

5 SUMMARY

When a sample of ion exchange resin is brought in contact with a solution, there may occur one or more of the four types of phenomena :

1. ion exchange,
 2. sorption of strong electrolytes,
 3. sorption of weak or nonelectrolytes,
- and 4. sorption of solvent or swelling of the resin.

In the present work, our interest has been in the first three directions.

1. Ion exchange :

Ion exchange equilibria with three types of salts, (1) strong acid-strong base salts (lithium chloride, lithium sulfate and sodium chloride), (2) strong acid-weak base salts (aniline hydrochloride) and (3) weak acid-strong base salts (sodium formate and sodium acetate), with styrene-divinylbenzene copolymer based sulfonic acid cation exchange resins of different degree of crosslinking (% nominal divinylbenzene content), 1,2,4,8,12,16 and 20, and of different particle size were studied. For the first type of salts, the value of the selectivity coefficient, K_{Li}^{H} was less in the chloride solution than in the sulfate solution. As the mole fraction of the counter ion in the resin phase, \bar{X}_M , increased, the selectivity coefficient decreased. The order of the selectivity was mostly $\text{Li} < \text{H} < \text{Na}$ in the chloride solution, while it was $\text{H} < \text{Li} < \text{Na}$ in the sulfate solution. The variation of the particle size did not have any significant

effect on the exchange equilibria within the range studied. For the second type of salts, the selectivity coefficient first increased and then decreased as the degree of crosslinking and the mole fraction of the counter ion in the resin phase increased. This behaviour was different from that observed for the first type of salts. For the third type of salts, the % exchange was high and increased to almost complete exchange as the ratio of the resin concentration to the salt concentration increased, for the resins of different degree of crosslinking studied.

2. Sorption of strong electrolytes :

The separation of naphthalene-2-sulfonic acid from sulfuric acid was attempted by the method based on solubility of their barium salts but it was not found to be quantitative.

The ultraviolet absorption spectrum of naphthalene-2-sulfonic acid and its sodium and ammonium salt were studied and it was observed that acid (sulfuric acid or hydrochloric acid upto 0.05 N), alkali (sodium hydroxide upto 0.05 N) and salt (sodium sulfate upto 0.005 N) have no effect on the maxima.

The sorption of strong electrolytes, naphthalene-2-sulfonic (NF) acid, sulfuric acid and hydrochloric acid in aqueous solution was studied on a strongly acidic cation exchange resin, a weakly acidic cation exchange resin, a strongly basic anion exchange resin and a weakly basic anion exchange resin with a view to obtain the separation of NF acid from sulfuric acid and hydrochloric acid. It was

observed that all the resins, except weakly acidic cation exchange resin were unsuitable for such separation. Next sorption of these acids in a column of monofunctional carboxylic acid cation exchange resin (of different degree of crosslinking : 2.5, 6, 8, 11 and 16) was studied. It was observed that, while the quantity of the acid sorbed per equivalent of the resin decreased as the degree of crosslinking, X , increased, the ratio (NF acid sorbed per equivalent of the resin / sulfuric acid or hydrochloric acid sorbed per equivalent of the resin) increased, reached a maximum and then decreased as X increased. The sorption of sulfuric acid and hydrochloric acid was essentially same.

Next, the resin of degree of crosslinking as 6 was tried for the column separation of binary mixtures of NF acid with the other two and fair degree of separation was achieved.

3. Sorption of weak and nonelectrolytes :

The ultraviolet absorption spectrum of phenylacetic acid in aqueous solution was studied and it was observed that the presence of aliphatic monocarboxylic acids studied have no significant effect.

(A) Sorption of monocarboxylic acids of the type $R-CH_2COOH$.

(a) Sorption equilibrium : The sorption equilibria of nine monocarboxylic acids, acetic, propionic, n-butyric, n-valeric, n-caproic, ^{n-caprylic,} isobutyric, isovaleric and phenylacetic acid, on three styrene divinylbenzene copolymer based sulfonic acid cation exchange resins of degree of crosslinking as 4, 8 and 12 were studied. It was observed that the acid

sorbed, per unit capacity of the resin was directly proportional to the equilibrium concentration of the acid, inversely proportional to the degree of crosslinking of the resin and related to the structure of the acids.

The value of $\log BX$ for the acids studied may be represented by

$$\log BX = 0.24 n_c + 0.04 n_b + 0.92 n_r - 0.30$$

where

$$B = (C_0 - C_e) / C_e \cdot C_r$$

C_0, C_e = the initial and the equilibrium concentration of the acid in gram equivalents per liter,

C_r = capacity of the air dry resin added per liter of the acid solution,

X = the degree of crosslinking of the resin,

n_c, n_b, n_r = the number of the straight chain and the branched chain carbon atoms and the benzene ring in R of the acid molecules $R-CH_2COOH$.

(b) Separation studied :

The resin of the degree of crosslinking as four was applied for the column separation of such acids from each other in binary mixtures. It was observed that as the value of B for an acid in the homologous series increased, the elution band became broader and reduced in height and the effluent volume before the breakthrough of the acid increased. The separation of the two acids in binary mixture was obtained, provided the two acids differ by at least two carbon atoms in the straight chain length. This was

illustrated by the separation of the binary mixtures of acetic and n-valeric, acetic and n-caproic, acetic and phenylacetic, propionic and n-caproic, propionic and phenylacetic, isobutyric and n-caproic, isobutyric and phenylacetic, n-butyric and phenylacetic and isovaleric and phenylacetic acid.

(B) Sorption equilibrium in organic solvents :

Sorption equilibria of some of above monocarboxylic acids of $R-CH_2COOH$ type on the resin of the degree of crosslinking as four in seven organic solvent were studied.

The sorption equilibria may be treated in term of the equation.

$$S = B C_e^{\alpha}$$

where B and α are constants.

The values of $\log B$ and α for the solvents used may be given by the following equations.

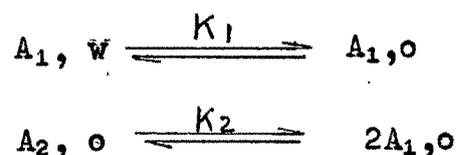
<u>Solvent</u>	<u>Equation</u>
n-Hexane	$-\log B = 0.06 + 0.38 n_c + 0.44 n_r$ $\alpha = 0.46 - 0.03 n_c - 0.00 n_r$
Cyclohexane	$-\log B = 0.03 + 0.40 n_c + 0.55 n_r$ $\alpha = 0.49 - 0.04 n_c - 0.02 n_r$
Benzene	$-\log B = (0.36 - 0.01 n_{Me}) + (0.23 + 0.02 n_{Me}) n_c$ $+ (0.80 - 0.06 n_{Me}) n_r$ $\alpha = (0.54 - 0.05 n_{Me}) + (0.03 + 0.00 n_{Me}) n_c$ $+ (-0.19 + 0.03 n_{Me}) n_r$
Toluene	
Xylene	

The results obtained indicate that the values for o-, m-, and p-xylene are essentially same and the contribution of side chain carbon atom is dependent on the position of the straight chain carbon atom to which the side chain carbon atom is attached. The over-all energy of interactions is essentially an additive function in such (*homologous series*) cases. However, when a wider range of solutes is considered in different solvents, constitutive effects also become significant.

(C) Distribution equilibrium :

The distribution equilibria of some of these acids of R-CH₂COOH type between water and seven organic solvents were studied at room temperature ($\sim 28 \pm 2^{\circ}$) with a view to compare distribution equilibrium and sorption equilibrium.

For the distribution of organic acids studied, following equilibria may be considered.



where K_1 is distribution constant and K_2 is dissociation constant of A_2 into $2A_1$; hence,

$$C_o / C_w = K_1 + (2K_1^2 / K_2) C_w$$

In cases, where the second term of the above equation is much larger than the first,

$$C_o^{1/2} / C_w = (2 / K_2)^{1/2} K_1 = K$$

where K is a constant (it is assumed that $K_2^{1/2}$ is not very substantially altered from acid to acid studied.).

The values of log K when the organic solvent used is n-hexane or cyclohexane and log K_1 when the organic solvent used is benzene, toluene or o-m- or p-xylene, may be given by the following equations.

<u>Solvent</u>	<u>Equation</u>
n-Hexane	$-\log K = 0.875 - 0.58 n_c - 1.42 n_r$
Cyclohexane	$-\log K = 0.875 - 0.585 n_c - 1.45 n_r$
Benzene	$-\log K_1 = (1.86 + 0.08 n_{Me}) - (0.58 + 0.005 n_{Me}) n_c$ $- (1.55 + 0.03 n_{Me}) n_r$
Toluene	
Xylene	

The values of log K and log K_1 calculated from above equation are in good agreement with the values obtained experimentally. The values are essentially same in o-, m-, and p-xylene. The comparison of sorption equilibria and distribution equilibria indicates that there is a close similarity between the two.

D. Sorption of coumarins :

The ultraviolet absorption spectra of some substituted coumarins in aqueous methanol (10 % by volume) and methanol were compared. The general shape of spectrum was same in aqueous methanol and in methanol but definite small change in the values of ϵ and maxima was observed.

The sorption equilibria of coumarin on three styrene-divinylbenzene copolymer based sulfonic acid cation exchange resins of degree of crosslinking as 4, 8, and 12 in water and aqueous methanol (10 %, 20 %, 30 % and 40 % by volume) and ten substituted coumarins on the resin X4 in aqueous methanol (10 %, 20 %, 30 % and 40 % by volume) were studied.

The effect of crosslinking, X, for the sorption of coumarin may be given by the equation :

$$\log B = \log \beta - \gamma \log X$$

where β and γ are constants.

The effect of percent methanol content, P, on the sorption of coumarin and ten substituted coumarins may be given by the equation :

$$\log (P+10) = a-b.B$$

where a and b are constants. The order of sorption was found to be as : coumarin and hydroxy coumarin < methyl or methoxy coumarin .

The separation of some binary mixtures of coumarins with a sulfonic acid cation exchange resin of relative degree of crosslinking as four was studied. The elution band became broader and reduced in height and the breakthrough volume increased as the value of B increased. The complete separation of coumarin and hydroxycoumarins from methyl and methoxycoumarins was obtained in the cases studied.

Papers :

A. Published :

1. Molecular sorption on ion exchange resins : Effect of

- degree of crosslinking of resin ; D.J.Patel and S.L. Bafna., Ind.Eng.Chem.Prod.Res.and dev. 4,1 (March 1965)
2. Sorption of strong electrolytes on ion exchange resins : Separation of binary mixtures of some strong acids ; D.J. Patel and S.L.Bafna., J.Ind.Chem.Soc., 42, 523 (1965).
 3. The selectivity coefficient of sulfonic acid cation exchange resins in sulfate solution ; S.S.Kanhere, D.J.Patel, R.S.Shah, R.A.Bhatt and S.L.Bafna., J.Ind. Chem.Soc., 42, 589 (1965).

B. Communicated :

1. Ion exchange equilibrium studied with some weak acids-strong base salts : D.J.Patel, R.A.Bhatt and S.L.Bafna., J.Ind.Chem.Soc.,
2. Separation of coumarins : D.J.Patel and S.L.Bafna, Nature.