Exchange studies of 5-sulphosalicylic acid in amberlite IRA 401 Cl anion exchange resin

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Abstract. Exchange studies of 5-sulphosalicylic acid in Amberlite IRA 401 Cl anion exchange resin have been carried out at 25°C in a stirred vessel. The exchange rates have been interpreted on the basis of a simple diffusion model.

Keywords. Ion exchange; kinetics; diffusion; anion exchange resin; exchange rate studies; 5-sulphosalicylic acid.

1. Introduction

Interest in ion exchange kinetics has grown rapidly in recent years. Knowledge of rate constants, mass transfer coefficients or diffusion coefficients, derived from rate investigations will be extremely useful in the design of ion exchange columns. Several authors have used kinetic models (Thomas 1944) in explaining ion exchange rates and some have used the mass transfer coefficient (Guggenheim 1944; Barrer 1948; Gregor *et al* 1955; Bonner *et al* 1956) concept in relating the mass transfer coefficient to the physical properties of the system. Glueckauf and Coates (1947) used a slightly modified approach where it is assumed that the rate at any time is proportional to the distance the system is from equilibrium. Smith and Dranoff (1964) have clearly brought out the merits and demerits of various approaches to the treatment of ion exchange kinetic data and have said that fairly reliable and accurate analysis of such data could be easily obtained by the simplest approach.

In the present work the exchange of 5-sulphosalicylic acid in Amberlite IRA 401 Cl resin has been studied over a range of concentrations. The data have been interpreted by a simple model.

2. Experimental

All exchange experiments were carried out in a 500 ml Corning beaker whose base was blown to a spherical shape held in a plastic cup and kept immersed in a thermostat maintained at 25° ± 1°C. Stirring of the experimental solution was achieved with the help of a glass paddle type stirrer fitted to a Tullu FHP Motor (National Manufacturing Ltd. India), and stirred at a fixed speed of 1000 rpm, as

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A list of symbols is given at the end of the paper

measured by a stroboscope. This speed was chosen after it was found that beyond this speed there was no effect on the rate of exchange when the speed of the stirrer was increased. Each experimental run utilised 200 ml of solution at a definite concentration of 5-sulphosalicylic acid. The sulphosalicylic acid was of BDH AR grade and was estimated by potentiometric titration against standard alkali. Exchange experiments were carried out with 0·5 g of resin Amberlite IRA 401 Cl (25–60 mesh, BSS, exchange capacity 3·6 m equivalents/g), carefully weighed and allowed to swell overnight by immersion in water. The resin was filtered and dried with filter paper before each experiment and added to the experimental solution maintained at 25°±1°C. Variation of the conductance of the solution was monitored by a conductivity cell (cell constant 0·1) whose resistance was measured by a Leeds and Northrup Bridge Cat. 7645 through a Null detector (Ajco-Poona). Figure 1 represents plots of conductance of sulphosalicylic acid solution with time for several concentrations. The data are represented in table 1.

3. Discussion

The results in figure 1 indicate the variation of conductance of the experimental solutions with time. The plot of log concentration of sulphosalicylic acid remaining in solution with time is found to be fairly linear after about 2 minutes of the run indicating that the exchange follows an exponential trend.

The hydroxyl group in the sulphosalicylic acid is expected to remain ionised in solution to a small extent in view of its low dissociation constant ($32·3 \times 10^{-4}$ at 25°C). It is therefore to be expected that the anion of the acid will exchange with
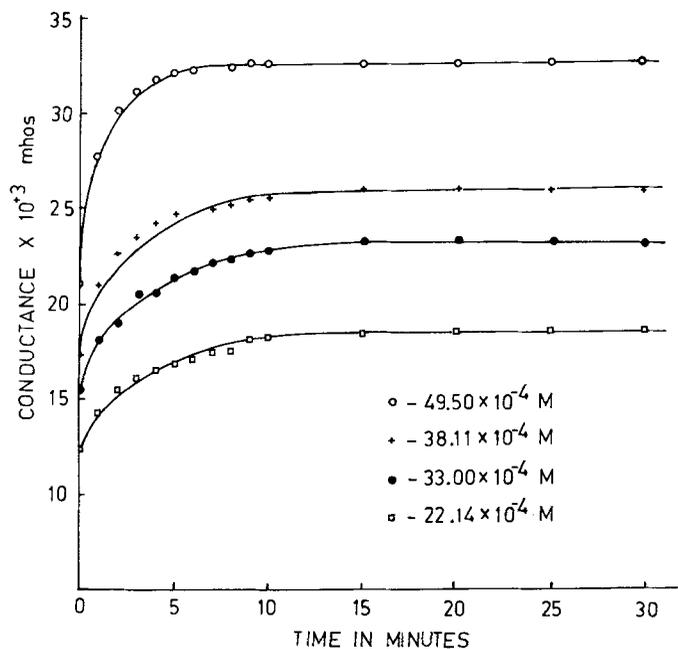

FIG 1   CONDUCTANCE vs TIME

Table 1. Exchange rate data of 5-sulphosalicylic acid in Amberlite IRA 401 Cl at 25°C at various concentrations of sulphosalicylic acid.

Time	49.5×10^{-4} M				38.11×10^{-4} M				33.0×10^{-4} M				22.14×10^{-4} M			
(min)	$A \times 10^{+3}$	$B \times 10^{+4}$	$C \times 10^{+4}$	D	$A \times 10^{+3}$	$B \times 10^{+4}$	$C \times 10^{+4}$	D	$A \times 10^{+3}$	$B \times 10^{+4}$	$C \times 10^{+4}$	D	$A \times 10^{+3}$	$B \times 10^{+4}$	$C \times 10^{+4}$	D
0	24·00	49·50	26·97		17·40	38·11	22·47		15·40	33·00	20·27		12·40	22·14	15·09	
1	27·70	35·40	15·18	0·883	20·80	25·67	12·04	0·784	17·99	23·92	12·33	0·578	14·17	16·38	10·09	0·421
2	29·90	28·45	10·78	1·639	22·50	19·50	8·27	1·348	18·90	20·29	9·83	0·861	15·30	11·95	6·55	0·886
3	30·90	25·50	9·43	2·064	23·49	17·55	7·05	1·629	20·50	14·18	6·60	1·409	16·00	9·95	5·27	1·129
4	31·60	23·50	8·40	2·580	24·20	15·24	5·86	2·009	20·60	14·15	6·17	1·511	16·50	7·74	3·95	1·458
5	32·08	22·00	7·67	3·236	24·70	14·22	5·30	2·250	21·40	13·20	5·38	1·734	16·89	7·08	3·47	1·611
6	32·10	21·75	7·55	3·400	24·75	13·62	4·98	2·428	21·60	11·55	4·63	1·999	17·00	6·53	3·12	1·737
7	32·18	21·60	7·50	3·478	25·00	13·25	4·82	2·527	22·00	10·23	4·03	2·285	17·39	5·53	2·59	1·973
8	32·30	20·50	7·44	3·580	25·10	12·75	4·55	2·722	22·20	9·73	3·76	2·443	17·40	5·42	2·47	2·035
9	32·56	20·50	7·04	4·830	25·50	11·13	4·00	3·294	22·59	8·25	3·13	2·949	18·00	3·66	1·65	2·601
10	32·59	20·40	6·94	5·810	25·60	10·93	3·89	3·463	23·70	7·93	3·00	3·105	18·20	3·33	1·46	2·786
15	32·59	20·40	6·94	—	26·00	9·53	3·32	—	23·10	6·64	2·44	—	18·60	1·66	1·44	—
20	32·65	20·30	6·88	—	26·00	9·43	3·28	—	23·30	5·94	2·19	—	18·70	1·33	0·57	—
30	32·65	20·30	6·88	—	26·00	9·43	3·28	—	23·30	5·94	2·19	—	18·70	1·33	0·57	—

A – Conductance of solution, mhos; B – Total concentration of sulphosalicylic acid from standard graph moles/litre; C – Calculated concentration of ionised form of sulphosalicylic acid g ions/litre; D – ln $(C_{A_0} - C_{A_r})/(C_{A_t} - C_{A_r})$, C_{A_r} in each case is estimated from figure 1.

two chloride ions of the resin, as per the mechanism,

$$2R^+Cl^- + (SA^{2-})H^{2+} \rightarrow 2R^+(SA^{2-}) + 2H^+ + 2Cl^- \tag{1}$$
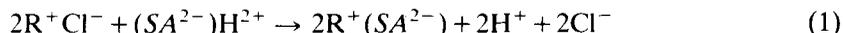
where (SA^{2-}) represents the anion of the sulphosalicylic acid, less both dissociable protons. This type of exchange was verified by chloride estimation of the solution at the end of the experiment. In order to follow the exchange after equation (1), sulphosalicylic acid of the same concentration as that used in the experiment (mole/lit) was used in preparing various mixtures of solutions by volume, with hydrochloric acid of double the strength as of the weak acid. This is because one mole of 5-sulphosalicylic acid is replaced in solution by two moles of HCl. A plot of conductance of these mixtures against their composition served as a standard curve for each experimental run from which the composition of the sulphosalicylic acid and chloride ion present at a given conductance value could be estimated. For a given value of conductance in figure 1 it was possible therefore to estimate the amount of chloride ion and sulphosalicylic acid present in solution at any given instant (cf. column B, in table 1). With the help of the dissociation constant of the OH^- group of the acid it was possible to calculate the concentration of the anion (SA^{2-}) (cf. column C, table 1).

The following simple approach could then be utilised to explain results in figure 1.

If the total concentration of exchangeable ions, i.e., (SA^{2-}) in solution is C_{A_0}, and C_{A_e}, the concentration at equilibrium, then $x_A = C_{A_e}/C_{A_0}$. Similarly if C_{A_s} represents the concentration of exchanged ions present on the resin per ml and Q_s the total concentration of exchangeable ions that could be present on the resin then $y_A = C_A/Q_s$.

From the experiments in the present case with 5-sulphosalicylic acid it can be inferred from table 1 that the corresponding value of x_A and y_A at the end of the kinetic run lie on an isotherm which is fairly linear (Coulson and Richardson 1971; Perry and Chilton 1973).

The problem is therefore simplified in the present work and the following ideas are explored. This is based on the following assumptions:

   (i) it is assumed that the system has achieved a steady state over short intervals of time;

  (ii) an equilibrium exists at the solid-liquid interface;

 (iii) the resin is treated as a homogeneous medium;

 (iv) the resin is free from the exchanging ions at time, $t = 0$;

  (v) the linear driving force approximation with a correction factor of unity for solid phase diffusivity is assumed;

 (vi) the experimental data is assumed to be independent of the speed of stirring;

(vii) the electrostatic forces and charge on the species are neglected;

(viii) the isotherm of y_A vs. x_A is linear.

The diagram in page 611 indicates the actual state of affairs at the resin surface-solution boundary.

Considering one cm^2 of the resin surface, then the rate of exchange reaction-depicted in (1) could be defined as:

$$R = k_L(C - C_i) = k_S(q_i - q) \tag{2}$$
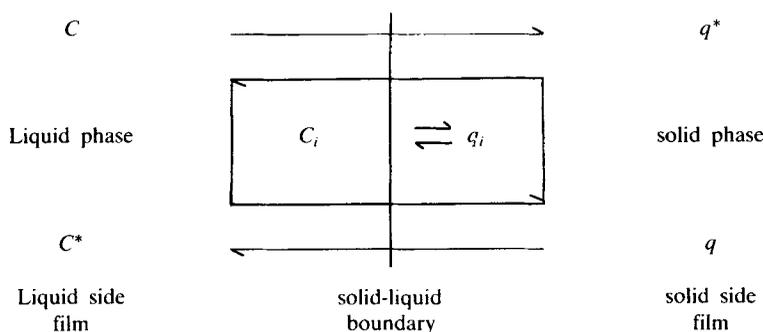
k_L and k_S represent the liquid and solid mass transfer coefficients, respectively. C and C_i represent the concentrations of the species (SA^{2-}) in the bulk of the solution and at the surface of the resin respectively. Analogously, q_i and q represent the concentrations of the same ion in the solid phase.

If Q represents the exchange capacity of the resin, then because of the fact that the equilibrium (1) lies on a fairly linear portion of an isotherm of y_A vs x_A one can show that:

$$q_i/Q = p\, C_i/C_{A_0},\tag{3}$$

where p is a constant. Here y_A as defined earlier is equal to q_i/Q and x_A is equal to $C_i/C_{A_0}, C_{A_0}$ being the initial concentration of the species (SA^{2-}). For a given system and at a given initial concentration of (SA^{2-}) in solution $Q \cdot P/C_{A_0}$ is constant and represented by α so that $q_i = \alpha C_i$.

From (2) it therefore follows that:

$$k_L C + k_S q = C_i(k_L + k_S\alpha).\tag{4}$$

Hence,

$$C_i = (k_L C + k_S q)/(k_L + k_S\alpha).\tag{5}$$

The rate of exchange can now be rewritten as:

$$R = k_L\,[C - (k_L C + k_S q)/(k_L + k_S\alpha)],\tag{6}$$

which on simplification gives

$$R = k_L\,[(k_S\alpha C - k_S q)/(k_L + k_S\alpha)].\tag{7}$$

As depicted in the diagram, at any instant q will always be in equilibrium with a corresponding concentration value in the bulk, represented by C^*, so that

$$k_S q = k_S\alpha C^*.$$

It therefore follows that

$$R = [k_L k_S\alpha(C - C^*)]/(k_L + k_S\alpha),\tag{8}$$

which, on rearrangement becomes,

$$R = (C - C^*)/\left(\frac{1}{k_S\alpha} + \frac{1}{k_L}\right).\tag{9}$$

Unless $p \to \infty$ and hence $\alpha \to \infty$, k_L can have a value such that

$$k_L \gg k_S \alpha. \tag{10}$$

If we now assume that k_L is very much greater than $k_S \alpha$, then

$$R = k_S \alpha (C - C^*). \tag{11}$$

In analogy with the relation between q and C^* as mentioned above, one should expect a similar relation between C and q^* where q^* now represents the equilibrium value in the solid phase corresponding to C at any instant. It is therefore obvious, that

$$R = k_S (q^* - q). \tag{12}$$

The assumption $k_L \gg k_S \alpha$ would mean that

$$C_i = C,$$

and

$$q_i = q^*. \tag{13}$$

Using the definition, that the rate R is,

$$R = -\left(\frac{dc}{dt}\right) \frac{V \times (D/6)}{(w/d)} \tag{14}$$

(it is assumed that the resin particles are uniform spheres), then comparing (14) and (12) it follows that

$$-\left(\frac{dc}{dt}\right) = (6/D)(w/d)(k_S/V)(q^* - q). \tag{15}$$

At any instant of time one can show that

$$(C_{A_0} - C)V = (w/d)q.$$

Therefore

$$q^* - q = \alpha C - (C_{A_0} - C)(Vd/w) \tag{16}$$

At equilibrium i.e. when no more of the ionic species (SA^{2-}) are exchanged, then

$$q^* = q_e = q \text{ and } C = C_{A_e}.$$

Therefore

$$\alpha C_{A_e} = (C_{A_0} - C_{A_e})(Vd/w),$$

which leads to

$$\alpha = [(C_{A_0} - C_{A_e})/C_{A_e}](Vd/w). \tag{17}$$

Using this value of α in (16) and simplifying, it can be shown that

$$q^* - q = (vd/w)(C_{A_0}/C_{A_e})(C - C_{A_e}), \text{ which on substitution into (15)}$$
leads to

$$-\left(\frac{dc}{dt}\right) = (6/D)(k_S C_{A_0}/C_{A_e})(C - C_{A_e}). \tag{18}$$

Integration of this equation between the limits 0 and t and noting that at $t = 0$, $C = C_{A_0}$ and at $t = t$, $C = C_{A_t}$, leads to

$$\ln [(C_{A_0} - C_{A_e})/(C_{A_t} - C_{A_e})] = (6/D)(k_S C_{A_0}/C_{A_e})\, t. \tag{19}$$

In other words a plot of

$$\ln (C_{A_0} - C_{A_e})/(C_{A_t} - C_{A_e}) \text{ vs time should be a straight line.}$$

The values of C_{A_0}, C_{A_t} are all actual ionic concentrations present in solution, calculated as per standard procedure (Maron and Prutton 1967). Values of C_{A_e} were estimated from experimental curves in figure 1.

A plot of $\ln (C_{A_0} - C_{A_e})/(C_{A_t} - C_{A_e})$ vs time is seen to be fairly linear (figure 2) bringing out the validity of (19). The slope of this plot is found to be

$$\text{slope} = (6/D)k_S(C_{A_0}/C_{A_e}).$$

Since D is 0·047 cm in the present case then for an initial sulphosalicylic acid concentration of $22\cdot14 \times 10^{-4}$ M this slope has a value equal to 0·4166 leading to a value of $k_S = 2\cdot05 \times 10^{-6}$ cm/sec. Since the slopes are all nearly the same as seen from figure 2, it can be inferred that the value of k_S is independent of the initial acid concentrations. The value of the diffusion coefficient D_S calculated using the expression

$$D_S = k_S D/10$$

works out to $0\cdot964 \times 10^{-8}$ cm²/sec suggesting that the order is as to be expected for surface diffusion.
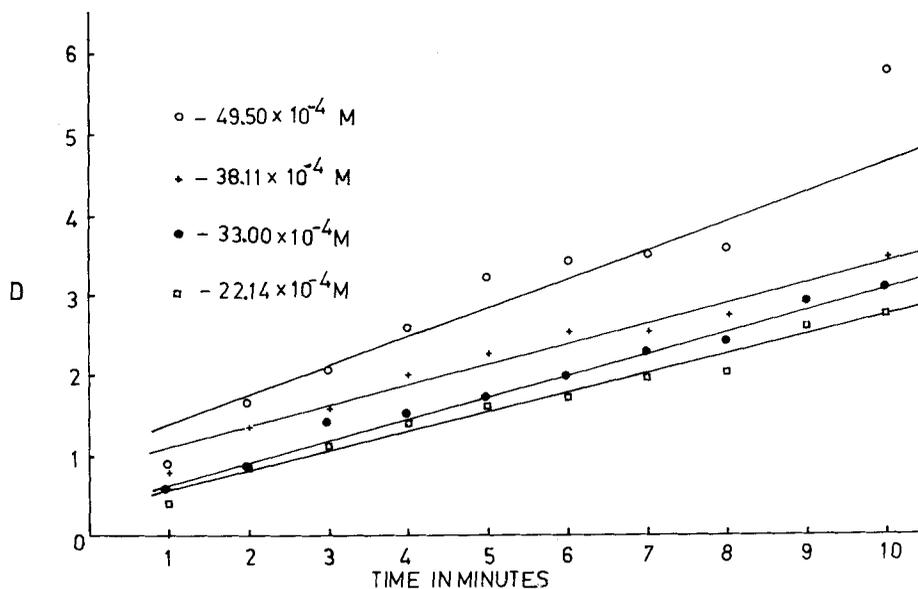

Figure 2. Verification of equation 19.

Further the value of α as calculated by the expression

$$\alpha = [(C_{A_0} - C_{A_e})/(C_{A_e})](Vd/w)$$

assuming a density of 1·1 is 1285. The assumption, $k_L \gg k_S \alpha$ would hence be valid, since $k_S \alpha = 0.00263$, which is very small compared to the k_L values calculated from the slope at time $t = 0$ using the plot of C/C_0 vs t. This slope would give $k_L a_p$, where a_p is the outer surface area of resin particle per unit volume of particle free slurry (cm^{-1}) and a value of k_L as 0·025 was obtained in the present case.

4. Conclusion

In conclusion it can be inferred that a simple model based on the linear driving force approximation can be very well employed to explain the exchange of 5-sulphosalicylic acid anion on Amberlite IRA 401 (Cl) anion exchange resin. The diffusion coefficient value estimated in the present case justifies the assumption that the process is surface diffusion controlled.

List of symbols

C_{A_0} Initial concentration of the species (SA^{2-}) in g ions/ml;
C^* concentration of species (SA^{2-}) in equilibrium in bulk solution at any time, g ions/ml;
C concentration of the species (SA^{2-}) in the bulk of the solution (g ions/ml);
C_i concentration of the species (SA^{2-}) at the surface of the resin (g ions/ml);
C_{A_t} concentration of species (SA^{2-}) at any time, g ions/ml;
C_{A_e} concentration of species (SA^{2-}) at equilibrium, g ions/ml;
C_{A_s} concentration of exchanged ions present on the resin g ions/ml;
d density of resin particles, g/ml;
D average diameter of resin particles in cm;
D_s diffusion coefficient cm^2/sec.
k_L liquid side mass transfer coefficient, cm/sec;
k_S solid side mass transfer coefficient, cm/sec;
P constant;
Q exchange capacity of the resin in g ions/ml;
Q_s total concentration of exchangeable ions on the resin g ions/ml;
q concentration of species (SA^{2-}) on the resin at any time g ions/ml;
q^* concentration of species (SA^{2-}) on the resin at equilibrium in the solid phase, g ions/ml;
q_i concentration of species (SA^{2-}) on the surface of the resin g ions/ml;
R rate of exchange g ions of (SA^{2-}) transferred per cm^2 resin surface per unit time;
t time in minutes;
V volume of experimental solution in ml;
w weight of resin in gms;
α constant;

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