temperature.

Nomenclature

a	: Concentration of metal ion in the resin.	K_s	: First order rate constant for the surface reaction.
A_s	: Saturation constant.	PVP	: Poly (4-vinyl pyridine)
c	: Concentration of metal ion in the solution.	QPVP	: Quaternized poly (4-vinyl pyridine).
C_B	: Concentration of B in the liquid phase.	R	: Radius of resin particle.
C_o	: Initial solution concentration.	X	: Fractional conversion of the resin.
D_e	: Effective diffusion coefficient.	t	: Time
K	: Stability constant.	ρ_p	: Particle density.
K_l	: Mass transfer coefficient in the liquid phase.		

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