Journal of Chromatography, 201 (1980) 121–129
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,030

EXAMINATION OF RADIATION DAMAGE TO ION EXCHANGERS BY DIFFUSE REFLECTANCE SPECTROSCOPY

T. MATSUURA*
Institute for Atomic Energy, Rikkyo University, 2-5-1, Nagasaka, Yokosuka 240-01 (Japan)
Y. YAMAMOTO
Department of Radiology, Komazawa Junior College, 1-23-1, Komazawa, Setagaya-ku, Tokyo 154 (Japan)
H. KURIHARA
Institute for Atomic Energy, Rikkyo University, 2-5-1, Nagasaka, Yokosuka 24-01 (Japan)
and
K. MIZUMACHI
College of Science, Rikkyo University, 3-34-1, Nishi-ikebukuro, Toshima-ku, Tokyo 171 (Japan)

SUMMARY

The browning of an anion-exchange resin when it is loaded with hydroxide ion or when it is irradiated was studied by diffuse reflectance and transmission spectroscopy in the wavelength range 900–300 nm. The hydroxide form of the resin showed a higher absorbance than the other ionic forms of the resin in the low wavelength region in both spectra. Irradiation of the resin resulted in an increase in absorbance in both spectra also in this wavelength region, depending on the dose. Temporary colour changes induced by low-temperature irradiation were also studied.

INTRODUCTION

It is a well known but intriguing phenomenon that a white anion-exchange resin such as Dowex 1 becomes brown when the loaded ion is converted from the usual form, such as chloride, into hydroxide or carbonate, although all of these anions are colourless in aqueous solution. In this work we investigated this effect by measurement of the diffuse reflectance (DRF) and transmission (TR) spectra of the resin.

A second aim was to study the darkening of ion-exchange resins on irradiation with gamma rays or other types of radiation, *i.e.*, radiation damage, by using the same spectroscopic methods. The dependence on, or correlation with, various parameters, such as type of resin, ionic form of the resin, integral dose of radiation, decrease in ion-exchange capacity, irradiation temperature and degree of dryness of the resin, was investigated.

0021-9673/80/0000–0000/$02.25

EXPERIMENTAL

Only one type of anion-exchange resin has so far been tested; from newly purchased batches of Dowex AG 1-X8, 50–100 and 100–200 mesh, fractions of 80–100 and 100–120 mesh were sieved. An exploratory experiment showed that there was no difference in the DRF spectra of the samples of 80–100 and 150–200 mesh,although grinding of the resin greatly decreased the log $F(R_\infty)$ value (Kubelka–Munk function)[1] in the DRF spectra, *i.e.*, the fine particles give a low absorption/scattering ratio.

For the unirradiated samples, hydroxide, chloride, sulphate, acetate, nitrate, fluoride, bromide and iodide forms of the resin were studied (these are referred to such as ROH, etc.). The preparation of the resin loaded with these ions was as follows: a sufficient volume of a *ca.* 1 *N* aqueous solution of the respective salts was passed through the chloride form of the resin, which was then thoroughly washed with pure water. For the preparation of fluoride, bromide and iodide forms of the resin, reagents of Merck (Darmstadt, G.F.R.) Suprapur grade were used, as it was found that a small amount of an impurity such as free iodine present in an extra-pure grade of potassium iodide caused darkening of the yellow colour of the resin and gave extraordinary spectra, presumably owing to the concentration of I_3^- species in the resin phase.

For the measurement of exchange capacity and for the study of the effect of the drying conditions, some samples of the ROH and RCl forms of the resin were kept in a desiccator at a constant relative humidity of *ca.* 76%, using saturated sodium chloride solution. Studies on the effects of irradiation dose were also made only for these two forms of the resin, and the irradiation and optical measurements were carried out in both wet and dry conditions. As the radiation source, radiation of up to $2.2 \cdot 10^8$ rad (6, 12 or 18 h irradiation in the "F-ring" position) or $7.0 \cdot 10^6$ rad (5 h irradiation in "R.S.R." position) using a 100-kW TRIGA reactor at our Institute was employed. Some irradiation runs with the ROH form were carried out while the dry samples were kept at dry-ice temperature during irradiation and measurements were made below room temperature.

The instrument used for the measurements of DFR and TR spectra was a Hitachi 200-010 double-beam spectrophotometer with an integrating sphere attachment (Type 200-0430), and the wavelength region covered was 900–*ca.* 300 nm. The cells employed were a cylindrical quartz cell of 1 cm thickness and 2.2 cm diameter with black tape covering the surfaces except for the light-incident face, and a rectangular quartz cell of 0.2 cm thickness, for DFR and TR measurements, respectively. For the measurement of DRF spectra, magnesium oxide was used as the reference, and also for the TR spectra the integrating sphere attachment with two magnesium oxide plates was employed after the cell, to collect the transmitted light as effectively as possible, as shown in Fig. 1.

The measurements of both spectra were made on resin samples either immersed in pure water or in the dry state, but the data given are those obtained in a wet condition, unless stated otherwise. When the same batch of sample was used and the measurements were made at almost the same time after the sample had been prepared and irradiated, the reproducibility of the data was good. Even for different batches of samples the general trends were similar, although the values of log $F(R_\infty)$ and absorbance differed considerably in some instances especially at longer wavelengths.

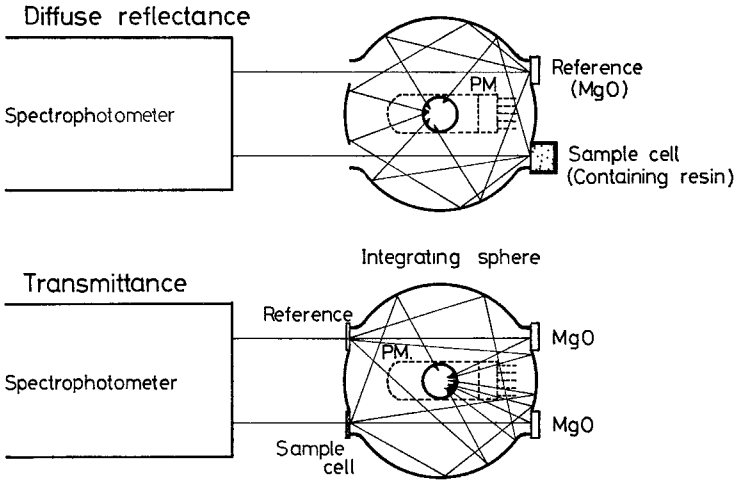


Fig. 1. Schematic diagram of the apparatus for the measurement of diffuse reflectance and transmission spectra of the resin.

The change in exchange capacity due to irradiation was also measured for the ROH and RCl forms of the resin. The measurements were made either by a gravimetric method, *i.e.*, by weighing the silver chloride precipitate obtained after eluting the RCl form with *ca.* 2 *N* potassium nitrate solution and adding silver nitrate[2], or by a potentiometric method, *i.e.*, by using a chloride ion-selective electrode in the potassium nitrate eluate, as these methods were found to give much more reproducible and reliable data than the usual titration method for the capacity of anion-exchange resins.

RESULTS AND DISCUSSION

Unirradiated samples

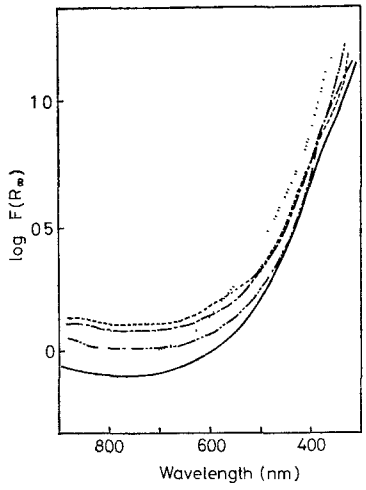
Figs. 2 and 3 show the DRF and TR spectra, respectively, of the unirradiated ROH, RCl, RSO_4, RNO_3 and RCH_3COO forms of the resin. Figs. 4 and 5 show the DRF and TR spectra, respectively, of the unirradiated resin in various halogen forms. Figs. 6 and 7 show the DRF and TR spectra, respectively, of the unirradiated ROH and RCl forms measured in the dry state (Fig. 6 contains the data for irradiated resins).

From these data one can observe the following general tendency for unirradiated resins:

(1) The ROH form of the resin, which is brown, has the highest absorption in both spectra, especially in the short wavelength region.

(2) For halogen ions, there is regularity between the series of ionic forms in both spectra. However, whereas the TR spectra show such a regularity over almost the whole wavelength region studied, for the DRF spectra this applies only at longer wavelengths.

(3) The results of measurements on the resin in the dry condition show almost the same tendency as in the wet condition, although the absorption/scattering ratio



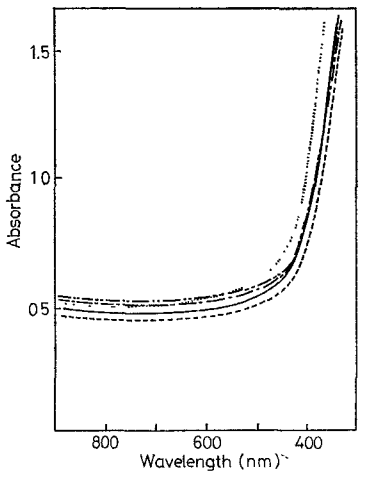
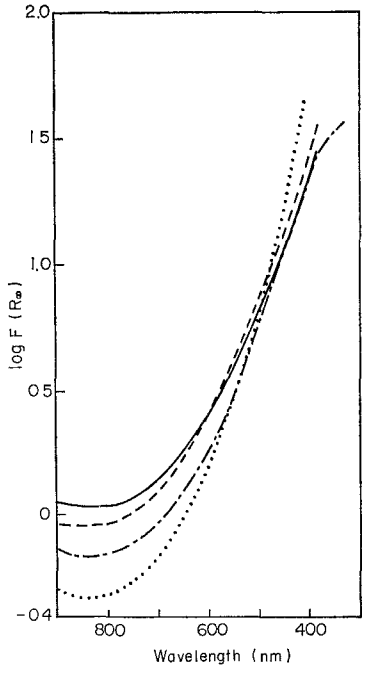


Fig. 2. Diffuse reflectance spectra of unirradiated resins. ———, RCl; - - -, RCH_3COO; —·—·, RSO_4; —··—, RNO_3; ·····, ROH.

Fig. 3. Transmission spectra of unirradiated resins. Curves as in Fig. 2.



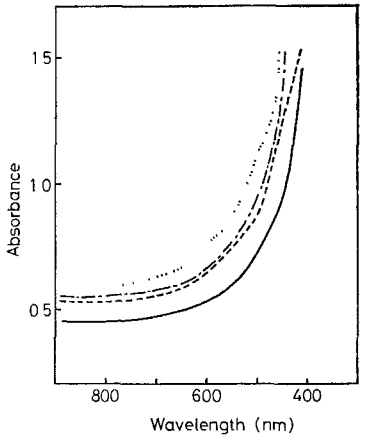
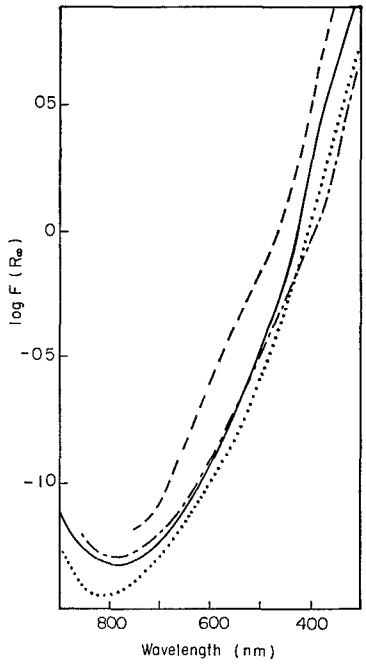


Fig. 4. Diffuse reflectance spectra of unirradiated resin. ———, RF; — — —, RCl; —·—·, RBr; ·····, RI.

Fig. 5. Transmission spectra of unirradiated resin. Curves as in Fig. 4.



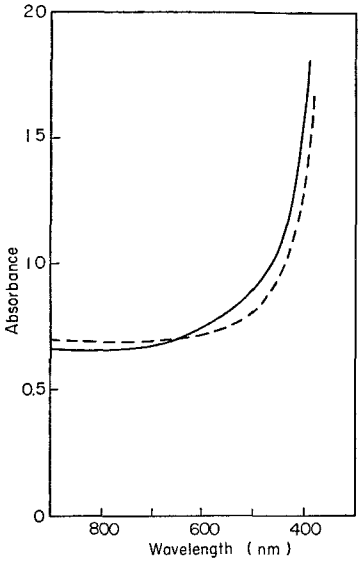


Fig. 6. Diffuse reflectance spectra of dry resin and effect of irradiation. —·—·, Unirradiated ROH; — — —, irradiated ROH; ·····, unirradiated RCl; ———, irradiated RCl. Irradiation dose: $7.0 \cdot 10^6$ rad.

Fig. 7. Transmission spectra of unirradiated resin measured in dry conditions. ———, ROH; — — —, RCl.

was lower in the DRF spectra and the absorbance was higher in the TR spectra for resin in the dry condition.

Irradiated samples

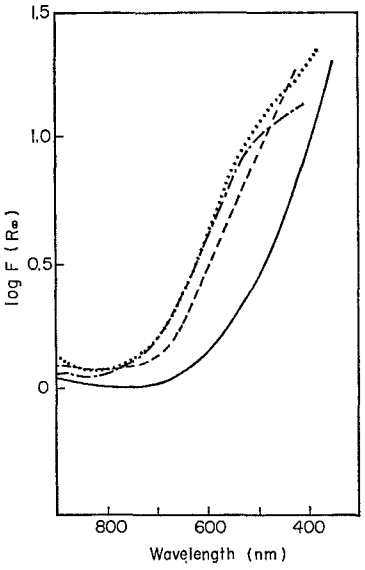
Effects of ion form and irradiation dose. Figs. 8 and 9 show the DRF spectra of the irradiated ROH and RCl forms of the resin respectively, with increasing dose. Fig. 10 shows the TR spectra of the irradiated RCl form of the resin with increasing dose. These are data for samples irradiated and measured in wet conditions.

From these data and the other data given below, the following conclusions can be drawn.

(1) The ROH form, which shows more pronounced browning on irradiation, experiences a greater change in the spectra than the RCl form, especially with relatively small doses, and it shows some saturation effect as the dose increases.

(2) Both spectra shift to an extent that depends on the dose received, but the spectral shifts occur in limited wavelength regions: *ca.* 700–*ca.* 500 nm in the DRF spectra of ROH, *ca.* 650–*ca.* 450 nm in those of RCl, and only below *ca.* 650 nm in the TR spectra of RCl.

Effect of drying conditions. Fig. 6 shows the change in the DRF spectra on irradiation with $7.0 \cdot 10^6$ rad for the ROH and RCl forms of the resin, which were



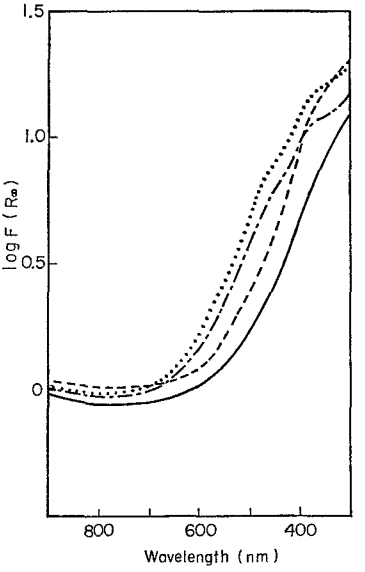


Fig. 8. Effect of irradiation dose on diffuse reflectance spectra of ROH form of the resin. ———, Unirradiated; – – –, $7.2 \cdot 10^7$ rad; —·—·, $14.4 \cdot 10^7$ rad; · · · · · ·, $21.6 \cdot 10^7$ rad.

Fig. 9. Effect of irradiation dose in diffuse reflectance spectra of RCl form of the resin. Curves as in Fig. 8.

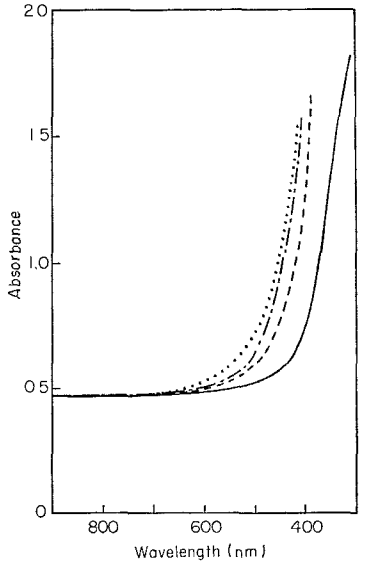


Fig. 10. Effect of irradiation dose in transmission spectra of RCl form of the resin. Curves as in Fig. 8.

irradiated and measured in dry conditions. As in wet conditions, the ROH form shows a larger absorption due to irradiation than the RCl form in the DRF spectra over the whole wavelength region. Although the data are not shown here, the TR spectra measured in dried conditions showed an increase in absorbance only at shorter wavelengths, as in wet conditions, depending on the dose.

Correlation with the decrease in the exchange capacity. Fig. 11 shows the decrease in the exchange capacity with increasing dose for samples irradiated in wet conditions. This shows clearly that the extent of the decrease in the exchange capacity of the resin is the same for the ROH and RCl forms.

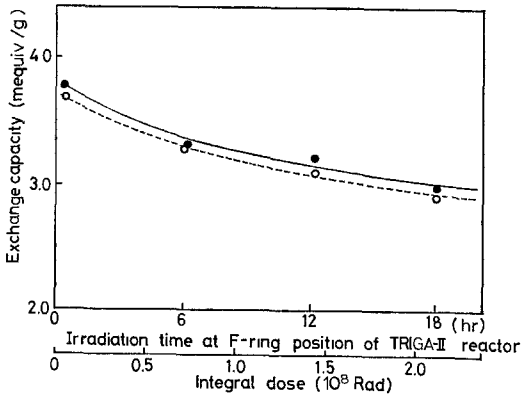


Fig. 11. Decrease in exchange capacity on irradiation of the resin. ●——●, RCl form; ○ - - - ○, ROH form.

Considering the other findings, that the decrease in capacity due to irradiation was also independent of the drying conditions and that there is some saturation effect in the spectra for the irradiated resin, as stated above, it can be concluded that the correlation between the apparent colour changes of an ion-exchange resin and the decrease in its capacity is not straightforward; we consider that the radiation damage that causes the apparent colour change of the resin occurs mainly as a result of some structural change in the skeleton of the resin, such as cross-linking.

Effect of irradiation temperature. Fig. 12 shows the effect of irradiation temperature on the DRF spectra of the ROH form of the resin, both irradiation ($7.0 \cdot 10^6$ rad) and measurement being carried out in dry conditions. It was observed visually that the sample irradiated at dry-ice temperature showed a definitely different apparent colour while it was still cold, but as it was warmed to room temperature the greenish colour disappeared and the colour became almost the same as that of a sample that had been irradiated at room temperature.

Fig. 13 shows the DRF spectra of the same resins measured in wet conditions. Although the apparent colour became almost the same as described above, the DRF spectrum of the sample irradiated in low temperature is between those of the unirradiated sample and the sample irradiated at room temperature. This indicates that the low-temperature irradiation resulted in a smaller degree of radiation damage than

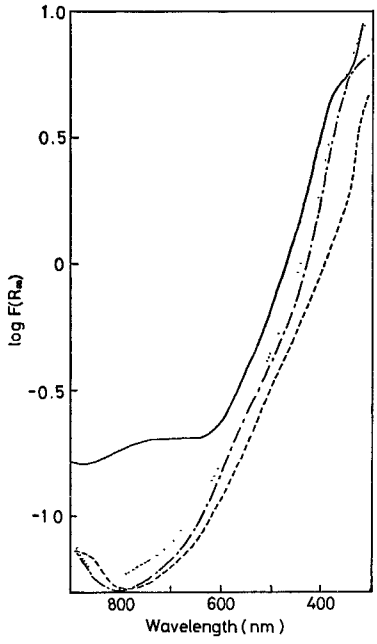
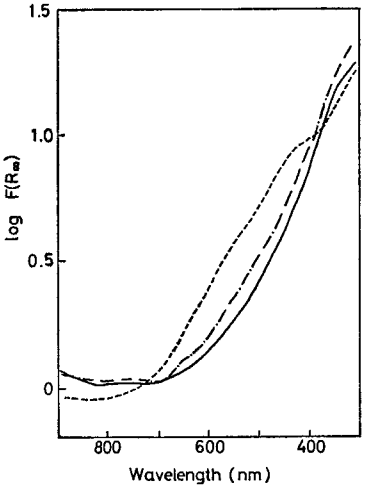


Fig. 12. Effect of irradiation temperature on diffuse reflectance spectra of ROH form of the resin. Irradiation with $7.0 \cdot 10^7$ rad was carried out at dry-ice temperature in dry conditions, and the measurements were made in dry conditions. – – –, Unirradiated; ———, measured while cold (*ca.* 1 h elapsed after irradiation); ·····, after warming to room temperature (*ca.* 2 h elapsed after irradiation); —·—·, 18 h elapsed after irradiation.



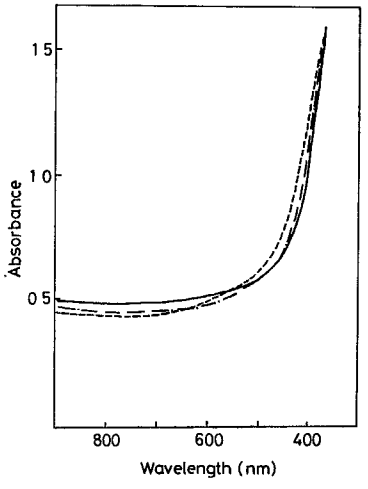


Fig. 13. Effect of irradiation temperature on diffuse reflectance spectra of ROH form of the resin, which was irradiated in dry and measured in wet conditions. ———, Unirradiated; – – –, room-temperature irradiation; —·—·, dry-ice temperature irradiation.

Fig. 14. Effect of irradiation temperature on transmission spectra of ROH form of the resin. Irradiation and measurement conditions as in Fig. 13.

room-temperature irradiation, and this effect was also apparent from the difference in the decrease in exchange capacity of these samples.

Fig. 14 shows the TR spectra of the same samples as in Fig. 13, and indicates that below *ca.* 600 nm the absorbance increases as the radiation damage increases.

CONCLUSION

The nature of the colour change of the unirradiated resin due to the loading of hydroxide ion on this type of resin is still unknown. We can speculate that hydroxide ion in an anion-exchange resin of this type may possibly form some chemical structure that can absorb light in the short wavelength region, probably by the formation of hydrogen bonds, and possibly with some correlation with the aromatic skeleton structure of this type of resin.

For the irradiated resin samples, the results suggest that there are several modes of radiation-induced damage to the resin, *i.e.*, the damage to the resin may be classified roughly into the following three categories, although these may occur at the same time:

(1) that leading to a decrease in the exchange capacity;

(2) some change in the skeleton part of the resin (cross-linking or degradation); and

(3) some temporary trapping of electrons, appearing only at low temperature.

ACKNOWLEDGEMENTS

The authors express their thanks to Professors T. Ishimori, K. Nakano and S. Kondo of the College of Science, Rikkyo University, for their encouragement of this study. This study was supported by a grant-in-aid for scientific research from the Ministry of Education, Science and Culture in Japan in Fiscal 1979 and also by funding from the Japan Private School Promotion Foundation. In addition, one of the authors (T. M.) thanks the Kashima Scientific Foundation for giving him the opportunity to participate in the 4th International Symposium on Ion Exchange.

REFERENCES

1 G. Kortum, *Reflectance Spectroscopy*, Springer, Berlin, 1969.
2 T. Hashimoto, *Genshiro Riyô Jisseki Hôkoku*, (Institute for Atomic Energy, Rikkyo University), 10 (1977) 45.