

# Uptake of sodium chloride by mixture of weakly acidic and weakly basic ion exchange resins: equilibrium and kinetic studies

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## Abstract

The equilibrium and kinetic behaviour of weakly acidic resin (WAR) with alkali and weakly basic resin (WBR) with acids have been studied by many research teams. But little work is reported in literature regarding equilibrium and kinetic behaviour of mixture of WAR and WBR.

In the present study, detailed analysis of equilibrium and kinetic behaviour of mixed resins with sodium chloride has been undertaken. From equilibrium studies, no adsorption is observed taking place, when salt solution is brought in contact with WAR or WBR individually; however adsorption is observed taking place, when salt solution is brought in contact with the mixture of WAR and WBR. The salt uptake depends on the concentration of salt solution, the amounts of individual ion-exchange resins as well as their proportion.

Mixture of resins and salt solution has three phases interacting with each other and a number of resistances can influence salt uptake rate either individually or in combination. A series of possible resistances to the salt uptake are identified, namely, diffusion across films surrounding the resin particles, diffusion inside the resin particles, and dissociation of carboxylic group (-COOH) in WAR.

To minimize the mathematical complexity, *limiting case approach* is adopted in this study. The underlying assumption in this approach is that resistance to the entire process lies in that limiting step.

It is finally concluded that generation of H<sup>+</sup> ions (by interaction of WAR particles and salt solution) followed by adsorption of acid by WBR governs the salt uptake process in mixed resin systems.

**Keywords:** Adsorption; Equilibrium; Kinetics; Ion-exchange resins; Mathematical modeling; Sodium chloride

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## 1. Introduction

Desalination of water by thermally regenerable ion-exchange processes like 'Sirotherm' (CSIRO Australia, 1960-1970) and 'Cycling Zone Adsorption' (USA, 1970-1980) led to the interest in the study of equilibrium and kinetics of adsorption, of mixture of weak electrolyte ion-exchange resins. These processes exploit the thermal dependence of equilibrium of these resins. These resins adsorb salt at room temperature and are regenerated by hot water at 80-90° C. Both these processes use tailor made

weak acid/weak base amphoteric resins which are not commercially available.

Present studies started with the aim of using commercially available mixtures of weakly acidic and weakly basic ion exchange resins for the above purpose. But due to the shortage of literature available on equilibrium and kinetic behaviour of mixture of ion-exchange resins, the need was felt to study the equilibrium and kinetics of salt uptake by mixture of weak resin pair.

The pair of commercially available weakly acidic resin (WAR) and weakly basic resin (WBR), chosen for this study are:

(1) TULSION CXO-9H+ (WAR), (2) TULSION-A-2X (MP) free base (WBR).

(Both these resins were made available by M/s Thermax India Ltd., Pune.)

## 2. Aim and scope

1. To study the equilibrium and kinetics of salt uptake by mixture of WAR and WBR in different ratios with sodium chloride.
2. To interpret above information with the help of appropriate mathematical models.

## 3. State of the art

The equilibrium and kinetic behaviour of WAR with alkali and WBR with acids have been studied by many research teams (Kunin, 1958; Helfferich, 1965; Adams et al., 1969; Warner et al., 1970; Native et al., 1975; Rao and Gupta, 1982a, b; Helfferich and Hwang, 1985; Bhandari et al., 1992, 1993). Starting with Helfferich in 1965 most of the above workers have confirmed the shrinking core mechanism accompanied by chemical reaction in case of carboxylic acid resin (WAR) and strong base. The present study with (WAR + NaOH) also confirms this observation. Similarly, in case of adsorption of acids on weakly basic resins (WBR) Helfferich and Hwang (1985) suggested that acid sorption by most commercial weak base ion exchangers can be correlated by shrinking core model considering sorption to be irreversible. However Juvekar et al. (1992) indicated that the sorption is significantly reversible.

Not much work is reported regarding equilibrium and kinetic behaviour of mixture of WAR and WBR with adsorption of salts. Warner et al. (1970) have stated "The kinetics of mixed beds are complex." Bolto and Weiss (1977) have conducted equilibrium and kinetic studies of sodium chloride with mixtures of various resin pairs, but have not proposed any rate model. Light (1973) and Latty (1974) selected DUOLITE CC-4 (WAR) and DUOLITE A-368 (WBR) for their studies. It was concluded by them that 0.66 g of WAR per gram of WBR was optimum ratio and equilibrium capacity of resin pair was 0.937 meq/g at pH 6.25.

## 4. Experimental

### 4.1. Materials

TULSION-CXO-9H+ (WAR) is a gel type poly-acrylic co-polymer with H<sup>+</sup> ions attached to carboxylic group and TULSION-A-2X (MP) freebase (WBR) is macroporous tertiary amine type resin. Other standard laboratory grade chemicals like sodium hydroxide, hydrochloric acid, sulphuric acid, sodium chloride and sodium sulphate (anhydrous) were used in the study.

### 4.2. Procedure

First of all, resins were swollen in distilled water and conditioned. Equilibrium studies were conducted by batch method taking 1-5 g of resins and a fixed volume (100 ml) of acid/alkali/salt solution. Equilibration was carried out with occasional shaking for more than 36 h (25°C). Adsorption of salt remained constant after 24 h in each case. Concentration change was measured by conductivity meter.

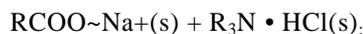
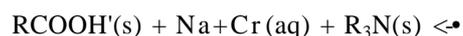
For kinetic studies 1-5 g resin mixtures in the weight ratio of (WAR/WBR) 0.5, 1 and 2 were stirred with salt solutions (conc. 1000, 5000 and 10,000 ppm) at fixed volume (100 ml). Laboratory type magnetic stirrer with te: on coated needle inside 250 ml glass beaker was used for these studies. Speed of the stirrer was kept in the middle range. Probe of conductivity meter was directly immersed in the solution and change in conductivity was noted with time.

## 5. Equilibrium studies

### 5.1. Salt uptake by mixed resins (MR)

Salt uptake was observed when mixtures of weakly acidic resin (WAR) and weakly basic resin (WBR) were equilibrated with sodium chloride or sodium sulphate salt solutions.

(a) *Sodium chloride system.* The salt uptake may be represented as



Equilibrium studies were carried out with initial sodium chloride salt solution concentrations of 1000 ppm (17.1 eq=m<sup>3</sup>), 5000 ppm (85.45 eq=m<sup>3</sup>) and 10,000 ppm (170.94 eq=m<sup>3</sup>) along with varying ion-exchange resin ratios. The results are shown in Figs. 1 and 2. The plots show that at low concentrations, uptake of salt varies linearly with solution concentration, however at higher concentrations, the salt uptake does not increase significantly. During the equilibrium studies pH of the process ranged between 6.5 and 7.5. This has been already reported in literature (Bolto and Weiss, 1977).

WBR is responsible for shifting of equilibrium towards forward direction. As such sorption capacity of mixed resins calculated with respect to WBR carries more meaning. Capacity of resin in terms of eq/kg (WBR) increases with increase in resin ratio. This means that with increase in resin ratio, the WBR decreases in the mixture and it gets saturated to a larger extent. In a limiting case when WAR/WBR tends to infinity, it should mean that salt uptake per kg of WBR should correspond to the sorption capacity of acid uptake by WBR. Therefore it is expected that salt uptake

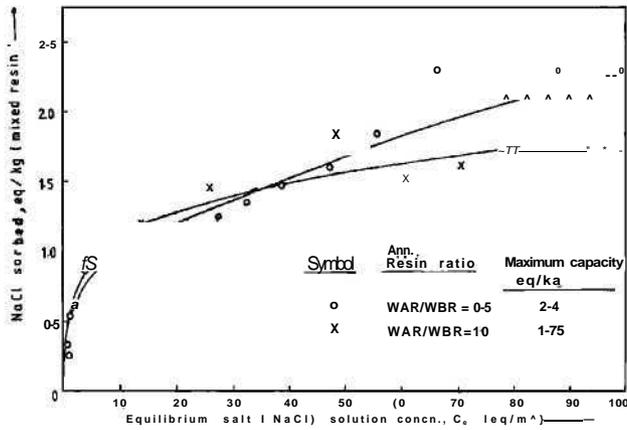


Fig. 1. Experimental equilibrium data for adsorption of NaCl on mixture of resins (WAR + WBR).

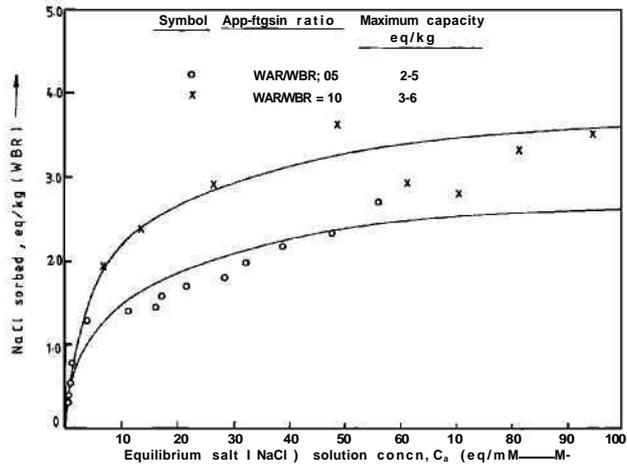


Fig. 2. Experimental equilibrium data for adsorption of NaCl on mixture of resins (WAR + WBR).

Table 1  
Capacities of mixed resin with NaCl system

Approx. resin ratio	Total resin (eq/kg)	WBR (eq/kg)
WAR=WBR = 0.50	2.40	2.50
WAR=WBR = 1.00	1.75	3.66

per unit weight of WBR will always be less than acid uptake capacity of WBR (i.e. 4.5 eq=kg). Table 1 shows salt uptake per kg of total resin and per kg of WBR for different ratios. These are the highest values of salt uptake as indicated in equilibrium curve. Hsu and Pigford (1989) have studied salt uptake by amphoteric resins Amberlite XD-2 and Amberlite XD-5 with sodium chloride solution. The maximum equilibrium capacities of Amberlite XD-2 reported are 1.0 eq=kg and that of Amberlite XD-5  $\ll$  1.3 eq=kg.

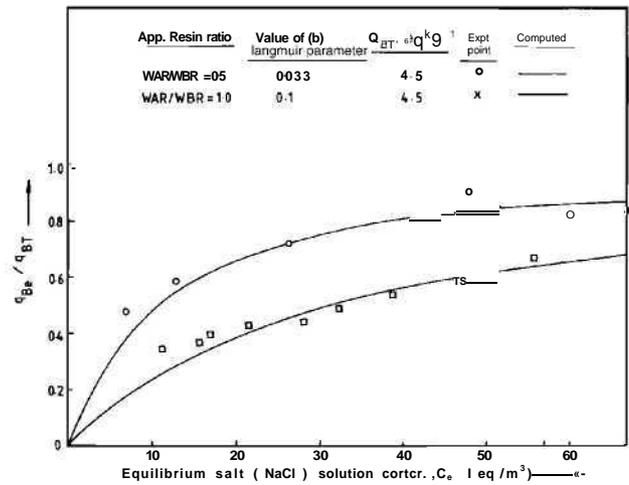


Fig. 3. Langmuir behaviour for mixed resin (WAR + WBR) and NaCl system.

Table 2  
Langmuir isotherm parameters (MR + NaCl system)

Approx. resin ratio	b	q <sub>BT</sub>
WAR=WBR=0:500.0334.50	0.033	4.50
WAR=WBR = 1:100	0.100	4.50

5.2. Analysis of equilibrium data

From the equilibrium behaviour of mixed resins and sodium chloride system, it may be observed that mixed resins and sodium chloride system show reversible behaviour.

The equilibrium data may be represented by Langmuir isotherm.

$$q_{Be} = \frac{q_{BT} \times b \times C_e}{1 + b \times C_e}; \tag{1}$$

where  $q_{Be}$ , eq. of salt sorbed per kg WBR;  $C_e$ , equilibrium solution concentration eq=m<sup>3</sup>; b, constant;  $q_{BT}$ , total capacity of WBR.

The plot of  $q_{BT} = q_{Be}$  vs.  $1/C_e$  was regressed by second-order polynomial and values of b (from slope of the line) were calculated. Fig. 3 shows the plots predicted by Langmuir isotherm behaviour and actual experimental points. There is a good correlation. Table 2 shows values of  $q_{BT}$ .

It may be noted that the value of  $q_{BT}$  is same as to be actual sorption capacity of WBR for the acid uptake. Also it may be noted that for low values of  $C_e$ ,  $q_{Be} = q_{BT} \approx b \times C_e$ . This implies that salt uptake by the mixture resin varies linearly at low salt solution concentration  $C_e$ . Further the value of b indicates that the salt uptake will be more pronounced with increase in the ratio of WAR/WBR. This has been discussed earlier as well. The uptake of salt by mixed resins could become possible because of generation of H<sup>+</sup> ions from WAR and subsequent adsorption of acid by WBR.

Also concentration of free  $H^+$  ions in MR + salt system is almost zero (neutral pH). It suggests that presence of WAR in mixed resins and salt system is equivalent to presence of free hydrogen ion in the acid + WBR system. This is further supported by the fact that salt uptake per gram of WBR at a given salt concentration increases with the ratio WAR/WBR.

### 5.3. Conclusions: equilibrium studies

It is well established that WAR or WBR, when placed individually in sodium chloride solutions of any concentration do not take up the salts. But uptake of salt is observed when mixture of WAR and WBR is equilibrated with the salt solution. The other important observations are:

- (i) The extent of adsorption of salt depends on the quantity of WAR, that of WBR, and salt solution concentration. It increases with increase in each parameter keeping the other two constant.
- (ii) Salt uptake by the mixture of resins takes place near neutral conditions. The pH values noted during the process lie between 6.5 and 7.5.
- (iii) Overall equilibrium capacity of mixed resins in different ratios is always less than the equilibrium capacity of WAR with sodium hydroxide and WBR with strong acids, i.e. hydrochloric acid.
- (iv) The equilibrium capacity of mixed resins (in agitated state) can be enhanced by varying resin ratios.

## 6. Kinetic studies

### 6.1. Experimental observations

Experimental conditions for mixed resin and sodium chloride system are given in Table 3. Experimental data were analysed looking at salt uptake as function of time (Fig. 4). It was observed that the total uptake of salt as well as the rate of uptake depends upon each of the three independent parameters, namely initial solution concentration, amount of WAR and the amount of WBR present. It increased with increase in each parameter, keeping other two parameters fixed.

It was decided to determine the combined effect of all three parameters at the same time. For this purpose initial rate analysis was employed taking initial rate of salt uptake for each run by second-order polynomial approximation with time. It was concluded that rate of salt uptake is proportional to all the three parameters namely masses of WAR, WBR and salt solution concentration.

### 6.2. Mechanism of salt uptake

Salt is taken up, when both WAR (RCOOH) and WBR (R<sub>3</sub>N) are present in salt solution. It implies that Na<sup>+</sup>

Table 3

Experimental conditions for mixed resin and sodium chloride system: kinetic studies

Expt. no.	Initial soln. concn. (eqm ~ <sup>3</sup> ) (ppm)	WAR (kg x 10 <sup>-3</sup> )	WBR (kg x 10 <sup>-3</sup> )	Approx. resin ratio
K-29	170.94 (10,000)	1.519	3.222	0.50
K-28	170.94 (10,000)	2.148	2.026	1.00
K-27	170.94 (10,000)	3.545	1.879	2.00
K-26	170.94 (10,000)	2.279	1.208	2.00
K-22	85.47 (5000)	1.025	2.043	0.50
K-23	85.47 (5000)	1.032	1.049	1.00
K-24	17.10 (1000)	0.526	1.053	0.50
K-25	17.10 (1000)	1.026	1.050	1.00
R-2	89.31 (5225)	0.7816	3.960	0.190
R-3	88.20 (5160)	0.3814	2.226	0.170
R-5	88.37 (5170)	0.2019	4.097	0.050
R-6	86.21 (5050)	0.0760	2.126	0.035

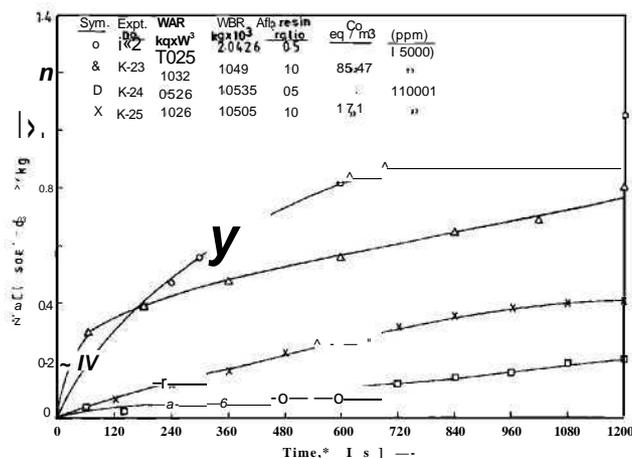
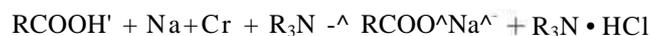
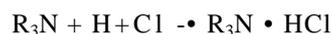


Fig. 4. Experimental kinetic data for adsorption of NaCl on mixed resin system.

ions from NaCl solution exchange  $H^+$  ions with RCOOH (WAR) and  $H^+CP$ , thereby generated, gets adsorbed by R<sub>3</sub>N (WBR). It was again observed in all kinetic experiments that concentration of  $H^+$  ions in bulk solution was almost zero. As such WBR acts as a sink and drives this reaction to proceed in forward direction.



Thus the following sequence of steps for salt uptake by mixture of WAR and WBR is being proposed:

1. From the bulk solution, diffusion of Na<sup>+</sup> ions across the fluid film surrounding WAR particles.
2. (a) Diffusion of Na<sup>+</sup> ions inwards in WAR particles.

- (b) Dissociation of -COOH group accompanied by exchange of Na<sup>+</sup> and H<sup>+</sup> ions inside WAR particles.
- (c) Diffusion of H<sup>+</sup> ions outwards.
- 3. Diffusion of H<sup>+</sup> ions across film surrounding WAR particles, and mixing in the bulk solution.
- 4. Diffusion of HCl (H<sup>+</sup> ions generated and Cl<sup>-</sup> ions from bulk solution) across the film surrounding WBR particles.
- 5. Adsorption of HCl on the microspheres of WBR particles.

One or more than one step may be slow, affecting the rate. Furthermore 'proximity' of WBR particles to WAR particles where H<sup>+</sup> ions are available is of utmost importance, otherwise WAR simply holds back H<sup>+</sup> ions. In order to understand the behaviour of mixed resin and salt system a new approach named 'proximity factor approach' was adopted. Proximity factor is defined as ratio of actual sorption of salt at equilibrium for particular experimental conditions to the maximum possible sorption value:

$$PF = \frac{\text{actual uptake of salt at equilibrium}}{\text{maximum possible salt uptake}}$$

In present studies equilibrium capacity of WAR with NaOH system is 11.5 eq/kg and that of WBR with strong acids is 4.5 eq/kg. The amount of Na ions initially present in the salt solution is also known. So maximum possible salt uptake will be the least value among eqs of WAR, WBR and salt solution.

If the capacity of WBR is least then WBR will have major controlling influence on the salt uptake. Similarly WAR and initial solution concentration will have their influences. From above cited capacities of individual resins, for every 1 kg of WAR, 0.39 kg of WBR will have the same capacity. Therefore, it is likely that,

1. If WAR=WBR > 0.39, salt uptake will depend on amount of WBR present in the mixture.
2. If WAR=WBR < 0.39, salt uptake will be limited to generation of H<sup>+</sup> ions by WAR.
3. If the amount of Na<sup>+</sup> ions in the bulk solution is less than H<sup>+</sup> ions generating capacity of WAR, the salt uptake will depend on Na<sup>+</sup> ions present in the solution.

Experimental data in the resin ratios of (WAR/WBR) 0.035-0.197 show the effect of WAR.

## 7. Results and discussion

The mechanism of salt uptake explained above led to the limiting case approach theory, which minimized the mathematical complexity in modeling. The underlying assumption in this approach is that resistance to the entire process lies in that particular limiting step. The four limiting cases thus identified for this process are discussed hereunder in detail.

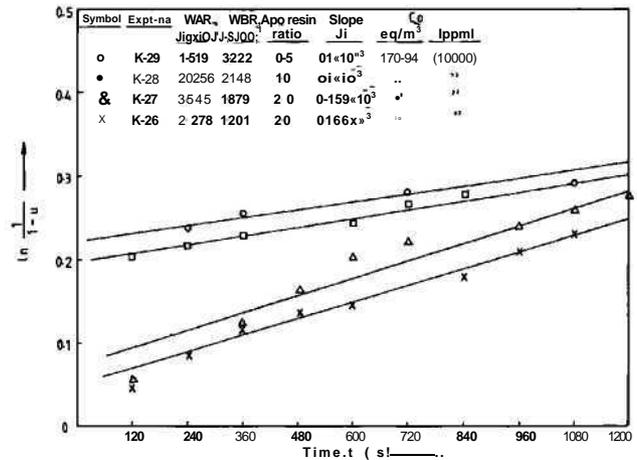


Fig. 5. Case I model for fluid film SURR. WBR controlling—NaCl and mixed resin system.

### 7.1. Limiting cases

#### 7.1.1. Case I: Sorption of acid on WBR is the slowest step

The effect is observed when WAR/WBR > 0.39.

As mentioned earlier, WBR drives the salt uptake in resin mixture, hence influence of WBR becomes all the more important. It has also been mentioned already that salt uptake takes place near neutral conditions, it implies that extremely low concentrations of acid exist in solution and it is being taken up by WBR continuously.

It is expected that with dilute solution concentrations the rate of adsorption will be film diffusion controlled (Helfferich, 1962). The following Eq. (2), is expected to correlate the experimental data for this situation:

$$\ln(1-u) = k_m C_a = Q_{Be} \times 3RP_B \times t \tag{2}$$

(see Appendix A).

(i) *Mixed resins and sodium chloride system:* In  $\ln(1-u)$ , as a function of time was plotted for various experimental runs as shown in Figs. 5 to 7. In Figs. 5 and 6, straight lines do not pass through origin. It may be recalled that in the actual experimental condition the concentration of solution is changing, fractional saturation of WAR is also changing. After a brief 'initial period' the rate of change of solution concentration as well as fractional saturation of WAR, would decrease, i.e. a 'pseudo-steady state' would be established. Thereafter the Eq. (2), should co-relate the data. In other words the plot of  $\ln(1-u)$  vs.  $t$  is not likely to pass through origin and straight line behaviour is observed in the 'later period'. It is expected that the 'initial period' for which the model does not hold good, will in general, decrease with increase in WAR/WBR ratio. This will be reflected by the intercept of the plot.

In  $\ln(1-u)$  vs.  $t$ , as larger the intercept, larger the 'initial period' (during which the model is not likely to hold good). This is evident in Figs. 5 and 6.

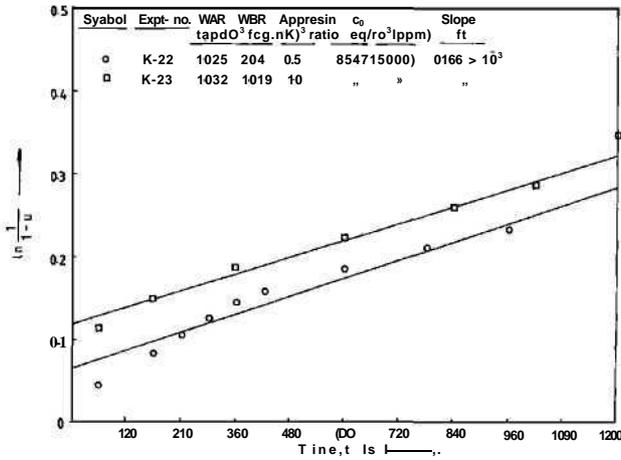


Fig. 6. Case I model for fluid film SURR. WBR controlling—NaCl and mixed resin system.

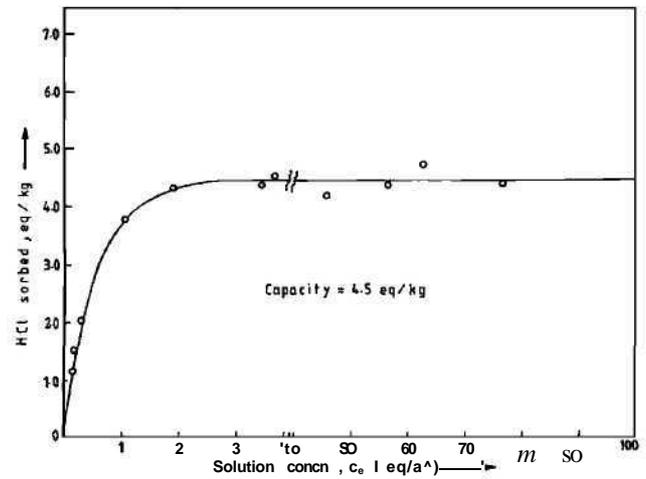


Fig. 8. Experimental equilibrium data for adsorption of hydrochloric acid on weakly basic resin (WBR).

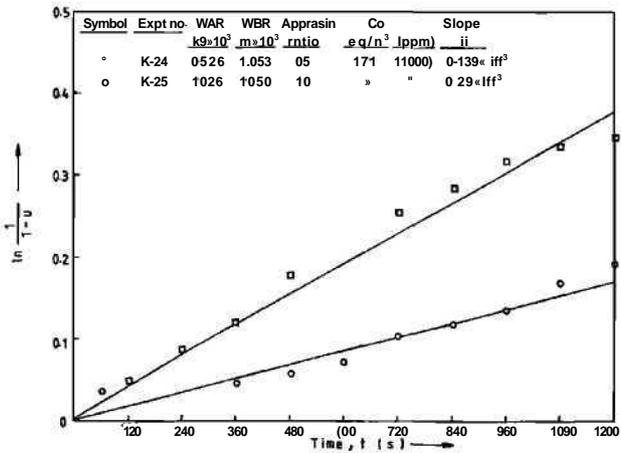


Fig. 7. Case I model for fluid film SURR. WBR controlling—NaCl + mixed resin system.

Fig. 7 shows that when initial concentration of salt is equal to 1000 ppm, the 'initial period' is almost zero. It indicates that at low solution concentrations, effect of both (WBR as well as initial salt concentration) are important. From Eq. (2),

$$\text{Slope} = k_m C_a = Q_{Be} \times 3 = R_{PB}$$

To determine the correctness of the proposed model and values of mass transfer coefficient  $k_m$  (and film thickness  $d$ ), values of individual parameters like  $R_{PB}$  and  $q_{Be} = C_b$  should be known. The average particle size of WBR particles is  $0.33 \times 10^{-3}$  m.

(ii) *Determination of  $q_{Be} = C_a$ :* As observed during experimentation, the concentration of  $H^+$  ions, in mixed resins and salt systems, is extremely low and not measurable. But for a system having WBR in contact with acid solution of such low concentration, the amount of  $H^+$  ions picked up per unit weight of WBR, will be very low (Fig. 8, Equilibrium Stud-

ies). However in the mixed resins and salt systems, a little amount of  $H^+$  ions are sorbed by WBR. This could become possible because of presence of WAR. Therefore it can be stated that there is an equilibrium between the generation of  $H^+$  ions (due to the interaction of salt and WAR) and sorption of the same by WBR, with the net result that concentration of  $H^+$  ions in the bulk fluid phase is extremely low.

From Fig. 2 Section 5 it is seen that for particular concentration of sodium chloride in the bulk fluid phase, the amount of  $H^+$  ions picked up per unit weight WBR increases with the ratio WAR/WBR. For example, at NaCl solution concentration of  $55 \text{ eq/m}^3$  (Fig. 2),  $q_{Be}$ , (at WAR=WBR = 0.5) is equal to  $2.5 \text{ eq/kg}$  and  $q_{Be}$ , (at WAR=WBR = 1) is equal to  $3.66 \text{ eq/kg}$ .

The corresponding  $H^+$  ion concentration in the WBR + HCl system from Fig. 8, are  $0.30$  and  $0.80 \text{ eq/m}^3$ , respectively, and these  $H^+$  ions concentration from WBR + HCl system are taken as values of  $C_a$  for mixed resin and salt systems. The values of  $C_a$  determined by this procedure are sort of 'latent' concentration of  $H^+$  ions which would be in equilibrium with WBR at any point of time during the process of salt uptake. And its value can only be approximated from independent studies of WBR and acid. As WBR and HCl system equilibrium curve (Fig. 8) is linear at low acid concentration, the value  $q_{Be} = C_a$  is constant and equal to  $3 = 0.5 \times 1.03 \times 10^{-3} = 6.8 \times 10^{-3}$  (where  $q_{Be} = 3 \text{ eq/kg}$ ,  $C_a = 0.5 \text{ eq/m}^3$ ,  $p_B = 1.03$ ).

Also,  $k_m = \frac{R_{PB}}{d}$

Table 4 gives the values of mass transfer coefficients  $k_m$  and film thickness for various experimental runs. Ideally there should have been a unique value of film thickness as it is a function of hydrodynamic conditions (i.e. agitation only). However the values are varying in a narrow range. These film thickness values are close to the ones obtained for sorption of NaOH by WAR at low solution concentrations. It may be noted that resistance to salt uptake, other

Table 4

Case-1 (model) values of mass transfer coefficients and film thickness. Mixed resin and sodium chloride system

Expt. no.	WAR (kg X 10 <sup>-3</sup> )	WBR (kg x 10 <sup>-3</sup> )	Resin ratio	Mass transfer coeff. (k <sub>m</sub> x 10 <sup>-3</sup> m=s)	5B (urn)	Slope (s <sup>-1</sup> )
Initial solution concentration, C <sub>0</sub> = 10,000 ppm (170.094 eq=m <sup>3</sup> )						
K-29	1.519	3.222	0.50	0.068	49	0.10 x 10 <sup>-3</sup>
K-28	2.148	2.026	1.00	0.068	49	0.10 x 10 <sup>-3</sup>
Initial solution concentration, C <sub>0</sub> = 5000 ppm (85.470 eq=m <sup>3</sup> )						
K-22	1.025	2.043	0.50	0.112	30	0.166 x 10 <sup>-3</sup>
K-23	1.032	1.049	1.00	0.112	30	0.166 x 10 <sup>-3</sup>
Initial solution concentration, C <sub>0</sub> = 1000 ppm (17.100 eq=m <sup>3</sup> )						
K-24	0.526	1.054	0.50	0.094	36	0.139 x 10 <sup>-3</sup>
K-25	1.026	1.051	1.00	0.197	17	0.290 x 10 <sup>-3</sup>

Table 5

Experimental conditions for very low resin ratio kinetic runs

S. no.	Expt. no.	WAR (kg x 10 <sup>-3</sup> )	WBR (kg x 10 <sup>-3</sup> )	Resin ratio	NaCl/initial soln. concn. (eq=m <sup>3</sup> )	(M <sup>-1</sup> )
1	R-2	0.781	3.960	0.190	89.31	(5225)
2	R-3	0.381	2.226	0.170	88.20	(5160)
3	R-5	0.202	4.097	0.050	88.37	(5170)
4	R-6	0.076	2.126	0.035	86.32	(5050)

Table 6

Analysis of experimental run R-3 by homogeneous sphere model

S. no.	Experimental		Theoretical ( Helfferich, 1962)	
	t (s)	u	T	ijt
1	122	0.300	0.0095	0.770 x 10 <sup>-4</sup>
2	171	0.370	0.0150	0.870 x 10 <sup>-4</sup>
3	236	0.440	0.0250	1.060 x 10 <sup>-4</sup>
4	336	0.500	0.0375	1.116 x 10 <sup>-4</sup>
5	495	0.560	0.0425	0.850 x 10 <sup>-4</sup>
6	764	0.635	0.0600	0.780 x 10 <sup>-4</sup>
7	997	0.660	0.0675	0.670 x 10 <sup>-4</sup>

than diffusion across WBR would also be present (total resistance concept).

7.1.2. Case II: counterdiffusion of Na<sup>+</sup> and H<sup>+</sup> ions is slowest the step

When WAR is limiting, it means that counterdiffusion of Na<sup>+</sup> and H<sup>+</sup> ions inside WAR particles and/or reaction may be controlling. This effect is pronounced when resin ratio WAR=WBR<sup>0.39</sup>. In this case, WAR will get more saturated as compared to WBR. Hence in this range, WAR will be limiting the salt uptake, if salt solution concentration is adequate. However, WBR will still be driving the reaction and will act as sink.

Four experimental runs were available in this range, which were analysed for this effect. Table 5 shows experimental conditions of these runs. The experimental data were analysed by

$$u = 1 - 6/Tt^2 \sum_{l=1}^{\infty} l^{-2} \exp[(-n^2Dt)/R^2_{PA}] \tag{3}$$

(see Appendix B).

From experimental values of t and u, dimensionless time z (=tD=R<sup>2</sup><sub>PA</sub>) was found out from solution of this equation from the literature (Helfferich, 1962). Table 6, gives the analysis of one experimental run (R-3) by this method. It is evident that we do not have a unique value of z/t(=D/Rj><sub>A</sub>). The values of z/t range from 0.67 x 10<sup>-4</sup> to 1.116 x 10<sup>-4</sup> s<sup>-1</sup>. Data for other runs were also analysed and those also did

not yield any unique value of z/t. Taking a representative value in the above range, say 0.85 x 10<sup>-4</sup> s<sup>-1</sup> the value of D<sub>r</sub> was calculated, i.e. z/t=D<sub>r</sub>/R<sup>2</sup><sub>PA</sub> = 0.85 x 10<sup>-4</sup> s<sup>-1</sup>, R<sub>PA</sub> = 0.44 x 10<sup>-4</sup> m, D<sub>r</sub> = 1.64 x 10<sup>-11</sup> m<sup>2</sup>=s. This value is order of magnitude lower than expected for diffusion in ion exchange resins. This suggests that counter-diffusion of Na<sup>+</sup> and H<sup>+</sup> ions in WAR is not the controlling resistance. It may be pointed out that this model assumes the instantaneous generation of H<sup>+</sup> ions from reaction between Na<sup>+</sup> ions coming from the solution and -COOH group of the ion exchange matrix. However it is not necessary that generation of H<sup>+</sup> ions is fast.

The experimental data were analysed by homogeneous sphere model.

7.1.3. Case III: generation of H<sup>+</sup> ions inside WAR particles or dissociation of-COOH group is the slowest step

For very low values of WAR/WBR the generation of H<sup>+</sup> ions inside WAR particles will be limited by amount of WAR. It is also expected that the rate of generation of H<sup>+</sup> ions will depend upon the concentration of salt in the solution.

Experiments R-2, R-3, R-5 and R-6 (WAR/WBR in range of 0.035-0.19) and experiments K-24, K-25 (C<sub>0</sub> << 1000 ppm for NaCl system) were analysed with the help of

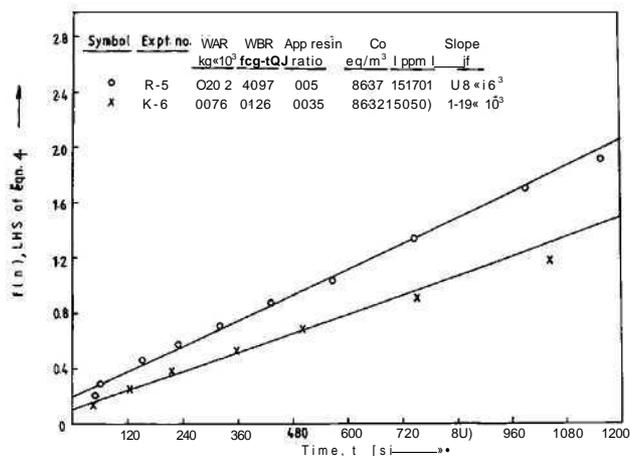


Fig. 9. Case III model: generation of  $H^+$  ions inside war particles controlling NaCl and mixed resin system (V-low—WAR/WBR).

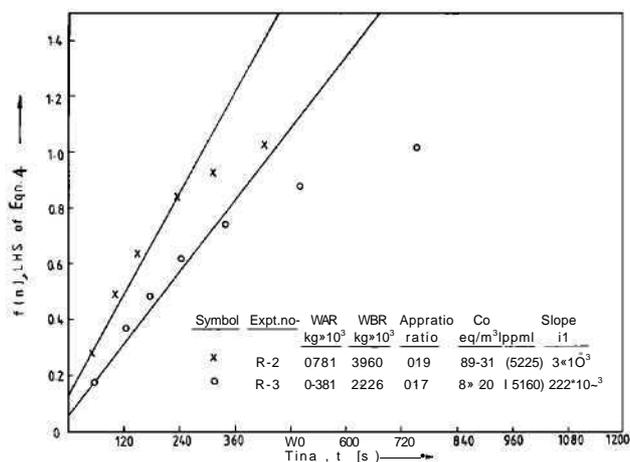


Fig. 10. Case III model: generation of  $H^+$  ions inside war particles controlling NaCl and mixed resin system (V-low—WAR/WBR).

this approach. Eq. (4), is expected to correlate the experimental data

$$\ln \left( \frac{1 - U}{1 - XU} \right) = k_r C_0 t \quad (4)$$

(see Appendix C).

The left-hand side (LHS) of Eq. (4), was plotted as a function of time as shown in Figs. 9 and 10. The experimental points fall on the straight lines but do not pass through origin for a brief initial period. It indicates the existence of other resistances as well. It may be noted that in Eq. (4), the underlying assumption is that salt solution penetrates WAR particles instantaneously,  $H^+$  ions generated diffuse out rapidly and the acid thus produced in the bulk fluid phase is adsorbed very quickly. Since all these steps, will take finite time, this is reflected in the intercept of these figures. From the slopes of these straight lines, values of reaction rate parameter were obtained (Table 7). The values of  $k_r$  are in close range and indicate that dissociation of -COOH in WAR is the controlling step. The experimental runs K-24

Table 7

Case III (model): values of reaction rate parameter  $k_r$

s. no.	Expt. no.	WAR (kg $\times 10^3$ )	WBR (kg $\times 10^3$ )	Resin ratio	Reaction rate $k_r$ (m $^3$ =eq s)
1	R-2	0.7816	3.960	0.190	$33.60 \times 10^{-6}$
2	R-3	0.3814	2.226	0.170	$25.00 \times 10^{-6}$
3	R-5	0.2019	4.097	0.050	$16.75 \times 10^{-6}$
4	R-6	0.0760	2.126	0.035	$13.80 \times 10^{-6}$

Initial salt solution concentration approximately  $85.47 \text{ eq}=\text{m}^3$  (5000 ppm).

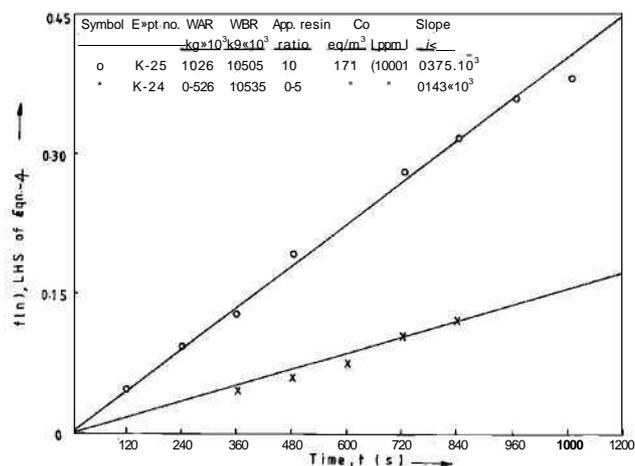


Fig. 11. Case IV model: generation of  $H^+$  ions inside war particles controlling NaCl and mixed resin system (V-low—C0).

Table 8

Case III (model): values of reaction rate parameter  $k_r$ . Mixed resin and NaCl system

S. no.	Expt. no.	WAR (kg $\times 10^3$ )	WBR (kg $\times 10^3$ )	Resin ratio	Reaction rate $k_r$ (m $^3$ =eq s)
CO = 1000 ppm = 17.1 eq=m $^3$					
1	K-24	0.526	1.054	0.50	$8.36 \times 10^{-6}$
2	K-25	1.026	1.050	1.00	$21.60 \times 10^{-6}$

and K-25 were also analysed similarly (Fig. 11, Table 8). It is observed that the plot of LHS vs.  $t$  (Eq. (4)) passes through origin. It suggests that the proposed mechanism for generation of  $H^+$  ions is controlling the rate from the beginning. The values of rate parameter obtained for these runs are in the same range as for runs R-2, R-3, R-5 and R-6. It may be noted that the experimental conditions for the two cases are widely different.

The variation in the values of  $k_r$  for different runs is perhaps because of the fact that other resistances are not necessarily equal.

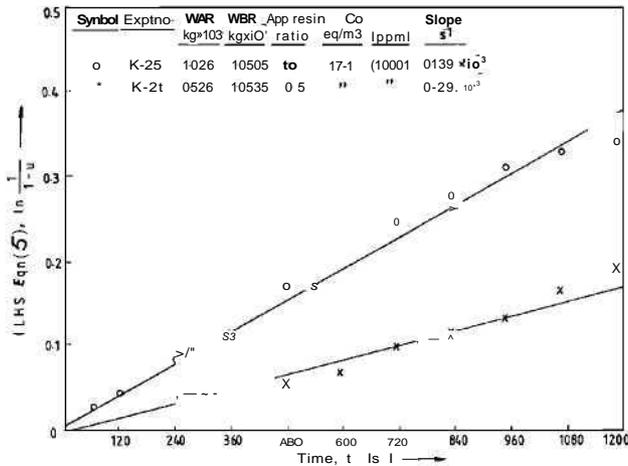


Fig. 12. Case IV model: diffusion of Na+ ions SURR. WAR particles controlling NaCl and mixed resin system.

It may be noted that from the total resistance concept, adsorption of acid on WBR would also affect the overall rate. From the above analysis it may be concluded that, generation of H+ ions by dissociation of -COOH group in WAR, by reacting with salt solutions is also a slow step. This also contributes towards the slow uptake of salt by mixed resin.

7.1.4. Case IV: diffusion of Na+ ions across the film surrounding WAR is the slowest step

This effect will be pronounced when salt solution has very low concentration and sufficient quantities of WAR and WBR are available.

Moreover this effect will be evident in the initial stages of the salt uptake process.

The following Eq. (5), is expected to correlate the data.

$$\ln(1-u) = k_{11} \times t \tag{5}$$

(see Appendix D) where  $k_{11} = 3 \times \text{WAR} \times k_{mA} / R_{PA} \rho_A V$ .

The experimental runs K-24 and K-25 have low initial salt solution concentrations of 1000 ppm and only early experimental points were considered. It may be pointed out that change in solution concentration in bulk liquid phase would be more distinct during the early stages. Also it is well established in mass transfer processes (when more than one resistances are important) that effect of film diffusion in early stages is very significant. Hence it is more relevant to analyse the experimental data of initial periods.

Plots of  $\ln(1-u)$  vs.  $t$ , for these runs show the straight lines passing through the origin (Fig. 12). From slope of straight line, the mass transfer coefficient  $k_{mA}$  was calculated and their values are presented in Table 9.

The high values of film thickness indicate that liquid film across the WAR particles may not be the controlling step, the higher values show the effect of combined resistances. It suggests that in the process of salt uptake by mixed resins,

Table 9

Case IV (model): values of mass transfer coefficients and film thickness. Mixed resin and NaCl systems

s. no.	Expt. no.	WAR (kg x 10 <sup>-3</sup> )	WBR (kg x 10 <sup>-3</sup> )	Resin ratio	Mass transfer coeff. $0 \times 10^{-3}$ m=s)	h (μm)
CO - 1000 ppm = 17.1 eq/m <sup>3</sup>						
1	K-24	0.526	1.054	0.50	0.0445	360
2	K-25	1.026	1.050	1.00	0.0470	340

$$(D_{NaCl} = 1.6 \times 10^{-9} \text{ m}^2=\text{s}).$$

the other resistances like generation of H+ ions by WAR and subsequent adsorption of acid by WBR are more important than this resistance.

8. Conclusions

- (a) Adsorption of sodium chloride or sodium sulphate is not observed, when WAR or WBR is equilibrated separately in these salt solutions. The salt uptake is observed only when both WAR and WBR are present in the salt solution. WBR actually drives the uptake of salt in the mixture of resins and acts as sink for the acid produced in the process,
  - The adsorption of salt on the mixture of resins takes place near neutral conditions.
- The maximum capacity of WAR determined by equilibrating it with NaOH was found to be 11.5 eq=kg and that of WBR with acids, was found to be 4.5 eq=kg.
- (a) The salt uptake increases with increase in each parameter, namely WAR, WBR and initial salt solution concentration.
  - In the mixture of resins and salt solution system, salt uptake capacity per unit weight of mixed resins is much lower than the capacity of individual resins determined independently and is limited by amount of WBR. The capacity of 1 kg of WAR is equivalent to 2.55 kg of WBR and this capacity matching ratio of WAR=WBR = 0.39.
  - With very low ratios of WAR/WBR it was found out that all the H+ ions in WAR could be replaced by Na+ ions.
  - With high ratios of WAR/WBR, i.e. 0.5, 1 or 2 the highest capacity in case of NaCl is 2.40 eq=kg (total weight of mixed resin basis).
- (a) The rate of salt uptake also increases with increase in each of the three parameters (WAR, WBR, CO).
  - The rate of formation of H+ ions by salt solution and WAR is exactly equal to rate of adsorption of acid by WBR.
- Generation of H+ ions inside WAR particles and their subsequent adsorption as acid on WBR are the two major controlling resistances of salt uptake.

## Notation

$a_1$	initial rate, eq s <sup>-1</sup>
$c$	$(1/I - 1)^{1/3} = a$ constant
$C$	concentration of salt solution at time $t$ , eq m <sup>3</sup>
$C_0$	initial concentration of salt solution, eq m <sup>3</sup>
$C_a$	concentration of acid in bulk fluid phase, eq m <sup>3</sup>
$C_b$	concentration of NaOH bulk fluid phase, eq m <sup>3</sup>
$C_e$	concentration of salt solution at equilibrium, eq m <sup>3</sup>
$C_{Nab}$	concentration of Na <sup>+</sup> ions in bulk fluid phase, eq m <sup>3</sup>
$C_{Nae}$	concentration of Na <sup>+</sup> ions in bulk fluid phase at equilibrium, eq m <sup>3</sup>
$C_{Nas}$	concentration of Na <sup>+</sup> ions at the surface of the particle, eq m <sup>3</sup>
$C_{as}$	concentration of acid at surface of WBR particle, eq m <sup>3</sup>
$A$	diffusion coefficient (in shrinking core model), m <sup>2</sup> s <sup>-1</sup>
$D_f$	diffusion coefficient in bulk fluid phase, m <sup>2</sup> s <sup>-1</sup>
$A$	effective diffusion coefficient in resin particle, m <sup>2</sup> s <sup>-1</sup>
$A$	diffusion coefficient of adsorbate in microspheres, m <sup>2</sup> s <sup>-1</sup>
LHS	left-hand side
$k_m$	mass transfer coefficient for acid across fluid film surrounding WBR particles, m s <sup>-1</sup>
$k_{mA}$	mass transfer coefficient for Na <sup>+</sup> ions across fluid film surrounding WAR particles, m s <sup>-1</sup>
$k_r$	reaction rate parameter, m <sup>3</sup> eq <sup>-1</sup> s <sup>-1</sup>
MR	mixed resin (oven dry basis)
$T_{ip}$	total number of resin particles per kg of WAR or WBR
$N$	number of particles of resin
$q_H$	concentration of H <sup>+</sup> ions in weakly acidic resin (WAR), eq kg <sup>-1</sup>
$q_{Na}$	concentration of Na <sup>+</sup> ions in WAR at any time $t$ , eq kg <sup>-1</sup>
$q_{Ae}$	capacity of WAR at equilibrium (specific to each experiment), eq kg <sup>-1</sup>
$q_{AT}$	total capacity of WAR with alkali (NaOH), eq kg <sup>-1</sup>
$q_{Be}$	capacity of WBR at equilibrium (specific to each experiment), eq kg <sup>-1</sup> total capacity of WBR with acids, eq kg <sup>-1</sup>
$Q_{Ae}$	equilibrium capacity of WAR ( $Q_{Ae} = q_{Ae} XPA$ ) with alkali (NaOH), eq m <sup>3</sup>
$Q_{Be}$	equilibrium capacity of WBR ( $Q_{Be} = q_{Be} xps$ ) with acids, eq m <sup>3</sup>
$r_c$	radius of microspheres, m
$RPA$	radius of WAR particles, m
$RPB$	radius of WBR particles, m
$t$	time, s
$u$	fractional attainment of equilibrium
$V$	solution volume, m <sup>3</sup>

WAR weight of weakly acidic resin (oven dry basis), kg  
 WBR weight of weakly basic resin (oven dry basis), kg

## Greek letters

$\delta A$	thickness of fluid film surrounding WAR particles, m
$\delta B$	thickness of fluid film surrounding WBR particles, m
$\eta_c$	$= R_c / R_{PA}$
$\lambda$	$= \frac{\text{Total sorption capacity of adsorbent}}{\text{Total adsorbate initially present in solution}}$ $= \frac{WAR q_{Ae} - WBR q_{Be}}{C_0 V} = \frac{C_0 V}{C_0 V} = 1$
$\rho_A$	density of WAR particle, kg m <sup>-3</sup>
$\rho_B$	density of WBR particle, kg m <sup>-3</sup>
$\tau$	$= t D_c = r C_2$ or $t D_p = R P 2$ dimensionless time

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## Appendix A. Case I: adsorption of acid by WBR is the slowest step: film diffusion

During experimentation it was established, that it is the adsorption of acid (generated by interaction of salt solution and WAR) on WBR, which drives the salt uptake process. Also the concentration of acid is extremely low, therefore it is likely that absorption of the acid on WBR is the slowest step.

The assumptions for this situation are as follows:

1. All particles of WBR are of equal radius— $RPB$ .
2. Concentration of acid in the bulk fluid phase is very low and also constant.
3. Diffusion inside the WBR is very fast.
4.  $C_{as} = C_a = u$  (i.e. linear equilibrium).

$$WBR \times q_{Be} du = dt = k_m (C_a - C_{as}) A, \quad (A.1)$$

where  $A$ , surface area of all particles =  $4\pi R_{PB}^2 N$ ;  $N$ , number of particles =  $n_p WBR$ ;  $n_p$ , total number of particles per kg of WBR kg<sup>-1</sup>;  $RPB$ , radius of WBR particles, m;  $k_m$ , mass transfer coefficient, m s<sup>-1</sup>;  $t$ , time, s;  $C_a$ , concentration of acid in solution, eq m<sup>3</sup>;  $C_{as}$ , concentration of acid at surface of WBR particles, eq m<sup>3</sup>.

Substituting values of  $A$  and  $N$  in Eq. (A.1)

$$WBR q_{Be} du = dt = k_m (C_a - C_{as}) n_p WBR 4\pi R_{PB}^2,$$

or

$$du=dt = k_m n_p 4nR^2_{PB}/q_{Be}(C_a - C_{as}); \tag{A.2}$$

Let

$$k_m n_p 4nR_{PB}/q_{Be} = k_2 I; \tag{A.3}$$

Eq. (A.2) reduces to

$$du=dt = k_2 I (C_a - C_{as}),$$

or

$$du=dt = k_2 I C_a (1 - C_{as}/C_a), \tag{A.4}$$

or

$$du=dt = k_2 I C_a (1 - u), \tag{A.5}$$

where

$$M = C_{as} = C_a. \tag{A.6}$$

Eq. (A.6) implies linear equilibrium behaviour, i.e. adsorbate uptake at equilibrium by adsorbent is directly proportional to concentration of adsorbate in the bulk fluid phase. This also implies reversible behaviour. This was the case in the present experimental situation.

Therefore,  $du = 1 - u = k_2 I C_a dt$ .

Integrating

$$\ln[1 - u]_0^t = -k_2 I C_a t,$$

or

$$\ln 1 - u = -k_2 I C_a t; \tag{A.7}$$

The LHS of Eq. (A.7), can be computed for different values of  $u$  and plotted as function of time  $t$ . If data fall on a straight line, it may indicate that adsorption of acid on WBR is rate controlling step in the process.

Slope of this straight line =  $k_2 I C_a$

$$\begin{aligned} k_m n_p 4nR^2_{PB} \times C_a &= q_{Be} \\ &= k_m n_p \frac{4}{3} n R_{PB} \times C_a / R_{PB} \times q_{Be}; \end{aligned} \tag{A.8}$$

where

$$n_p \frac{4}{3} n R_{PB} / q_{Be} = 1 = Q_{Be}.$$

Substituting Eq. (A.8) in Eq. (A.7) and rearranging we get

$$\ln 1 - u = k_m C_a \times 3 \times t = Q_{Be} R_{PB}. \tag{A.9}$$

Eq. (A.9) is identical to equation for film diffusion control situation ( Helfferich, 1962) in;nite volume condition and linear equilibrium behaviour.

### Appendix B. Case II: counter diffusion of Na<sup>+</sup> ions and H<sup>+</sup> ions in WAR is slowest step

This situation will arise if the steps other than this are much faster. This implies that concentration differences in bulk fluid phase are negligible and concentration gradients of Na<sup>+</sup> and H<sup>+</sup> ions in WAR are significant. Also -COOH is completely dissociated and exchange between Na<sup>+</sup> and H<sup>+</sup> ions is instantaneous.

The fundamental equation for salt uptake will be

$$(a) \text{WAR } q_{Ae} \times du=dt = \text{WAR } dq_A=dt,$$

(b)

$$q_A = \int_0^{R_p} 4\% q_A R^2 dR / \int_0^{R_p} 4\% R^2 dR, \tag{B.1}$$

or

$$q_A = 3 \int_0^{R_{PA}} q_A R^2 dR = R^3_{PA}$$

Also

$$b q_A / b t = 1 = R^2 \times d[SR/R^2 D d q_A / dR], \tag{B.2}$$

where  $D$ , diffusivity of H<sup>+</sup> ions and Na<sup>+</sup> ions inside WAR particles for binary exchange, i.e. Na<sup>+</sup> and H<sup>+</sup>

$$D = \frac{D_H D_{Na} (q_H + q_{Na})}{q_H D_H + q_{Na} D_{Na}}, \tag{B.3}$$

$q_{Na}$ ,  $q_H$ , concentrations of Na<sup>+</sup> and H<sup>+</sup> ions at a point inside WAR particle.

For Eq. (B.2),

$$IC \quad t \geq 0 \quad q_{Na} = 0;$$

$$0 < R < R_{PA};$$

$$BC - 1 \quad t \geq 0 \text{ at } R = R_{PA};$$

$$q_{Na} = q_{Ae};$$

It means that surface of WAR particles gets saturated with Na<sup>+</sup> instantaneously and concentration is same as at equilibrium condition.

$$BC - 2: \quad R = Q, \quad dq_{Na} / SR = 0$$

(radial symmetry condition).

**Assumptions:** (1) The diffusion characteristics of isotopic exchange hold good.

(2) Sum of concentration of H<sup>+</sup> ions and concentration of Na<sup>+</sup> ions at any point inside WAR is constant, i.e.  $q_{Na} + q_H = \text{constant}$ .

For the situation that  $H^+$  ions from  $-COOH$  groups are completely replaced by  $Na^+$  ions the relevant equation is given below

$$q_A = q_{Ae} = 1 - \frac{6}{n^2} \exp(-n^2 Dt) / R_{PA}^2 \quad (B.4)$$

or

$$M = 1 - \frac{6}{n^2} \exp(-n^2 Dt) / R_{PA}^2 \quad (B.5)$$

The values of experimental data ( $u$  and  $t$ ) can be introduced in this equation and values of diffusion parameter determined.

The value of  $D$  is overall effective diffusion coefficient for hydrogen ions and sodium ions in WAR for the entire exchange. This statement is being brought out for the reason that diffusion coefficient for binary exchange at a given location in ion-exchanger particle is not a constant, but depends upon the relative magnitudes of the two ions (at a given instant and which are changing with time).

### Appendix C. Case III: generation of $H^+$ ions inside WAR particles or dissociation of $-COOH$ group is the slowest step

This situation will arise when ratio  $WAR/WBR < 0.39$ ; salt solution concentration will also have a pronounced effect. Generation of  $H^+$  ions inside WAR is the slowest step and counter-diffusion of  $Na^+$  and  $H^+$  ions is faster along with other steps mentioned in mechanism.

$$WAR \times q_{Ae} \times du = dt = k_r q_{Ae} (1 - u) WAR \times C \quad (C.1)$$

It may be noted that  $q_{Ae} u WAR$  represents the total  $H^+$  ions which have been generated till time  $t$ , and hence  $q_{Ae}(1 - u) WAR$  is equal to amount of  $H^+$  ions which would be subsequently generated in a given experiment. It is assumed that reaction is first order with respect to salt as well as hydrogen ions. Therefore,

$$du = dt = k_r C (1 - u), \quad (C.2)$$

where  $k_r$  reaction rate constant and  $C = C_0(1 - Xu)$ .

Therefore

$$du/dt = k_r C_0 (1 - Xu) (1 - u), \quad (C.3)$$

or

$$du = (1 - Xu) (1 - u) = k_r C_0 dt, \quad (C.4)$$

Integrating

$$1/A - 1 \ln 1 - U = 1 - Xu = k_r C_0 dt. \quad (C.5)$$

This mechanism will be valid if a unique value of parameter  $k_r$  is obtained for different experimental conditions, i.e. varying amounts of WAR, WBR and different initial solution concentrations.

### Appendix D. Case IV: diffusion of $Na^+$ ions across the film surrounding WAR particles is the lowest step

This is likely to be governing situation when initial concentration of salt in the bulk fluid phase is very low. Equation of salt uptake is

$$V dC_{Nab} = dt = WAR n_p 4n R_{PA}^2 k_{mA} \times (C_{Nab} - C_{Nas}),$$

where  $k_{mA}$ , mass transfer coefficient for  $Na^+$  ions across film surrounding WAR particles.

$$dC_{Nab} = (C_{Nab} - C_{Nas}) = WAR n_p 4n R_{PA}^2 k_{mA} dt = V; \quad (D.1)$$

$$k_{I1} = WAR n_p 4n R_{PA}^2 k_{mA} / V.$$

Therefore,

$$C_0 d(1 - Xu) / [C_0(1 - Xu) - C_{Nas}] = k_{I1} dt; \quad (D.2)$$

$$LHS = XC_0 du / [C_0(1 - Xu) - C_{Nas}].$$

The value of  $C_{Nas}$  is not known a priori. Therefore making a simplifying assumption,  $C_{Nas} = C_{Nae}$ , where  $C_{Nae}$  is concentration of  $Na^+$  ions in the bulk fluid phase at equilibrium.

From material balance of  $Na^+$  ions

$$[C_0 - C_{Nae}]V = WAR q_{Ae},$$

$$1 - C_{Nae}/C_0 = WAR q_{Ae} / VC_0;$$

$$WAR q_{Ae} / VC_0 = XC_{Nae} = C_0(1 - X). \quad (D.3)$$

Substituting Eq. (D.3) in Eq. (D.2) and rearranging

$$du = 1 - u = k_{I1} dt; \quad (D.4)$$

Integrating

$$\ln 1 - u = k_{I1} t; \quad (D.5)$$

Slope of the plot  $\ln 1 - u$  vs.  $t$  would be

$$k_n = WAR n_p 4n R_{PA}^2 k_{mA} / V, \quad (D.6)$$

$k_{I1}$  can be written as

$$k_{I1} = 3V_A k_{mA} / R_{PA} V;$$

where  $V_A$ , volume of all WAR particles;  $V$ , solution volume;  $V_A = WAR/p_A$ .

Slope

$$k_n = 3WAR k_{mA} / R_{PA} V. \quad (D.7)$$

Also

$$k_{mA} = D_{Na^+H^+} / d_A,$$

$d_A$ , film thickness surrounding WAR particle.

It may be noted that Eqs. (D.5) and (A.9) are similar however they represent completely different controlling mechanisms.

The experimental data have been analysed in the light of the foregoing discussion in the results and discussion.

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