CHROMSYMP. 808

RELATIONSHIP BETWEEN THE MASS-EXCHANGE RATE IN AN ION EXCHANGER AND IN SOLUTION FOR SELECTIVE SYSTEMS IN THE CASE OF A CONCAVE EXCHANGE ISOTHERM

A. I. KALINITCHEV*, E. V. KOLOTINSKAYA, T. D. SEMENOVSKAYA and V. T. AVGUL

Institute of Physical Chemistry, Lenin-Prospect 31, 117915 Moscow (U.S.S.R.)

SUMMARY

The kinetic dependences characterizing the influence of equilibrium factors on the diffusion processes in selective ion exchangers and in the solution film around the bead have been compared. A formal similarity of these dependences is shown to eliminate the possibility of identifying the kinetic mechanism in selective systems using conventional methods for non-selective exchange. The relationship between mass-transfer rates in the ion exchanger AV-17 and in the solution film has been analyzed for the desorption of $Ag(S_2O_3)_2^{3-}$, selectively retained by the exchanger, using sodium chloride solutions. The results of the analysis confirm the above conclusions.

INTRODUCTION

The conditions under which desorption processes are conducted in technological schemes for the extraction of valuable components from industrial wash waters and natural waters are dictated by the mechanism of mass exchange between the ion exchanger and the solution. The widely used methods of identifying the kinetic mechanism[1] are applicable only to a limited extent in non-ideal systems. In particular, they cannot be used to analyze the desorption processes of selectively retained ions. This conclusion is based on the numerical analysis of ion-exchange kinetics in complex-forming ion exchangers, using a mathematical model[2–4].

Theoretical studies, confirmed by experiments, have shown the interdiffusion rate in the ion exchange phase to depend on the external solution concentration and the isotherm shape[2–4]. These dependences are formally similar to those observed in external diffusion kinetics, as seen by comparing the results of calculating the mass-exchange rate in the bead[4] and in the solution film[1] in the case of a concave exchange isotherm, presented in Fig. 1. It should also be noted that a linear time dependence of the fractional conversion, $F(t^{1/2})$, characterizing the exchange kinetics in the ion-exchange phase in non-selective processes, can be observed for selective ion exchangers only in the case of convex isotherms[2–4].

A distorted view of the rôle of external and interdiffusion factors in selective systems also results from applying the Helfferich–Tunitsky criterion[1,5], since the dif-
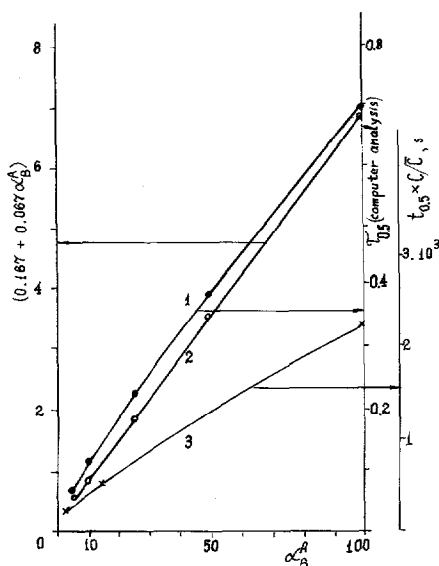
Fig. 1. Dependence of the dimensionless half time of conversion on the separation coefficient, α_B^A where A is the displaced ion: 1, for complex-forming ion exchangers; 2, for film kinetics; 3, $t_{0.5}(\alpha_B^A)$ for $Ag(S_2O_3)_2^{3-}$–Cl^- exchange in AV-17-8P.

fusion coefficients in the ion exchanger that enter into this criterion can undergo very sharp changes with a change in exchange direction, which is not accounted for in the theoretical expressions for non-selective processes.

A deviation from the ideal exchange kinetics, caused by the influence of selectivity, can occur in any ion-exchange system when relatively free and bound ions of the same kind are present in the ion-exchange phase. This is true for complex-forming, weakly dissociating, chemically and structurally non-homogeneous ion exchangers. In the general theory of sorption dynamics, it is regarded as necessary to account for the influence of the equilibrium distribution upon the ion-exchange sorption kinetics in a bi-porous adsorbent (micropore–macropore)[6], under conditions of selective sorption, when the isotherm shape is close to rectangular.

In the present work we have analyzed the experimental data on the desorption kinetics of the silver thiosulphate complex, $Ag(S_2O_3)_2^{3-}$, selectively retained by anion-exchangers having various porosities, using sodium chloride solutions of different concentration. Investigation of this system offers an opportunity to observe the variation in exchange rate over a wide range of the exchange isotherm parameters, since, with the displacement of triply charged ions by the singly charged ones, the shape of the isotherm, in accordance with the electroselectivity condition, depends on the solution concentration. The sorption and desorption of $Ag(S_2O_3)_2^{3-}$ have been studied previously[7-9] with the aim of extracting silver from various solutions.

EXPERIMENTAL

Kinetic determinations were performed with the help of a home-made flow cell (6 mm I.D.) with a thin layer of ion exchanger. The variation of the concentration

TABLE I

SPECIFIC VOLUME (V) AND VOLUME CAPACITY ($\bar{C}$) OF AV-17 ANION EXCHANGERS

Anion exchanger	Amino group	V_{beads} (cm³/g)	$\bar{C}$(mequiv./cm³)
AV-17-8 (gel)	Quaternary	1.3	2.5
AV-17-8P (porous)	Quaternary	2.9	1.2
AV-17-20P (porous)	Quaternary	1.8	1.1

of ions desorbed in the flow was estimated by use of an UV detector, type DU-1 of the Model 304 Tsvet-300 liquid chromatograph. The ion exchanger was presaturated under static conditions with $Ag(S_2O_3)_2^{3-}$, which was prepared by the interaction of diluted 0.006 M silver nitrate and 0.012 M sodium thiosulphate solutions. The concentration (c_0) of sodium chloride solution was varied between 0.1 and 2 M. Sodium chloride solutions are the most convenient in this case as they have a low optical density. A noticeable decomposition of the thiosulphate complex with the formation of silver chloride takes place at solution chloride concentrations higher than 2 M[10]. The flow-rate through the monolayer in the cell was constant, $v = 5$ cm/min; the sample of ion exchanger weighed 0.01–0.005 g, the average radius (r_0) of the wet resin particles was 0.04 cm. Under these conditions the relative concentration of $Ag(S_2O_3)_2^{3-}$ in the eluate, i.e., in the course of its desorption, did not exceed $2 \cdot 10^{-3}$. Table I shows the specific volume, V, and the volume capacity, $\bar{C}$, of the strongly basic AV-17 anion exchanger having differing porosities.

In addition to $Ag(S_2O_3)_2^{3-}$–Cl^- exchange, the CNS^-–Cl^- ion-exchange rate was measured as described above.

Because of the slow course of the $Ag(S_2O_3)_2^{3-}$ desorption at low sodium chloride concentrations, the time $t_{0.1}$, corresponding to the experimental $F = 0.1$, was used to characterize the exchange rate.

RESULTS AND DISCUSSION

Fig. 2 (curves 1–3) presents the data on the rate of desorption of $Ag(S_2O_3)_2^{3-}$ from anion exchangers of the same chemical nature but with differing internal structures. The exchange rate increases with increasing sodium chloride concentration, more rapidly with the increasing water content in the ion exchanger. This is especially clear when comparing the processes taking place in exchangers AV-17-8P and AV-17-20P which have the same volume capacity but differ in their moisture contents (Table I).

An increase in exchange rate with increasing solution concentration, caused by penetration of the free electrolyte into the ion exchanger, has often been noted previously[11,12], not only for macroporous but also for gel ion exchangers. The experiments discussed, however, are characterized by the fact that in the same concentration range the exchange rate of singly charged ions (Fig. 2, curves 4, 5) varies to a considerably smaller extent than that of multiply charged ions. The rate variations are, therefore, associated not only with the concentration factor, $\bar{C}/C$, but also with the value of the separation coefficient, α_B^A, where A = $Ag(S_2O_3)_2^{3-}$, and B = Cl^-, which, in the case of triply charged ions displaced by singly charged ones, sharply increases with decreasing solution concentration.
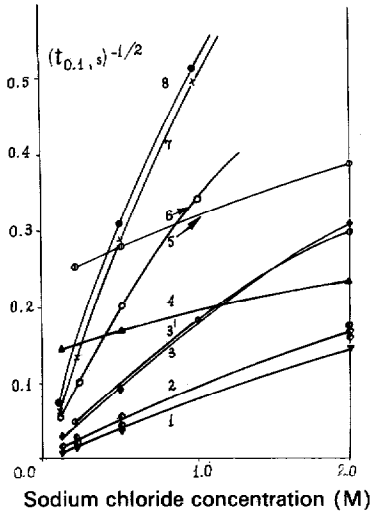
Fig. 2. Dependence of desorption rate of different ions on the sodium chloride concentration in the eluent: 1, 2, 3, experimental data on the desorption of $Ag(S_2O_3)_2^{3-}$ from AV-17-8 (1), AV-17-20P (2), AV-17-8P (3); 4, 5, experimental data on the desorption of CNS^- from AV-17-8 (4), AV-17-20P (5); 3', 6, 7, 8, calculated results for film exchange kinetics in AV-17-8 (6), AV-17-8P (7, 3'), AV-17-20P (8).

Despite the explicit dependence of the rate of desorption of $Ag(S_2O_3)_2^{3-}$ on the transport conditions in the bead, one should not discard the possibility of the effect of external diffusion factors. Fig. 2 gives the results of calculations based on the equation for film kinetics[1]:

$$\ln(1 - F) + (1 - 1/\alpha_B^A)\,F = -\frac{3DC}{r_0\delta\bar{C}\alpha_B^A} \tag{1}$$

The following initial values were taken in the calculations: $D = 0.5 \cdot 10^{-5}$ cm^2/s, $\delta = 0.2\,r_0/(1 + 70r_0v) = 0.007$ cm, $r_0 = 0.04$ cm and $v = 5$ cm/min. The separation coefficient was assumed to vary in accordance with the expression[1]:

$$\alpha_B^{A|z_A|} = K_B^A \left(\frac{\bar{C_A}}{C_A}\right)^{|z_A| - |z_B|} \tag{2}$$

where z_A and z_B are the charges.

TABLE II

VARIATION OF SEPARATION COEFFICIENTS (α_B^A) WITH THE CONCENTRATION OF SOLUTION (C_0)

C_0 (equiv./l)	$\alpha_B^{A\star}$
0.1	104
0.2	49
0.5	13
1.0	3
2.0	1

$\star$ At $|z_A| = 3$, $|z_B| = 1$, $K_B^A = 3$, $\bar{C} = 1.2$ mequiv./cm^3.

Table II shows the separation coefficients found from eqn. 2 for $\bar{C}/C_0 = 0.01$. The equilibrium coefficient, K_B^A, was determined from independent experiments. Assuming all the three AV-17 samples to have the same selectivity, α_B^A, towards $Ag(S_2O_3)_2^{3-}$, the equilibrium characteristics were found for only one of the anion exchangers (AV-17-8P).

From eqn. 1 it follows that the mass-exchange rate in a film (Fig. 2, curves 6–8) is considerably higher than the exchange rate in experiments with all the ion exchangers.

On the basis of the analysis performed, the experimental kinetic dependences can be referred to the mass-exchange process in the ion exchange phase. The influence of selectivity on the mass-exchange rate is caused by the presence of "free and bound" ions in the bead, located in the bead pores and in the vicinity of the ion-exchanger functional groups, respectively. When the local equilibrium is established instantaneously, the ionic composition of the parallel diffusion fluxes in the bead pores and gel phase is determined, along with kinetic parameters, by the shape of the exchange isotherm. If the mobility of ions in the pores is much higher than that in the gel, the system is adequate for ion exchange accompanied by the association of counter ions with fixed charges, and the kinetic dependences for macroporous ion exchangers are similar to those for weakly dissociating or complex-forming ion exchangers.

It seems impossible to make a quantitative comparison of the experimental and the calculated kinetic dependences for complex-forming ion exchangers because of the absence of sufficiently exact equilibrium and kinetic parameters necessary for computer analysis.

Fig. 1 illustrates an attempt at qualitative comparison of the theoretical and experimental results. The experimental exchange rate is represented by the $t_{0.5}$ $C/\bar{C}$ value, as the theoretical analysis has been performed at a constant $\bar{C}/C$ ratio, and in the experiments the solution concentration varies from 0.1 to 2 M ($t_{0.5}$ is the half time for exchange).

With the $Ag(S_2O_3)_2^{3-}$–Cl^- ion exchange taken as an example, it has thus been shown that, first, the dependence of the exchange rate on the isotherm shape, observed experimentally, is a manifestation of the peculiarities characterizing the kinetic mechanism of interdiffusion, and not external diffusion; and secondly, the effect of equilibrium factors can be interpreted within the framework of the model proposed[2–4] for complex-forming ion exchangers. The use of this model is more justified in cases where the exchange takes place in ion exchangers containing a large quantity of non-exchangeable electrolyte.

The non-exchangeable, absorbed electrolyte can also be regarded as a "stagnant mobile phase" (a term from liquid chromatography). The ion transfer rate in the immiscible liquid in the pores can be assumed to depend on the same factors as those acting in the immiscible solution film at the particle surface. This is confirmed by the similarity between experimental curve 3 and curve 3' calculated for film kinetics at a certain effective film thickness, $\delta_{ef} = 6\delta$ (Fig. 2). This seems to explain the difficulty in identifying the kinetic mechanism in the systems in question.

From a practical point of view, it is important that the exchange process can be strongly retarded in macroporous ion exchangers in the case of a concave isotherm, because of the absence of compulsory (with the flow) removal of the displaced ions from the "stagnant phase".

REFERENCES

1 F. Helfferich, *Ionites*, Inostrannaya Literatura, Moscow, 1962, pp. 150, 240, 257.
2 A. I. Kalinitchev, T. D. Semenovskaya and K. V. Chmutov, *Sorption and Chromatography*, Nauka, Moscow, 1979, p. 144.
3 A. I. Kalinitchev, E. V. Kolotinskaya and T. D. Semenovskaya, *J. Chromatogr.*, 243 (1982) 17.
4 A. I. Kalinitchev, E. V. Kolotinskaya and T. D. Semenovskaya, *Zh. Fiz. Khim.*, 58 (1984) 2807.
5 N. N. Tunitsky, V. A. Kaminsky and C. F. Tymaschev, *Metodi Phisiko Khimitcheskoi Kinetiki*, Chimia, Moscow, 1972, p. 79.
6 G. E. El'kin, *Ion Exchange and Chromatography*, Nauka, Leningrad, 1984, p. 104.
7 A. E. Agadzhanyan, K. A. Ter-Arakelyan and G. G. Babayan, *Arm. Khim. Zh.*, 35 (1982) 151.
8 B. N. Laskorin, G. I. Sadovnikov, Yu. P. Novikov, A. P. Lebedeva and A. N. Eryomkina, *Zh. Prikl. Khim. (Moscow)*, 47 (1974) 254.
9 A. B. Davankov, V. M. Laufer and L. B. Zubakova, *Theory and Practice of Sorption Processes*, VGU, Voronezh, 1968, No. 2, p. 180.
10 A. E. Agadzhanyan, K. A. Ter-Arakelyan and G. G. Babayan, *Chemistry and Chemical Technology*, EGU, Erevan, 1982, No. 1, p. 99.
11 D. Richman and H. C. Thomas, *J. Phys. Chem.*, 60 (1956) 237.
12 N. I. Nikolaev, M. D. Kalinina and G. T. Tchuvileva, *Zh. Fiz. Khim.*, 44 (1970) 3110.