Part I : INTRODUCTION

1. Scope and object
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3. Ion exchange equilibria
4. Sorption of weak and nonelectrolytes

1.

SCOPE AND OBJECT :

The scope of the studies here, of which this is a part, is to study the exchange and sorption behaviour of ion exchangers which may also be of interest towards the applied aspect.

The object of this study is to undertake such studies with cinchona alkaloids and coumarins.

2.

ION EXCHANGE MATERIALS : (1-10)

Introduction :

Ion exchange materials are of a wide variety. These may be inorganic or organic and of different shape and size. The common general structural principle is a framework with electric surplus charge and mobile counter ions. However, the various types of materials behave markedly differently.

Inorganic ion exchange materials :

Most natural ion exchange materials are crystalline aluminosilicates with cation exchange properties. The zeolites have a rigid three-dimensional framework structure with cavities and channels permeable to counter ions. Clays have a layer structure and the counter ions move in between the layers. Glauconites have a dense, three-dimensional framework structure and the exchange can occur essentially only at the crystal surface. A few minerals such as apatite can act as natural inorganic anion exchangers.

Synthetic aluminosilicate cation exchangers have been prepared by fusion and precipitation methods. Recently, zeolites with regular crystal structure have been prepared. These are useful as molecular sieves as these can sorb small molecules, but exclude molecules which may be larger than the channel width. Interesting cation and anion exchangers, have also been prepared from zirconium and tin hydroxides.

Organic ion exchangers :

Organic ion exchange resins are the most significant of the ion exchange materials. These are gels and the matrix consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains. The ionic groups attached to the matrix may be of various types such as,

$$-SO_3^- \quad -COO^- \quad -PO_3^{--} \quad -AsO_3^{--}$$

for cation exchangers and

$$-NH_3^+ \quad >NH_2^+ \quad >N^+< \quad >S^+$$

for anion exchangers. Hence, ion exchange resins are crosslinked polyelectrolytes. They are insoluble, but have a limited swelling in water, depending on the crosslinking. The ion exchange behaviour of the resins is mainly dependent on the nature of the fixed ionic groups.

Certain coals are natural weak acid cation exchangers. Others may be converted into ion exchangers by chemical treatment, such as sulfonation. Many other natural or synthetic materials can act as ion exchangers or can be converted into ion exchangers, by introducing fixed ionic groups or by crosslinking. Ion exchange papers and phosphorylated cotton are of interest.

Commercial ion exchangers are insoluble solids. Recently liquid ion exchangers, such as long chain aliphatic amines and fatty acids or alkyl phosphates have become of great interest.

Organic synthetic resins in general, have superior chemical and mechanical stability, exchange capacity, exchange rates and versatility. Inorganic materials possess better thermal stability and resistance to radiation.

Preparation :

A wide variety of organic ion exchange resins have been prepared and some are available commercially under various trade names. Tables (2.1 and 2.2) give the trade names and the manufacturers of commercially available ion exchange resins.

The synthesis of ion exchange resin should yield a three-dimensional, crosslinked matrix of hydrocarbon chains carrying ionic groups. The resins can be prepared by condensation polymerisation or addition polymerisation and the ionogenic groups can be introduced, before, during or after the polymerisation. These groups may be of one or more types giving monofunctional or multifunctional cation exchange or anion exchange or amphoteric resins.

Most of the earlier cation exchange resins were condensation products of phenol derivatives and aldehydes.

Most of the present commercial resins are addition polymers prepared from vinyl monomers. These resins have a better chemical and thermal stability than the condensation polymers and their degree of crosslinking and particle size can be more easily controlled.

Table 2.1

Some common commercial cation exchange resins

Matrix	Ionic group	Trade name	Manufacturer	Physical form	Remarks
Crosslinked polystyrene.	$-SO_3^-$	Amberlite IR-120	Rohm and Haas Co.	Spherical beads	Standard resin, 8 % DVB.
Strongly acidic.		Amberlite 200	Rohm and Haas Co.	Sph.Beads.	Higher mech.and chem.stability.
		Amberlyst 15	Rohm and Haas Co.	Sph.Beads.	Macroreticular resin.
		Dowex 50	Dow Chemical Co.	Sph.Beads.	Dowex 50 X 2 has 2 % DVB etc.
		Imac C-12	Activit Hollands.	Sph.Beads.	Standard resin, 8 % DVB.
		Permutit Q	Permutit Co.,U.S.A.	Sph.Beads.	Standard resin.
		Zeo-Karb 225	Permutit Co.,England	Sph.Beads.	Standard resin, 8 % DVB.
Vinyl addition polymers.	-COOH	Amberlite IRC-50	Rohm and Haas Co.	Sph.Beads.	

Table 2.1 (Continued)

Matrix	Ionic group	Trade name	Manufacturer	Physical form.	Remarks
Weakly acidic		Duolite CS-101	Chemical Process Co.	Sph.Beads.	
		Zeo-Karb 226	Permutit Co.England.	Sph.Beads.	
Vinyl addition polymers.		Permutit C	Permutit A.G. W.Germany.	Sph.Beads.	
Weakly acidic		Permutit H-70	Permutit Co., New York.	Sph.Beads.	
Phenolic	$-SO_3^-$	Duolite C-10	Chemical Process Co.	Granules.	More porous
		Zeo-Karb 215	Permutit Co.England.	Granules.	
	-COOH	Duolite CS-100	Chemical Process Co.	Granules.	
		Permutit H	Permutit Co., New York.	Granules.	
		Zeo-Karb 216	Permutit Co., England.	Granules.	

Table 2.2

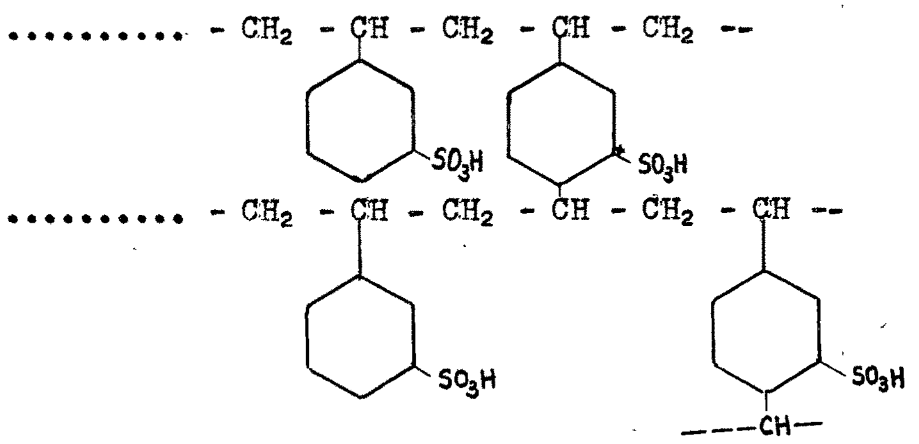
Some common commercial anion exchange resins

Matrix	Ionic group	Trade name	Manufacturer	Physical form	Remarks
Crosslinked Polystyrene	$-N(alkyl)_3^+$	Amberlite IRA-400	Rohm and Haas Co.	Spherical Beads.	Standard resin, 8% DVB.
		De-Acidite FF	Permutit Co., England.	Sph.Beads.	Standard resin, 7-9% DVB.
		Dowex 1	Dow Chemical Co.	Sph.Beads.	Standard resin, Dowex 1-X8.
		Dowex 21 K	Dow Chemical Co.	Sph.Beads.	Improved mech. Stability.
		Duolite A-101	Chemical Process Co.	Sph.Beads.	Improved resins.
		Permutit S-1	Permutit Co., New York.	Sph.Beads.	
	$-N(alkylol)-(alkyl)_2^+$	Amberlite IRA-410	Rohm and Hass Co.	Sph.Beads.	Standard resin, (∽ 6 % DVB)
		Dowex 2	Dow Chemical Co.	Sph.Beads.	Standard resins, Dowex 2-X8.
		Duolite A-102	Chemical Process Co.	Sph.Beads.	Improved resins.
		Permutit S-2	Permutit Co., New York.	Sph.Beads.	

Table 2.2 (Continued)

Matrix	Ionic group	Trade name	Manufacturer	Physical form	Remarks
”	Weak base Amino groups	Amberlite IR-45	Rohm and Hass Co.	Sph.Beads.	
		De-Acidite M	Permutit Co., England.	Sph.Beads.	Polyamine groups.
		De-Acidite G	Permutit Co., England	Sph.Beads.	$-N(C_2H_5)_2$ groups only
		Dowex 3	Dow Chemical Co.	Sph.Beads.	
Condensation polymers.	$-N(alkyl)_3^+$	Imac S-3	Activit Holland	Granules.	Highly porous resin.
	Weak base Amino groups	Amberlite IR-4B	Rohm and Haas Co.	Granules.	
		Duolite A-2	Chemical Process Co.	Granules.	
	Strong and weak base groups.	Permutit A	Permutit Co., New York.	Granules.	

The monofunctional sulphonic acid cation exchange resins available are crosslinked polystyrenes with sulphonic acid groups, introduced by sulphonation of the polymer. The crosslinking agent used is divinylbenzene. Amberlite IR-120, Dowex 50, Nalcite HCR, Permutit Q, Duolite C-20 and C-25 and Lewalit S-100 are resins of this type. The structure may be imagined as :



Pure divinylbenzene is not readily available ; hence the resins are prepared with a commercial product consisting of a mixture of the different divinylbenzene isomers (about 40 to 55 %) and ethylstyrene (about 45 to 60 %). Ethylstyrene is also incorporated into the matrix.

By varying the divinylbenzene content, the degree of crosslinking can be adjusted in a simple and reproducible manner. The nominal DVB content is used to indicate the degree of crosslinking ; it refers to mole percent of pure divinylbenzene (not of the commercial product) in the polymerisation mixture. Resins with low degree of crosslinking, swell strongly and are soft and gelatinous. Resins with high DVB content swell much less and are tough and mechanically more stable.

The copolymer beads are prepared by the pearl polymerisation technique. The monomers, from which stabilisers have been removed, are mixed and a polymerisation catalyst, such as benzoylperoxide is added. The mixture is then added to a thoroughly agitated aqueous solution at a required temperature (usually 85° to 100° C). The mixture forms small droplets, which remain suspended. A suspension stabiliser (gelatin, polyvinylalcohol etc.) in the aqueous phase prevents agglomeration of the droplets. The size of the droplets depends mainly on the nature of the stabilizer, the viscosity of the solution and the agitation and can be varied within wide limits. The polymer is obtained in the form of fairly uniform beads.

The sulphonation of the beads is simple, if proper precautions are taken. The cracking of beads may be avoided by first swelling the beads in an organic solvent such as toluene, nitrobenzene etc. It is advisable to transfer the sulphonated beads first to a highly concentrated electrolyte solution, which causes less swelling and then to dilute the solution stepwise. Sulphonation with concentrated sulphuric acid or chlorosulphonic acid results in practically complete monosulphonation of all the benzene rings.

Highly porous, 'macromolecular ion exchange resins' are prepared by a variation in the conventional pearl polymerisation technique. An organic solvent, which is a good solvent for the monomers, but a poor solvent for the polymer is added to the polymerisation mixture. As polymerisation progresses, the solvent is squeezed out by the growing copolymer regions. In this way, spherical beads are obtained with wide pores which permit access to the interior of the beads even when nonpolar solvents are used. The recent Amberlyst ion exchange resins are of this type.

Cation exchangers with specific preference for certain cations can be made by introducing groups which form strong complexes, preferably chelates with these cations. Resins with chelating iminodiacetic acid are now commercially available.

Most of the earlier anion exchange resins were condensation products of aromatic or aliphatic amines and aldehyds, dihaloparaffins or haloepoxides. Most of these contain weakly basic groups.

The more important anion exchangers are corss-linked polystyrenes, into which strong or weakly basic groups are introduced by chloromethylation and subsequent amination. Reaction with tertiary alkylamines gives strong base quaternary ammonium groups and reaction with primary or secondary alkylamines or ammonia gives weak base amino groups. Anion exchangers with strong base quaternary phosphonium and tertiary sulphonium groups have also been prepared.

Amphoteric ion exchangers contain both acidic and basic groups. 'Snakecage' polyelectrolytes are a novel variety of amphoteric resins. These are prepared from conventional ion exchangers by polymerisation of monomeric counter ions within the resin.

For specific purposes ion exchangers in the form of pellets, rods, belts etc. have been prepared by cementing ion exchange particles together with an inert binder or by impregnating suitable supporting carriers.

Ion exchange membranes have been prepared by various methods. The membranes may be homogeneous or heterogenous and have become of significant interest recently, particularly for desalting of water.

References :

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3.

ION EXCHANGE EQUILIBRIA

The fundamental understanding of equilibria and kinetics is essential for fruitful utilisation of ion exchange as a practical tool. It is, therefore, not surprising that a large number of investigations, by both academic and industrial centres, have been carried out in these directions and during the past two decades, it has been possible to make significant progress towards the basic understanding of this complex problem. An important factor, for this, has been the availability of stable and monofunctional resins of known and variable structure. For these modern resins, ion exchange equilibria are fully reversible. Thus, the cation exchange equilibrium between the resin, RA, in the A form and the cations B^+ in the solution may be represented by

$$RA + B^{+}_{aq.} \rightleftharpoons RB + A^{+}_{aq.} \qquad (3.01)$$

and the selectivity coefficient, K^{B}_{A} is given by

$$K^{B}_{A} = \frac{\left[\bar{B}^{+}\right]\left[A^{+}\right]}{\left[\bar{A}^{+}\right]\left[B^{+}\right]} \qquad (3.02)$$

where $\left[A^+\right]$ denotes the concentration of cations A^+ in solution in gm.equivalents per litre,

$\left[B^+\right]$ denotes the concentration of cations B^+ in solution in gm. equivalents per litre,

$\left[\overline{A}^+\right]$ denotes the concentration of A form of resin in gm.equivalents per litre of solution.

and $\left[\overline{B}^+\right]$ denotes the concentration of B form of resin in gm.equivalents per litre of solution.

The selectivity coefficient is significantly dependent on the chemical nature of the ions A^+ and B^+, on the resin used and often on other substances present in the solution. The principal theoritical problem is to explain and to predict selectivity quantitatively.

Formal thermodynamic treatment :

The thermodynamic equilibrium constant K_a is given by

$$K_a = \frac{\left[\overline{B}^+\right] \cdot \gamma_B \cdot \left[A^+\right] \cdot \gamma_A}{\left[\overline{A}^+\right] \cdot \gamma_A \cdot \left[B^+\right] \cdot \gamma_B} \qquad (3.03)$$

$$= K_A^B \cdot \frac{\bar{\gamma}_B \cdot \gamma_A}{\bar{\gamma}_A \cdot \gamma_B} \qquad (3.04)$$

where γ_A, γ_B are the activity coefficients for cations A^+ and B^+ in solution,

and $\bar{\gamma}_A$, $\bar{\gamma}_B$ are the activity coefficients for cations A^+ and B^+ in resin phase.

In general the ratio $\bar{\gamma}_A / \bar{\gamma}_B$ may not be equal to unity or equal to the ratio γ_A / γ_B.

Ion exchange as a Donnan membrane equilibrium :

Bauman and Eichorn in 1947 suggested that Ion Exchange resins could be regarded as concentrated solid electrolyte solutions. Hence, when a cation exchange resin is in equilibrium with an aqueous solution containing electrolytes $\overset{+}{A}\overset{-}{X}$ and $\overset{+}{B}\overset{-}{X}$, the Donnan equation may be applied to both of these electrolytes, and

$$\bar{a}_{A^+} \cdot \bar{a}_{X^-} = a_{A^+} \cdot a_{X^-} \qquad (3.05)$$

and $$\bar{a}_{B^+} \cdot \bar{a}_{X^-} = a_{B^+} \cdot a_{X^-}$$

where a_{A^+}, a_{B^+} and a_{X^-} denote the activities of ions A^+, B^+ and X^- in solution, and $\bar{a}_{A^+}$, $\bar{a}_{B^+}$ and $\bar{a}_{X^-}$ denote the activities of ions $\bar{A}^+$, $\bar{B}^+$ and $\bar{X}^-$ in the resin phase.

Hence we have, by substituting activities by products of concentration and activity coefficient,

$$\frac{\bar{y}_A \cdot y_B}{\bar{y}_B \cdot y_A} = \frac{\left[\bar{B}^+\right]\left[A^+\right]}{\left[\bar{A}^+\right]\left[B^+\right]} \qquad (3.07)$$

or

$$K_A^B = \frac{\bar{y}_A \;/\; \bar{y}_B}{y_A \;/\; y_B} \qquad (3.08)$$

calculation, using the available values of activity coefficients for concentrated solutions of electrolytes, gives value~~s~~ for selectivity coefficient, which is of right order of magnitude but is not accurate quantitatively. Also, for a given series of ions of similar type, the order of increasing affinity for the resin is, the order of decreasing activity coefficients in concentrated solution. For example, the three such series are

increasing affinity for resin, and decreasing activity coefficient in concentrated solution

1. $Li^+ < H^+ < Na^+ < K^+ \approx NH_4^+ < Rb^+ < Cs^+ < Ag^+ < Tl^+$

2. $Mn^{++} < Mg^{++} \approx Zn^{++} < Cu^{++} \approx Ni^{++} < Co^{++} < Ca^{++} < Sr^{++} < Pb^{++} < Ba^{++}$

3. $F^{-} < HCO_3^{-} < Cl^{-} < HSO_4^{-} < Br^{-} < NO_3^{-} < I^{-} < ClO_4^{-}$

naphthalene-sulphonate^{-}.

The above series show no exact correlation with any one simple property of the ions, but partial correlation with increasing atomic weight or increasing crystallographic radius has been noted. The principal factors concerned are (a) the hydrated ionic radius, which limits the coulombic interaction between ions and (b) the polarisability of the ions, determining the van der Waals attraction. These factors together control the total energy of interaction between cations and anions. The problem of explaining the selectivity is thus the problem of treating the activity in concentrated solutions - a problem which has not yet been fully solved from fundamentals.

Support for the treatment of ion exchange equilibria as simple Donnan systems is provided from the studies of influence of charge density on selectivity. According to the theory, selectivity should increase with internal ionic concentration. This has been found to be so with sulphonated polystyrene resins of different degree of crosslinking : the selectivity being greater for higher degree of crosslinking. The latter are less swollen and hence constitute more concentrated solution. Since, these results may as well be due to the effect of crosslinking per se, the point is better proved by work of Boyd on polystyrene resins in which the crosslinking was kept constant, but the degree of sulphonation was varied. This point is further more clearly proved by Deuel from work on soluble (noncrosslinked) polystyrene sulphonic acids of different degrees of esterification. The conclusion, therefore seems well established that interionic forces inside the resin are a major factor in determining selectivity.

Swelling energy theory :

Gregor, in 1951 pointed out that the influence of the elastic properties of the resin should be taken into consideration. The sorption of water causes the polymer network to stretch and set up an internal swelling pressure (actually tension), π, which has exactly the same thermodynamic effect as an externally applied osmotic pressure - it increases the chemical potential of any species, i, inside the resin, by an amount $\pi \overline{V}_i$, where $\overline{V}_i$ means the partial molar volume of i in the resin. Hence, the chemical potential of ions A^+ and B^+ will differ by $\pi(\overline{V}_A - \overline{V}_B)$ and the selectivity coefficient is given by

$$RT \ln K_A^B = \pi(\overline{V}_A - \overline{V}_B) \qquad (3.09)$$

Complete Donnan theory :

According to complete Donnan theory the selectivity coefficient is given by

$$\ln K_A^B = \ln (\gamma_B / \gamma_A) - \ln (\overline{\gamma}_B / \overline{\gamma}_A) + \pi (\overline{V}_A - \overline{V}_B) / RT \qquad (3.10)$$

The theory involves the plausible assumption that the chemical and mechanical work terms can be separated. It is not possible to check this equation accurately by direct experiment, its approximate validity is indicated by the work of Glueckauf and others. The method employed may be explained as follows. The term ln (γ_B / γ_A) for the solution can be calculated by the extended Debye-Huckel theory, since the external solution is quite dilute. The $\overline{\gamma}$ values can be determined by isopiestic vapour pressure measurements, on resins of very low degree of crosslinking, for which π is negligible, the assumption being made that $\overline{\gamma}$ is dependent only on the internal molality of the ions and independent of crosslinking. This assumption is certainly not accurately true, but at least the evidence supports the analogy between a swoolen resinate and an ordinary concentrated solution.

There is also the problem of calculating $\overline{\gamma}_B$ / $\overline{\gamma}_A$ ratio for the mixed resinate from the data obtained for the A and B forms separately. The assumption usually made is that the mixed resin salts follow the empirical 'Harned rule' , observed for certain pairs of salts in aqueous solution. However, this proves to be the weakest link in the chain of calculations, as the 'Harned rule' is not widely applicable and in particular, is invalid for a mixture of p-toluene-sulphonic acid and its sodium salt, substances chosen for their structural similarity to a sulphonic acid resin.

Finally, there is the problem of swelling pressure π. This has been calculated from water vapour sorption isotherms determined by the isopiestic method with resins of the same salt form but different degrees of crosslinking. The assumption is made that at equal water contents (per gm.equivalent), two resins of different crosslinking have the same chemical activity coefficients, but differ in water vapour activity on account of different swelling pressure. The free energy change on transferring a mole of water from a resin of low crosslinking ($\pi \approx 0$) to one of higher crosslinking (at the same molality) is then given by

$$\Delta G = RT \ln P_2 / P_1 \qquad (3.11)$$

where P_1 and P_2 are the equilibrium vapour pressures over the two resins, and this can be equated with the mechanical work involved in transferring the water of molar volume V_w (= 18 ml.) from a negligible pressure to one at pressure π. Hence,

$$\pi V_w = RT \ln (P_2 / P_1) \qquad (3.12)$$

Calculations have indicated that only approximate agreement with experimental values is obtained even in most favourable case of alkali metal ions. The experimental finding that K_A^B is not a true equilibrium constant but changes considerably with change in the proportion of $\bar{A}^+ : \bar{B}^+$ in the resin is qualitatively accounted for but is not accurately represented.

The conclusion to be drawn from this work is that although the equation provides a sound representation of ion exchange equilibria, it is not to be thought of as a valuable method of predicting selectivity coefficients. The chief difficulty is in assessing the important activity coefficient ratio $\overline{\gamma}_B$ / $\overline{\gamma}_A$. The influence of swelling energy is generally negligible except for highly crosslinked resins or large ions.

Other factors affecting selectivity :

(i) The sieve effect, exclusion of large ions :
Ion exchange resins exhibit 'ionic sieve' effect, but the cut-off is not sharp, as resins are expansible, and can be thought of as elastic sieves. The tension increases with the degree of crosslinking. This ionic sieve effect is somewhat off-set by the existence of an additional force of attraction between large ions and the resin framework, favouring sorption.

(ii) Sorption by van der Waals forces :

Considerable noncoulombic forces of attraction, van der Waals forces, come into play with large, particularly, organic ions. The attraction is probably,chiefly of the nature of London (dispersion) forces between the cation and the benzene rings of the resin, but ion induced dipole forces probably contribute. In some cases resins may sorb nonionic substances by van der Waals adsorption.

(iii) Semispecific effects : reversal of affinity series :

In some cases, the lyotropic series of cations is reversed or is rather different. This must be attributed to specific interaction of the cations and the resin in addition to normal forces. Such effects reduce the hope of explaining the selectivity in terms of a few simple factors.

(iv) Change of selectivity with ion fraction $\bar{\bar{X}}$ in the resin :

It is observed that K_A^B decreases markedly as the ion fraction of B, ($\bar{X}_B$) in the resin increases. In other words, the resin predominantly in the A form exhibits a greater affinity for B (compared with A) than it does when predominantly in the B form. A small decrease may be attributed to the changing extent of swelling, but it seems impossible to account for larger effects on this basis.

It may be that practical resins, particularly those of high crosslinking are microheterogeneous in structure, containing regions of different degree of crosslinking. The different regions would take up the competing ions in different proportions and small amounts of B would go at first to sites with the greatest affinity for B, whereas less favourable sites for B would be increasingly difficult to fill.

The heat of exchange :

The exchange of similar ions such as Na for K is not accompanied by a large heat change. It is usually only a few kilocalories per gram ion. This can be estimated from

$$\frac{\delta \ln K_A^B}{\delta T} = \frac{\Delta H_A^B}{RT^2} \qquad (3.13)$$

strictly, K_A^B in this equation should be the thermodynamic equilibrium constant, but approximate values may be obtained by using selectivity coefficient based on concentrations. A more rigorous thermodynamic treatment has been given by Duncan, which makes it possible to obtain heats of exchange for different stages in the replacement of A by B. Larger selectivities should, of course, result from longer heats of exchange.

Other aspects of equilibria :

(i) Sorption of water :

The swelling changes are best treated by the Donnan theory. The equilibrium state is determined chiefly by the balance between the osmotic forces on one hand- the tendency of water to enter and dilute the internal electrolyte solution - and the elastic contraction of the crosslinked chains on the other hand. The water content therefore, depends primarily on the activity coefficient of the internal ions and the degree of crosslinking of the resin. A marked contraction of a resin is usually indicative of formation of undissociated ion pairs of low activity.

(ii) Sorption of electrolytes :

The penetration of soluble electrolytes by resins is also covered by the Donnan Theory. Neglecting activity coefficients and swelling energy effects, the elementary theory gives as the condition of distribution of any permanent electrolyte X^+Y^-, between resin and external solution,

$$[\bar{X}^+]\,[\bar{Y}^-] = [X^+]\,[Y^-] \qquad (3.14)$$

An important consequence of this is that, for strong acid cation exchange resins, ions of the same sign as the resin structure are largely excluded from the resin. Determination of the actual amount of soluble electrolyte can be used to obtain the information about the activity coefficients in the resin phase. This effect is also the basis of the selective permeability exhibited by ion exchange membranes.

(iii) Sorption of nonelectrolytes (Chapter 4)

(iv) Effect of nonexchanging ions and other solutes :

The influence of nonexchanging ions and other solutes in the external solution on ion exchange equilibria is also understandable but not often quantitatively predictable. They have negligible effect, unless they alter the activity coefficients of exchangable ions to different extents. Thus there are many salts, which exist partly or almost wholly as complex ions in solution, and hence show very low activity for the simple ions.

(v) Ion exchange in nonaqueous or mixed solvents:

Ion exchange reaction can take place in some nonaqueous or mixed solvents, provided the electrolytes are appreciably soluble and ionised to some extent. Equilibrium constants are, in general, different from those in aqueous solution, but the theoretical problem of interpreting the changes due to the solvent is very complicated.

4

SORPTION OF WEAK AND NONELECTROLYTES : (1)

Sorption of nonelectrolytes :

A quantitative theory for nonelectrolyte sorption on ion exchangers has not yet been developed. However, general rules have emerged,which may explain qualitatively in terms of physical forces and interactions and, with due caution, qualitative prediction of sorption equilibria can be made.

In the absence of interactions of any kind, the molal distribution coefficient should be unity ; actually, it is rarely so and the various interactions which cause deviations from ideality are discussed in the following.

Ionic solvation and salting out :

The fixed ionic groups and the counter ions in the ion exchanger form solvation shells and hence, only a fraction of the total internal solvent is free, in which the non-electrolyte is dissolved. Hence, in the absence of any other interactions, the nonelectrolyte concentration in the free water in the ion exchanger should be same as the nonelectrolyte concentration in the external solution. Thus the molality of the nonelectrolyte in the ion exchanger, which refers to the total solvent in the ion exchanger is less than that in the external solution. The nonelectrolyte is then 'salted out' .

'Salting out' effects should be more pronounced when the fraction of solvent in the ion exchanger, which is free, is smaller. This is the case when the resin is highly crosslinked and the counter ions are strongly solvated. Hence, with salting out as predominant effect, the molal distribution coefficient decreases with increasing degree of crosslinking and increasing solvation number of the counter ion.

If salting out effect is the predominant effect, sorption of the nonelectrolyte solute can be increased by adding an electrolyte to the external solution. Addition of electrolyte results in 'salting out' in the solution also and thus counteracts 'salting out' in the ion exchanger.

Interactions with counter ions, 'salting in' and complex formation :

In certain systems, exactly the opposite of salting out is observed. The mechanism, which is responsible for such 'salting in' effects is not yet quite clear. Analogous effects are observed with ion exchange resins.

Interactions between nonelectrolyte and the counter ions become more pronounced when inorganic counter ions are replaced by organic ions. The most striking effects are noted when the solute forms complexes with counter ions.

London and dipole interactions :

Sorption of organic nonelectrolytes with hydrocarbon groups by ion exchange resins with hydrocarbon matrices is likely to be affected by two kinds of interactions. First, sorption is favoured by London interactions between the solute and the matrix. These forces are rather weak. A second and stronger contribution may come from dipole-dipole interactions of the polar solvent molecules with one another and with polar groups of the solute. The result of such interactions is that the hydrocarbon groups tend to coagulate or to be squeezed out of the polar solvent into a phase boundary. Both the London and the dipole interactions favour local adsorption of the hydrocarbon groups of the solute on the matrix and thus enhance the sorption of the nonelectrolyte. Both interactions are more pronounced when the hydrocarbon group of the solute is larger (provided that the polar group~~s~~ remains the same). Hence, in a homologous series, the distribution coefficient usually increases with increasing molecular weight of the solute, at least as long as sorption is not limited by molecular size effects.

London forces are specific interactions and depend on the molecular structure of the solute and the matrix. Different types of resins may widely differ in their sorption behaviour. Strong sorption may be expected when the chemical configurations of the solute and the matrix are similar. Large molecules with very strong affinity may even be sorbed irreversibly.

Molecular size, swelling pressure and sieve action :

The molecular size of the solute, in combination with the crosslinking of the resin, may considerably influence the sorption of the nonelectrolyte. The interior of the swollen resin is under rather high swelling pressure, which tends to squeeze the solvent and solute molecules out of the resin. Larger molecules are more strongly affected. This may be expressed by the equation,

$$\pi v_N = - RT \ln \frac{\bar{a}_N}{a_N} \qquad (4.1)$$

A given swelling pressure π reduces the internal activity $\bar{a}_N$ of a species N more strongly, if the partial molar volume v_N of the species is large. The equilibrium swelling pressure,in turn,is high if the resin is highly crosslinked. With resins of moderate crosslinking and smaller nonelectrolyte molecules, this swelling-pressure effect is rather small and is often overshadowed by other interactions which favour sorption of larger molecules. However, with increasing size of the solute molecule or increasing degree of crosslinking, the effect becomes more important. The distribution coefficient in a homologous series may then have maximum value at medium molecular size.

Sorption of larger molecule is further restricted by the purely mechanical sieve action of the matrix. Molecules, which are too large for passing through the meshes of the matrix are excluded by the resin.

Of course, sieve action does not impose a sharp limit on the molecular size of the solute,since the mesh width of the matrix is not uniform.Swelling pressure and sieve effects are, hence,difficult to distinguish. Also, the sorption rate becomes very low, when the molecular size of the solute approaches the critical range. Hence, uptake of large molecules under ordinary experimental conditions may be low, because sorption equilibrium, no matter how favourable, is not attained.

Dependence on solution concentration :

The uptake of the solute by the resin increases with increase in the concentration of the solution. The sorption isotherm usually has a negative curvature. This is particularly true for solutes which are strongly sorbed even from dilute solutions. Here, the saturation of the resin is fairly complete at relatively low solution concentrations, so that the isotherm flattens out after an initial steep rise. However, in a number of cases, isotherms with positive curvature are observed. Usually, a Langmuir or Freundlich isotherm can be fitted reasonably to the experimental results.

Dependence on temperatures and pressure :

The effect of temperature on sorption equilibria is complex and has not yet been studied systematically. Not only the heat of the actual sorption process is involved, but also the temperature dependence of swelling, solvation and in some cases, of the dissociation of ion pairs or complexes in the resin. Usually the temperature dependence of sorption is small. In cases of strong specific sorption, the temperature coefficient is likely to be negative.

The effect of pressure on sorption of solutes has so far received little attention. However, one may expect that the pressure dependance is insignificant, since sorption usually occurs without much change in the volume of the total system.

Sorption of weak electrolytes :

Weak electrolytes are little affected by Donnan exclusion and thus are sorbed in essentially the same way as nonelectrolytes. The dissociation of weak electrolytes and hence, their uptake by ion exchangers depends on the pH of the solution. The pH dependence can be used for elution. Weak electrolytes can also be sorbed, without simultaneous ion exchange, by resins containing multivalent counter ions.

Reference :

(1) Helfferich, F., Ion Exchange, McGraw-Hill Book Company, Inc., U.S.A., 1962.