

# Studies on Applications of Natural Polyphenol–Phenol–Formaldehyde Copolymer Based Cation Exchange Resins

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## SYNOPSIS

Naturally occurring polyphenol(condensed tannin)–phenol–formaldehyde copolymer matrix based cation exchange resins have been successfully used as a solid catalyst (in  $H^+$  ion form) in the inversion of sucrose and hydrolysis of methyl acetate. Apart from the normal advantages of the solid catalysts over the acid catalysts in the solution phase, the values of the activation energy, entropy, and enthalpy of activation of the reactions involved reveal that the resins prepared acted as a catalyst with characteristics comparable to those of the commercially available resins based on a styrene–DVB matrix. The resins have also been successfully used for softening of hard water and enrichment of metal ion concentration from very dilute solutions. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Condensed tannins are present in the bark and heartwood of various plants found in different parts of the world. Tannins are flavonoids in the polycondensed form and have found wide applications as partial substitute of phenols in the production of polyphenol–phenol–formaldehyde adhesive<sup>1–5</sup> resins. But their use in the preparation of cation exchange resins has only been recently reported<sup>6,7</sup> wherein the cation exchange properties of these newly produced resins (sulfonated condensed tannin–phenol–formaldehyde) were studied. The  $H^+$  ion form of one of these resins<sup>7</sup> (viz. R-604  $SO_3H$ ) was studied to evaluate the catalytic activities and capability of water softening and metal ion concentration from very dilute solutions.

## EXPERIMENTAL

Resin<sup>7</sup> R-604  $SO_3Na$  (30–50 mesh size), Sucrose (AR grade), methyl acetate (AR), samples of water from different sources, EDTA (AR), zinc chloride, silver nitrate etc. were used in this study.

## Hydrolysis Reactions

The hydrogen ion form of the R-604  $SO_3H$  resin was used in the catalytic inversion of sucrose studied by the polarimetric method and in the hydrolysis of methyl acetate studied<sup>8</sup> by the analytical method.

## Inversion of Sucrose

A weighed quantity (ca. 5 g) of R-604  $SO_3Na$  was converted to the  $H^+$  form by using 1 N HCl, and washed thoroughly in order to make it free from any soluble acid until the wash liquid was free from  $H^+$  ions. The R-604  $SO_3H$  was added to 100 mL of 20% sugar solution previously thermostatted with a stirring arrangement. Portions of the solution were taken out at known time intervals and the rotation of polarized light was noted with the help of a Lipich type polarimeter. Care was taken so that no resin particle adhered to the sides of the polarimeter tube. After taking the solution in the polarimeter tube, the angle of rotation was noted as quickly as possible in each case. Thereafter the solution was immediately returned to the reaction mixture each time. Similarly, angles of rotation were also noted at several other temperatures. The reading taken after heating the reaction mixture at 65°C for 30 min was taken as the infinity reading. The enthalpy of activation,  $\Delta H^\ddagger$ , entropy of activation,  $\Delta S^\ddagger$ , and

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energy of activation,  $E_a$  of the process were calculated from the experimental data.

### Hydrolysis of Methyl Acetate

A weighed quantity (ca. 5 g) of resin<sup>7</sup> R-604 SO<sub>3</sub>Na was similarly converted to the H<sup>+</sup> ion form and placed into 100 mL of water, thermostatted, and 5 mL of methyl acetate (AR) was added after noting the time of addition of the ester. Stirring of the mixture was done continuously and 5 mL aliquots were taken out at known time intervals, chilled, and titrated against 0.01 N NaOH solution using phenolphthalein as indicator. The experiment was repeated at several other temperatures. The infinity reading in each case was taken after heating the reaction mixture at 65°C for 30 min.  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $E_a$  values of the reaction were calculated in a similar manner.

To ascertain whether there is any loss of exchange capacity of the resin, the capacity was determined before and after both the hydrolytic reactions.

### Softening of Hard Water

Samples of hard water were collected from different areas of Calcutta (and its suburbs) and treated with one of the new resins in Na<sup>+</sup> ion form. It was observed that the hardness may be totally removed by using a requisite amount of resin. Their regeneration was easy to perform by using a common salt solution.

About 5 g of R-604 SO<sub>3</sub>Na was taken in a burette type exchange column. Samples of hard water were passed through the columns at the rate of 3 mL/min as influent and the effluent liquids were analyzed. In each case 20 mL of the effluent liquid was pipetted out and titrated against 0.01M EDTA solution using Erio T as indicator. Hardness was also

estimated in each sample prior to its treatment with the resin, using the same 0.01M EDTA solution and Erio T as the indicator. Regeneration of the resin bed was effected by passing 1 N NaCl solution through the resin bed at the rate of 2 mL/min.

Experiments were performed to find the actual volume of the samples of hard water required to saturate the resin bed with the metal ions present. In each case, the hard water sample was allowed to pass through the resin column at the rate of 3 mL/min until the effluent liquid showed any reaction of metal ion or ions (viz. that of Ca, Mg, etc.). At this stage the volume of hard water required was recorded as the actual volume of the sample needed to exhaust the resin column (Table I).

### Enrichment of Metal Ion Concentration from Dilute Solution

#### Silver Ion

As an exploratory study the following experiments were conducted. The resin (4.252 g of R-604 SO<sub>3</sub>Na) taken in a burette column was converted to the H<sup>+</sup> ion form by using 1 N HNO<sub>3</sub> and rinsed thoroughly with distilled water to make the bed free from any electrolyte. AgNO<sub>3</sub>, 1000 mL of 1.455 × 10<sup>-4</sup> molar solution, was passed through the resin bed at a rate 3 mL/min. A little portion of the effluent liquid was tested from time to time near the end of this operation and it was observed that no silver was coming out. After this the sorped silver was leached down in the following way. Nitric acid, 10 mL of 1 N, was used as eluant and allowed to stand for 6 h. After that the effluent was collected at the rate of 1 mL/min. Another 10 mL portion of 1 N nitric acid was used as eluant allowing the same standing time and

**Table I** Hardness of Water Before and After Treatment with Resin

Sample of Water	Hardness (ppm)				Vol. of H <sub>2</sub> O <sup>a</sup>	
	Before Treatment	After Treatment with		Calculated	Actual	
		R-604 SO <sub>3</sub> H	R-604 SO <sub>3</sub> Na			
Distilled	0	0	0	—	—	
Calcutta municipal supply	81	6	0	Hardness within reason. lim.		
Salt Lake City supply	695	152	0	960.28	947.50	
Salt Lake tube well	650	136	0	1026.77	1010.20	
Baranagar municipal supply	580	93	0	1150.68	1123.60	

<sup>a</sup> Volume of water softened before the resin column (containing 5.255 g of R-604 SO<sub>3</sub>Na of capacity 2.54 meq/g) was exhausted.

rate of collection. In this way five installments of the nitric acid were necessary to be used as eluant. Finally the bed was rinsed with 20 mL of distilled water at the same rate. All effluents were collected in the same conical flask. The total quantity of silver released was estimated by Volhard's method using a standard solution of KSCN and  $\text{Fe}^{3+}$  ions as indicator (vide Table II).

### Zinc Ion

The resin (5.255 g of R-604  $\text{SO}_3\text{Na}$ ) taken in a burette column was converted to the  $\text{H}^+$  ion form by using 1 N HCl and rinsed thoroughly with distilled water.  $\text{ZnCl}_2$ , 1000 mL of  $1.00 \times 10^{-4}$  molar solution, was passed through the resin bed in the same way as in the previous case. The sorped zinc was leached down by two installments of 5 mL each of 1 N HCl that happened to be sufficient for zinc. A time of 3 h was allowed after each addition of acid instead of the 6 h in the case of silver. Finally the bed was rinsed with 30 mL of water as before and the total quantity of zinc released was estimated by using 0.01M EDTA solution and Erio T as indicator (vide Table II).

## RESULTS

### Hydrolysis Reactions

#### Inversion of Sucrose

The angles of rotation of the sugar solution with time were regarded as basic data and the rate constant for each temperature was calculated (Table III).

#### Hydrolysis of Methyl Acetate

The volumes of alkali solution required to titrate the liberated acid with the elapse of time were re-

corded as basic data and the rate constants were calculated therefrom (Table IV).

Both the inversion of sucrose and hydrolysis of methyl acetate being pseudounimolecular reactions, the Eyring equation<sup>9</sup> may be suitably applied in the following form:

$$K = ekT/h \cdot \exp(T\Delta S\# - \Delta H\#)/RT$$

where  $K$  is the rate constant and other symbols bear usual significance. The equation leads to

$$\log(K/T) = \log(ek/h) + \Delta S\#/2.303R - \Delta H\#/2.303RT.$$

Thus a plot of  $\log(K/T)$  vs.  $1/T$  should give a straight line, the slope and intercept of which may be used to compute  $\Delta H\#$  and  $\Delta S\#$  values, respectively.

Again, following the Arrhenius equation one can write

$$\log K = -E_a/2.303RT + C$$

and as such a plot of  $\log K$  vs.  $1/T$  will give a straight line from the slope of which  $E_a$  may be calculated.

Figure 1 shows the straight line plots of  $\log K$  vs.  $1/T$  (upper part of the figure) and  $\log(K/T)$  vs.  $1/T$  (lower part of the figure) for both the reactions. The slopes of the former straight lines (shown on the upper part) were used to calculate  $E_a$  values (Table V) and the slopes and intercepts of the latter lines (shown on the lower part) give  $\Delta H\#$  and  $\Delta S\#$  values, respectively (Table V).

The exchange capacity of the resin before it was used as catalyst was found to be 2.54 meq/g and that determined after the inversion of sucrose and hydrolysis of methyl acetate was found to be 2.40 and 2.34 meq/g, respectively.

Table II Enrichment of Metal Ion Concentration

Solution of Metal	Conc. of Dilute Solution (M)	Vol. of Solution <sup>a</sup> (mL)	Vol. Acid and H <sub>2</sub> O <sup>b</sup>			Enrichment Ratio
			Acid (1 N) to Leach (mL)	Water to Rinse (mL)	Total (mL)	
Silver	$1.455 \times 10^{-4}$	1000	50	20	70	14.1
Zinc chloride	$1.00 \times 10^{-4}$	1000	10	30	40	25

<sup>a</sup> Passed through resin bed.

<sup>b</sup> Used for "elution" of the "sorped" metal ions.

**Table III Rate Constants for Inversion of Sucrose at Different Temperatures**

Temperature (°K)	$1/T \times 10^4$	Rate Constant ( $K \times 10^3 \text{ min}^{-1}$ )	$\log K$	$\log(K/T)$
303	33	0.954	-3.02	-5.50
313	32	2.842	-2.55	-5.04
323	31	6.850	-2.16	-4.67
333	30	15.701	-1.80	-4.33

### Softening of Hard Water

Hardness data of the samples of water before and after the treatment with R-604  $\text{SO}_3\text{Na}$  are tabulated in Table I. The results of treatment of the same samples with the  $\text{H}^+$  ion form of the resin are also shown in the same table that indicates that  $\text{Na}^+$  ion form of the resin is more efficient than R-604  $\text{SO}_3\text{H}$  ( $\text{H}^+$  ion form). As expected the "exhaust" capacity is comparable with the theoretical value.

### Enrichment of Metal Ion Concentration from Dilute Solutions

Table II shows how enrichment of metal ion concentration could be achieved with the help of the resin. The volumes of 1 N acid and water used for leaching and rinsing, respectively, were sufficient to wash down the sorped ions.

## DISCUSSION

### Hydrolysis Reactions

Using the resin catalyst R-604  $\text{SO}_3\text{H}$  sucrose solutions were converted to inverted sugar solutions within a short time (depending on temperature of reaction); moreover, the catalyst could be easily and quantitatively removed from the system and used repeatedly. Inversion up to any desired degree remains in the hands of the experimenter and the difficulties in using any soluble electrolyte catalyst in

such cases are also avoided. The inverted sucrose solution is quite popular because the mixture of dextrose and fructose derived from the hydrolysis of sucrose has better nutritional and medicinal values than sucrose solution itself. As such, the above resin has immense commercial potential as a catalyst for the conversion of sucrose to dextrose and fructose.

Hydrolysis of methyl acetate was carried out by using the  $\text{H}^+$  ion form of the same resin. Thus the resins have the potential of hydrolyzing esters in general without involving the process of separation of soluble acids from the products of hydrolysis.

Helfferich<sup>10-12</sup> made an important contribution to the ion exchange catalysis by assuming that the  $\text{H}^+$  forms of the ion exchange resins are pseudoacids of reduced degrees of freedom and suggesting that ion exchange resin catalysts may be compared with soluble electrolytes containing similar active ions (viz.  $\text{H}^+$  ions).

There are several apparent advantages<sup>10</sup> of the use of ion exchange materials in regard to their catalytic activities. Some of these are:

1. by a simple filtration step, catalyst-free products can be obtained;
2. the catalyst can be separated and recovered as and when required by means of a simple filtration or even decantation;
3. continuous reactions can be achieved by passing the reactants through beds of ion exchange resin catalyst;

**Table IV Rate Constants for Hydrolysis of Methyl Acetate at Different Temperatures**

Temperature (°K)	$1/T \times 10^4$	Rate Constant ( $K \times 10^3 \text{ min}^{-1}$ )	$\log K$	$\log(K/T)$
305	32.78	2.18	-2.66	-5.15
311	32.15	3.82	-2.42	-4.91
318	31.45	9.95	-2.00	-4.50

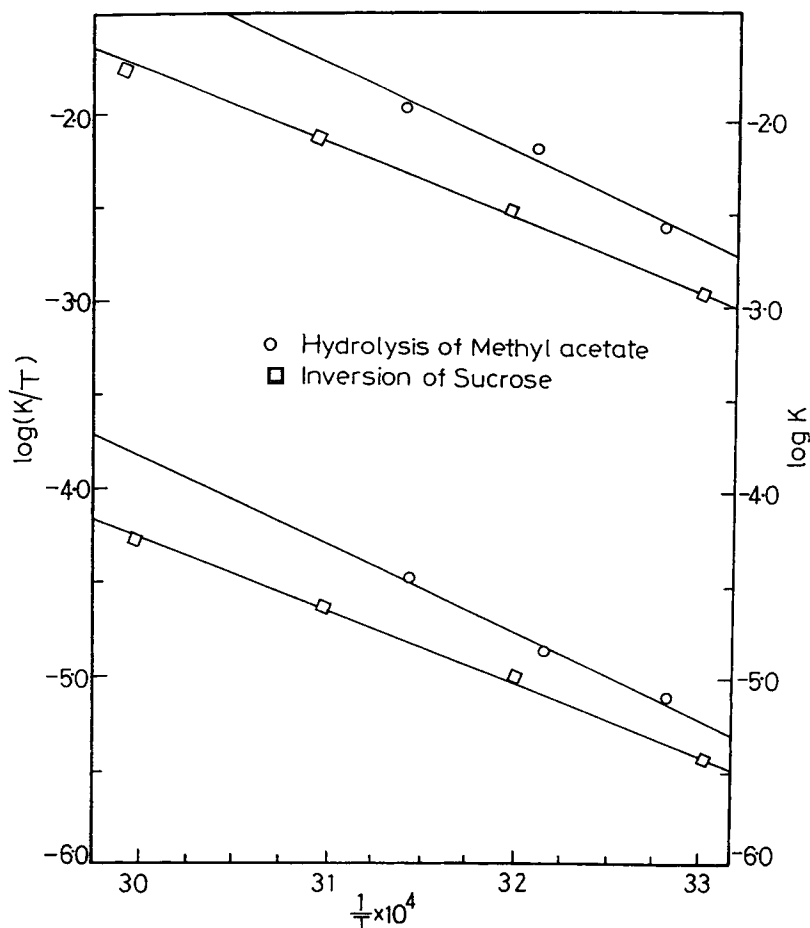


Fig.1  $\log K$  vs.  $1/T$  (upper portion)  
 $\log(K/T)$  vs.  $1/T$  (lower portion)

**Figure 1**  $\log K$  vs.  $1/T$  (upper portion),  $\log(K/T)$  vs.  $1/T$  (lower portion)

4. side reactions can be kept at a minimum;
5. special corrosion-resistant equipment is not necessary as with some soluble catalysts.

The type of resin under discussion has natural renewable resources and is commercially attractive. The applicability of a resin catalyst is, however, restricted by the thermal and chemical stability of the resins. With the resin used here being stable at least up to  $100^{\circ}\text{C}$ , the possibility of its applications below  $100^{\circ}\text{C}$  is encouraging, particularly in acid and neutral media. Moreover, as the capacity of the resin remains almost unchanged after the hydrolytic processes studied, it can be used repeatedly without further regeneration.

The enthalpy of activation,  $\Delta H^{\#}$ , and the entropy of activation,  $\Delta S^{\#}$ , are associated with the formation of activated complex in the processes. According to

Hammett et al.,<sup>13-15</sup> the entropy change of the activated complex is an important factor in determining the efficiency of a catalyst. Their hypothesis is that the formation of the activated complex in the ion exchanger involves some kind of fixation to the

**Table V**  $\Delta S^{\#}$ ,  $\Delta H^{\#}$ , and  $E_a$  Values Using R-604  $\text{SO}_3\text{H}$  as Catalyst

Reaction	$\Delta S^{\#}$ (cal/degree/mol)	$\Delta H^{\#}$ (kcal/mol)	$E_a$ (kcal/mol)
Inversion of sucrose	-10.19	19.44	19.80
Hydrolysis of methyl acetate	-17.28	16.01	22.18

fixed ionic groups on the matrix. Thus the reactant molecule suffers a loss of some internal degrees of freedom. Reactant molecules with many degrees of freedom have more entropy to lose. For these  $\Delta S^\ddagger$  becomes negative. In the hydrolysis processes studied in this work,  $E_a$  values and negative  $\Delta S^\ddagger$  values obtained are comparable to the literature values. This indicates that the new tannin-phenol-formaldehyde resin, R-604  $\text{SO}_3\text{H}$ , performs its catalytic functions more or less as expected. Thus for the hydrolysis of methyl acetate, the value of  $E_a$  obtained, 22.18 kcal/mol, is comparable to the literature<sup>13</sup> values, 17.50 kcal/mol, for DVB-4, 17.10 kcal/mol for Dowex-50, and 17.10 kcal/mol for hydrochloric acid. Further, for inversion of sucrose the value of energy of activation obtained in this work, 19.80 kcal/mol using R-604  $\text{SO}_3\text{H}$ , and the literature<sup>16</sup> value, 24.2 kcal/mol using DVB-4, are also comparable.

In other approaches by Thomas and Davies<sup>17,18</sup> and Helfferich,<sup>10-12</sup> the heterogeneous nature of catalysis exhibited by the ion exchangers was made the starting point for interpreting the catalyst activity. The pores of an ion exchanger that are in contact with a solution contain solvent, solutes, and counterions. The counterions are mobile and solvated and thus in a condition that is, in principle, not different from that in a corresponding homogeneous solution. It can therefore be expected that counterions that display catalytic activity in homogeneous solutions are equally active in the pores of a resin, and that the reaction mechanism in homogeneous catalysis by a dissolved electrolyte and heterogeneous catalysis by a resin is essentially the same. The comparable  $E_a$  values mentioned are in conformity with this idea.

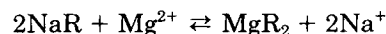
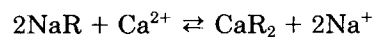
It is known that a decrease in entropy in any process corresponds to a more ordered or less random molecular configuration. Using R-604  $\text{SO}_3\text{H}$  as catalyst, the reactions mentioned above have negative entropy of activation (Table V). This leads to the conclusion that the reactant molecules are bound together in the transition state with a considerable loss of degrees of freedom. As such the experimental  $\Delta S^\ddagger$  values also provide indications of the nature of the transition state, that is, in the activated state the reactant molecules are tightly bound, and as a result the reactions are a bit slower than the homogeneous ones.

### Applications of Resins in Water Softening

The softening of water by means of ion exchange resins has developed considerably with the availability of the sulfonated styrene-DVB copolymers.

These resins are now being used extensively for the softening of water in industry, on a municipal scale, and even in domestic application. A large section of the population living in cities and municipalities depend on hard water. Application of ion exchange resins will continue to grow considerably because the advantages of using soft water have not yet been fully appreciated by all those residing in hard water areas.

The softening equilibria, except for minor ionic trace constituents, involve merely the calcium, magnesium, and sodium ions and may be written as



It is evident that, for the softening process, the equilibrium of either of the processes should proceed to an appreciable extent to the right hand direction in order to obtain a high degree of softening. The greater the value of equilibrium constant the greater the softening ability or the softening efficiency of the exchanger. However, it should be recognized that an increase in softening efficiency must be accompanied by a decrease in regeneration efficiency. Thus an exchanger having an equilibrium that is far to the right will show marked softening efficiency, but its practicability will be poor because its regeneration ability will be much below the required level.

The equilibria for sulfonic acid cation exchangers are such that the softening process is efficient but still permits an efficient<sup>19</sup> regeneration. In this respect the sulfonic acid type resin under discussion also shows quite satisfactory exchange efficiency and regeneration ability.

It is interesting to note that, for the sulfonic acid exchanger, the efficiency of the column method far exceeds<sup>19</sup> the efficiency of the batch procedure. This is the reason for adopting the columnar procedure in this work.

Although cation exchangers perform best when they are completely regenerated (i.e., all the exchange spots are occupied by  $\text{Na}^+$  ions), the use of a completely regenerated bed is not economical. And it is quite possible to soften hard water utilizing a bed that has been regenerated with an amount of sodium chloride that is insufficient to remove all the calcium and magnesium from the exchanger. The most economic level for regeneration is not a single valued function, but it depends on variables, such as type of exchanger, concentration, and water composition. The most economic regeneration level is described as the minimum amount of salt required

to yield water that will have the maximum permissible degree of hardness. Moreover, there is no capacity limit stipulated in this description.<sup>19</sup> In actual practice, 80% of the theoretical efficiencies are utilized. Although regeneration efficiency is of economic importance, the quantity of resin and capital equipment costs must be balanced against the above factors. In actual practice some efficiency may be sacrificed in order to minimize capital costs.

In the water softening process small quantities of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and other polyvalent cations are replaced by  $\text{Na}^+$ . From hard water (i.e., solutions containing low concentration of calcium, magnesium, etc.), polyvalent ions are preferentially taken up by the resin because of the electroselectivity effect, but in equilibria with highly concentrated solutions sodium ion is preferred. Thus the ion exchanger can be regenerated with only a little more than the stoichiometric amount of concentrated brine, although equilibrium in the sorption step is highly favorable. Much of the success of ion exchange in water softening is due to this fortunate coincidence.

It is important that the concentration and the electrolyte composition of the water to be softened determine to a large extent the minimum regeneration level that may be utilized in order to obtain a maximum degree of softening. As the concentration or  $\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})$  ratio increases, the hardness leakage increases at a fixed regeneration level. Therefore, it follows that for any desired quality of water (i.e., the water having desired degree of hardness), the minimum regeneration level and the regeneration efficiency will vary with water composition.

The major factors that control the rate of exchange are:

1. particle size;
2. resin type;
3. flow rate; and
4. temperature.

Any factor that alters or influences the rate of exchange affects both the exhaust capacity and the leakage. For example, a decrease in particle size results in an increased rate and therefore an increased exhaust capacity.

For sulfonic acid cation exchangers the regeneration flow rate is more important than the exhaustion flow rate. On the laboratory bench a flow rate of 3 mL of hard water/min/5 g of the resin (viz. R-604  $\text{SO}_3\text{Na}$ ) for the softening operation and 2 mL of 1 N NaCl solution/min for regeneration has been found to be satisfactory. In line with the conclusions

found from the above studies, the regeneration process was maintained more slowly in comparison to the softening operation.

### Enrichment of Metal Ion Concentration from Dilute Solutions

The technology of recovering metal values from aqueous solutions and the ability of ion exchange resins to selectively concentrate many metals of economic and strategic importance fall under the purview of hydrometallurgy. In addition one must keep in view that:

1. new regulations are being imposed to the effect that stream and river pollution is to be prevented;
2. the important ore reserves are of low grade;
3. it has become urgently necessary to recover metal values from the industrial waste streams.

Ion exchange resins are now being utilized throughout most of the world for exploitation of low-grade ore reserves and also to recover metal values from waste water. In many instances the concentration of the metal to be recovered is such that unless this can be increased at a relatively low cost, it becomes uneconomical to recover the metal.

Ion exchange resins may be employed in hydrometallurgical operations in one of the following ways:

1. the resins are used to concentrate and purify the valuable metal contained in the leach liquors of some ores;
2. they are used to recover metal values in the tailings of other hydrometallurgical operations;
3. they are employed to upgrade the impure concentrates;
4. the resins can be used for enrichment of metal ion concentration from waste water.

The last process has been successfully adopted to explore the applicability of the new resin developed by the authors for concentration of metal ions from dilute solution on a laboratory scale. Two cases, namely the concentration of silver ion and zinc ion, were reported here (Table II). It is evident from the table that the process is more efficient (higher enrichment ratio) in the case of zinc ions with higher valence due to electroselectivity effect.<sup>10</sup> The potential of the above method lies in the recovery of metals

such as silver and zinc from waste liquids of the photographic and blockmaking industries, respectively.

## REFERENCES

1. D. C. Roy, A. Sarkar, and B. N. Rajak, *Indian Plywood Ind., Res. Inst. J.*, **3**, 81 (1973).
2. H. M. Saayman and J. A. Oatley, Proceedings of the IUFRO Conference on Wood Gluing, U.S. Forest Product Lab., September 22–23, 1975.
3. A. Pizzi, *Adhesive Age*, **20**, 27 (1977).
4. A. Pizzi, *Forest Prod. J.*, **28**, 42 (1978).
5. A. Pizzi, *Wood Adhesives*, Marcel Decker, New York, 1983.
6. A. Sarkar, N. C. Mitra, and R. S. Banerjee, *J. Polym. Sci., Polym. Lett. Ed.*, **27**, 331–332 (1989).
7. N. C. Mitra, R. S. Banerjee, and A. Sarkar, *J. Appl. Polym. Sci.*, **42**, 2499–2508 (1991).
8. N. C. Mitra, R. S. Banerjee, and A. Sarkar, Proceedings of the 27th Annual Convention of Chemists, India, 1990.
9. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw–Hill, New York, 1941.
10. F. Helfferich, *Ion Exchange*, McGraw–Hill, New York, 1962.
11. F. Helfferich, *J. Am. Chem. Soc.*, **76**, 5567 (1954).
12. F. Helfferich, *Angew. Chem.*, **66**, 241, 327 (1954).
13. S. A. Bernard and L. P. Hammett, *J. Am. Chem. Soc.*, **75**, 1798, 5834 (1953).
14. V. C. Haskell and L. P. Hammett, *J. Am. Chem. Soc.*, **71**, 1284 (1949).
15. P. Riesz and L. P. Hammett, *J. Am. Chem. Soc.*, **76**, 992 (1954).
16. G. Bodemer and R. Kunin, *Ind. Eng. Chem.*, **43**, 1082 (1951).
17. G. G. Thomas and C. W. Davies, *Nature*, **159**, 372 (1947).
18. C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, 1607 (1951).
19. R. Kunin, *Ion Exchange Resins*, Wiley, New York, 1963.

Received October 19, 1993

Accepted June 30, 1994