The Effect of Temperature on the Stability of Ion-Exchange Resins in Aqueous Medium

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Synopsis

The effect on ion-exchange resins of the polystyrene type of a thermal treatment has been studied by heating strong cation and strong anion resins in water at 95°C and 250°C and obtaining the IR spectra of the remaining resins as well as those of the decomposition products extracted by the water. The degradation of the resins is highly dependent on their ionic form. The —(OH⁻) and the —(H⁺) forms are more labile, losing completely their exchange capacity at 250°C, while the —(Li⁺) form retains considerable ion-exchange capacity. On the other hand, the hydrothermal process affects differently the backbone of the anion and the cation resins. There are similarities in the type of decomposition products found after hydrothermal treatment with those observed after radiolytic exposure of the resins. Heating the resins in water reduces the crosslinking of the polystyrene matrix.

INTRODUCTION

The decomposition of ion exchange resins (IXR) can be increased by exposing them to ionizing radiation or to high temperatures. The damage produced in IXR by radiation exposure has been studied by different authors.[1-6] This work is generally related to the loss of ion-exchange capacity and the results obtained are sufficient for the interpretation of the radiation effect on resins, but it does not provide an adequate insight into the degradation mechanisms. The hydrolysis of functional groups induced by radiation has been studied in detail in the case of anionic resins by Hall and Streat[7] and by Basinski, Narebska, and Tempczyk.[4] In some radiolytic studies[8-10] IR and EPR spectroscopic techniques have been used, and observations have been made about the degradation of the resin matrix. Grangwer et al.[11] have reviewed the effects of radiation on IXR.

Data on thermal and chemical stability of IXR have been summarized by Polyanskii and Tulupov,[12] where a detailed comment on different analytical methods and results is presented. Finally, Nagy et al.[13] have studied the thermal behavior of irradiated IXR and were able to establish relationships between the peaks observed in differential thermal analysis, with the ionic forms and the divinylbenzene content of the resins.

The field covered by previous work on IXR refers to their use on various processes where the chemical environment is aggressive and/or they are subject to strong radiation doses (like reprocessing plants and radwaste disposal).

On the other hand, IXR have found a widespread use in the cyclic clean-up processes of water for both thermal and nuclear power stations. Although IXR are essentially insoluble materials, traces of compounds which are not normally

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detected can affect the efficiency of resin bed performances and introduce contaminants in the fluid being cleaned up by the resins.

The very stringent requirements for water quality in steam cycles as well as in primary circuits of pressurized water reactors are such that they imply in turn special requirements on the IX material being employed and on their thermal, radiolytic, and chemical stability. Efforts have been devoted to the production of better grades of IXR as, for instance, nuclear grade resins having a specially low quantity of the aggresive chloride ion.[14]

Manufacturers usually recommend maximum operating temperatures for IXR, e.g., 120°C for strong cationic and 70°C for strong anionic IXR. These limits imply that the IX cleaning systems do not operate properly above those values and that the material may deteriorate severely either in their IX capacity or because fouling of the resins by decomposition products may also occur.

In the present work we have studied the thermal decomposition of IXR to gain a better understanding of the nature of the thermal decomposition processes in the special context of high purity water. IR spectroscopy was preferred as a direct instrumental method for recording changes of structure instead of the usual measurements of loss of exchange capacity, water content, solubility, swelling, weight change, etc. The experiments were performed at 95°C and 250°C and were aimed to studying the transformation of the material as well as to the type of substances produced in their decomposition, which may finally contribute to the formation of an aggressive medium.
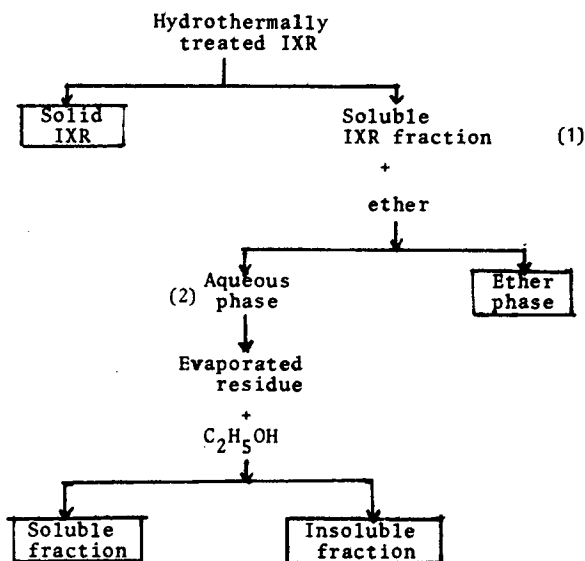
EXPERIMENTAL

Thermal Treatment of Resins. The IXR were heated with deionized water inside tightly closed glass or stainless steel vessels containing water; the vessels were maintained in an oven for 1 week either at 95°C or at 250°C. When the experiments were completed, it was possible to observe that the remaining solid material was very similar in appearance to the original resins. It was, however, evident that the amount of the IXR, as well as the average bed size, were appreciably reduced.

Separation of Decomposition Products. The decomposition products that are leached out of the thermally decomposed resins will consist of a complex mixture of substances which may include ionic compounds as well as compounds of different polarity. In order to characterize the various decomposition products, the solid resins remaining after thermal degradation were separated from the liquid by filtration. The filtrate was then subjected to the simple solvent separation procedure as depicted in Scheme 1.

The procedure allows a first separation of ionic and highly polar products (aqueous phase) from the slightly polar fraction (ether phase). The dry residue of the aqueous phase was further separated into an ethanol-soluble and an ethanol-insoluble portions.

Infrared Spectra. The IR spectra of the various fractions of filtrate were obtained as follows: from the ether phase a film was deposited by evaporation on KBr windows for IR observation. The aqueous phase was dried, and the dry residue was then extracted with a very small amount of absolute ethanol, which was allowed to form a film on the KBr windows.

The remaining insoluble residue was dried again and then mulled in Nujol

Hydrothermally
treated IXR

Solid IXR Soluble IXR fraction (1)

+

ether

(2) Aqueous phase Ether phase

Evaporated residue

+

C_2H_5OH

Soluble fraction Insoluble fraction

Scheme 1. Sample processing to obtain the IR spectra of the various fractions. (1) For anion XR the solution was acidified. (2) For cation XR, $BaSO_4$ was precipitated and filtered off before evaporating the aqueous phase.

for its IR examination. In order to determine the IR spectra of solid IXR, it was necessary to grind the material to a very find powder, which was then mixed with KBr; in this way it was possible to prepare a pellet from which a clear spectrum could be obtained. Only the resins treated 1 week at 250°C could be mechanically ground with ease. The IR spectrum of nondegraded resin was obtained for comparison using a highly ground material which was available in our laboratory.

In the case of cationic resins, sulfate produced by thermal degradation was precipitated with $BaCl_2$ after the extraction with ether. The precipitated $BaSO_4$ was filtered off, and, with the filtrate, the normal procedure, to obtain the IR spectrum, was followed.

The IR spectra were recorded with a Beckman IR-33; the interpretation of the spectra and band assignment was done with the help of the correlation tables of Cross[15] and Bellamy.[16]

Ion-Exchange Capacity and Water Content. The ion-exchange capacity of the resins was determined in samples of ca. 1.5 g of resin. They were completely converted into the (H^+) form with 200 cm³ of $6N$ HCl solution (cation exchange resins) or with 200 cm³ of 10% NaOH solution (anion exchange resins). They were throughly washed with deionized water and finally eluted with 200 cm³ of 20% NaCl solution. The effluent of the cation exchange resin was titrated against standard $0.1N$ NaOH and that of the anion exchange resin against standard $0.1N$ HCl.

The water content of the resins was established from the weight loss upon drying the resins to constant weight at 60°C.

The resins employed throughout this work were nuclear grade commercial

TABLE I
Hydrothermal Degradation of IXR[a]

Resin	Dissolved material (%)	Water content (%)	Loss of capacity (%)	SO_4^- produced (5)
Anionic/OH⁻, untreated	0.1	60.7	—	—
Anionic/OH⁻ heated to 95°C	1	53.7	14	—
Anionic/OH⁻ heated to 250°C	31	3.4	100	—
Cationic/H⁺, untreated	0.1	57	—	—
Cationic/H⁺ heated to 95°C	1	48.3	1	0.07
Cationic/H⁺ heated to 250°C	27	6	~100 (from IR)	—
Cationic/Li⁺, untreated	—	42	—	—
Cationic/Li⁺ heated to 250°C	36.5	30.1	56	65

[a] Resins were heated for 7 days at stated temperature.

products with a polystyrene backbone crosslinked with divinylbenzene in H⁺, Li⁺, and in OH⁻ ionic forms.

RESULTS AND DISCUSSION

Table I summarizes the observed effect of temperature on the water content and on the IX capacity. The amount of dissolved matter for both types of resins and, for the cationic resin, the amount of $SO_4^=$ produced are reported as well. We shall now consider the IR evidences for both resin types.

Strong Anion-Exchange Resins

Ether Soluble Fraction. From the experiments carried out at 95°C the spectrum in Figure 1 was obtained for the low polarity fraction. The decomposition products in this fraction show the effect of oxidation because bands typical of —C=O and —C—O—C groups are present[16,17] ($\nu^* = 1740, 1290, 1130$, and 1080 cm⁻¹).

Ethanol Insoluble Aqueous Fraction. At 95°C and 250°C the spectra showed a strong band at 1100 cm⁻¹, which can be assigned to a C—O—C group. This band has also been observed by Kazanjian[10] in strong anion IXR after ir-
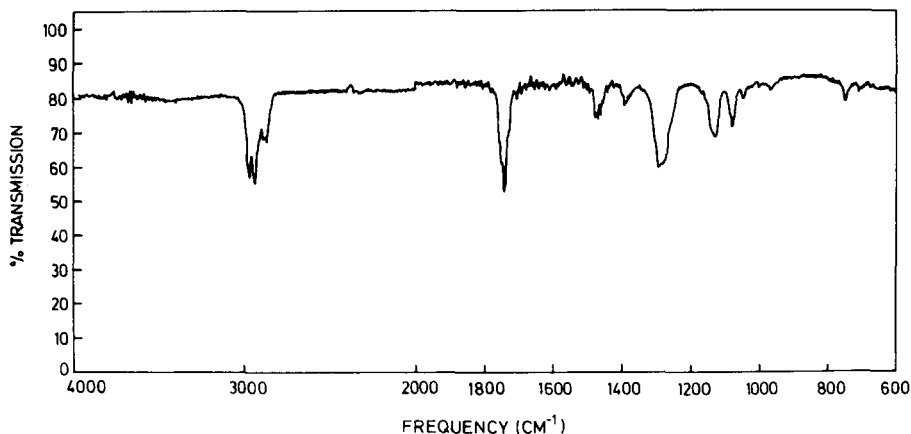

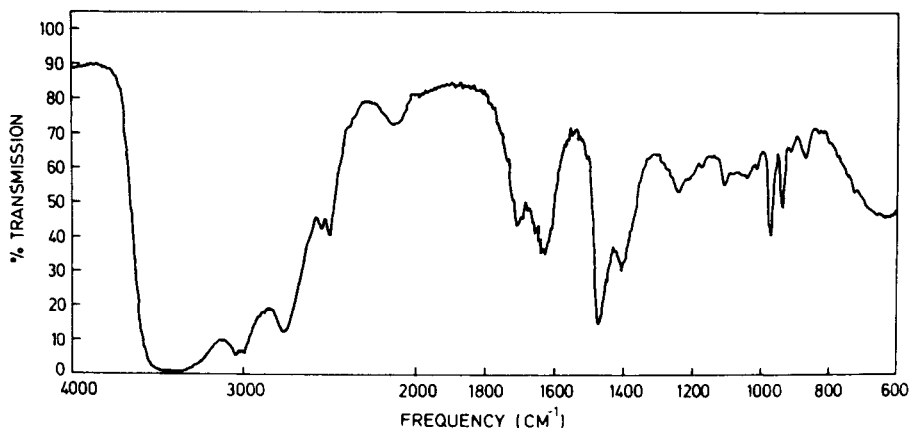Fig. 1. IR spectrum of film deposited from ether soluble fraction: anionic IXR, 95°C.

Fig. 2. IR spectrum of film deposited from ethanol soluble dry residue of the aqueous phase: anionic IXR, 95°C.

radiating and heating the resins.

Ethanol Soluble Aqueous Phase.   The IR spectrum (Fig. 2) has similar features with those reported by Litowska and co-workers[9] in their study of the effect of radiation upon IXR.   This fraction probably consists of compounds produced by thermal hydrolysis of functional groups and also by partial degradation of the resin matrix.   The group of bands between 2800 and 2000 cm^{-1} has been assigned[9] in analogy with the spectrum of $HN(CH_3)_3I$, where, in particular, the band at 2700 cm^{-1} is assigned to the H—N— stretching mode.[18]   The band at 940 cm^{-1} indicates the presence of double bonds which also originate in the cleavage of the polymer backbone.   There is also evidence in this fraction of a —C=O band (1740 cm^{-1}).   This corroborates an oxidation mechanism already noted by Jellinek.[19]   In the case of the IXR heated at 250°C, the IR spectrum (Fig. 3) corresponds to the whole aqueous phase.   It is important to mention that CO_2 evolved from this fraction upon acidification.

All the bands that appeared at 95°C are again present at 250°C, except for a new band at 1260 cm^{-1} (tentatively assigned to a C—O—C linkage bond) and for the disappearance of the —C=O band.
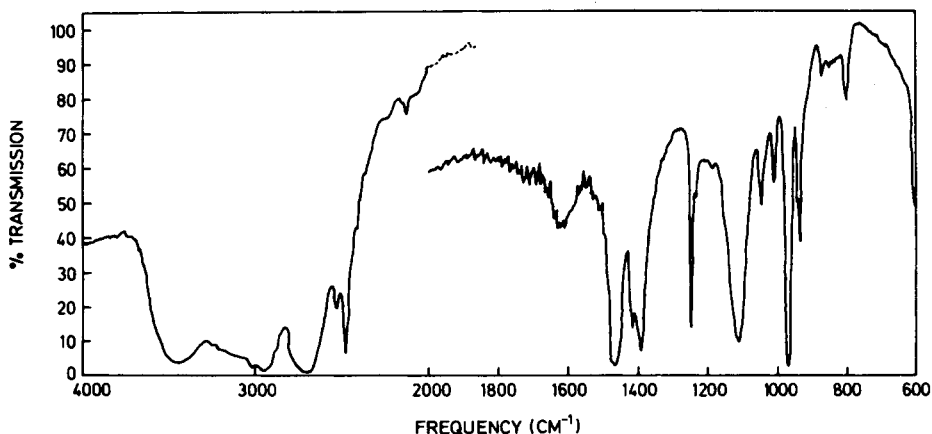

Fig. 3. IR spectrum of complete aqueous phase after ether extraction, KBr pellet: anionic IXR, 250°C.

These observations, indicate that this resin is thermally decomposed by formation first of —C=O and C—O—C groups in the backbone. When the decomposition advances further, the —C=O is converted to CO_2. Moreover, it appears that the functional groups are cleaved from the backbone through the benzyl C—N bond, yielding weak bases in the liquid phase.

SOLID RESINS

It is interesting to compare to above observations with those obtained from the spectra of the solid IXR shown in Figure 4. The assignment of bands is given in Table II.

The spectrum of a nondegraded anion exchange resin [Fig. 4(a)] is compared to that of a sample heated at 250°C [Fig. 4(b)] and to that of a sample which was slightly charred in an open vessel heated at 110°C [Fig. 4(c)]. Together with the spectra, a proposed assignment is also reported which follows that of Strasheim and Buijs.[20] The effects of the thermal treatment can be seen both on the functional groups and on the resin matrix. The absence of the 890 cm^{-1} band from the spectrum [Fig. 4(b)] of the resin treated at 250°C indicates the total loss of the functional $[—N(CH_3)_3^+]$ groups. This agrees with the loss of exchange capacity reported in Table I. The difference in intensity of the 3440 cm^{-1} (—OH stretching in water) and the disapperance of the 1628 cm^{-1} band (—OH bending in water) also agree with the dramatically reduced water content shown by Table I for the anion IXR treated at 250°C. There changes in the intensity of the —C—H deformation frequencies (1460, 1425, and 1370 cm^{-1})

TABLE II
Assignment of IR Bands (cm^{-1}) for Anionic IXR[a]

Untreated resin [cf. (4a)]	Heated 250° [cf. (4b)]	Charred dry [cf. (4c)]	
3440	3450	3450	OH str. (H_2O)
2995	3040, 2940	3050, 2950	CH str.
	2870	2880	
		2740	$\overset{+}{N}$—H str.
		2660, 2320	$(CH_3)_3 \overset{+}{N}H$
		2100	
	1710		—C=O group
1628	—	1660	O—H deform. (H_2O)
1615	1615		C=C phenyl group
1507	1520		no assignment
1486	—	1485	C=C phenyl group
1499, 1427	1460, 1425	1460	C—H def.
1417	—	1420	Crosslinking
1385	1370	1380	
		1130	C—O—C bond
889	—	890	C—N bond
828, 763	820, 760	835, 770	C—H bent out of plane
702	700	710	

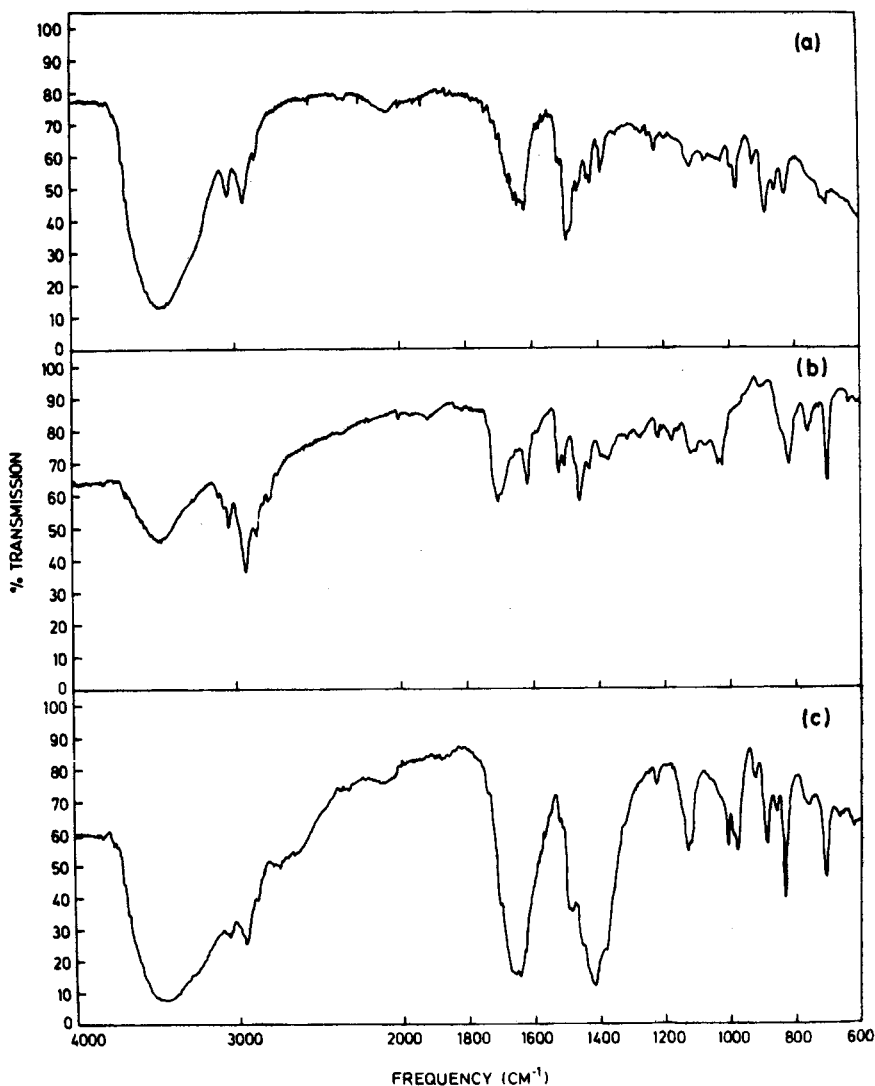[a] The assignment was made following Ref. 20 for untreated resins.

Fig. 4. IR spectrum of solid anionic IXR, KBr pellets: (a) untreated resin; (b) anionic IXR heated at 250°C; (c) anionic IXR charred dry state.

are also observed. Another important feature is the appearance of the band corresponding to the —C=O group that shows the effect of thermal degradation over the material.[21]

It is possible to recognize in the charred sample some of the bands corresponding to degradation products leached from the resins in the hydrothermal experiments. Near 2700 cm^{-1} a weak band can be seen corresponding to the degradation on functional groups (N^{+}—H) [Fig. 4(c)] and at 1130 cm^{-1} a band assigned to a C—O—C bond from the degradation of the resin matrix.

When this spectrum is compared to (4a) some important changes can be observed in the deformation bands: the 1485 cm^{-1} band has the same intensity as in a nondegraded resin, but the 1460, 1420, and 1380 cm^{-1} show a noticeable

increase in intensity. The 1420 cm^{-1} band has been attributed by Strasheim and Buijs[20] to the crosslinkings between adjacent chains in the polystyrene; its intensity, as shown in spectrum [Fig. 4(c)], is much greater than in the original resin [Fig. 4(a)] and an increase in crosslinkage is assumed. On the other hand, this band is barely visible in the resin heated in water in a closed vessel at 250°C. This clearly points to the breakdown of the crosslinkings in the process of hydrothermal decomposition.

The strong band at 1660 cm^{-1} can be attributed, besides the OH deformation of the water, to the —C=O (there is a shoulder at 1700 cm^{-1}) and the 1655 cm^{-1} of the —C=O stretching of phenyl groups. These two bands are barely visible.

It is possible that the Hoffmann degradation contributes to the elimination of the positively charged ionogenic groups in the anion XR; however, other processes must also take place due to the appearance of —C=O groups in the polymeric matrix which are not observed in the heated cation XR (see below).

STRONG CATION-EXCHANGE RESINS

Ether Phase. The spectrum of this fraction when the resin was heated at 95°C is identical to that of the analogous fraction for the anion resin decomposition products (Fig. 1).

The complete similarity between the low polarity decomposition products, corresponding to anion and to cation exchange resins, suggests a common origin, probably arising from the degradation of the polymeric backbone.

Ethanol-Insoluble Aqueous Fraction. The IR spectrum of this fraction which was done in Nujol was very similar at 95°C and 250°C; the spectrum in Figure 5 illustrates the fraction obtained at the highest temperature. No evidence of functional groups is observed in this fraction (absence of —SO$_3$ and C—S bands).

The band at 1110 cm^{-1} is again assigned to a C—O—C bond and emphasizes once more the similarity of decomposition products of both types of IXR.

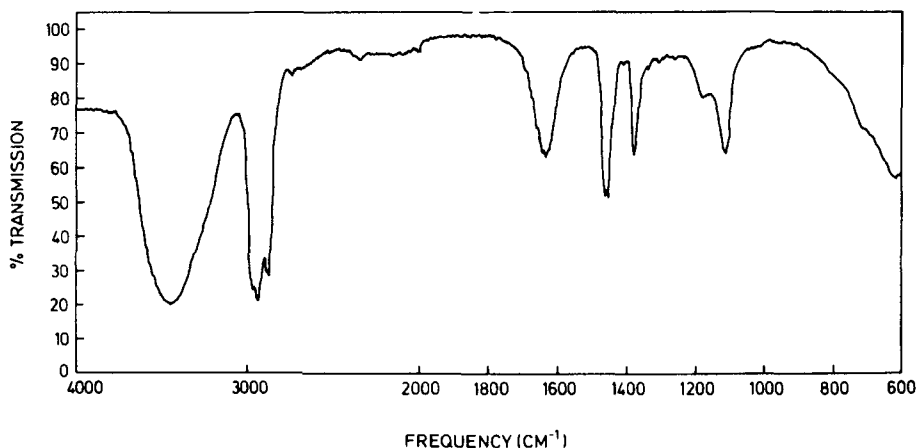**Ethanol-Soluble Aqueous Fraction.** It was possible to identify, in the

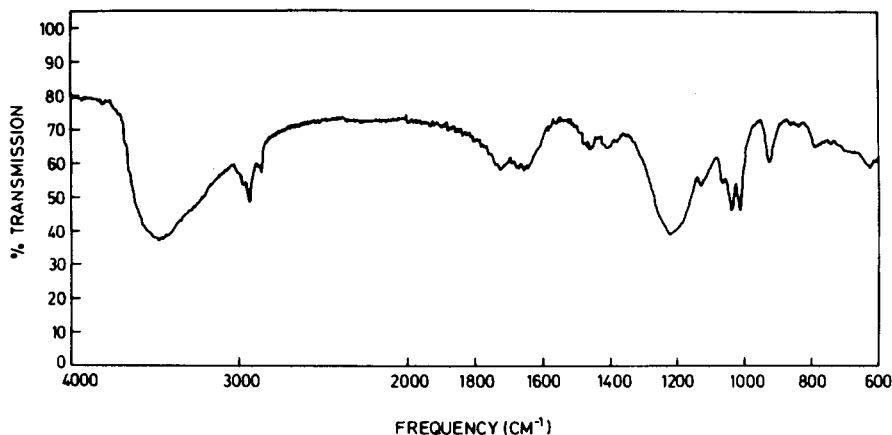Fig. 5. IR spectrum of ethanol insoluble aqueous fraction: Nujol mull, cationic IXR, 250°C.

Fig. 6. IR spectrum of film deposited from ethanol soluble dry residue of the aqueous phase: cationic IXR, 95°C.

fraction obtained after heating at 95°C, the presence of soluble sulfonates through the bands 1220 and 1010 cm^{-1} (Fig. 6). A weak —C=O band is also observed in the IR spectrum.

Solid Resin. The spectrum of a nondegraded cation exchange resin [Fig. 7(a)] is compared to those of the (Li$^+$) [Fig. 7(b)] and the (H$^+$) [Fig. 7(c)] ionic forms after thermal exposure to 250°C. At 250°C the —(H$^+$) resin gave a strongly acid solution that corroded the stainless steel vessel, preventing further analysis of the filtrate. It can be seen in the spectrum [Fig. 7(c)] that the stretching and deformation frequencies of —C—H are very close to those characteristic of polystyrene. There is an almost complete loss of ionic groups (very low intensity of —SO$_3^-$ and —C—S bands) and loss of crosslinkings shown here by the absence of the 1420 cm^{-1} band. The assignment of bands is given in Table III.

TABLE III
Assignment of IR Bands (cm^{-1}) for Cationic IXR[a]

Untreated resin [cf. (7a)]	Li$^+$ heated 250°C [cf. (7b)]	H$^+$ heated 250°C [cf. (7c)]	
3450	3450	3450	O—H str. (H$_2$)
	3040	3080, 3045	C—H str.
2930, 2870	2940, 2860	2940, 2870	IXR, polystyrene
1631	1630	—	O—H deform. (H$_2$O)
1604	1610	1610	C=C phenyl group
1497	1500	1500	C=C phenyl group
1455	1460	1460	C—H deform.
1416	1420	—	Crosslinking
1219, 1176	1220, 1175	1230, 1160	
1130, 1046	1130, 1035	1120, 1030	—SO$_3$H group
1009	1010	1010	
834, 776	835, 760	830, 760	
699	700	700	
675	—	—	C—S bond

[a] The assignment was made following Ref. 20 for untreated resins.
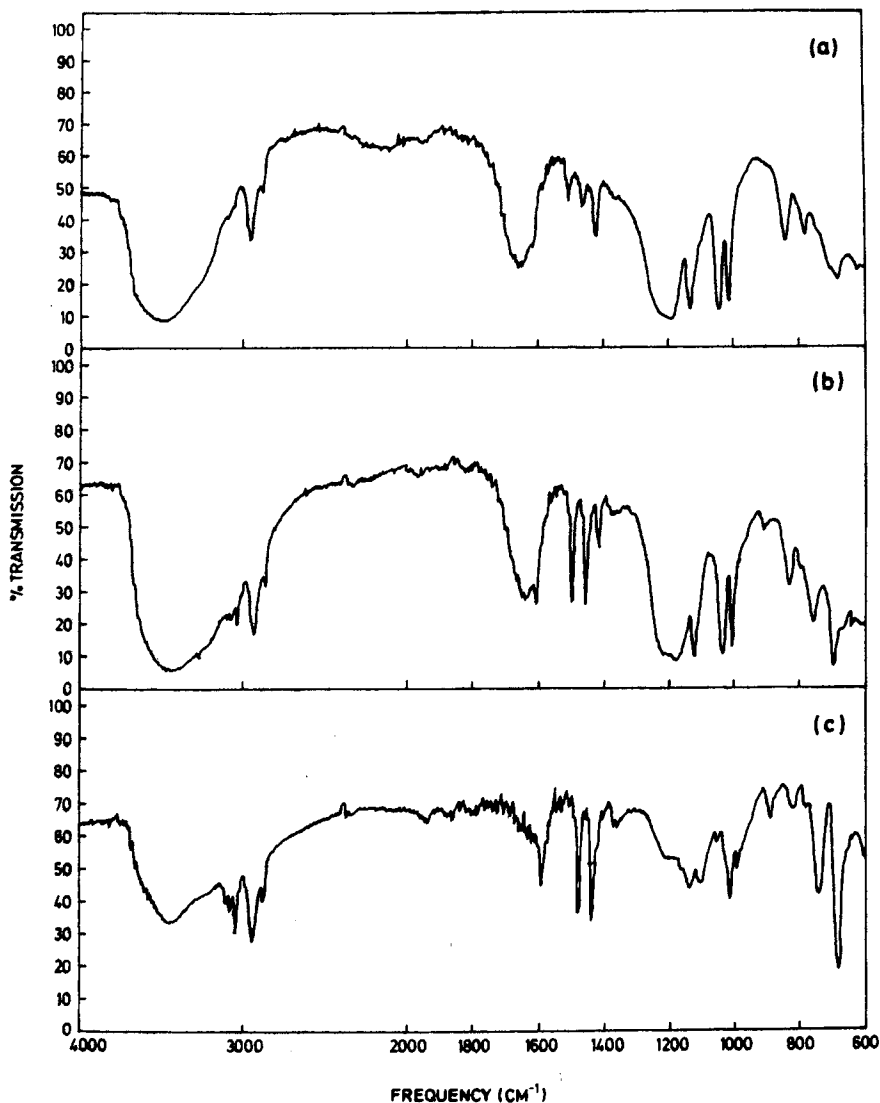
Fig. 7. IR spectrum of solid cationic IXR, KBr pellets: (a) untreated resin; (b) cationic/Li$^+$ heated at 250°C; (c) cationic/H$^+$ heated at 250°C.

For the —(Li$^+$) resin, on the other hand, degradation is not so severe.   There is still a considerable amount of sulfonic groups in the matrix and part of the crosslinkings (1420 cm^{-1}) remain in the polystyrene structure.   The values of the remaining ion-exchange capacity and water content in these two cation exchange resins (cf. Table I) are in agreement with the IR evidences.

CONCLUSIONS

Results from experiments done with both ion-exchange resins suggested the usefulness of a parallel study of their hydrothermal decomposition.   The anion exchange resin heated at 250°C yielded a solid having no IX capacity and the backbone bears witness to the oxidation of the polymeric matrix.   On the other

hand, CO_2 was found in the filtrate and the functional benzyltrimethyl ammonium groups, yielding a weak base related to trialkylamines. Similarities are found in this case with the results of irradiation experiments reported in the literature.

For the cation exchange resin in the (H^+) form, there is also a complete loss of IX capacity, and the remaining solid has almost the same IR spectrum of polystyrene, giving no indication of further oxidation of the backbone. The (Li^+) form retains appreciable IX capacity, its matrix being much less affected by the heating than in the case of the anionic resin.

Polyanskii and Tulupov[12] arrived at a similar conclusion about the nonoxidative degradation of the polymeric matrix of sulfonated resins in air.

It is noticeable, however, that the amount of solid lost upon heating is almost the same for all the different ionic type of resins. This implies that, besides the Hoffmann reaction, which is to be expected in the case of the anion-exchange resin, there must be a different degradation mechanism for each type of resin which may originate in the different methods of synthesis, since it is well known that during the chloromethylation step (for the anionic resin) lateral reactions take place which end up in the formation of new intermolecular bonds between the polymer chains, many times referred to as additional crosslinking.[22,23] In this way the characteristics of the anionic resin depend both on the original polymer and on the steps for the synthesis of the IX material.

It is important to mention that the thermal degradation of IX resins in closed vessels with water does not contribute to further crosslinking, but rather the opposite. In the case of the anion exchange resin which was slightly charred in an open vessel, evidence was found on the formation of more crosslinkings. This has been also reported for irradiated resins.

Finally it must be said that the different operating temperatures for both types of resins as normally recommended appears justified by the present work, and it was also possible to verify that the (H^+) form suffers a more severe degradation than the corresponding alkali metal ionic form leading to the formation of a much more aggressive medium by decomposition.

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