Aldehyde Separation by Polymer-Supported Oligo(ethyleneimines)

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ABSTRACT: Chlorosulfonated styrene (10%) divinylbenzene resin beads reacted with an excess of ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) to give the corresponding sulfonamides with pendant oligo(ethyleneimines). The resulting modified resins are useful in the separation of aldehydes from hydrocarbon mixtures. Sorption of aldehydes occurs through formation of both Schiff base and five-membered (imidazoline) rings. Sorbed aldehydes can readily be stripped from the resins by treating with dilute acid solutions. Since the sulfamide bond has a reasonable stability toward acid–base hydrolysis, the loaded resins can be regenerated and recycled by simple acid–base washings, without losing their activity. In the present study, sorption and desorption kinetics of acetaldehyde, benzaldehyde, and salicylaldehyde have been investigated under different conditions. The aldehyde sorption obeys second-order kinetics. The method presented is applicable for all aromatic aldehydes. However, in the case of aliphatic aldehydes carrying an α-hydrogen, aldol condensation products form in solution. So aliphatic aldehydes and their aldol products are sorbed together by the resins. This limits the recovery of aliphatic aldehydes. Consequently, the resins described are cost effective sorbents for the removal and recovery of aromatic aldehydes from various mixtures. © 1997 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem **35:** 2857–2864, 1997

Keywords: aldehyde separation; polymeric sulfonamides; polymer with oligo(ethyleneimines)

INTRODUCTION

The separation and purification of the reagents or products is perhaps the most tedious process in chemical reactions. Polymer-supported reagents offer simplicity for isolation of one of the entities included. The preference is mainly given to cross-linked polymeric supports, since these are insoluble in all solvents. Moreover, polymers with suitable functional groups can serve as entrapping agents for a class of low molecular weight compounds. Thus, it is possible to pick up and separate any desired component from the reaction mixtures.

There are two main factors governing the use of a polymer in selective binding: (i) Selectivity: Functional groups attached must be reactive only toward the target molecule. The reverse reaction must be quantitative and performed easily in mild conditions. (ii) Nature of the polymeric support: Chemical inertness is an important factor to ensure recycling of the supported reagent and to avoid side reactions on the support itself. Polymers carrying hydrolyzable groups or functionalities that are susceptible to redox reactions are not suitable because they are difficult to recycle. In view of this, polystyrene-based resins are the most widely used supports, even though they have the disadvantages of slow reagent diffusion that

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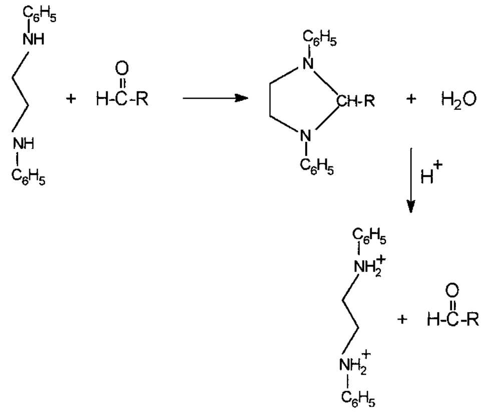


Scheme 1.

in many cases lowers the reaction rate. Change of swelling behavior during the course of the reaction is another limitation. Obviously, these properties hardly meet the above requirements. However, in the literature there are few reports on successful trapping or protecting of various compounds. For instance, crosslinked polystyrene having methyl chloroformate groups has been used to protect amines.[1] Moreover, a polystyrene resin carrying alcohol units with hydrocarbon spacer chains has been applied for the protection of carboxylic acids via esterification.[2–4] Protection of aldehydes and ketones through acetal or ketal formation has been achieved by using pendant glycidol moieties attached to crosslinked polystyrene[5,6] and poly(methylmethacrylates).[7] It is interesting to note that, when highly crosslinked supports are used, monoprotection of terephthaldialdehyde can be achieved with low capacities due to kinetic site isolation by less flexible chains.[8]

The present work deals with the separation of aldehydes by using polystyrene-based resins having 1,2-diaminoethane pendant units. Dianilinoethane has been reported to give imidazoline by treating with aldehydes. This reaction is reversible in acid conditions. Upon treatment with dilute acids, the imidazoline decomposes into its components (Scheme 1). This reaction has been demonstrated to be useful in the selective separation of aldehydes.[9] However, this process is not straightforward, because, during the regeneration with acid, aldehydes can also undergo acid-catalyzed condensation reactions with the phenyl groups as usual.[10] In order to avoid these side reactions, we have searched for a suitable polymer for the selective separation of aldehydes which fulfills the above requirements. In order to avoid side reactions, we have developed a suitable polymer, crosslinked polystyrene carrying oligo(ethyleneimine) functionalities. For this purpose oligo(ethyleneimines) ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) were treated with chlorosulfonated polystyrene resin. Aldehyde sorption and desorption characteristics of these polymers were investigated.

EXPERIMENTAL

Carbonyl-free methanol was prepared from commercial methanol (Merck) according to the procedure described in the literature.[11] Inhibitors in styrene (Fluka) and divinylbenzene (DVB) (Aldrich) were removed properly before use. Ethylenediamine (Merck), diethylenetriamine (Merck), triethylenetetramine (Merck), chlorosulfonic acid (Merck), and other analytical grade chemicals and solvents were used without any further purification.

Preparation of Spherical Beads of Crosslinked Styrene–10% DVB Copolymers

This was prepared according to the procedure described elsewhere.[12] The resulting spherical beads were sieved, and the 210–420 μm fraction was used for further modifications.

Chlorosulfonation of the Styrene–DVB Resin Beads

The reaction was performed by a treatment of styrene–DVB spherical beads with chlorosulfonic acid in the cold as described before.[12] The degree of the chlorosulfonation was determined by boiling the product with a 10% NaOH solution for 4 h. The chlorine content of the solution was determined by the mercuric thiocyanate method.[13] The chlorine analysis indicates a 63.65% chlorosulfonation.

Sulfamidation of the Chlorosulfonated Resins by Oligo(ethyleneimines)

Sulfamidation of the chlorosulfonated resins was performed by treating the resin samples with an excess of oligo(ethyleneimines) ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) in dimethoxyethane. A typical procedure is as follows:

Table I. Aldehyde Loading Capacities of the Resins[a]

Sorbent	Amine Content of Resin[b] (mmol/g of Resin)	Sorbed bzd (mmol/g of Resin)	NH_2/bzd[c] (mmol/mmol)	Sorbed acd (mmol/g of Resin)	NH_2/acd[c] (mol/mol)	Sorbed sld (mmol/g of Resin)	NH_2/sld[c] (mol/mol)
Resin 1	3.44	0.95	3.62	1.3	2.65	0.9	3.8
Resin 2	5.99	2.0	3	2.1	2.9	1.3	4.6
Resin 3	7.96	3.8	2.10	3.9	2.04	2.08	3.8

[a] bzd, benzaldehyde; acd, acetaldehyde; sld, salicylaldehyde.
[b] Including sulfamide groups.
[c] The ratio of amine content to the sorbed aldehyde (mol/mol).

The chlorosulfonated resin (15 g) is placed in a 250 mL round bottom flask which is kept in an ice-bath. Cold dimethoxyethane (40 mL) is added to the flask. The mixture of 40 mL (0.596 mol) of ethylenediamine with 20 mL of dimethoxyethane is added dropwise to the reaction mixture in the flask while it is being stirred. Stirring is continued for 24 h at room temperature. The content of the flask is filtered and washed with 20 mL of ethanol and an excess of water. To remove HCl, the product is dispersed in 100 mL of 5% NaOH and stirred for 30 min. The solution is decanted, and 100 mL of water is added to it and boiled for 30 min. While hot, the mixture is filtered and washed successively with an excess of water and 20 mL of ethanol. The resulting product is dried under vacuo at 40°C for 24 h (yield 17 g). Resins R-EDA, R-DETA, and R-TETA are prepared in this way using ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA), respectively. The yields for the latter two are 17.5 and 18.2 g, which can be explained in terms of mechanical losses.

Aldehyde Loading Capacities of the Resins

To estimate the maximum aldehyde binding capacities of the resins, 1 g of each sample was combined with 30 mmol of aldehyde in 25 mL of methanol for 18 h at room temperature. This amount was chosen in order to have a 7.5–8.7-fold excess of the theoretical capacities. Sorption capacities of each resin were examined for acetaldehyde, benzaldehyde, and salicylaldehyde. At the end of this period the resins were removed by filtration and a sample of each filtrate (1 mL) was diluted with methanol up to appropriate concentrations ($\sim 10^{-5} M$).

Quantitative determinations of aldehydes were carried out colorimetrically according to the procedure based on 2,4-dinitrophenylhydrazone formation yielding an absorption maximum around 480 nm.[11]

The amounts of sorbed aldehydes were calculated by subtracting the final aldehyde contents (nonsorbed amounts) from the initial contents of the interacted solutions. The experimental data obtained are compiled in Table I.

Aldehyde Sorption Kinetics of the Resins

Simple batch kinetic experiments were performed as follows: A sample of resin (1 g) was added to 50 mL of methanolic aldehyde solution ($6.04 \times 10^{-2} M$). The mixture was stirred gently. After appropriate intervals of time, aliquots (1 mL) were taken from the solution and transferred through filter paper into volumetric flasks. The sample solutions were diluted properly, and the aldehyde content was measured colorimetrically. Concentration–time plots for the aldehyde sorptions are shown in Figures 1 and 2. The solutions

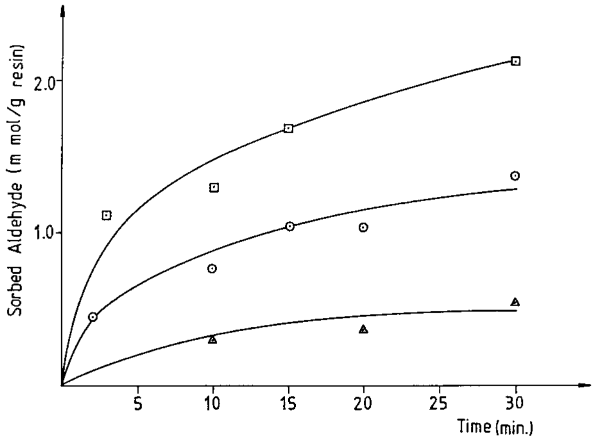


Figure 1. Sorption kinetics of various aldehydes by the Resin 3: acetaldehyde (⊡); benzaldehyde (⊙); salicylaldehyde (△).

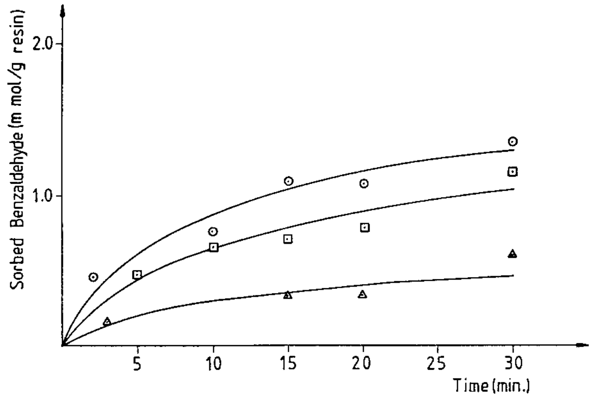


Figure 2. Benzaldehyde sorption by the resins: Resin 1 (△); Resin 2 (⊡); Resin 3 (⊙).

were not buffered during the experiments. The sorption kinetics were found to be second order. By the plotting of $1/\beta$ versus time (where β represents the molar ratio of unreacted aldehyde), the rate constants were calculated from the slope of the linear curves. The rate constants found for different aldehyde and resin combinations have been tabulated in Table II.

Kinetics of the Desorption of Aldehydes from Loaded Resins

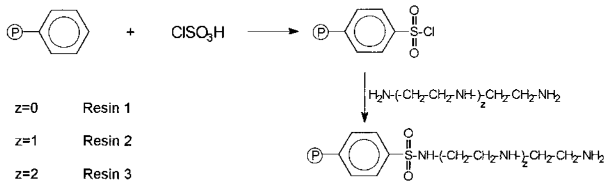
In order to investigate the desorption kinetics, aldehyde-loaded samples (1 g) were treated with acidified solutions of carbonyl-free methanol/water (1 : 1) mixtures. Methanol/water mixtures were chosen as a solvent to obtain good kinetic data.

RESULTS AND DISCUSSION

The reversible aldehyde binding ability of *N,N'*-dialkyl- or *N,N'*-diaryl-1,2-diaminoethanes has encouraged us to investigate the use of polymer-supported oligo(ethyleneimines) in aldehyde separation. Attachment of oligo(ethyleneimines) to the polymeric support was achieved by treating excess amounts of oligo(ethyleneimines) with chlorosulfonated styrene–divinylbenzene (10%) crosslinked resin, as outlined in Scheme 2.

Table II. Rate Constants for the Sorption of Aldehydes by the Resins

Resin	Aldehyde	Rate Constants 10^3k (mol^{-1} s^{-1})
Resin 1	Benzaldehyde	1.63
Resin 2	Benzaldehyde	3.30
Resin 3	Benzaldehyde	3.37
Resin 3	Acetaldehyde	17.93
Resin 3	Salicylaldehyde	1.13



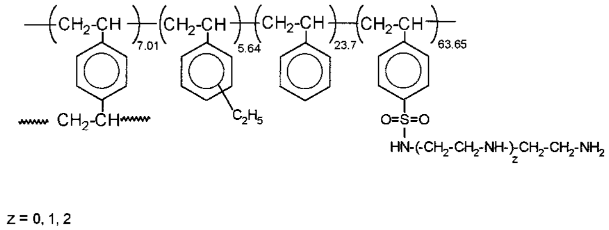
Scheme 2.

In this reaction, ethylenediamine, diethylenetriamine, and triethylenetetramine are bound to the polymer through sulfamide bonds. Since the reaction of amines with chlorosulfone groups is fast and an excess of amines is used, the sulfamidation reactions were assumed to proceed quantitatively on the basis of residual chlorine analysis. The full structure of the modified resins can be written as depicted in Scheme 3.

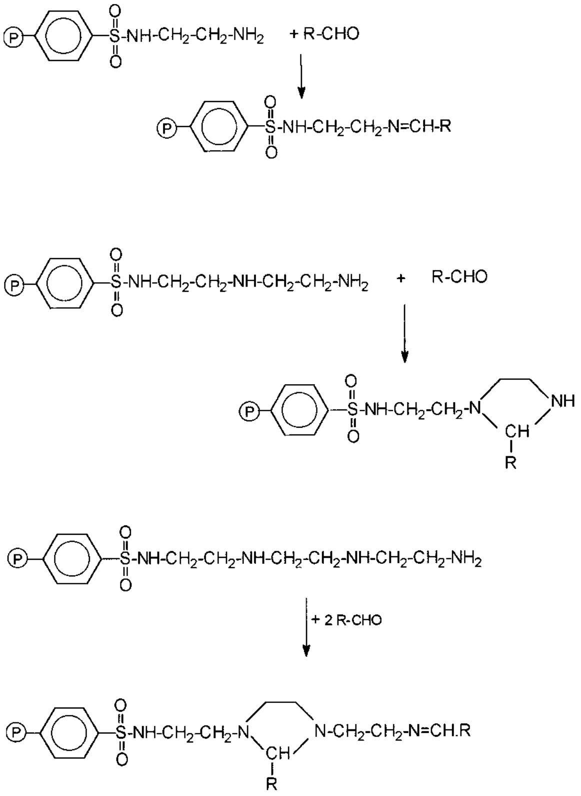
The amine contents of these resins (including sulfamide group) calculated are summarized in Table I. These resins having oligo(ethyleneimine) moieties were treated with alcohol solutions of benzaldehyde, salicylaldehyde, and acetaldehyde separately to test their aldehyde binding abilities.

Aldehyde Binding Capacities of the Resin Samples

To estimate the maximum capacity for aldehydes, each of the samples (1 g) was contacted with 50 mL of a 1.182*M* aldehyde solution, which contained a 7.5–8.7-fold excess of the theoretical capacities. Capacities were measured indirectly by monitoring the residual aldehyde content of test solutions. The representative data shown in Table I indicate that the maximum loading capacities of each resin for benzaldehyde and acetaldehyde are



Scheme 3.



Scheme 4.

high and almost identical. It is important to note that, in Resin 1, 2 mol of amino groups is used for 1 mol of aldehyde sorption. In Resins 2 and 3, 3 and 2 mol of amino groups are consumed to bind 1 mol of aldehyde, respectively. These results seem to be inconsistent with each other. If, however, we assume that all reactive amine groups have been blocked by aldehydes, the sulfamide group nitrogen must not take part in aldehyde binding. On the basis of this assumption, each primary amine group of Resin 1 binds one aldehyde molecule via Schiff base formation. On the other hand, in Resin 3, 1.5 mol of amine group is used for 1 mol of aldehyde consumed. In other words, two aldehyde molecules are bound by three amino groups. This implies that aldehyde binding preferable occurs through five-membered ring (imidazoline) formation by the secondary amines and the remaining primary amine end group can bind aldehyde by forming Schiff base. Notably, ring formation will be favored if a neighboring secondary amino group is available. Indeed, in Resin 2 one secondary amino group and one primary amino group takes up one aldehyde molecule by forming a five-membered ring. According to these considerations, aldehyde binding of the resins must be as shown in Scheme 4.

Consequently, in Resin 1 aldehyde is bound through Schiff base formation and 1 mol of primary amine is consumed per 1 mol of aldehyde. In Resin 2, one aldehyde molecule is bound through a five-membered ring by two amino groups, whereas, in Resin 3, two secondary amines are used to form five-membered rings with one aldehyde molecule and the remaining primary amino groups form Schiff base with the second aldehyde molecule. In total, 2 mol of aldehyde is bound for each function in Resin 3. This mode of aldehyde sorption is clearly shown by the loading data represented in Table I.

Sorption capacities of the resins are apparently lower for salicylaldehyde, probably because of its high strong steric effect arising from phenolic OH groups. On the other hand, in the case of acetaldehyde sorption, the solution becomes colored during the experiment due to the base-catalyzed aldol condensation which is common for aldehydes carrying an α-hydrogen. Indeed, the colored solution exhibits the characteristic odor of crotonaldehyde, which is the first condensation product of acetaldehyde. This is an important limitation in the use of these resins for sorption of many aliphatic aldehydes. Solid resin particles become colored during sorption of aliphatic aldehydes which means aldol condensation products are also sorbed by the resins. Moreover color development is faster for acetaldehyde than for butyraldehyde. Also aldol condensation products form in the solution, especially for long-term interactions.

Aldehyde Sorbtion Kinetics of the Resins

Aldehyde sorbtion kinetics of the resins were made by contacting the resin samples with diluted aldehyde solutions ($6.04 \times 10^{-2} M$). The amounts of sorbed aldehydes versus time plots (Fig. 1) show that the rates of benzaldehyde sorption are very close for Resins 2 and 3 (Fig. 2). As seen from Table II, benzaldehyde sorbtion is about two times faster in Resin 2 than that for Resin 1. This can be ascribed to differences in the rates of Schiff base formation and imidazoline formation, because although Schiff bases are more stable in basic conditions than in acid conditions, these are acid-catalyzed reactions. Consequently, imidazoline ring formation must be faster than Schiff base formation, which is in consistent with the result for Resin 3. According to this assumption in Resin

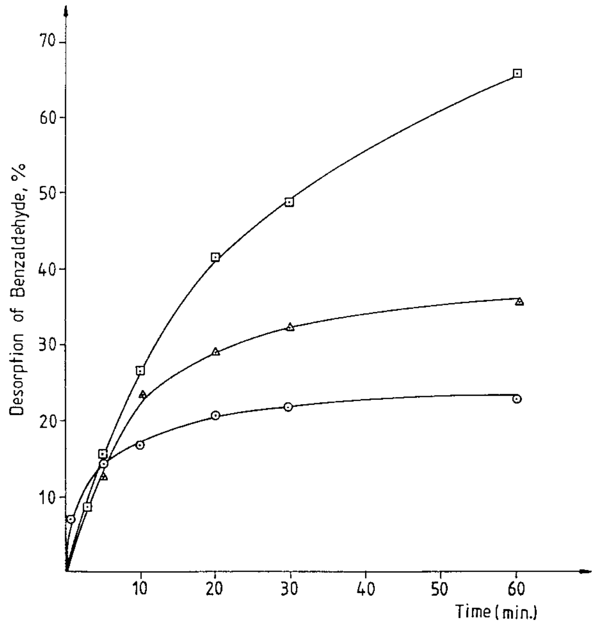


Figure 3. Percentage benzaldehyde releasing from the resins at pH = 1: Resin 1 (⊡); Resin 3 (△); Resin 2 (⊙).

3, aldehyde sorption occurs for both ring and Schiff base formations. Indeed the sorption rate constant for benzaldehyde by Resin 3 is 3.7×10^{-3} mol^{-1} s^{-1}, which is very close to the one for Resin 2. Another effect on aldehyde sorption kinetics might be spacer chain effect. Obviously, the length of ethyleneimine in Resin 3 is longer than that of the others. This causes a greater facility for aldehyde binding. Comparison of the kinetics of aldehyde binding to the Resin 3 (Fig. 1) indicates that the sorption rates are higher for acetaldehyde. This is in accordance with its molecular weight which provides fast diffusion. Interestingly, all the aldehyde sorptions studied obey second-order reaction kinetics. This fact has been inferred from $1/\beta$ vs time plots (where β represents the unreacted fraction of aldehyde). Rate constants for different aldehydes and resins are shown in Table II. The sorption rate constant for acetaldehyde (17.93×10^{-3} mol^{-1} s^{-1}) is about five times higher than that of benzaldehyde.

Aldehyde Desorption Kinetics of the Loaded Resins

To investigate the desorption kinetics, the loaded samples were subjected to hydrolysis in solution with different acid concentrations. The amounts of stripped aldehydes were measured by monitoring aldehyde concentrations of acid solutions. All experiments show that aldehyde concentrations of the acidified solutions increase with time. Benzaldehyde desorption kinetics of the loaded resins (Fig. 3) represent that the desorption rate of benzaldehyde from Resin 1 is higher than those of the others. This can be ascribed to the rapid hydrolysis of the Schiff bases. Hydrolysis of imidazoline rings must be somewhat difficult due to the greater stability of five-membered rings. Indeed, the rate of aldehyde desorption of resins is in the order Resin 1 > Resin 3 > Resin 2. This result is in accordance with type of aldehyde binding because Resin 1 binds aldehydes only through Schiff base, whereas, in Resin 3, aldehyde is

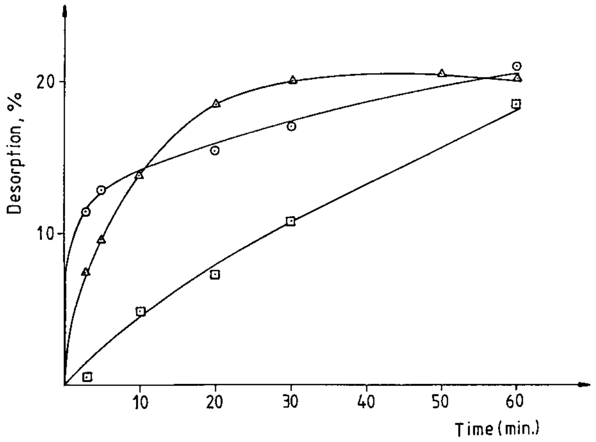


Figure 4. Percentage aldehyde releasing from the loaded Resin 3 at pH = 1: acetaldehyde (⊙); benzaldehyde (△); salicylaldehyde (⊡).

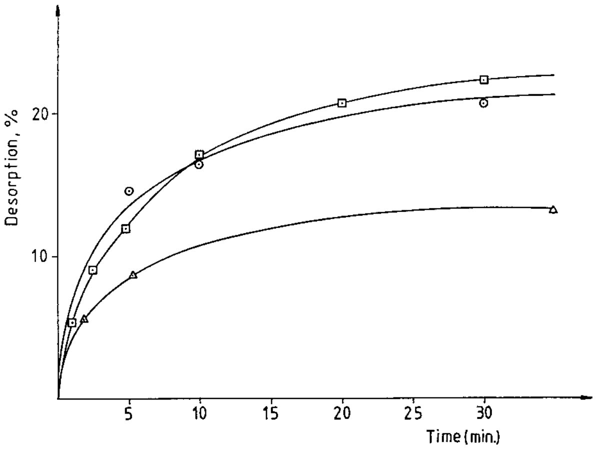


Figure 5. pH dependence of benzaldehyde desorption from Resin 3: $[H^+] = 1$ M (⊡); pH = 1 (⊙); pH = 3.2 (△).

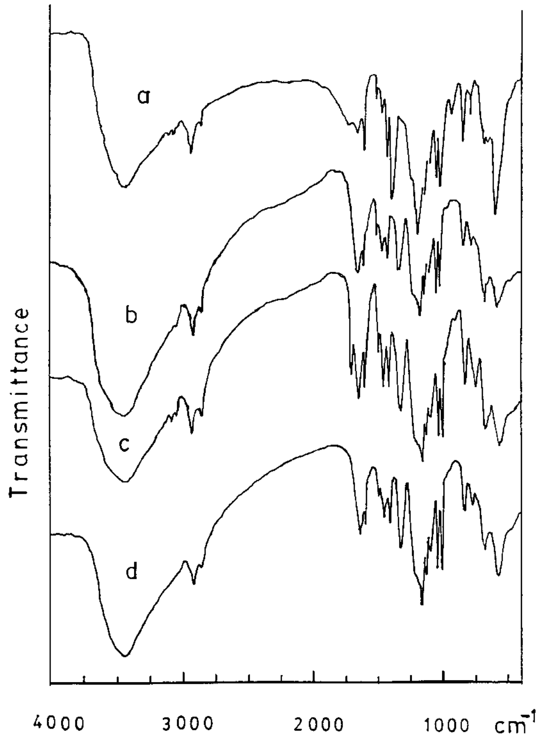


Figure 6. FT-IR spectra of chlorosulfonated resin (a), Resin 2 (b), benzaldehyde loaded Resin 2 (c), and the corresponding regenerated resin (d).

bound through both Schiff base and the five-membered ring. In contrast, in Resin 2 aldehyde must be bound through five-membered ring formation. Comparison of the stripping rates of the aldehydes from Resin 3 indicates that acetaldehyde and benzaldehyde are released with almost equal rates, whereas salicylaldehyde is stripped slowly (Fig. 4). As expected, aldehyde desorption is faster in higher acid concentrations (Fig. 5). Benzaldehyde is desorbed rapidly from Resin 3 with 1*M* HCl solution. Desorption experiments indicate that aldehyde are not entirely desorbed in methanol–water solutions even after 1 h. However, it has been observed that when the loaded samples are subjected to hydrolysis in 5*M* aqueous HCl solutions, all the aldehyde contents of the resins are eluted in about 30 min. The chemical transformation in each step can be followed by IR spectra (Fig. 6). Thus, S=O stretching vibrations of chlorosulfone groups appear at 1380 (asym.) and 1170 cm^{-1}. In the sulfamidation products, these bands shift to lower frequencies of 1328 and 1164 cm^{-1}, respectively. The positions of these bands do not change after treating with aldehydes. However, the strength of the N—H stretching vibration band at 3430 cm^{-1} slightly decreases after aldehyde treatment. Moreover aromatic C—H stretching vibration bands are almost invisible in the chlorosulfonated and sulfamidation products. After interaction with benzaldehyde these peaks become sharper and shift to 3080 (asym. str.) and 3040 (sym. str.) cm^{-1}, due to the additional phenyl rings of sorbed benzaldehyde (Fig. 6c). This evidence can be attributed to the aldehyde binding. After elution of the sorbed aldehydes from Resin 2, the IR spectra of the resin (Fig. 6d) become identical to those of the aldehyde-free resin (Fig. 6b). This reveals that no side reaction occurs during the regeneration. After aldehyde desorption, the resin becomes entirely free of aldehyde and it can be re-used.

Interfering Entities

Although we have not been able to carry out quantitative competitive extraction experiments, a qualitative test with acetone indicates that acetone is also bound to the resins. However, in this case stripping of acetone is impossible because of the formation of nonhydrolyzable acetone–amine products on the polymer. Furthermore, alkyl halogenides are important interfering entities in that they create tertiary and quaternary amino groups on the polymer by a simple Hoffmann alkylation reaction. Hence, aliphatic ketones and alkyl halogenides are interfering compounds in the aldehyde sorption. The method works well in the presence of aliphatic and aromatic hydrocarbons, alcohols, phenols, and water.

Regeneration of the Resins

During aldehyde stripping with acid solution, amino groups of the resin turn into the salt forms. These salts can easily be removed by treating with aqueous alkaline solutions. To avoid sodium salt formation through sulfamide groups, diluted (0.1*M*) NaOH solutions are used for alkaline washing. This procedure is followed by washing with boiling water. By this way, the resins can be recycled without losing aldehyde binding abilities.

In conclusion, aldehydes can be separated selectively from the mixtures by polymer-supported oligo(ethyleneimines). Aldehyde sorption capacities and rates of the resins increase with increasing number of amino groups. However, aldehydes with an α-hydrogen undergo a side reaction (aldol condensation) during the interaction with these resins. However, if the recovery of aldehydes is not a goal, the resins can be used for the removal of traces of amounts of aliphatic aldehydes such as acetaldehyde, propionaldehyde, and butyraldehyde. Further experiments involving the effect of concentration, temperature, polymer structure, and morphology are needed. However, since these resins are prepared from commercially available materials with acceptable costs, the system presented is very promising with respect to potential applications.

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