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ION-EXCHANGE KINETICS IN SELECTIVE SYSTEMS

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SUMMARY

Preliminary direct measurements, based on autoradiography, have confirmed indirect suggestions, obtained by potentiometric and isotopic techniques, that chloride–sulphate exchange on anionic resins at low salinity is not controlled by ion diffusion alone. Further, experimental evidence has shown that rate mechanisms vary not only among different anionic resins, but also for the same resin if direct or reverse exchange is considered.

INTRODUCTION

The study of the chloride–sulphate exchange on anionic resins, investigated to remove sulphates from sea water or brackish water and to prevent calcium sulphate scale in evaporation, reverse osmosis and similar processes[1], has shown definite evidence that diffusional ion-exchange rate theories do not apply to very selective systems, such as that investigated[2,3]. At low solution concentration ($1 \cdot 10^{-3}$–$6 \cdot 10^{-3} N$), where the selectivity of the resin towards the divalent ion is raised substantially by the electroselectivity effect[4], the experimental rates for the conversion of chloride to sulphate are not controlled by film diffusion, as expected. In fact, the experimental kinetics do not follow the corresponding Nernst–Planck model equations[5], the rates are unfavourably dependent on selectivity and the activation energies are too high. On the basis of these results, rate control by the chemical exchange reaction at the fixed charges of the resin has been hypothesized, and a correspondingly developed rate equation, derived from an S_N2 nucleophilic substitution reaction, has shown an excellent agreement with most of the experimental data. In order to obtain further confirmation of this chemical control hypothesis, which is unusual for such systems, and to collect direct evidence of the rate mechanism involved, other investigational

approaches are currently being employed, based on isotopic and autoradiographic techniques, applied both to direct chloride to sulphate and reverse sulphate to chloride exchange. This paper presents the preliminary results and the rate information obtained.

EXPERIMENTAL

Potentiometric, isotopic and autoradiographic techniques were used.

Potentiometric technique

A slightly modified Kressman–Kitchener stirrer–reactor, filled with about 10 mg of resin, previously converted into the Cl form with $6 \cdot 10^{-3} N$ hydrochloric acid–sodium chloride solution at pH 3, is immersed, still rotating (3000 rpm), in a jacketed vessel containing 0.8 l of $6 \cdot 10^{-3} N$ sulphuric acid–sodium sulphate solution at pH 3, the temperature being $25 \pm 0.1°C$. Release of chloride from the resin is followed potentiometrically with a chloride-selective electrode; the potentiometric data are automatically processed by a Hewlett-Packard 2100 S computer to obtain direct U (*i.e.*, Cl_t/Cl_∞) *vs.* time plots. The infinite solution volume condition (*i.e.*, negligible concentration in solution of the ion exchanged) is ensured in all of the experiments. Further details are given elsewhere[2].

Isotopic technique

If negligible concentrations of sulphates in solutions have to be monitored, as when the reverse sulphate to chloride exchange occurs, acceptable measurements are easily obtained using labelled sodium sulphate (^{35}S, β-emitter, 0.167 MeV, half-life 87.2 days, specific activity *ca.* 80 mCi/mmol). After the resin has been converted into the sulphate form, according to the procedure previously described, being immersed in a ^{35}S-labelled $6 \cdot 10^{-3} N$ sulphuric acid–sodium sulphate solution, it is then treated with $6 \cdot 10^{-3} N$ hydrochloric acid–sodium chloride solution:sulphate release is followed by periodically monitoring the build-up of radioactivity in solution using a Packard Tri-Carb 2002 liquid scintillation spectrometer and Insta-Gel scintillation cocktail. The data are automatically processed by the Hewlett-Packard 2100 S computer, as before.

To trace the mechanism of sulphate invasion of the resin, in some experiments the resin was loaded almost completely (up to $U = 0.7$–0.9) with ordinary sulphates, then an appropriate amount of labelled sulphate was suddenly added and the resin sulphation completed. By re-immersion in chloride solution, the time course of the release of radioactivity during the reverse exchange provides useful information on the ion-diffusion mechanism.

Autoradiographic technique

This technique has been adapted to these resins by Madi and co-workers in Debrecen, Hungary, and by Walis and co-workers in Warsaw, Poland. Madi and co-workers procedure was as follows: after contacting ^{35}S-labelled sodium sulphate solution, as previously described, for definite periods of time, corresponding to pre-determined U values, the resin was extracted from the reactor, washed with acetone, dried and embedded in a thermoplastic material; 90-μm thick slices were cut with a

microtome and placed on a Agfa-Gevaert 34B50 autoradiographic plate, with a 2.5-μm thick aluminium foil placed in between. After exposure for 1 h, the plates were developed for 2 min, then fixed for 10 min. The radioaudiograms were evaluated with a Zeiss GII densitometer (slit width 40 μm, slit height 2 mm). A substantially similar procedure was followed by Walis's group, to whom the resins, converted at Bari's laboratory with the appropriate amount of ^{35}S, were air-mailed for the autoradiographic measurements. The reproducibility of the autoradiograms, obtained independently on the same resins by the two groups, confirmed the viability of this technique.

Reference should be made to the publications of the two groups for other operating details[6-9].

RESULTS AND DISCUSSION

After unsuccessful attempts to apply the well known Fick and Nernst–Planck diffusional rate theories to these ion-exchange kinetics, the latter proved to fit the rate equation acceptably:

$$\ln \left(\frac{1}{1 - U} \right) = kCt \tag{1}$$

[where k = rate parameter (sec·equiv./l)$^{-1}$, C = solution concentration (equiv./l), and t = time (sec)], derived from S$_N$2 chemical reactions. This clearly supports the hypothesis of chemical control as the rate-determining step for the direct chloride to sulphate exchange reaction, where particularly high sulphate selectivities have been measured [the separation factor, α, is about 5, 22 and 46 for strong (Kastel A 500), medium (Kastel A 105) and weak (Kastel A 102) anionic resins, respectively[2]]. No direct information, however, was obtainable from potentiometric measurements on the mechanism(s) of ion diffusion within the resin bead. Use of labelled sulphates provided a first indication towards this objective. Autoradiograms of equatorial sections of beads, taken at different percentagesof conversion, indicate that on a strongly basic and less selective resin, sulphate invasion seems to occur homogeneously, according to the progressive conversion model, typical, for example, of the slow poisoning of catalyst pellets (see Fig. 1). This result is confirmed if the time course of the release of radioactivity during the reverse sulphate to chloride exchange on the same resin is measured. As shown in Fig. 2, either from the resin previously fully loaded with labelled sulphate (curve C), or when ^{35}S has been added only in the final stages of sulphation (curve D), radioactivity is released continuously throughout the reverse exchange. This again indicates that the sulphates taken up by this resin diffuse homogeneously within the bead, irrespective of the time course of their uptake. The contrary would have been expected with a Fickian gradient diffusion mechanism. A progressive conversion model for ion diffusion within the resin therefore seems thus to hold for such a resin, in a similar fashion to that discussed by Wen[10] and Kunii and Levenspiel[11].

The situation changes completely if a weakly basic, much more sulphate-selective resin is considered. As shown by the autoradiography of such a resin (Fig. 3), a well defined shell develops during the chloride to sulphate exchange, which finally reaches the core of the bead. The increased resin selectivity therefore seems to favour the unreacted core model for ion diffusion in the particle, first developed by Yagi and Kunii[12] and confirmed for several chelating systems[13-16].
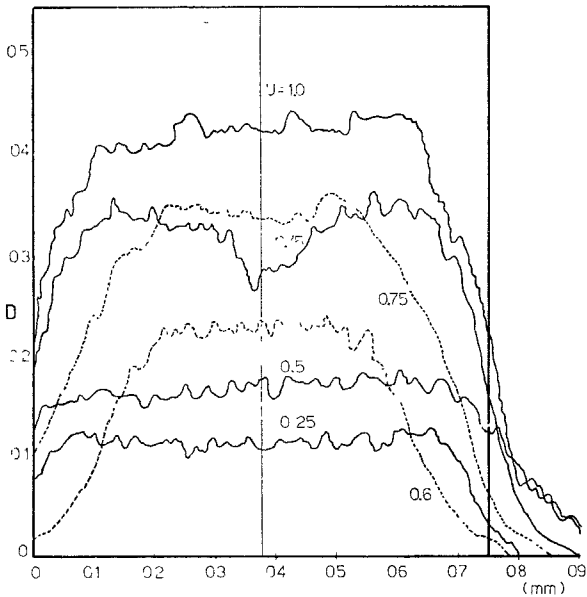
Fig. 1. Autoradiographic evaluation of sulphate distribution along equatorial sections of beads of Kastel A 500 resin at various degrees of conversion (magnification 200×). Mean bead diameter: 0.75 mm. Solid lines, direct exchange; broken lines, reverse exchange. $6 \cdot 10^{-3}$ N; 16–18-mesh resin. Abscissa, photometric scanning distance along sample diameter; ordinate, value of autoradiographic blackening, D, with respect to 24-h exposure time.
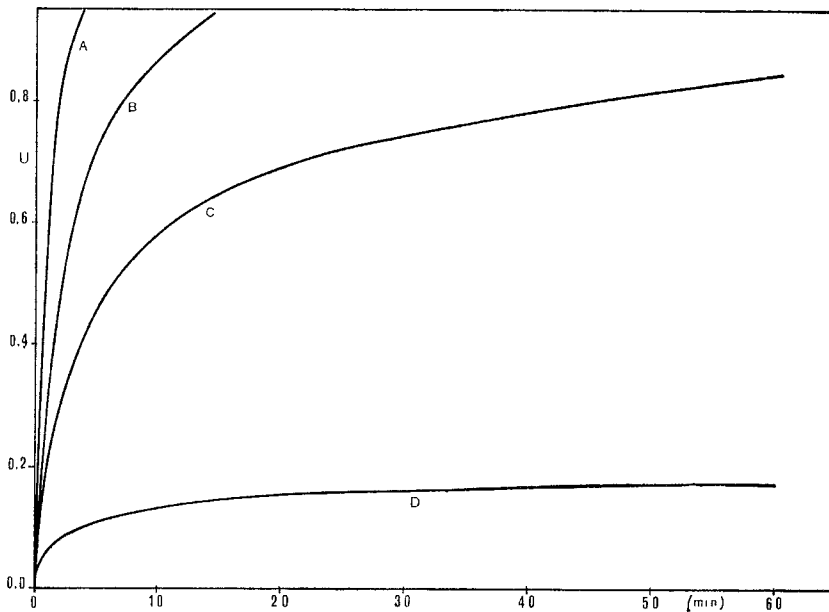

Fig. 2. Experimental exchange rates for (A) direct, (B) isotopic, (C) reverse (integral) and (D) reverse (last 10%) chloride–sulphate exchange on Kastel A 500 resin (20–30-mesh resin; $6 \cdot 10^{-3}$ N).
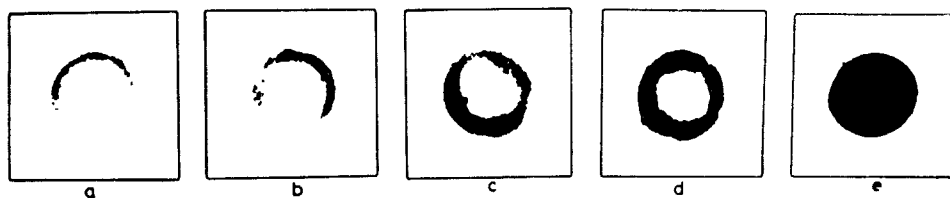
Fig. 3. Autoradiography of Kastel A 102 resin at various degrees of conversion (direct exchange) $(6 \cdot 10^{-3}\ N)$. Reaction time (a) 15 sec; (b) 30 sec; (c) 1 min; (d) 2 min; (e) 1 h.

Either for the strongly basic resin (progressive conversion model) or the weakly basic resin (unreacted core model), a high resin selectivity towards the entering ion seems to exclude the classic, Fickian gradient diffusional model.

Not only does the nature of the resin, as far as its selectivity is concerned, affect the mechanism of ion diffusion within the particle, the latter can also change if direct or reverse exchange (i.e., uptake or release of the preferred ion) is considered on the same resin. From the same data in Fig. 1 it appears that sulphates are no longer released in a strictly progressive manner from the strong resin, as in the direct exchange, provided that their autoradiographic profiles also virtually vanish at the external edges of the bead during the reverse exchange, with some formation of a concentration gradient.

Passing from direct to reverse or isotopic exchange, the rate-controlling step can also change for the same resin. In spite of the good agreement shown by eqn. 1 for the direct exchange, none of the investigated resins was found to obey the same rate law when the reverse (Fig. 4) and the isotopic (Fig. 5) exchanges are considered, as indicated by the absence of any linearity in these plots.

To complete the failure of classical rate theories based on diffusion to explain the behaviour of strongly selective ion-exchange systems, it should be noted that even the isotopic exchanges have not been explained by the commonly accepted Nernst–Planck model as indicated by the disagreements in Fig. 6.

CONCLUSIONS

Rate mechanisms in highly selective systems, for instance when a monovalent ion has to be exchanged for a polyvalent ion in very dilute solutions, do not seem to obey the well known models based on diffusion. Experimental evidence on the chloride–sulphate exchange on anionic resins, collected by potentiometric, isotopic and autoradiographic methods, confirms the lack of previous theories to explain simple ion-exchange processes not controlled by film and/or particle diffusion, and to describe diffusion within the resin particle according to other than Fickian gradient-dependent mechanisms.

Further research is planned to collect direct evidence of non-diffusion-controlled situations in this system, employing autoradiography and X-ray scanning microanalysis.
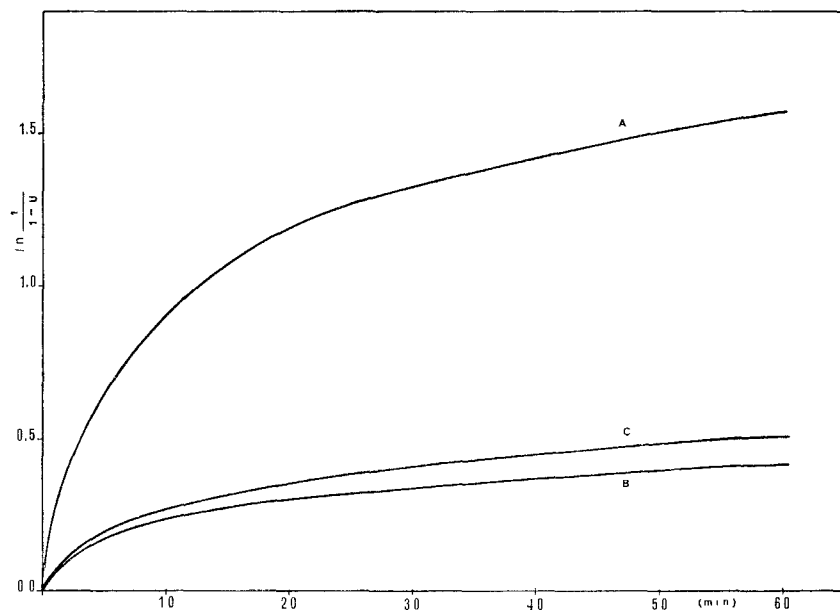
Fig. 4. Experimental reverse sulphate–chloride exchange rates for various anionic resins analysed according to the S_N2 model. 20–30-mesh resin; $6 \cdot 10^{-3}$ N. Resins: A, Kastel A 500; B, Kastel A 105; C, Kastel A 102.
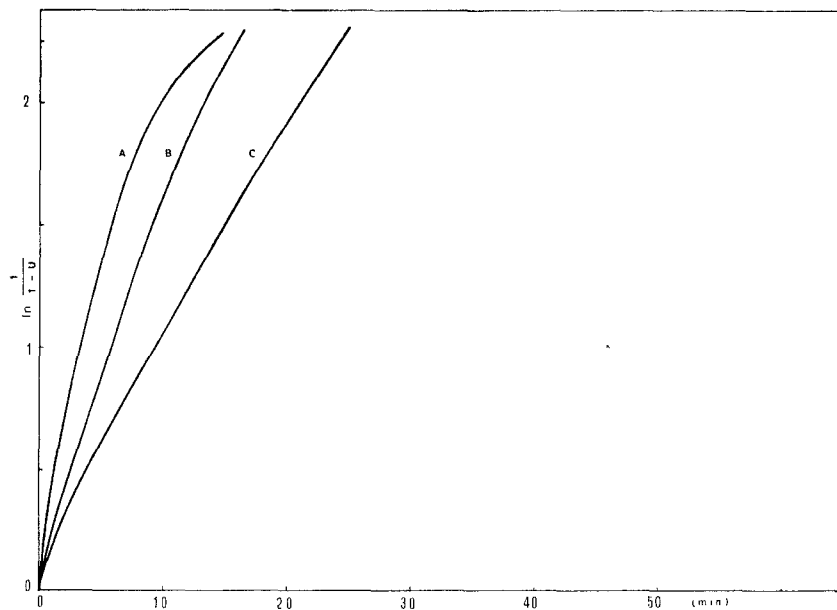

Fig. 5. Experimental isotopic sulphate–sulphate exchange rates for various anionic resins analysed according to the S_N2 model. 20–30-mesh resin; $6 \cdot 10^{-3}$ N. Resins: A, Kastel A 500; B, Kastel A 105; C, Kastel A 102.
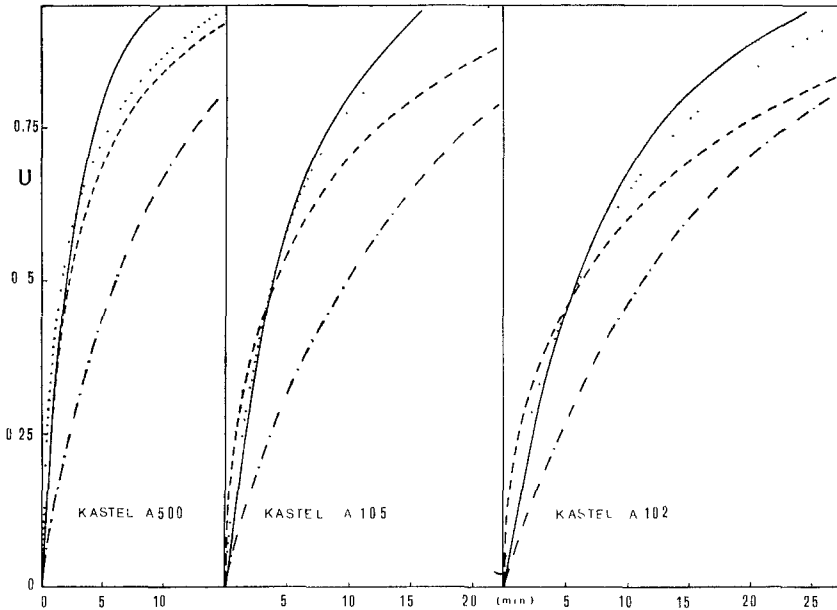
Fig. 6. Experimental isotopic sulphate–sulphate exchange rates (...) for various anionic resins analysed according to the Nernst–Planck model (see ref. 5). ——, Calculated for film diffusion control; - - - -, calculated for particle diffusion control; ·-·-·, calculated for film plus particle diffusion control. 20–30-mesh resin; $6 \cdot 10^{-3}$ N.

ACKNOWLEDGEMENTS

REFERENCES

1 G. Boari, L. Liberti and R. Passino, *J. Chromatogr.*, 102 (1974) 155.
2 L. Liberti, G. Boari and R. Passino, *Desalination*, 26 (1978) 181.
3 L. Liberti and G. Schmuckler, *Desalination*, 27 (1978) 253.
4 K. F. Bonhoeffer, L. Miller and U. Schindewolf, *Z. Phys. Chem.*, 198 (1951) 270.
5 F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962, Ch. 6.
6 I. Madi, T. Varro and E. Kovacs, *Int. J. Appl. Radiat. Isotopes*, 28 (1977) 473.
7 T. Varro, G. Somogyi, Zs. Varga and I. Madi, *Int. J. Appl. Radiat. Isotopes*, 29 (1978) 381.
8 K. Cichomska, A. Lutze-Birk and L. Walis, *Isotopenpraxis*, 14 (1978) 224.
9 H. Jaskolska, L. Rowinska and L. Walis, *J. Radioanal. Chem.*, 38 (1977) 29.
10 C. Y. Wen, *Ind. Eng. Chem.*, 60 (1968) 34.
11 D. Kunii and O. Levenspiel, *Fluidization Engineering*, Wiley, New York, 1969.
12 S. Yagi and D. Kunii, *Chem. Eng. (Tokyo)*, 19 (1955) 500.
13 M. Nativ, S. Goldstein and G. Schmuckler, *J. Inorg. Nucl. Chem.*, 37 (1975) 1951.
14 R. E. Bahu, M. J. Craske and M. Streat, *Proceedings of the International Conference on Theory and Practice of Ion Exchange, Cambridge, July 25–30, 1976*, Society of Chemical Industry, London, 1976, 19.1.

15 A. A. Efendiev, A. T. Shahtahtinskaja and P. Meares, *Proceedings of the International Conference on Theory and Practice of Ion Exchange, Cambridge, July 25–30, 1976*, Society of Chemical Industry, London, 1976, 18.1.
16 F. Helfferich, in J. A. Marinsky (Editor), *Ion Exchange*, Vol. I, Marcel Dekker, New York, 1966, p. 86.