2.

EQUILIBRIA WITH ALKALI SULPHATES :

2.1 Ion Exchange Equilibria (2-12)(of Section one)

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 significent 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

$$RA + B^+_{aq.} \rightleftharpoons RB + A^+_{aq.}$$

and the selectivity coefficient, K^B_A is given by

$$K^B_A = \frac{\left[\overline{B^+}\right]\left[A^+\right]}{\left[\overline{A^+}\right]\left[B^+\right]}$$

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,

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

and $[\overline{B}^{+}]$ 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 persent 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

$$K_a \equiv \frac{[\overline{B}^{+}] \cdot \overline{\gamma B} \cdot [A^{+}] \cdot \gamma A}{[\overline{A}^{+}] \cdot \overline{\gamma A} \cdot [B^{+}] \cdot \gamma B}$$

$$= K_{A}^{B} \cdot \frac{\overline{\gamma B} \cdot \gamma A}{\overline{\gamma A} \cdot \gamma B}$$

where γA, γB are the activity coefficients for cations A^{+} and B^{+} in solution,

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

In general the ratio $\overline{\gamma A} / \overline{\gamma B}$ may not be equal to unity or equal to the ratio $\gamma A / \gamma B$.

Ion exchange as a Donan 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 A^+X^- and B^+X^-, the Donnan equation may be applied to both of these electrolytes, and

$$\overline{a}_{A^+} \cdot \overline{a}_{X^-} = a_{A^+} \cdot a_{X^-}$$

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

where a_{A^+}, a_{B^+} and a_{X^-} denote the activities of ions A^+, B^+ and X^+ in solution,

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

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

$$\frac{\overline{\gamma}_A \cdot \gamma_B}{\overline{\gamma}_B \cdot \gamma_A} = \frac{[\overline{B^+}]\ [A^+]}{[\overline{A^+}]\ [B^+]}$$

or
$$K_A^B = \frac{\overline{\gamma}_A \,/\, \overline{\gamma}_B}{\gamma_A \,/\, \gamma_B}$$

calculation, using the available values of activity coefficients for concentrated solutions of electrolytes, give values 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. $Ba^{++} < Mn^{++} < Mg^{++} \approx Zn^{++} < Cu^{++} \approx Ni^{++} < Co^{++} < Ca^{++} < Sr^{++} < Pb^{++} < Ba^{++}$

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 polarizability 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 cross-linking : the selectivity being greater for higher degree of cross-linking. The later are less swollen and hence constitute more concentrated solution. Since, these results may as well be due to the effect of cross-linking per se, the point is better proved by work of Boyd on polystyrene resins in which the cross-linking was kept constant, but the degree of sulphonation was varied. This point is further more clearly proved by Devel from work on soluble (non-cross-linked) 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

$$RT \ln K_A^B = \pi (\overline{V_A} - \overline{V_B})$$

Complete Donnan theory :

According to complete Donnan theory the selectivity coefficient is given by

$$\ln K_A^B = \ln (\gamma_B / \gamma_A) - \ln (\overline{\gamma_B} / \overline{\gamma_A}) + \pi(\overline{V_A} - \overline{V_B}) / RT.$$

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 $\ln (\gamma_B / \gamma_A)$ 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 degrees of cross-linking, 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 cross-linking. 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 cross-linking. The assumption is made that at equal water contents (per gm. equivalent), two resins of different cross-linking have the same chemical activity coefficients, but differ in water vapour activity on account of different swelling pressures. The free energy change on transferring a mole of water from a resin of low cross-linking ($\pi \simeq 0$) to one of higher cross-linking (at the same molality) is then given by

$$\Delta G = RT \ln p2 / p1$$

where p1 and p2 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 Vw (= 18 ml.) from a negligible pressure to one at pressure π. Hence,

$$\pi \, Vw = RT \ln (p_2 / p1)$$

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 $\overline{A^+}$: $\overline{B^+}$ 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 cross-linked resins or large ions.

<u>Other factors affecting selectivity</u> :

(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 cross-linking. This ionic sieve effect is somewhat off-set by the existance of an additional force of attraction between large ions and the resin frame work, favouring sorption.

(ii) Sorption by van der Waals forces :

Considerable non-coulombic 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 non-ionic substances by van der Waals adsorption.

(iii) Semi-specific 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 $\overline{X}$ in the resin :

It is observed that K_A^B decreases markedly as the ion fraction of B, ($\overline{X_B}$) 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 chaning 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 cross-linking are micro-heterogeneous in structure, containing regions of different degree of cross-linking. 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, where-as 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

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

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 cross-linked chains on the other hand. The water content therefore, depends primarily on the activity coefficient of the internal ions and the degree of cross-linking 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 $\overset{+}{X}\overset{-}{Y}$, between resin and external solution,

$$\left[\overline{X^{+}}\right]\left[\overline{Y^{-}}\right] = \left[X^{+}\right]\left[Y^{-}\right]$$

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 non-electrolytes :

The sorption of non-electrolytes by ion exchange resins has been noted in several systems, but is rather unpredictable. Adsorption effects are well-known to be semi-specific,depending not only on the general nature of the substance, but also, on both, the shape and size of the molecules and the configuration of the surface on which they adsorb. Closeness of fitting of molecule-to-surface is probably important, as the force of adsorption involves the summation of the short-range van der Waals forces between the various atoms. Sorption by resins can be expected to increase with solute concentration according to a Freundlich isotherm, but the constants of the isotherm cannot be predicted theoretically.

(iv) Effect of non-exchanging ions and other solutes :

The influence of non-exchanging 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 non-aqueous or mixed solvents :

Ion exchange reaction can take place in some non-aqueous 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.

2.2. The selectivity coefficients of sulphonic acid cation exchange resins in sulphate solutions .

2.2.a. Introduction :

The cation exchange equilibria of univalent cations with sulphonic acid cation exchange resins in aqueous solution have been the subject of investigation of several workers. (2 - 26 , 28 - 30) In most of these studies chloride solutions have been used and the postulated theories have been applied with varying success. Since, there is no satisfactory method yet available for accurately predicting the selectivity coefficients, it was considered to be of interest to study the selectivity coefficients for sulphonic acid cation exchange resins with univalent cations in aqueous sulphate solution and to compare the results with those for univalent cinchona alkaloid cations in aqueous solution of cinchona alkaloid sulphates.

This study includes the effect of (a) the mole fraction $\overline{X_M}$, of the counter ion in the resin phase, (b) the relative degree of cross-linking, X , (nominal % divinyl benzene content) of the resin and (c) the average particle diameter 'a' (in mm.), of the resin, on the selectivity coefficients for sodium-hydrogen and potassium-hydrogen exchange in aqueous sulphate solution ($\sim$ 0.04 N) at room temperature ($\sim 30^{\circ}$C).

2.2.b. Experimental :

Resins : Resins used were the sulphonated styrene-

-divinyl benzene copolymer type sulphonic acid cation exchange resins of different X. These included Dowex 50 resins (Dow Chemical Co.) of X = 1,2,4,8,12 and 16 (these are further referred to as resins X 1, X 2, X 4, X 8, X 12 and X 16), prepared sample of a similar resin (from Permutit Co., London), of X = 20 (This is further referred to as resin X 20), Amberlite resins (Röhm and Haas Co.) IR - 120 and IR - 200 (these are further referred to as resins IR - 120 and IR - 200) and a resin Amberlyst - 15 (Rohm and Haas Co.) , (this is further referred to as resin Amb - 15)

Chemicals : Sodium sulphate, potassium sulphate, sodium chloride, potassium chloride and sodium hydroxide were of A.R.quality. Distilled water was used.

Moisture and capacity of the resins (1,27) :

The resins were washed with distilled water, cycled thrice between sodium chloride and hydrochloric acid, regenerated with a large excess of hydrochloric acid, washed free of acid, filtered, air-dried, sieved and stored in good containers. The resin Amb - 15 was first soaked in methanol and then washed with water before regeneration. A number of particles ($\sim$50 to 60) of each resin were measured for the particle diameter, with a travelling microscope and the average value was taken as the average particle diameter, a .

Moisture content was determined by heating weighed samples ($\sim$0.5 grams) of air-dried resin in clean, dry weighing bottles, in an oven (100 - 103°C) to a constant weight. % moisture content was then calculated.

For the estimation of the capacity of the resins, weighed samples ($\sim$0.5 gms.) of air-dried resins were contacted with 50 cc. of 1 N barium chloride solution in well-stoppered flasks with frequent shaking. After two to three days, the liberated acid was estimated by titration with standard sodium hydroxide solution, and then the capacity was calculated. Preliminary work had indicated that increase in contact time did not increase the amount of acid liberated. Table (2.01) gives the obtained values for % moisture content and capacity of different resins.

Solutions :

The solutions of salts were prepared by dissolving known weights in distilled water to known volumes. The sulphate solutions were reached by sulphate estimation (as barium sulphate). The solutions were then suitably diluted($\sim$0.04 N) and concentrations accurately calculated.

Determination of selectivity coefficients :

Weighed quantities of air-dry resins were contacted with known volumes of salt solutions ($\sim$0.04 N) in well stoppered flasks with frequent shaking at room temperature ($\sim 30^{\circ}$C). Preliminary work was carried out to find out the time, after which further exchange did not take place. After sufficiently more time than this, the solutions were analysed for acid liberated, by titration with standard sodium hydroxide solution.

The selectivity coefficient K_{H}^{M}, for the exchange reaction

$$\overline{H^+} + M^+ \rightleftharpoons \overline{M^+} + H^+$$

is given by

$$K_{H}^{M} = \frac{\left[\overline{M^+}\right]_e \left[H^+\right]_e}{\left[\overline{H^+}\right]_e \left[M^+\right]_e}$$

Where $\left[H^+\right]_e$ and $\left[M^+\right]_e$ denote the concentrations of hydrogen ions and alkali metal ions in gm. equivalents / litre, in aqueous solution at equilibrium,

and $\left[\overline{H^+}\right]_e$ and $\left[\overline{M^+}\right]_e$ denote the gm. equivalents of resin in the hydrogen form and in the alkali metal form, per litre of the solution, at equilibrium.

Hence the selectivity coefficient is given by

$$K_{H}^{M} = \frac{\left[H^+\right]_e^{2}}{\left\{\left[\overline{H^+}\right]_i - \left[H^+\right]_e\right\}\left\{\left[M^+\right]_i - \left[H^+\right]_e\right\}}$$

Where $\left[\overline{H^+}\right]_i$ denotes the gm. equivalents of resin in hydrogen form added initially, per litre of solution, and

$[M^+]_i$ denotes the initial concentration of cations M^+ in aqueous solution, in gm, equivalents per litre.

Hence, by substituting the proper values, the selectivity coefficients were calculated.

2.2.c. RESULTS :

Table 2.01 gives the values of % moisture content and capacity of different resins.

Table (2.02) and figure (2.01) gives the variation of the selectivity coefficient for resin X 8, with $\overline{X}_M$, in chloride solution, for sodium-hydrogen and potassium-hydrogen exchange.

Tables (2.03 to 2.06) and figures (2.02 and 2.03) give the variation of the selectivity coefficient for resins X 1, X 2, X 4, X 8, X 12, X 16 and X 20, with $\overline{X}_M$, in sulphate solutions, for sodium-hydrogen exchange.

Tables (2.10 to 2.13) and figures (2.04 and 2.05) give the variation of the selectivity coefficient for resins X 1, X 2, X 4, X 8, X 12, X 16 and X 20, with $\overline{X}_M$, in sulphate solution, for potassium-hydrogen exchange.

Tables (2.07 and 2.14) and figures (2.06) give for resin IR-120 of different particle diameters, the variation of the selectivity coefficient with $\overline{X}_M$, in sulphate solution, for sodium-hydrogen exchange and potassium-hydrogen exchange.

Tables (2.08, 2.09, 2.15 and 2.16) and figure (2.07) give for resin IR-200 of different particle diameters, the variation of the selectivity coefficent with $\overline{X}_M$, in sulphate solution, for sodium-hydrogen and potassium -hydrogen exchange.

Table (2.17) gives the selectivity coefficients (obtained from figures 2.02 and 2.03) for sodium-hydrogen exchange for resins X 1 to X 20 at definite values of $\overline{X}_M$, and figure (2.08) gives the plot of these selectivity coefficients at definite values of $\overline{X}_M$ against X for sodium-hydrogen exchange.

Table (2.18) gives the selectivity coefficients (obtained from figures 2.04 and 2.05) for potassium-hydrogen exchange for resins X 1 to X 20 at definite values of $\overline{X}_M$ and figure (2.09) gives the plot of these selectivity coefficients at definite values of $\overline{X}_M$ against X, for potassium-hydrogen exchange.

Table (2.19) gives the values of the selectivity coefficient for maxima in the plots of figures (2.08 and 2.09) and corresponding values of X , and figure (2.10) gives the plot of maximum selectivity coefficient for sodium-hydrogen and potassium-hydrogen exchange against definite values of $\overline{X}_M$.

Table (2.20) gives the values of X for resins IR-120 and IR-200 obtained from figures (2.08 and 2.09).

Table 2.01

Capacity of cation exchange resins

Resin	a (mm.)	Moisture (%)	Capacity	
			Meq.per gm. air dry resin	Meq.per gm. oven-dry resin
X 1	0.215	20.3	4.18	5.24
X 2	0.215	20.4	4.14	5.20
X 4	0.215	24.0	3.89	5.12
X 8	0.215	27.0	3.72	5.09
X 12	0.215	26.0	3.73	5.04
X 16	0.215	24.7	3.54	4.70
X 20	0.215	16.8	3.69	4.43
IR-120	0.84	30.0	3.47	4.96
IR-120	0.58	30.8	3.43	4.96
IR-120	0.37	29.9	3.48	4.96
IR-120	0.23	28.5	3.55	4.96
IR-200	1.13	27.2	3.48	4.78
IR-200	0.84	28.8	3.40	4.78
IR-200	0.58	28.1	3.44	4.78
IR-200	0.37	25.5	3.56	4.78
IR-200	0.23	26.1	3.53	4.78
Amb-15	1.13	25.9	3.39	4.58
Amb-15	0.84	25.4	3.42	4.58
Amb-15	0.58	26.7	3.36	4.58
Amb-15	0.37	23.5	3.51	4.58

Figure 2.07

Plot of the selectivity coefficient for resin X8 against $\bar{X}_M$, in chloride solution, for (A) potassium-hydrogen exchange and (B) sodium-hydrogen exchange.

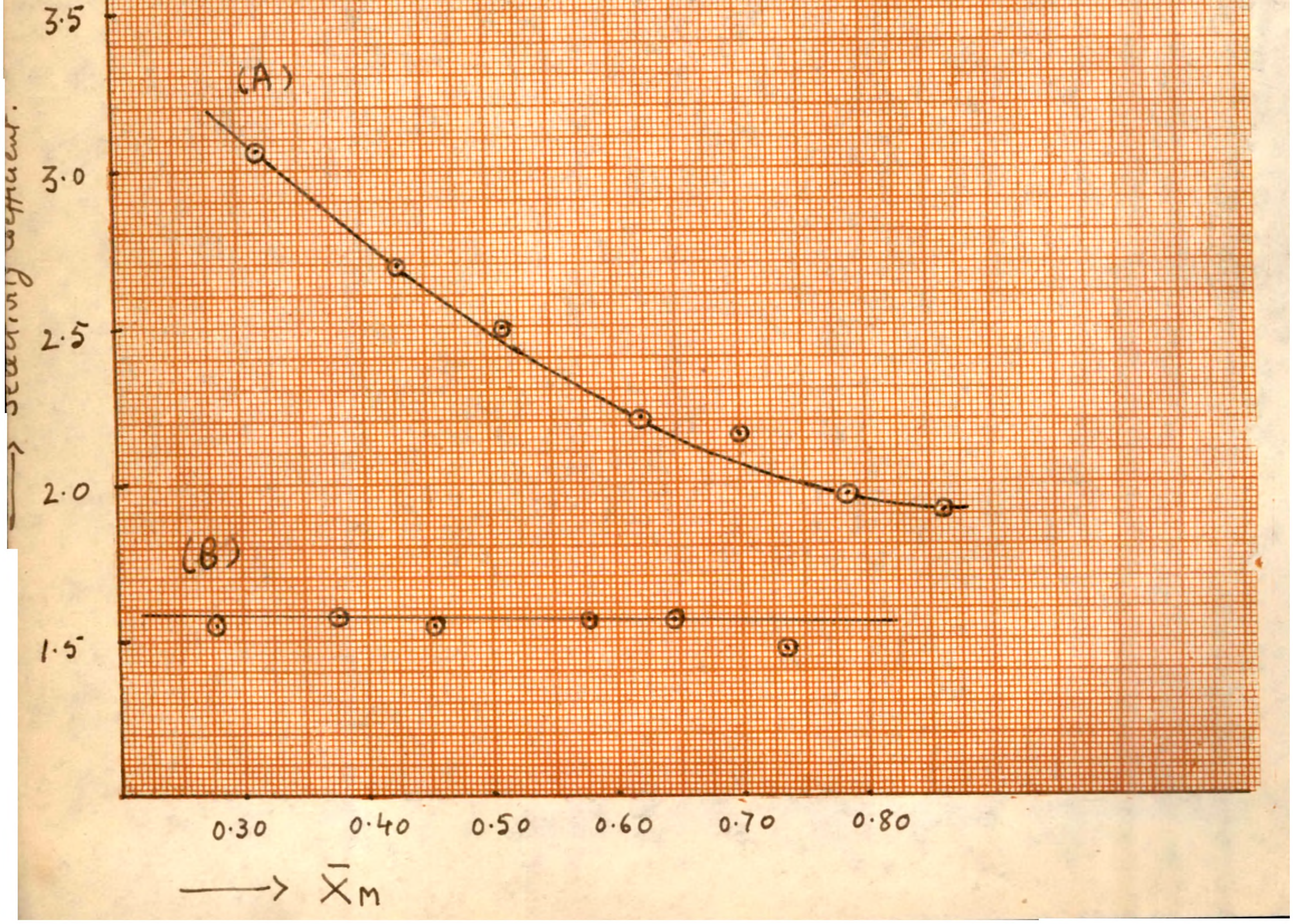


Table 2.02.a

Selectivity coefficients for sodium-hydrogen exchange with resin X 8 in chloride solution.

$[H^+]_e \cdot 10^2$	$[\bar{H}^+]_i \cdot 10^2$	K^{Na}_{H}	$\bar{X}_{Na^+}$	$[Na^+]_i \cdot 10^2$
3.082	11.11	1.540	0.2774	3.850
2.793	7.459	1.581	0.3744	3.850
2.503	5.527	1.539	0.4530	3.850
2.064	3.587	1.566	0.5754	3.850
1.788	2.783	1.559	0.6428	3.850
1.355	1.856	1.469	0.7303	3.850

Table 2.02.b.

Selectivity coefficients for potassium-hydrogen exchange with resin X 8 in chloride solution.

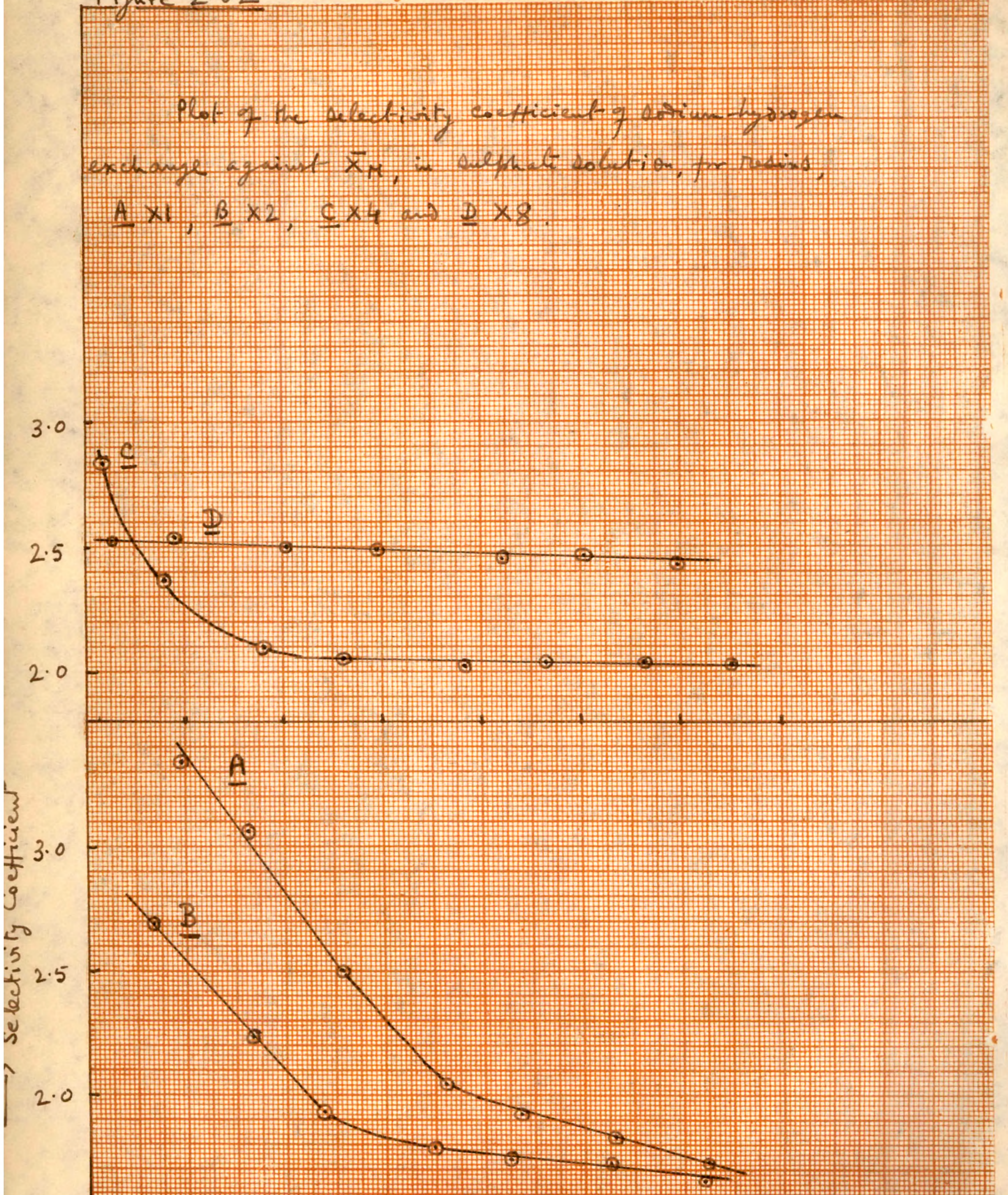
$[H^+]_e \cdot 10^2$	$[\bar{H}^+]_i \cdot 10^2$	K^{K}_{H}	$\bar{X}_{K^+}$	$[K^+]_i \cdot 10^2$
3.509	11.16	3.047	0.3143	4.037
3.164	7.446	2.679	0.4250	4.037
2.847	5.580	2.494	0.5104	4.037
2.312	3.718	2.203	0.6216	4.037
1.946	2.790	2.148	0.6976	4.037
1.445	1.859	1.945	0.7771	4.037
0.9632	1.122	1.900	0.8584	4.037

Table 2.03

Selectivity coefficients for sodium-hydrogen exchange

Resin	$[H^+]_e \cdot 10^2$	$[\bar{H}^+]_i \cdot 10^2$	K^{Na}_{H}	$\bar{X}_{Na^+}$	$[Na^+]_i \cdot 10^2$
X 1	3.725	12.550	3.335	0.2968	3.801
	3.216	8.399	3.065	0.3634	3.815
	2.860	6.268	2.514	0.4562	3.815
	2.350	4.194	2.045	0.5604	3.815
	1.995	3.135	1.918	0.6362	3.815
	1.531	2.091	1.832	0.7319	3.815
	1.036	1.259	1.732	0.8230	3.815
X 2	3.347	12.510	2.694	0.2675	3.801
	3.032	8.288	2.232	0.3657	3.815
	2.722	6.226	1.934	0.4371	3.815
	2.274	4.148	1.789	0.5480	3.815
	1.948	3.113	1.745	0.6258	3.815
	1.508	2.080	1.722	0.7246	3.815
	1.021	1.246	1.657	0.8191	3.815

Figure 2.02



Plot of the selectivity coefficient of sodium-hydrogen exchange against $\bar{X}_H$, in sulphate solution, for resins, A X1, B X2, C X4 and D X8.

Table 2.04

Selectivity coefficients for sodium-hydrogen exchange

Resin	$[\mathrm{H}^+]_e \cdot 10^2$	$[\overline{\mathrm{H}}^+]_i \cdot 10^2$	$K^{\mathrm{Na}}_{\mathrm{H}}$	$\overline{X}_{\mathrm{Na}^+}$	$[\mathrm{Na}^+]_i \cdot 10^2$
X 4	3.455	15.590	2.844	0.2216	3.801
	3.267	11.690	2.372	0.2796	3.801
	2.974	7.780	2.103	0.3822	3.849
	2.714	5.864	2.061	0.4629	3.849
	2.280	3.912	2.027	0.5824	3.849
	1.947	2.924	2.041	0.6661	3.849
	1.495	1.959	2.046	0.7630	3.849
	1.002	1.176	2.027	0.8519	3.849
X 8	3.401	14.890	2.516	0.2283	3.801
	3.267	11.140	2.538	0.2931	3.801
	3.022	7.438	2.501	0.4062	3.849
	2.762	5.578	2.495	0.4955	3.849
	2.310	3.724	2.455	0.6207	3.849
	1.963	2.790	2.473	0.7037	3.849
	1.479	1.858	2.435	0.7960	3.849

Table 2.05

Selectivity coefficients for sodium-hydrogen exchange

Resin	$[H^+]_e \cdot 10^2$	$[\overline{H^+}]_i \cdot 10^2$	K^{Na}_{H}	$\overline{X}_{Na^+}$	$[Na^+]_i \cdot 10^2$
X 12	3.482	14.950	3.314	0.2329	3.801
	3.358	11.230	3.233	0.2989	3.801
	3.112	7.470	3.250	0.4168	3.796
	2.864	5.598	3.219	0.5116	3.796
	2.380	3.736	2.945	0.6365	3.796
	2.011	2.803	2.861	0.7174	3.796
	1.507	1.874	2.702	0.8042	3.796
	0.989	1.125	2.580	0.8800	3.796
X 16	3.468	14.190	3.369	0.2443	3.801
	3.347	10.660	3.375	0.3141	3.801
	3.088	7.096	3.360	0.4351	3.796
	2.828	5.322	3.309	0.5313	3.796
	2.316	3.548	2.942	0.6528	3.796
	1.942	2.664	2.818	0.7291	3.796
	1.432	1.774	2.536	0.8069	3.796
	0.934	1.073	2.186	0.8704	3.796

Figure 2·03

Plot of the selectivity coefficient of sodium-hydrogen exchange against $\bar{X}_M$, in sulphate solution, for resins (A) X12, (B) X16 and (C) X20.

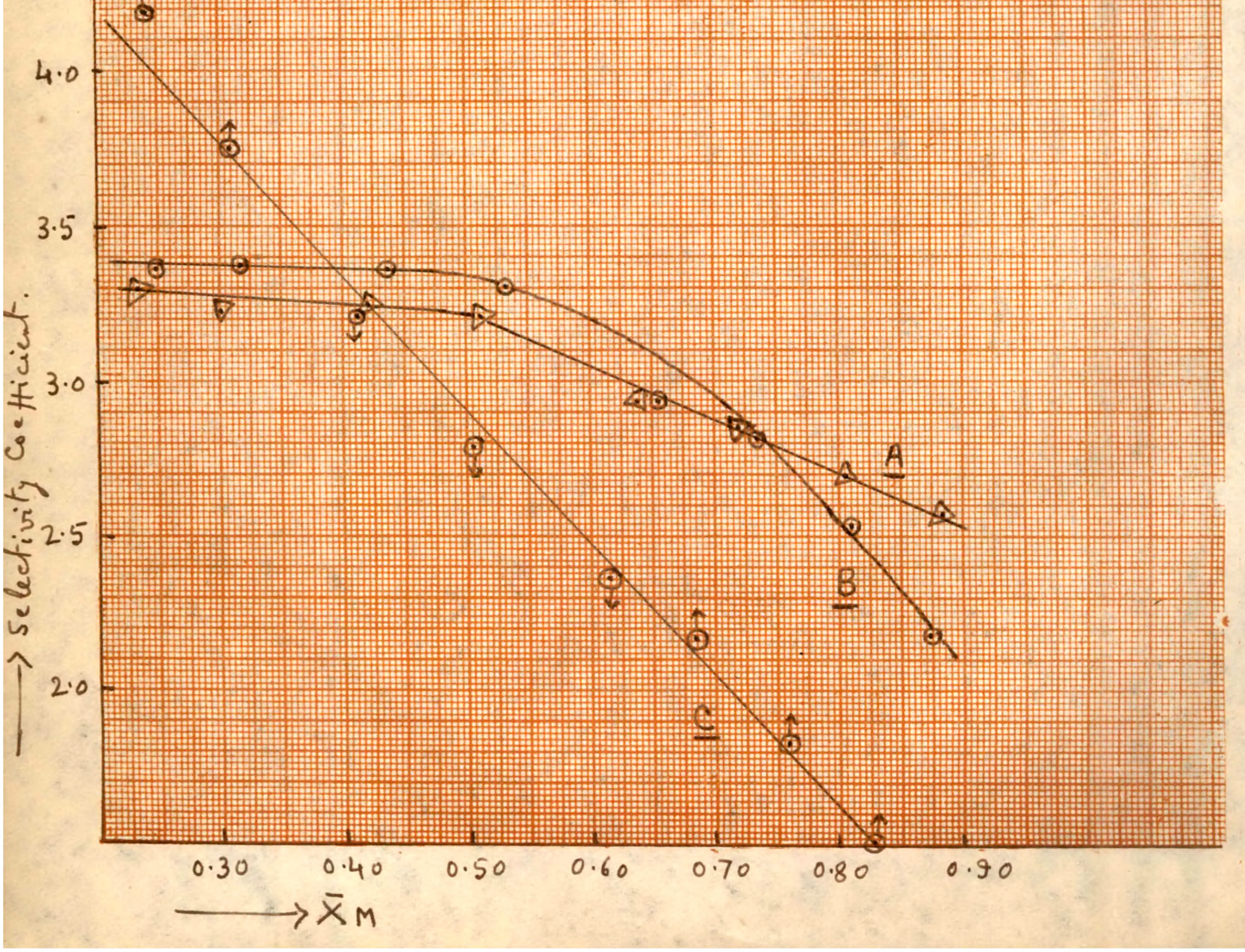


Table 2.06

Selectivity coefficients for sodium-hydrogen exchange

Resin	$[\overset{+}{\mathrm{H}}]_e \cdot 10^2$	$[\overline{\overset{+}{\mathrm{H}}}]_i \cdot 10^2$	$K^{\mathrm{Na}}_{\mathrm{H}}$	$\overline{X}_{\overset{+}{\mathrm{Na}}}$	$[\overset{+}{\mathrm{Na}}]_i \cdot 10^2$
X 20	3.536	14.780	4.198	0.2393	3.801
	3.401	11.100	3.756	0.3064	3.801
	3.092	7.540	3.221	0.4102	3.781
	2.788	5.546	2.794	0.5027	3.781
	2.266	3.694	2.374	0.6135	3.781
	1.895	2.773	2.168	0.6832	3.781
	1.406	1.862	1.826	0.7553	3.781
	0.915	1.108	1.512	0.8256	3.781

Table 2.07

Selectivity coefficients for sodium-hydrogen exchange with resin IR-120 of different particle diameters

a (mm.)	$[\overset{+}{H}]_e \cdot 10^2$	$[\overset{+}{\bar{H}}]_i \cdot 10^2$	K^{Na}_{H}	$\bar{X}_{\overset{+}{Na}}$	$[\overset{+}{Na}]_i \cdot 10^2$
0.37	3.212	10.460	2.417	0.3070	3.801
	2.962	6.998	2.518	0.4234	3.826
	2.690	5.228	2.508	0.5144	3.826
	2.218	3.500	2.382	0.6334	3.826
	1.892	2.620	2.543	0.7221	3.826
	1.414	1.756	2.421	0.8050	3.826
	0.934	1.054	2.505	0.8853	3.826
0.58	3.212	10.370	2.447	0.3096	3.801
	2.936	6.896	2.467	0.4256	3.818
	2.650	5.162	2.395	0.5134	3.818
	2.218	3.444	2.505	0.6436	3.818
	1.876	2.590	2.539	0.7243	3.818
	1.399	1.722	2.506	0.8127	3.818
	0.929	1.043	2.611	0.8904	3.818

Table 2.08

Selectivity coefficients for sodium-hydrogen exchange with resin IR-200 of different particle diameters.

a (mm.)	$[H^+]_e . 10^2$	$[\bar{H}^+]_i . 10^2$	K^{Na}_{H}	$\bar{X}_{Na^+}$	$[Na^+]_i . 10^2$
0.23	3.096	7.084	3.344	0.4370	3.815
	2.786	5.256	3.054	0.5301	3.815
	2.292	3.556	2.727	0.6443	3.815
	1.882	2.613	2.507	0.7204	3.815
	1.399	1.766	2.208	0.7921	3.815
	0.910	1.063	1.866	0.8563	3.815
0.37	3.698	21.360	7.519	0.1731	3.801
	3.536	14.270	4.397	0.2479	3.801
	3.375	10.720	3.639	0.3149	3.801
	3.108	7.138	3.420	0.4355	3.809
	2.786	5.288	3.034	0.5269	3.809
	2.292	3.566	2.716	0.6422	3.809
	1.901	2.650	2.528	0.7174	3.809
	1.622	2.141	2.318	0.7575	3.809
	0.923	1.075	1.936	0.8580	3.809

Table 2.09

Selectivity coefficients for sodium-hydrogen exchange with resin IR-200 of different particle diameters.

a (mm.)	$[\overset{+}{H}]_e \cdot 10^2$	$[\overline{\overset{+}{H}}]_i \cdot 10^2$	K_H^{Na}	$\overline{X}_{\overset{+}{Na}}$	$[\overset{+}{Na}]_i \cdot 10^2$
0.58	3.671	20.690	6.092	0.1774	3.801
	3.510	13.790	4.116	0.2545	3.801
	3.347	10.350	3.524	0.3235	3.801
	3.060	6.900	3.254	0.4433	3.809
	2.724	5.116	2.861	0.5326	3.809
	2.228	3.454	2.564	0.6454	3.809
	1.851	2.555	2.487	0.7247	3.809
	1.375	1.728	2.200	0.7956	3.809
	0.898	1.043	1.907	0.8602	3.809
0.84	3.671	20.460	6.176	0.1794	3.801
	3.510	13.660	4.170	0.2569	3.801
	3.375	10.230	3.899	0.3299	3.801
	3.076	6.814	3.469	0.4515	3.806
	2.748	5.092	3.047	0.5398	3.806
	2.238	3.426	2.689	0.6533	3.806
	1.837	2.538	2.444	0.7236	3.806
	1.362	1.707	2.202	0.7980	3.806
	0.894	1.035	1.948	0.8634	3.806

Table 2.10

Selectivity coefficients for potassium-hydrogen exchange

Resin	$[H^+]_e \cdot 10^2$	$[\overline{H^+}]_i \cdot 10^2$	K^K_H	$\overline{X}_{K^+}$	$[K^+]_i \cdot 10^2$
X 1	3.464	8.374	4.316	0.4136	4.030
	3.092	6.298	3.181	0.4911	4.030
	2.520	4.184	2.560	0.6022	4.030
	2.133	3.139	2.385	0.6795	4.030
	1.615	2.092	2.267	0.7721	4.030
	1.082	1.268	2.137	0.8541	4.030
X 2	3.617	12.480	3.542	0.2897	4.034
	3.292	8.314	2.926	0.3962	4.030
	2.970	6.232	2.548	0.4763	4.030
	2.474	4.148	2.351	0.5965	4.030
	2.095	3.111	2.232	0.6735	4.030
	1.585	2.086	2.050	0.7595	4.030
	1.052	1.245	1.923	0.8447	4.030

Figure 2.04

Plot of the selectivity coefficient of potassium-hydrogen exchange against $\bar{X}_M$, in sulphate solution, for resins, **A** X1, **B** X2, **C** X4 and **D** X8.

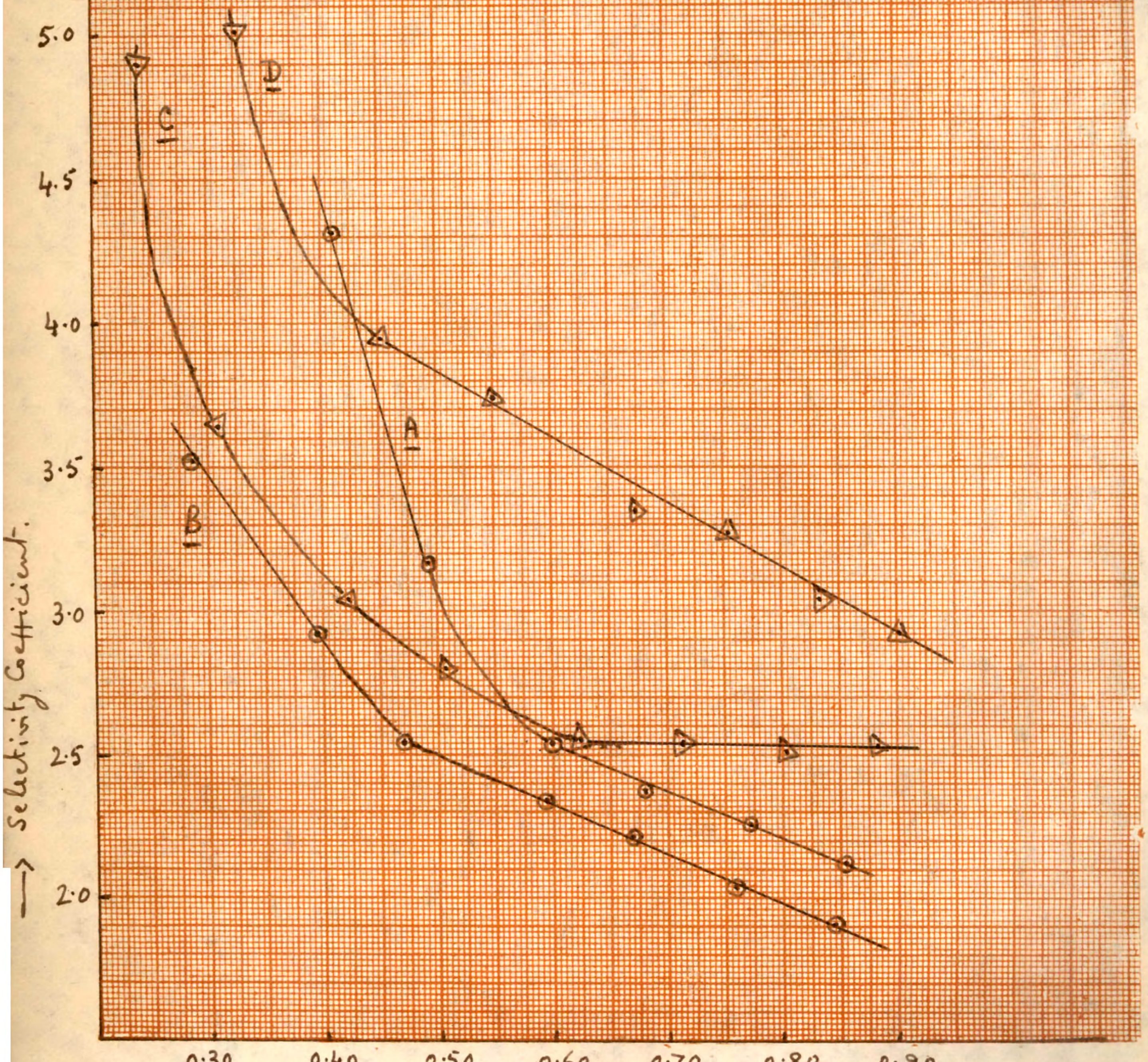


Table 2.11

Selectivity coefficients for potassium-hydrogen exchange

Resin	$[\overset{+}{H}]_e \cdot 10^2$	$[\overline{\overset{+}{H}}]_i \cdot 10^2$	K^K_H	$\overline{X}_{K^+}$	$[\overset{+}{K}]_i \cdot 10^2$
X 4	3.786	15.590	4.898	0.2429	4.034
	3.595	11.660	3.651	0.3082	4.034
	3.264	7.780	3.049	0.4196	4.038
	2.958	5.842	2.808	0.5062	4.038
	2.440	3.898	2.557	0.6261	4.038
	2.068	2.917	2.559	0.7091	4.038
	1.559	1.948	2.522	0.8002	4.038
	1.034	1.174	2.543	0.8810	4.038
X 8	3.677	11.210	5.027	0.3280	4.034
	3.346	7.438	3.952	0.4496	4.038
	3.054	5.582	3.750	0.5471	4.038
	2.504	3.726	3.348	0.6722	4.038
	2.101	2.796	3.278	0.7515	4.038
	1.552	1.869	3.053	0.8299	4.038
	1.007	1.121	2.935	0.8980	4.038

Table 2.12

Selectivity coefficients for potassium-hydrogen exchange

Resin	$[H^+]_e \cdot 10^2$	$[\bar{H}^+]_i \cdot 10^2$	K^K_H	$\bar{X}_{K^+}$	$[K^+]_i \cdot 10^2$
X 12	3.758	11.240	6.841	0.3345	4.034
	3.524	7.476	6.039	0.4713	4.044
	3.200	5.616	5.020	0.5697	4.044
	2.602	3.748	4.098	0.6945	4.044
	2.166	2.800	3.942	0.7738	4.044
	1.575	1.872	3.382	0.8414	4.044
	1.015	1.127	3.035	0.9001	4.044
X 16	3.786	10.650	8.420	0.3555	4.034
	3.512	7.116	6.428	0.4934	4.044
	3.162	5.342	5.202	0.5921	4.044
	2.528	3.556	4.098	0.7108	4.044
	2.098	2.674	3.927	0.7847	4.044
	1.513	1.782	3.361	0.8487	4.044
	0.977	1.072	3.285	0.9118	4.044

Figure 2.05

Plot of the selectivity coefficient of potassium-hydrogen exchange against $\bar{X}_M$, in sulphate solution, for resins, A X12, B X16 and C X20.

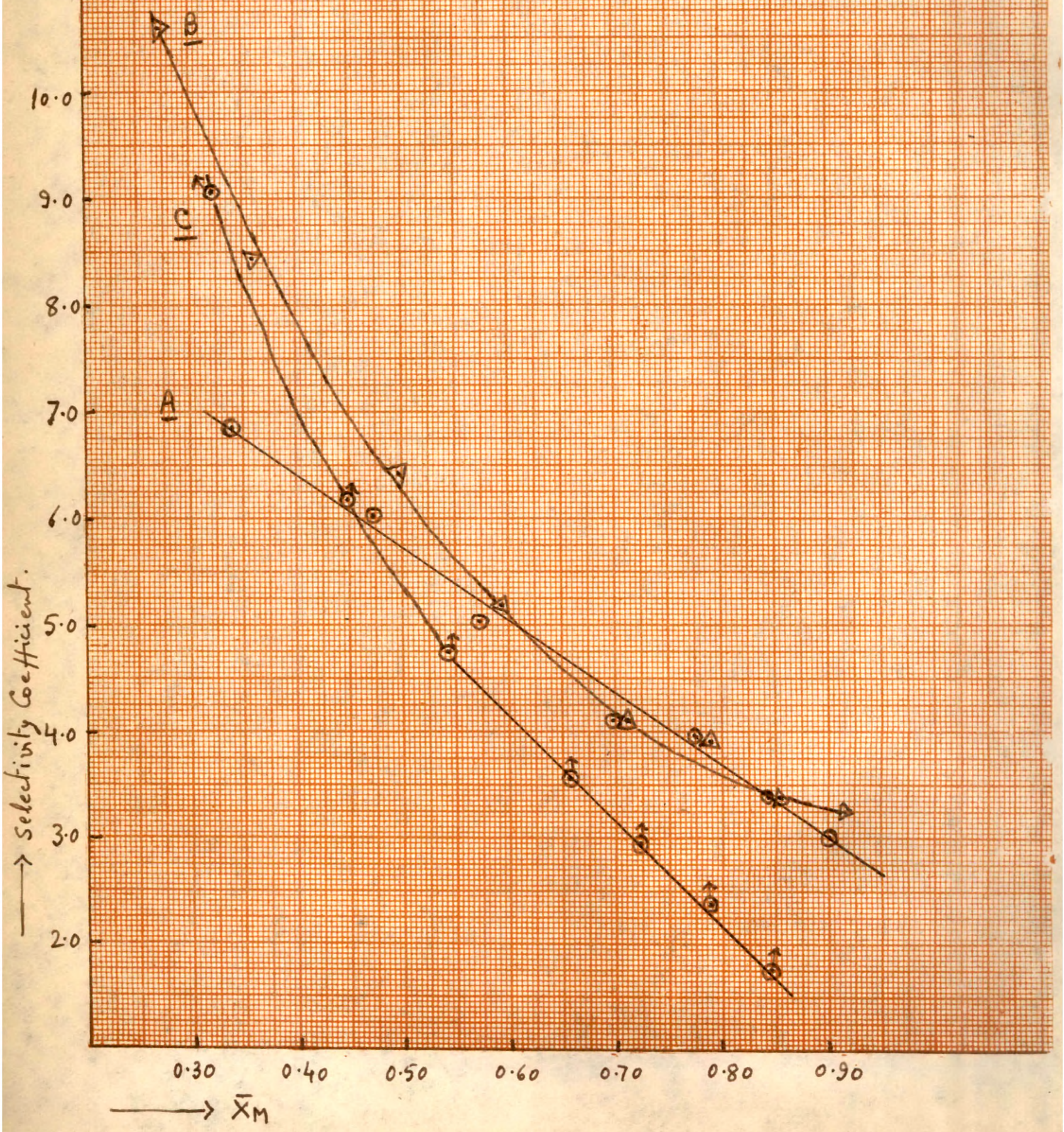


Table 2.13

Selectivity coefficients for potassium-hydrogen exchange

Resin	$[H^+]_e.10^2$	$[\overline{H^+}]_i.10^2$	K^K_H	$\overline{X}_{K^+}$	$[K^+]_i.10^2$
X 20	3.814	11.090	9.084	0.3440	4.034
	3.296	7.400	6.172	0.4455	3.725
	2.990	5.540	4.768	0.5398	3.725
	2.424	3.698	3.545	0.6552	3.725
	1.994	2.770	2.959	0.7197	3.725
	1.456	1.848	2.383	0.7883	3.725
	0.935	1.114	1.756	0.8397	3.725

Figure 2·06

Plot of the selectivity coefficient against $\bar{X}_M$, with resin IR-120, of different particle diameter 'a',

(△) a = 0·37 mm. and (O) a = 0·58 mm., for

A sodium-hydrogen exchange and B potassium-hydrogen exchange.

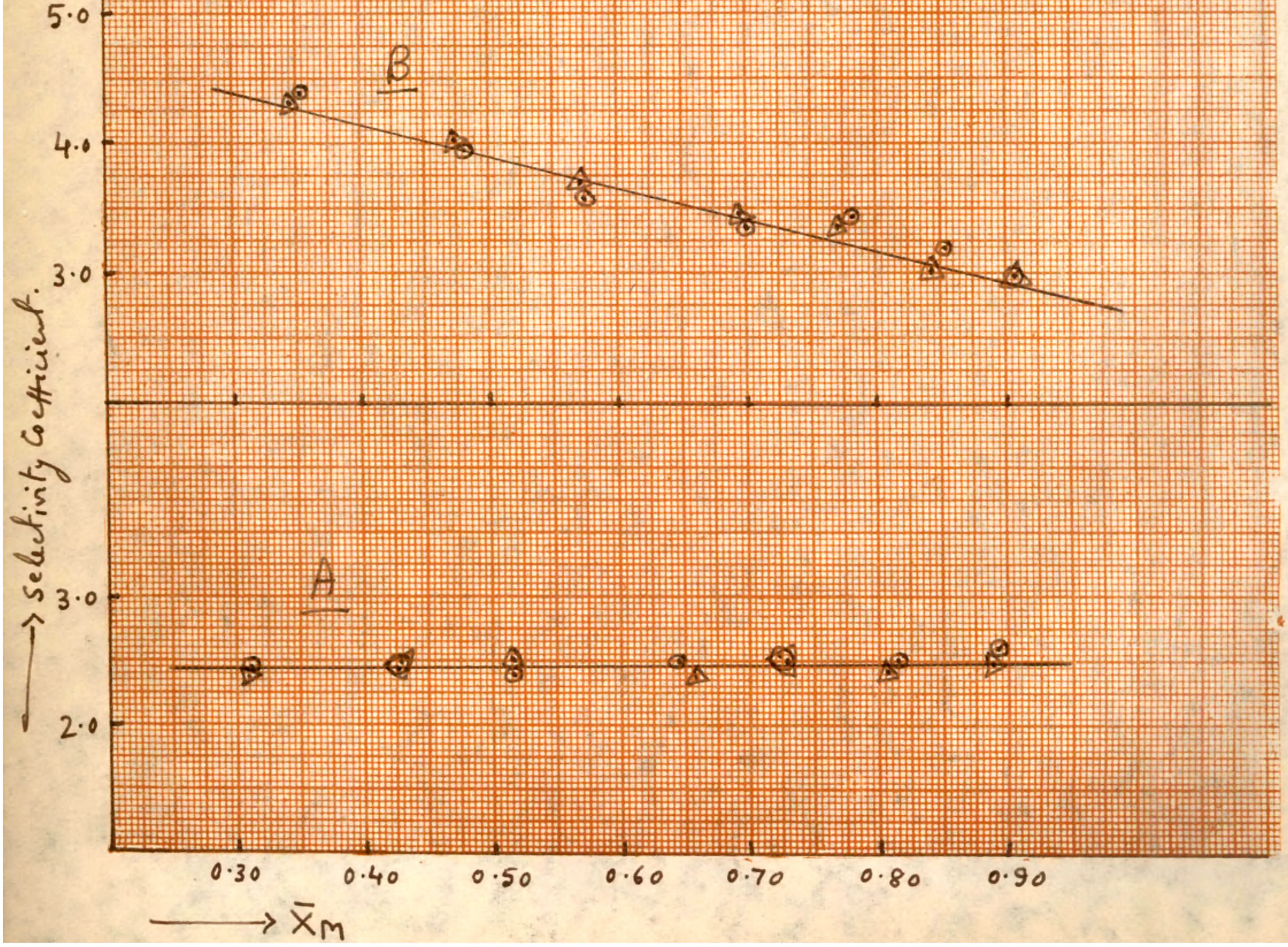


Table 2.14

Selectivity coefficients for potassium-hydrogen exchange with resin IR-120 of different particle diameters.

a (mm.)	$[H^+]_e . 10^2$	$[\overline{H^+}]_i . 10^2$	K^K_H	$\overline{X}_{K^+}$	$[K^+]_i . 10^2$
0.37	3.595	10.450	4.294	0.3441	4.034
	3.300	6.990	4.014	0.4720	4.035
	2.976	5.228	3.714	0.5692	4.035
	2.426	3.486	3.453	0.6963	4.035
	2.017	2.615	3.371	0.7713	4.035
	1.469	1.747	3.027	0.8412	4.035
	0.953	1.054	2.903	0.9031	4.035
0.58	3.595	10.310	4.384	0.3484	4.034
	3.282	6.878	3.956	0.4772	4.039
	2.936	5.116	3.583	0.5738	4.039
	2.402	3.442	3.389	0.6979	4.039
	1.994	2.560	3.435	0.7791	4.039
	1.468	1.729	3.210	0.8489	4.039
	0.947	1.046	2.949	0.9061	4.039

Figure 2·07

Plot of the selectivity coefficient against $\bar{X}_M$ with resin IR-200, of different particle diameter 'a',
(○) a = 0·23 mm. ($\overset{\uparrow}{\circ}$) a = 0·37 mm. (△) a = 0·58 mm. and (□) a = 0·84 mm.;
for A sodium-hydrogen exchange and B potassium-hydrogen exchange.

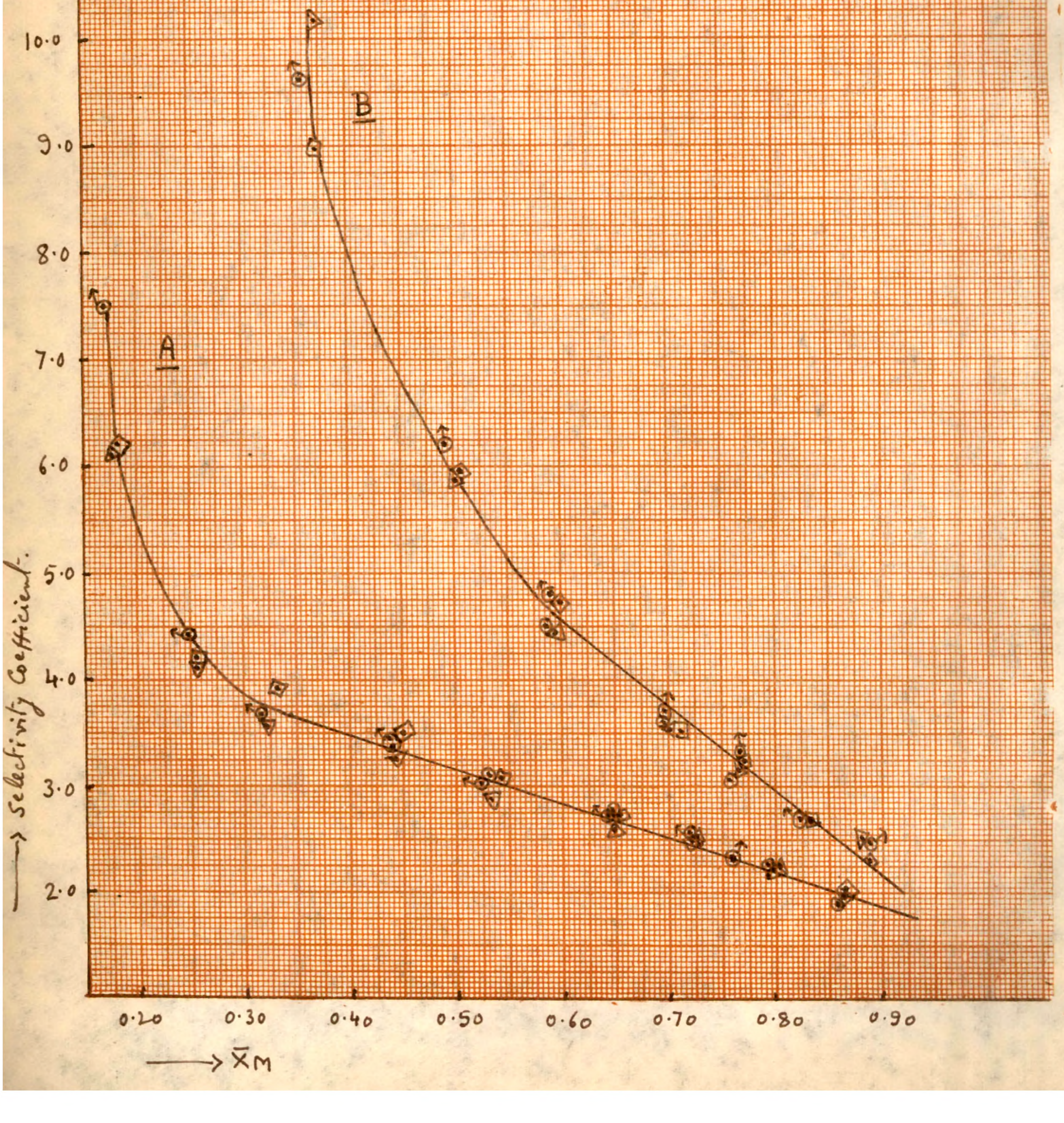


Table 2.15

Selectivity coefficients for potassium-hydrogen exchange with resin IR-200 of different particle diameters.

a (mm.)	$[\overset{+}{H}]_e . 10^2$	$[\overline{\overset{+}{H}}]_i . 10^2$	K^K_H	$\overline{X}_{\overset{+}{K}}$	$[\overset{+}{K}]_i . 10^2$
0.23	3.060	5.228	4.484	0.5852	4.023
	2.464	3.548	3.594	0.6944	4.023
	1.994	2.634	3.061	0.7568	4.023
0.37	3.814	10.700	9.598	0.3562	4.034
	3.492	7.132	6.216	0.4898	4.031
	3.108	5.288	4.801	0.5876	4.031
	2.490	3.574	3.709	0.6963	4.031
	2.031	2.657	3.295	0.7643	4.031
	1.473	1.789	2.686	0.8235	4.031
	0.954	1.075	2.436	0.8869	4.031

Table 2.16

Selectivity coefficients for potassium-hydrogen exchange with resin IR-200 of different particle diameters.

a (mm)	$[H^+]_e \cdot 10^2$	$[\overline{H}^+]_i \cdot 10^2$	K^K_H	$\overline{X}_{K^+}$	$[K^+]_i \cdot 10^2$
0.58	3.814	10.320	10.160	0.3693	4.034
	3.444	6.894	5.853	0.4994	4.031
	3.034	5.124	4.421	0.5924	4.031
	2.426	3.464	3.536	0.7008	4.031
	1.969	2.569	3.134	0.7663	4.031
	1.431	1.726	2.668	0.8290	4.031
	0.923	1.045	2.238	0.8828	4.031
0.84	3.786	10.240	8.954	0.3698	4.034
	3.442	6.828	5.921	0.5042	4.033
	3.052	5.074	4.699	0.6017	4.033
	2.408	3.422	3.520	0.7037	4.033
	1.964	2.541	3.232	0.7732	4.033
	1.423	1.716	2.650	0.8294	4.033
	0.918	1.036	2.300	0.8861	4.033

2.2.d. DISCUSSION :

According to complete Donnan theory, the selectivity coefficient, K_{H}^{M} is given by

$$\ln K_{H}^{M} = \ln (\gamma M / \gamma H) - \ln (\overline{\gamma M} / \overline{\gamma H}) - \pi (\overline{V_H} - \overline{V_M}) / RT \quad (1)$$

where γM, γH denote the activity coefficients of alkali metal ion and hydrogen ions in solution, $\overline{\gamma M}$, $\overline{\gamma H}$ denote the activity coefficients of alkali metal ions and hydrogen ions in the resin phase, π denotes the internal swelling pressure and $\overline{V_M}$, $\overline{V_H}$ denote the partial molar volume of alkali metal ions and hydrogen ions in the resin.

The change in the selectivity coefficient, should therefore, be considered to be due to the change in one or more of the three terms in equation (1).

Effect of non-exchanging ions :

The comparison of figures (2.01, 2.02 and 2.04) indicates that the selectivity coefficients for sodium-hydrogen and potassium-hydrogen exchange for resin X 8 are substantially higher when the non-exchanging ion is sulphate than when it is chloride. This is to be attributed to the changes in the first term of equation (1) and there may also be some contribution by changes in second term of equation (1), due to sorption of small quantities of electrolyte by the resin due to the Donnan membrane effect.

Figure 2.10

Plot of the maximum selectivity coefficient of (A) sodium-hydrogen exchange and (B) potassium-hydrogen exchange against definite values of $\bar{X}_M$ (from table 2.19).

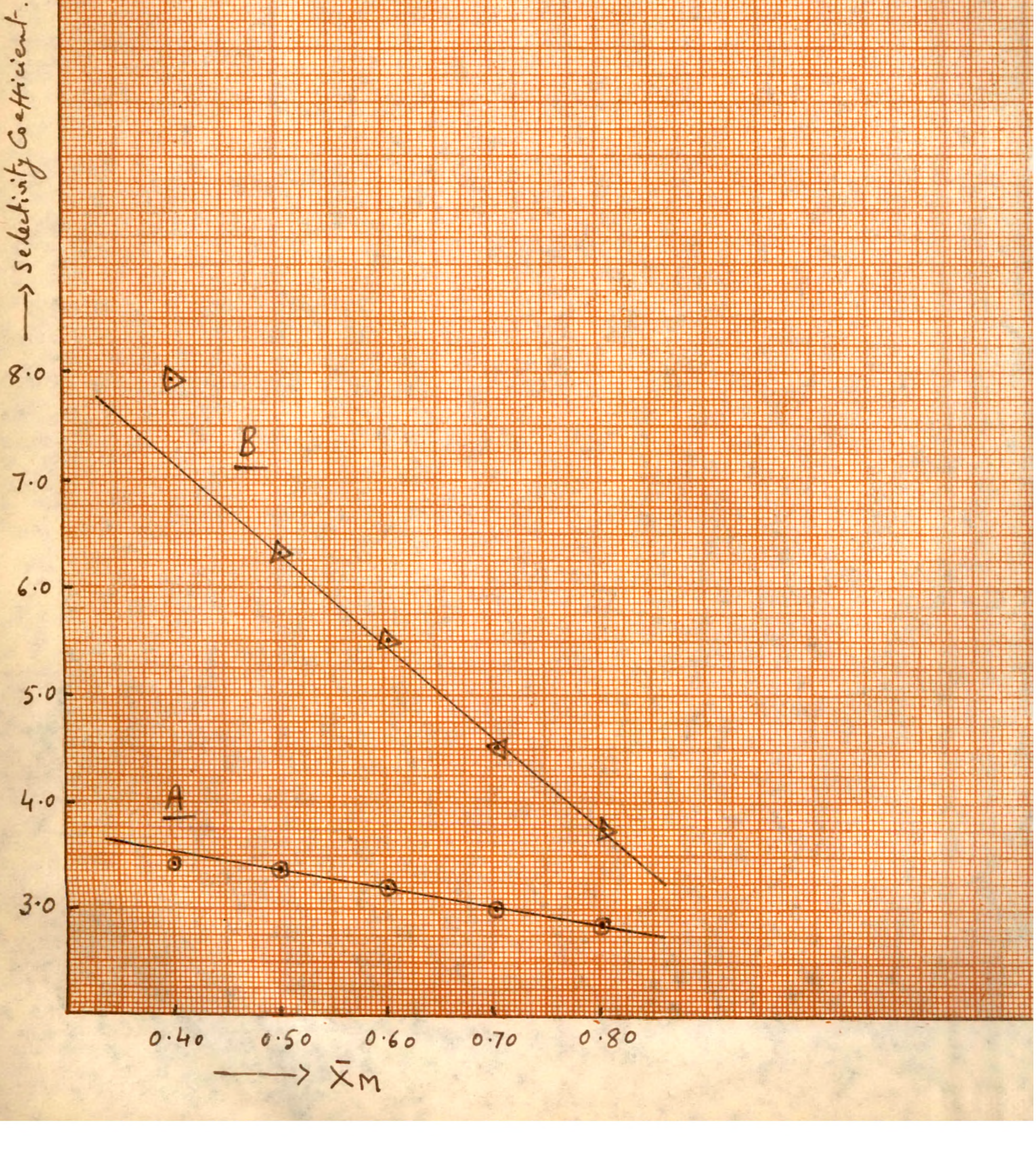


Figure 2.09

Plot of the selectivity coefficients for potassium-hydrogen exchange against % cross-linking X, for definite values of $\bar{X}_M$.

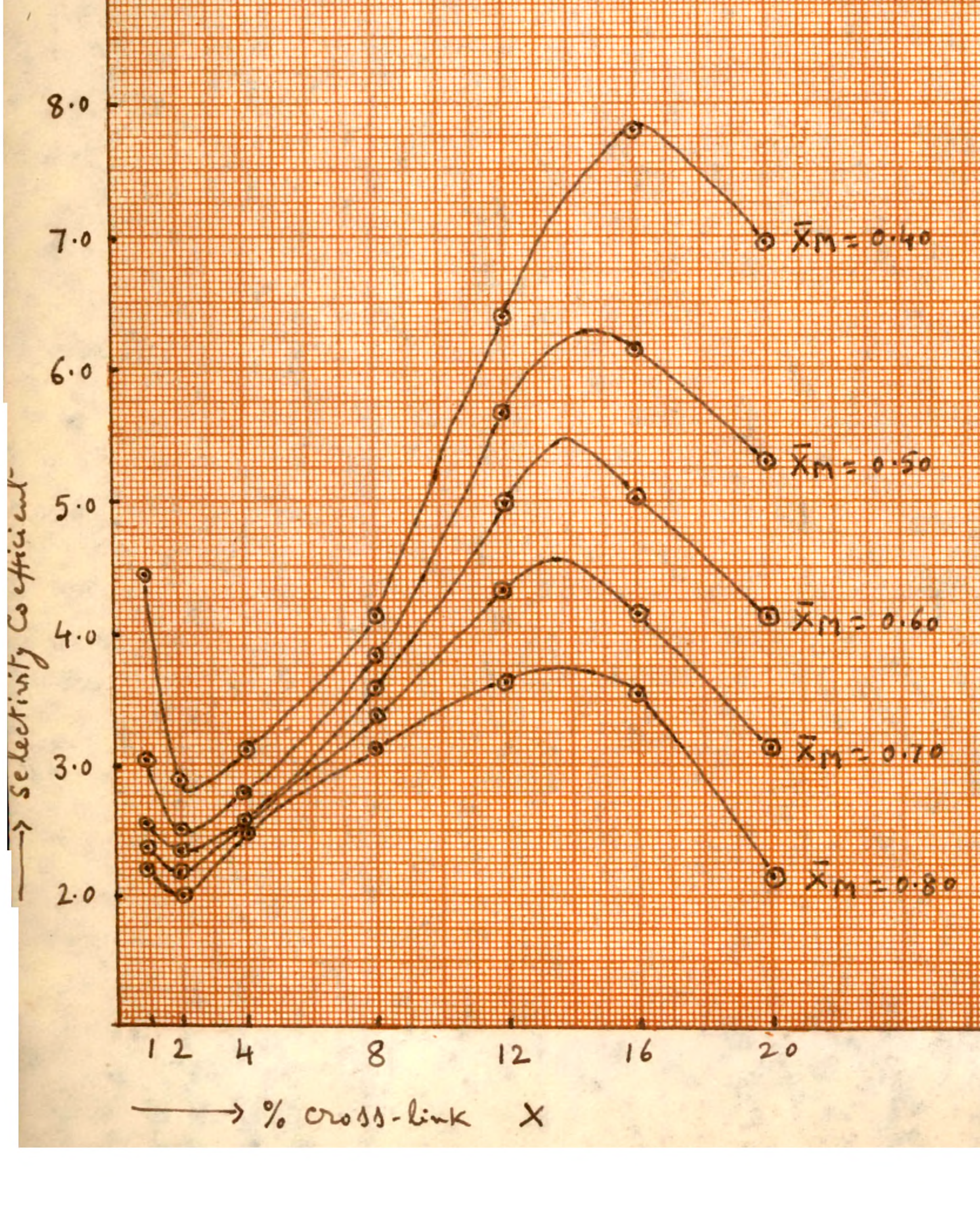


Figure 2.08

Plot of the selectivity coefficient for sodium-hydrogen exchange against % cross-linking X, for definite values of $\bar{X}_M$.

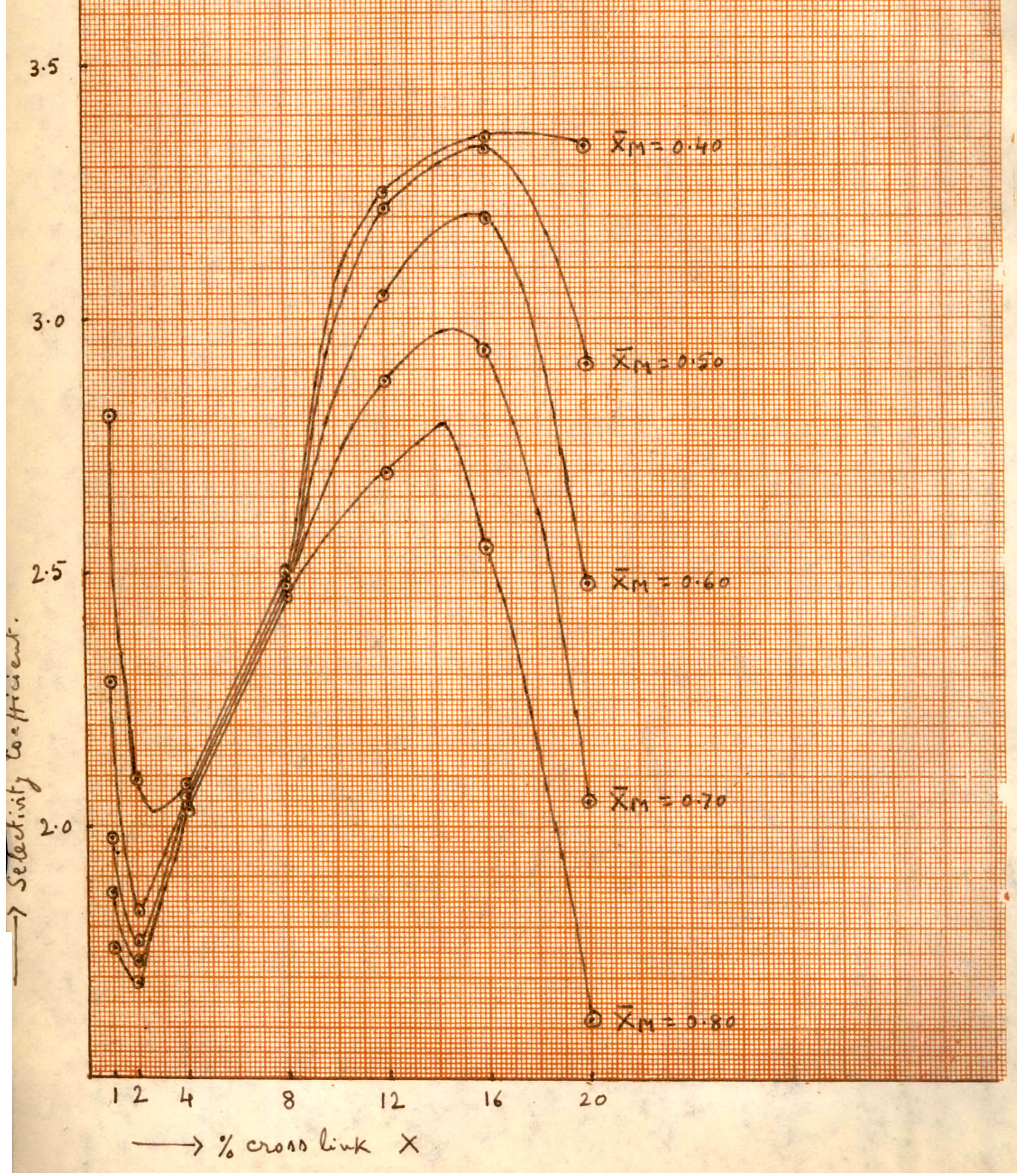


Table 2.17

Selectivity coefficients obtained from figures 2.02 and 2.03 for sodium-hydrogen exchange, for resins X 1 to X 20, at definite values of $\overline{X}_M$

$\overline{X}_M$	Values of K_H^{Na} for						
	X 1	X 2	X 4	X 8	X 12	X 16	X 20
0.40	2.81	2.10	2.08	2.50	3.25	3.36	3.34
0.50	2.29	1.83	2.06	2.49	3.22	3.34	2.91
0.60	1.98	1.77	2.05	2.48	3.05	3.20	2.48
0.70	1.87	1.73	2.04	2.47	2.88	2.94	2.05
0.80	1.76	1.69	2.04	2.46	2.70	2.55	1.62

Table 2.18

Selectivity coefficients obtained from figures 2.04 and 2.05 for potassium-hydrogen exchange, for resins X 1 to X 20, at definite values of $\overline{X}_M$

$\overline{X}_M$	Values of K_H^K for						
	X 1	X 2	X 4	X 8	X 12	X 16	X 20
0.40	4.45	2.91	3.12	4.15	6.40	7.77	6.95
0.50	3.06	2.51	2.80	3.84	5.70	6.15	5.30
0.60	2.55	2.35	2.58	3.60	5.00	5.02	4.15
0.70	2.38	2.17	2.56	3.38	4.35	4.15	3.15
0.80	2.22	2.00	2.55	3.16	3.65	3.55	2.15

Table 2.19

Values of the selectivity coefficient and X for maxima in the plots of figures 2.08 and 2.09 .

$\bar{X}_M$	K_H^{Na}	X	K_H^K	X
0.40	3.37	17.5	7.85	16.4
0.50	3.34	16.0	6.30	14.6
0.60	3.21	15.5	5.48	13.9
0.70	2.98	14.7	4.48	13.6
0.80	2.80	14.4	3.75	13.8

Table 2.20

Values of X for resins IR-120 and IR-200 obtained from figures 2.08 and 2.09 .

	Resin IR-120				Resin IR-200			
$\bar{X}_M$	K^{Na}_{H}	X	K^{K}_{H}	X	K^{Na}_{H}	X	K^{K}_{H}	X
0.40	2.45	7.8	4.12	7.9	3.45	-	8.00	-
0.50	2.45	7.8	3.90	8.2	3.13	11.0	5.90	12.5
0.60	2.45	8.0	3.65	8.2	2.80	9.6	4.55	10.8
0.70	2.47	8.2	3.40	8.1	2.47	7.8	3.73	9.5
0.80	2.47	8.2	3.15	8.0	2.15	5.0	2.93	6.6

Effect of $\overline{X}_M$:

Figures (2.02 to 2.05) indicate that for sodium-hydrogen exchange in sulphate solution, the selectivity coefficient either decreases with increase in $\overline{X}_M$ or decreases with increase in $\overline{X}_M$ over some range and is practically constant over some range. For potassium-hydrogen exchange in sulphate solution, the selectivity coefficient decreases with increase in $\overline{X}_M$. For a resin of particular X , this effect is to be attributed to the changes in the first two terms of equation (1). Small contribution may also be attributed to some volume changes in the resin particle as $\overline{X}_M$ increases. Another contributory reason may be that the resins, particularly of higher X , may be , to some extent , micro-heterogeneous (19 A) , containing regions of some-what different X . The competing counter ions M^+ , would be taken up by the different regions to different extents. For smaller values of $\overline{X}_M$, the counter ions would be mostly taken up, by regions having greater affinity for them ; for larger values of $\overline{X}_M$, the counter ions would be taken up relatively to greater extent , by regions having lower affinity for them.

Effect of X :

From figures (2.02 to 2.05) , the values of the selectivity coefficients were obtained for definite values of $\overline{X}_M$ (tables 2.17 and 2.18) for resins of different X . In figures (2.08 and 2.09) the selectivity coefficients for sodium-hydrogen exchange and potassium-hydrogen exchange are plotted against X , for definite values of $\overline{X}_M$. As the value of X increases, the charge density in the resin particle increases, since the relative degree of swelling decreases. With increase in X , and hence , the charge density ; at the definite $\overline{X}_M$ the selectivity coefficient first decreases as X increases from 1 to 2 ; then the selectivity coefficient increases , reaches a maximum and again decreases , as X increases . These variations in selectivity coefficients with X , at definite $\overline{X}_M$, should be attributed to changes in the second and third terms of equation (1) .

Table (2.19) gives the values of the selectivity coefficients and X for maxima in the figures (2.08 and 2.09) . It is observed that as $\overline{X}_M$ increases , the maximum selectivity coefficient is obtained with decreasing X.

Effect of a and structure :

Figure (2.06) indicates that for resin IR-120 the selectivity coefficient is essentially independent of a . From figure (2.06 A) , the values of the selectivity coefficients were obtained at definite values of $\overline{X}_M$, and then from figure (2.08), the values of X were read for sodium-hydrogen exchange. Similarly , from figure (2.06 B), the values of the selectivity coefficients were obtained for definite values of $\overline{X}_M$, and then from figure (2.09), the values of X were read for potassium-hydrogen exchange.

The values (table 2.20) indicate that X is fairely constant ($\sim$ 7.8 to 8.2) . This is in agreement with the fact that the resin IR-120 is of the same type structurally , as resins X 1 to X 20 and of X about 8.

For resin IR-200 , also, figure (2.07) , the selectivity coefficients are essentially independent of a . From figure (2.07 A) , the values of the selectivity coefficients were obtained for definite values of $\overline{X}_{M}$ and then from figure (2.08) , the values of X were read for sodium-hydrogen exchange. Similarly values were obtained from figures (2.07 B and 2.09) for potassium-hydrogen exchange . It is observed (table 2.20) that for some values of the selectivity coefficients , there are no corresponding values of X from figures (2.08 and 2.09), while other values obtained for X , vary significantly with $\overline{X}_{M}$. This means that the resin IR-200 is structurally of different type than other resins used . Though resin IR-200 is also based on styrene and divinyl benzene , and presumably of almost the same X , the polymerisation technique has been changed . The changes in the structure have also given better stability to artrition and temperature.

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