2. ION EXCHANGE EQUILIBRIA

2.1 Introduction (1-10 of chapter 1)

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

$$RA + B^+_{aq.} \rightleftharpoons RB + A^+_{aq.} \qquad (2.01)$$

and the selectivity coefficient, K^B_A is given by

$$K^B_A = \frac{[\bar{B}^+][A^+]}{[\bar{A}^+][B^+]} \qquad (2.02)$$

where $[A^+]$ denotes the concentration of cations A^+ in solution in gm. equivalents per liter,

$[B^+]$ denotes the concentration of cations B^+ in solution in gm. equivalents per liter,

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

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

$$K_a = \frac{[\overline{B^+}] \cdot \overline{\gamma}_B \cdot [A^+] \cdot \gamma_A}{[\overline{A^+}] \cdot \overline{\gamma}_A \cdot [B^+] \cdot \gamma_B} \qquad (2.03)$$

$$= K_A^B \cdot \frac{\overline{\gamma}_B \cdot \gamma_A}{\overline{\gamma}_A \cdot \gamma_B} \qquad (2.04)$$

where γ_A , γ_B 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 $\bar{y}_A \ / \ \bar{y}_B$ may not be equal to unity or equal to the ratio $y_A \ / \ y_B$.

Ion exchange as a Donhan 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 Donhan equation may be applied to both of these electrolytes, and

$$\bar{a}_{A^+} \cdot \bar{a}_{X^-} = a_{A^+} \cdot a_{X^-} \qquad (2.05)$$

and

$$\bar{a}_{B^+} \cdot \bar{a}_{X^-} = a_{B^+} \cdot a_{X^-} \qquad (2.06)$$

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 A^+ , B^+ and X^- in the resin phase.

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

$$\frac{\bar{y}_A \cdot y_B}{\bar{y}_B \cdot y_A} = \frac{\left[\overline{B^+}\right] \left[A^+\right]}{\left[\overline{A^+}\right] \left[B^+\right]} \qquad (2.07)$$

$$\text{or} \qquad K^{B}_{A} = \frac{\bar{y}_A \;/\; \bar{y}_B}{y_A \;/\; y_B} \qquad (2.08)$$

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

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-sulfonate$^-$.

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, determing 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 sulfonated polystyrene resins of different degree of crosslinking : the selectivity being greater for higher degree of crosslinking. The later 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 sulfonation was varied. This point is further more clearly proved by Deuel from work on soluble (noncrosslinked) polystyrene sulfonic 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 $\pi \bar{V}_i$, where $\bar{V}_i$ means the partial molar volume of i in the resin. Hence, the chemical potential of ions A^+ and B^+ will differ by $\pi(\bar{V}_A - \bar{V}_B)$ and the selectivity coefficient is given by

$$RT \ln K_A^B = \pi(\bar{V}_A - \bar{V}_B) \quad (2.09)$$

Complete Donnan theory :

According to complete Donnan theory the selectivity coefficient is given by

$$\ln K_A^B = \ln(\gamma_B / \gamma_A) - \ln(\bar{\gamma}_B / \bar{\gamma}_A) + \pi(\bar{V}_A - \bar{V}_B) / RT \quad (2.10)$$

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 expalined as follows. The term $\ln(\gamma_B / \gamma_A)$ for the solution can be calculated by the extended Debye-Hückel theory, since the external solution is quite dilute. The $\bar{\gamma}$ 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 $\bar{y}$ 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 $\bar{y}_B / \bar{y}_A$ 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-toluenesulfonic acid and its sodium salt, substances chosen for their structural similarity to a sulfonic 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

$$\Delta G = RT \ln p_2 / p_1 \qquad (2.11)$$

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,

$$\pi V_w = RT \ln (p_2 / p_1) \qquad (2.12)$$

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 $\overline{A^+}$: $\overline{B^+}$ 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 crosslinked 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 crosslinking. This ionic sieve effect is somewhat off-set by the existance 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 $\overline{X}$ in the resin :

It is observed that K^{B}_{A} 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 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 propertions 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

$$\frac{\delta \ln K_A^B}{\delta T} = \frac{\Delta H_A^B}{RT^2} \qquad (2.13)$$

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,

$$\left[\overline{X^+}\right]\left[\overline{Y^-}\right] = \left[X^+\right]\left[Y^-\right] \qquad (2.14)$$

An important consequence of this is that, for strong acid cation exchange resins, ions of the same sign as the resin structure are largely exclused 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 :

The sorption of nonelectrolytes by ion exchange resins has been noted in several systems, but is rather unpredictable. Adsorption effects are wellknown to be semispecific,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 shortrange 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 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.

2.2 Ion exchange equilibrium studies with different types of salts

2.2.1. Ion exchange equilibrium studies with strong acid-strong base type salts :

2.2.1. a Introduction :

The cation exchange equilibria of univalent cations with sulfonic acid cation exchange resins in aqueous solution have been the subject of investigation of several workers (2-26, 28,29). 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 sulfonic acid cation exchange resins with univalent cations in aqueous sulfate solution.

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 crosslinking, X, (nominal % divinylbenzene content) of the resin and (c) the average particle diameter, a (in mm.), of the resin, on the selectivity coefficients for lithium-hydrogen exchange in aqueous sulfate solution ($\backsim$ 0.04 N) at room temperature ($\backsim$ 30°C). For comparison, the selectivity coefficient have also been obtained when the counter ion Li^+ is replaced by Na^+ and when the co-ion $SO_4^=$ is replaced by Cl^- in the solution.

2.2.1. b Experimental :

Resins : Resins used were the sulfonated styrene-divinylbenzene copolymer type sulfonic 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 X1, X2, X4, X8, X12 and X16), prepared sample of a similar resin (from Permutit Co., London) of X=20 (this is further referred to as resin X 20) and Amberlite resins (Rohm and Haas Co.) IR-120 and IR-200 (these are further referred to as resins IR-120 and IR-200).

Chemicals : Lithium sulfate, lithium chloride, sodium 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. 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 gm.) of air-dry resin in clean, dry weighing bottles, in an oven (100-103°C) to a constant weight and % moisture content was then calculated.

For the estimation of the capacity of the resins, weighed samples (∽ 0.5 gm.) of air-dry 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 (2.2.1.01) gives the obtained values for % moisture content and capacity of different resins.

Solutions : The solutions of salts were prepared by dissolving known weight in distilled water to known volumes. Lithium sulfate solution was rechecked by sulfate estimation (as barium sulfate). Lithium chloride and sodium chloride solutions were rechecked by chloride titration (Mohr's method). The solutions were then suitabely diluted (∽ 0.04 N) and the concentrations accurately calculated.

Determination of selectivity coefficients :

Weighed quantities of air-dry resins were contacted with known volumes of the salt solution (∽ 0.04 N) in well-stoppered flasks with frequent shaking at room temperature (∽ 30°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 the acid liberated, by titration with standard sodium hydroxide solution.

The selectivity coefficient K_H^M, for the exchange reaction

$$\overline{H^+} + M^+ \rightleftharpoons \overline{M^+} + H^+ \qquad (2.15)$$

is given by

$$K_H^M = \frac{\left[\overline{M^+}\right]_e \left[H^+\right]_e}{\left[\overline{H^+}\right]_e \left[M^+\right]_e} \qquad (2.16)$$

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

Hence the selectivity coefficient is given by

$$K_H^M = \frac{\left[H^+\right]_e^2}{\left\{\left[\overline{H^+}\right]_i - \left[H^+\right]_e\right\}\left\{\left[M^+\right]_i - \left[H^+\right]_e\right\}} \qquad (2.17)$$

where $\left[\overline{H^+}\right]_i$ denotes the gm. equivalents of resin in hydrogen form added initially, per liter of solution, and $\left[M^+\right]_i$ denotes the initial concentration of cations M in aqueous solution, in gm, equivalents per liter.

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

2.2.1.c Results :

Table (2.2.1.01) gives the value of % mositure content and capacity of different resins.
Table (2.2.1.02) and figure (2.2.1.1) give the veriation of the selectivity coefficients for resins X1 to X16 with $\overline{X}_M$, in sulfate solution for lithium-hydrogen exchange.
Table (2.2.1.03) and figure (2.2.1.2) give the variation of the selectivity coefficients for resins X1 to X16, with $\overline{X}_M$, in chloride solution for lithium-hydrogen exchange.
Table (2.2.1.04) and figure (2.2.1.3) give the variation of the selectivity coefficient for resins X1 to X16,with $\overline{X}_M$, in chloride solution for sodium-hydrogen exchange.
Tables (2.2.1.05 and 2.2.1.06) and figure (2.2.1.4) give the variation of the selectivity coefficient for resins IR-120 and IR-200 of different particle diameter, in sulfate solution for lithium-hydrogen exchange.
Tables (2.2.1.07 and 2.2.1.08) and figure (2.2.1.5) give the variation of the selectivity coefficients for resins IR-200 of different particle diameter, in chloride solution for lithium-hydrogen and sodium-hydrogen exchange.
Table (2.2.1.09) gives the selectivity coefficients obtained from figure (2.2.1.1) for lithium-hydrogen exchange for resins X1 to X16 at definite values of $\overline{X}_M$ and figure (2.2.1.6) gives the plots of these selectivity

coefficients at definate values of $\overline{X}_M$, against X, for lithium-hydrogen exchange in sulfate solution.
Table (2.2.1.10) gives the values of X for resins IR-120 and IR-200 obtained from figure (2.2.1.6)

Table 2.2.1.01

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	0.58	30.8	3.43	4.96
IR-120	0.37	29.9	3.48	4.96
IR-200	0.84	28.8	3.40	4.78
IR-200	0.58	28.1	3.44	4.78

Table 2.2.1.02

Exchange equilibrium of cation exchange resins with lithium sulphate : $10^2 [M^+]_i = 3.905$

Resin	$10^2 [H^+]_i$	$10^2 [H^+]_e$	$\overline{X}_M$	K_H^M
X 1	1.263	1.020	0.8074	1.482
	2.113	1.505	0.7169	1.589
	3.434	1.961	0.6255	1.686
	4.186	2.302	0.5498	1.756
	6.264	2.818	0.4498	2.121
	12.60	3.837	0.3047	2.471
X 2	1.191	0.9714	0.8162	1.465
	1.966	1.421	0.7228	1.491
	2.949	1.852	0.6282	1.524
	3.930	2.170	0.5521	1.544
	5.892	2.626	0.4457	1.652
	7.874	2.926	0.3716	1.769
	11.89	3.382	0.2844	2.569

Table 2.2.1.02 (Continued)

Resin	$10^2 \left[\overline{H}^+\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
X 4	1.165	0.9594	0.8231	1.519
	1.931	1.409	0.7298	1.524
	2.885	1.817	0.6296	1.480
	3.844	2.134	0.5552	1.504
	5.761	2.554	0.4433	1.506
	7.672	2.843	0.3705	1.576
	11.51	3.238	0.2813	1.900
	15.36	3.554	0.2250	2.221
X 8	1.137	0.9294	0.8177	1.397
	1.878	1.361	0.7247	1.409
	2.796	1.751	0.6262	1.361
	3.734	2.050	0.5493	1.347
	5.588	2.470	0.4421	1.363
	7.459	2.783	0.3730	1.475
	11.17	3.118	0.2787	1.533
	14.89	3.310	0.2223	1.590

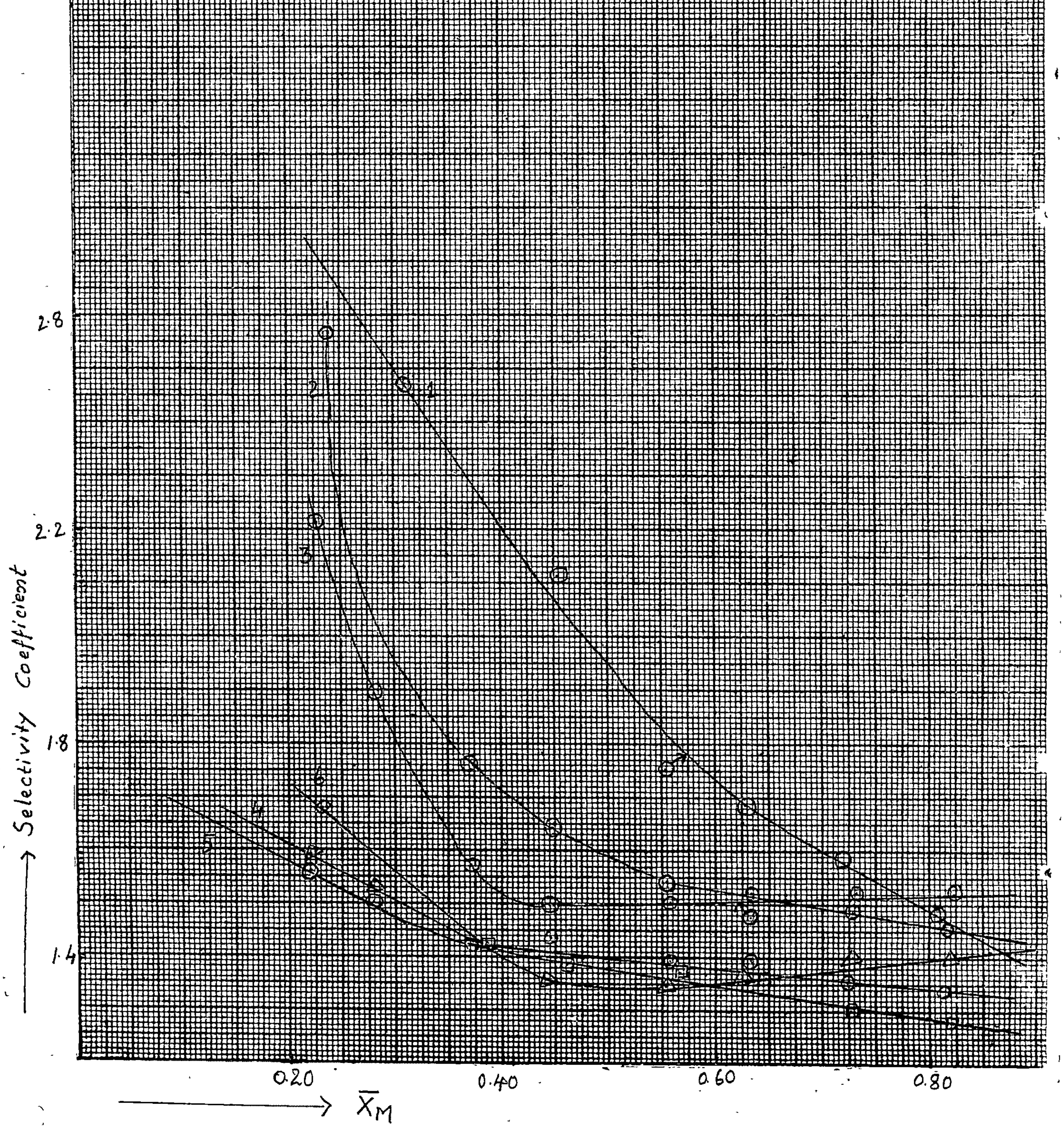

Fig. 2.2.1.1 Variation of the selectivity coefficient with $\overline{X}_M$ for the resins (1) X1, (2) X2, (3) X4, (4) X8, (5) X12 and (6) X16 in lithium sulfate solution.

Table 2.2.1.02 (Continued)

Resin	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K_H^M
X 12	1.137	0.9175	0.8072	1.283
	1.884	1.355	0.7193	1.361
	2.799	1.763	0.6299	1.401
	3.744	2.074	0.5540	1.407
	5.608	2.506	0.4469	1.446
	7.491	2.770	0.3698	1.432
	11.28	3.142	0.2786	1.590
	15.03	3.310	0.2203	1.571
X 16	1.072	0.8754	0.8166	1.286
	1.776	1.289	0.7257	1.305
	2.662	1.703	0.6392	1.369
	3.558	2.015	0.5662	1.392
	5.319	2.434	0.4576	1.395
	7.087	2.722	0.3841	1.435
	10.65	3.118	0.2727	1.640
	14.24	3.310	0.2325	1.685

Table 2.2.1.03

Exchange equilibrium of cation exchange resins with lithium chloride : $10^2 \left[M^+ \right]_i = 3.868$

Resin	$10^2 \left[\overline{H^+} \right]_i$	$10^2 \left[H^+ \right]_e$	$\overline{X}_M$	K^M_H
X 1	1.261	0.9309	0.7384	0.8939
	2.103	1.351	0.6422	0.9636
	3.147	1.734	0.5509	0.9970
	4.200	2.044	0.4867	1.063
	6.275	2.506	0.3994	1.224
	8.370	2.860	0.3417	1.472
X 2	1.195	0.8943	0.7487	0.8943
	1.982	1.296	0.6539	0.9324
	2.966	1.655	0.5580	0.9436
	3.944	1.946	0.4937	0.9870
	5.912	2.360	0.3993	1.040
	7.879	2.677	0.3397	1.156
	11.85	3.090	0.2607	1.402
	15.79	3.407	0.2158	2.053

Table 2.2.1.03 (Continued)

Resin	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
X 4	1.153	0.8760	0.7593	0.9258
	1.930	1.266	0.6558	0.9266
	2.891	1.624	0.5618	0.9272
	3.863	1.898	0.4914	0.9305
	5.776	2.299	0.3981	0.9692
	7.691	2.579	0.3354	1.009
	11.57	2.993	0.2587	1.193
	15.37	3.212	0.2090	1.293
X 8	1.112	0.8448	0.7530	0.8696
	1.867	1.225	0.6560	0.8678
	2.789	1.575	0.5645	0.8714
	3.738	1.834	0.4908	0.8678
	5.585	2.232	0.3997	0.8816
	7.459	2.498	0.3349	0.8878
	11.16	2.848	0.2552	0.9122
	14.91	3.089	0.2072	0.9740

Fig. 2.2.1.2 Variation of the selectivity coefficient with $\overline{X}_M$ for the resins (1) X1, (2) X2, (3) X4, (4) X8, (5) X12 and (6) X16 in lithium chloride solution.

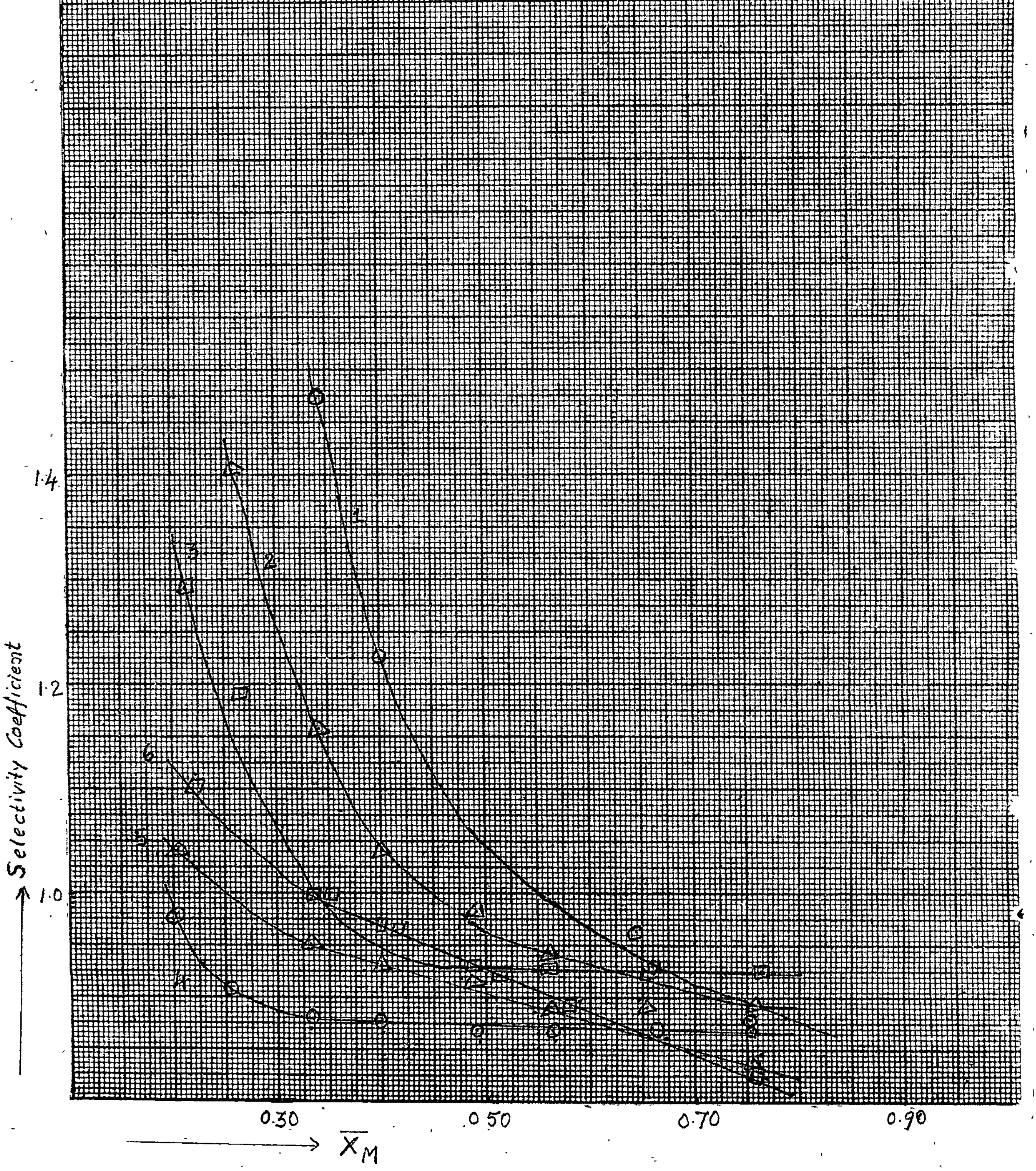

Table 2.2.1.03 (Continued)

Resin	$10^2\left[\overline{H}^+\right]_i$	$10^2\left[H^+\right]_e$	$\overline{X}_M$	K_H^M
X 12	1.140	0.8517	0.7474	0.8341
	1.941	1.259	0.6488	0.8910
	2.812	1.581	0.5624	0.8886
	3.834	1.886	0.4918	0.9210
	5.602	2.251	0.4018	0.9350
	7.532	2.530	0.3360	0.9566
	11.26	2.896	0.2572	1.031
	14.92	3.090	0.2071	1.038
X 16	1.079	0.8151	0.7553	0.8245
	1.803	1.192	0.6615	0.8696
	2.673	1.539	0.5757	0.8966
	3.590	1.825	0.5084	0.9241
	5.355	2.226	0.4159	0.9649
	7.124	2.506	0.3519	0.9986
	10.63	2.847	0.2678	1.020
	14.21	3.090	0.2175	1.104

Table 2.2.1.04

Exchange equilibrium of cation exchange resins with sodium chloride : $10^2 \left[M^+ \right]_i = 4.000$

Resin	$10^2 \left[\overline{H^+} \right]_i$	$10^2 \left[H^+ \right]_e$	$\overline{X}_M$	K_H^M
X 1	1.290	0.9851	0.7637	1.055
	2.096	1.397	0.6665	1.073
	3.118	1.817	0.5826	1.162
	4.219	2.157	0.5113	1.225
	6.246	2.634	0.4218	1.407
	8.341	2.996	0.3592	1.673
	12.47	3.561	0.2857	3.243
X 2	1.175	0.9194	0.7825	1.074
	1.936	1.339	0.6915	1.128
	2.892	1.745	0.6034	1.177
	3.921	2.070	0.5279	1.199
	5.773	2.490	0.4313	1.250
	7.847	2.808	0.3580	1.319
	11.57	3.243	0.2803	1.473
	15.44	3.532	0.2289	2.241

Table 2.2.1.04 (Continued)

Resin	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
X 4	1.942	1.397	0.7178	1.376
	2.892	1.803	0.6233	1.358
	3.877	2.113	0.5453	1.342
	5.773	2.533	0.4388	1.351
	7.745	2.837	0.3664	1.410
	11.56	3.185	0.2755	1.486
	15.52	3.474	0.2239	1.904
X 8	1.140	0.9482	0.8316	1.534
	1.864	1.390	0.7456	1.562
	2.797	1.831	0.6549	1.601
	3.773	2.172	0.5755	1.612
	5.593	2.620	0.4685	1.673
	7.476	2.924	0.3911	1.746
	11.19	3.243	0.2897	1.748

Fig. 2.2.1.3 Variation of the selectivity coefficient with $\bar{X}_M$ for the resins (1) X1, (2) X2, (3) X4, (4) X8, (5) X12 and (6) X16 in sodium chloride solution.

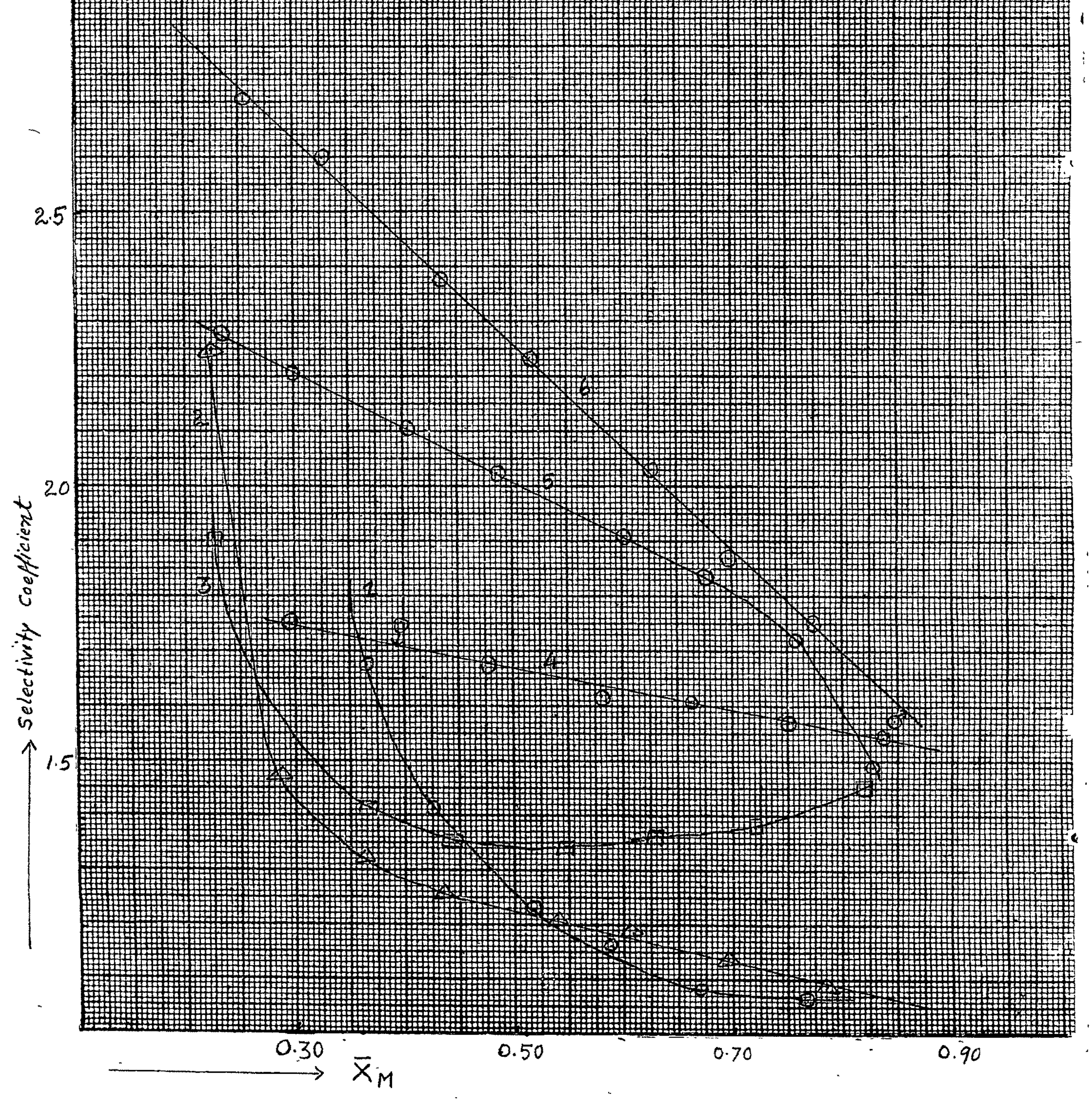

Table 2.2.1.04 (Continued)

Resin	$10^2\left[\overline{H^+}\right]_i$	$10^2\left[H^+\right]_e$	$\overline{X}_M$	K^M_H
X 12	1.169	0.9627	0.8233	1.479
	1.915	1.441	0.7521	1.711
	2.831	1.897	0.6701	1.832
	3.799	2.258	0.5944	1.900
	5.663	2.736	0.4831	2.023
	7.619	3.040	0.3990	2.102
	13.34	3.358	0.2961	2.201
	15.25	3.532	0.2315	2.275
X 16	1.095	0.9194	0.8397	1.559
	1.777	1.368	0.7698	1.739
	2.661	1.831	0.6884	1.863
	3.576	2.215	0.6195	2.020
	5.323	2.707	0.5087	2.217
	7.101	3.040	0.4282	2.371
	10.64	3.388	0.3183	2.586
	14.29	3.561	0.2493	2.693

Table 2.2.1.05

Exchange equilibrium of cation exchange resins with lithium sulphate :

Resin IR-120 ; $10^2 \left[M^+\right]_i = 3.905$

a (mm.)	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
0.58	1.035	0.8694	0.8395	1.503
	1.730	1.289	0.7453	1.441
	2.586	1.685	0.6515	1.419
	3.451	1.991	0.5768	1.418
	5.179	2.410	0.4652	1.403
	6.893	2.662	0.3862	1.348
	10.36	3.070	0.2962	1.548
	13.82	3.286	0.2376	1.657
0.37	1.058	0.8754	0.8271	1.386
	1.757	1.295	0.7370	1.391
	2.617	1.690	0.6459	1.392
	3.516	2.003	0.5697	1.393
	5.235	2.422	0.4627	1.406
	6.984	2.698	0.3863	1.407
	10.51	3.070	0.2921	1.517
	13.93	3.261	0.2342	1.548

Fig. 2.2.1.4 Variation of the selectivity coefficient with $\bar{X}_M$ for the resins (a) IR-120 ; O, a = 0.58 mm., △,a = 0.37 mm. and (b) IR-200 ; O ,a = 0.84 mm., △,a = 0.58 mm. in lithium sulfate solution.

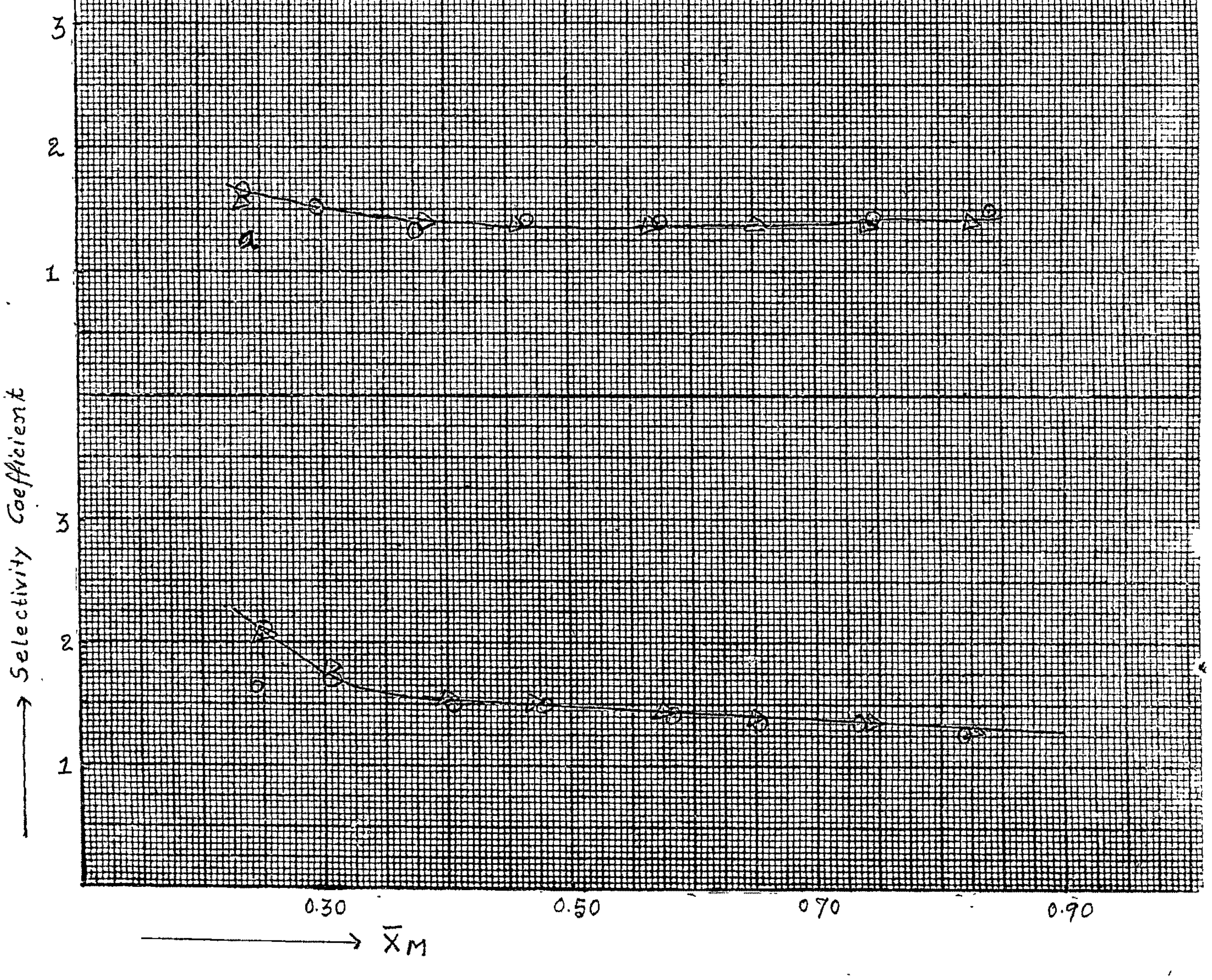

Table 2.2.1.06

Exchange equilibrium of cation exchange resins with lithium sulphate :

Resin IR-200 ; $10^2 \left[M^+\right]_i = 3.905$

a (mm.)	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
0.84	1.029	0.8453	0.8217	1.272
	1.720	1.265	0.7355	1.322
	2.560	1.666	0.6512	1.389
	3.438	1.991	0.5793	1.431
	5.122	2.434	0.4752	1.498
	6.832	2.734	0.4001	1.557
	10.28	3.098	0.3056	1.703
	13.69	3.383	0.2471	2.124
0.58	1.038	0.8574	0.8262	1.336
	1.730	1.277	0.7381	1.370
	2.582	1.679	0.6501	1.402
	3.475	2.003	0.5760	1.432
	5.176	2.446	0.4726	1.503
	6.901	2.746	0.3979	1.566
	10.31	3.142	0.3045	1.805
	13.80	3.383	0.2451	2.098

Table 2.2.1.07

Exchange equilibrium of cation exchange resins with lithium chloride :

Resin IR-200 ; $10^2 \left[M^+\right]_i = 3.868$

a (mm.)	$10^2 \left[H^+\right]_i$	$10^2 \left[H^+\right]_e$	$\bar{X}_M$	K^M_H
0.84	1.029	0.7785	0.7565	0.7830
	1.711	1.150	0.6719	0.8668
	2.558	1.503	0.5875	0.9053
	3.410	1.788	0.5244	0.9482
	5.108	2.202	0.4310	1.001
	6.829	2.494	0.3652	1.044
	10.29	2.896	0.2813	1.166
0.58	1.039	0.7909	0.7612	0.8193
	1.733	1.155	0.6671	0.8517
	2.587	1.527	0.5902	0.9396
	3.467	1.813	0.5229	0.9670
	5.163	2.214	0.4288	1.006
	6.898	2.519	0.3651	1.074
	10.40	2.920	0.2807	1.202
	13.78	3.163	0.2295	1.338

Fig. 2.2.1.5 Variation of the selectivity coefficient with $\bar{X}_M$ in (a) lithium chloride and (b) sodium chloride with the particle size ○, a = 0.84 mm. and △, a = 0.58 mm. of the resin IR-200.

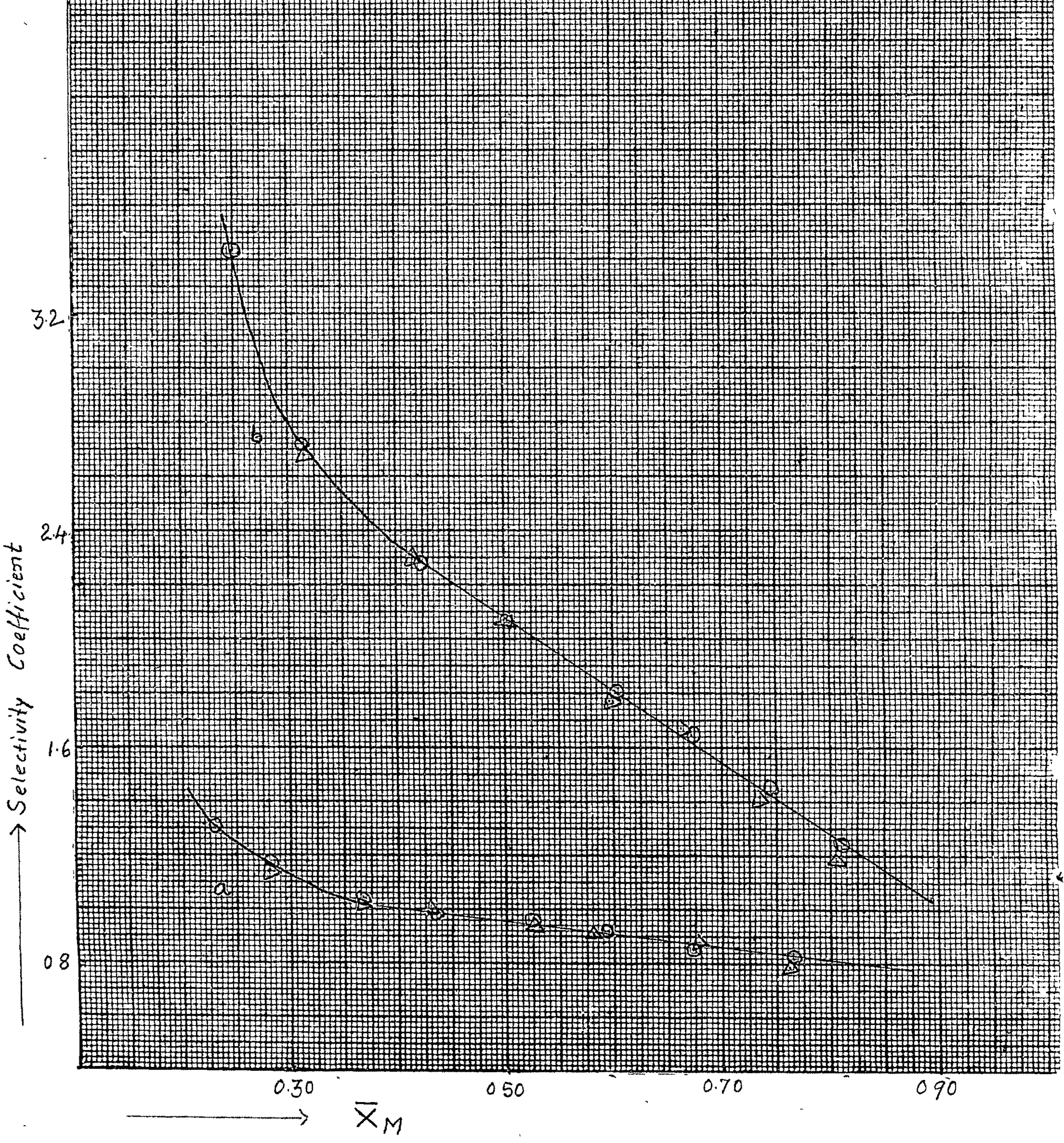

Table 2.2.1.08

Exchange equilibrium of cation exchange resins with sodium chloride :

Resin IR-200 ; $10^2 \left[M^+\right]_i = 4.000$

a (mm.)	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
0.84	1.108	0.8906	0.8042	1.173
	1.857	1.360	0.7324	1.409
	2.699	1.788	0.6625	1.662
	3.647	2.176	0.5967	1.764
	5.386	2.693	0.4999	2.060
	7.264	3.046	0.4193	2.305
	10.78	3.413	0.3163	2.694
0.58	1.121	0.9048	0.8071	1.225
	1.821	1.347	0.7396	1.442
	2.698	1.803	0.6683	1.653
	3.596	2.172	0.6039	1.811
	5.387	2.693	0.4999	2.059
	7.240	3.040	0.4200	2.293
	10.78	3.417	0.3167	2.719
	14.58	3.648	0.2501	3.456

2.2.1.d Discussion :

According to complete Donnan theory, the selectivity coefficient, K_H^M is given by

$$\ln K_H^M = \ln (\gamma_M / \gamma_H) - \ln (\bar{\gamma}_M / \bar{\gamma}_H) + \pi (\bar{V}_H - \bar{V}_M) / RT \qquad (2.10)$$

where γ_M , γ_H denote the activity coefficients of alkali metal ions and hydrogen ions in solution , $\bar{\gamma}_M$, $\bar{\gamma}_H$ denote the activity coefficients of alkali metal ions and hydrogen ions in the resin phase, π denotes the internal swelling pressure and $\bar{V}_M$, $\bar{V}_H$ 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 (2.10).

Effect of nonexchanging ions :

The comparison of figures (2.2.1.1 and 2.2.1.2) indicates that the selectivity coefficients are substantially higher when the nonexchanging ion is sulfate than when it is chloride. This is to be attributed to the changes in the first term of equation (2.10) and there may also be some contribution by changes in the second term of equation (2.10) due to sorption of small quantities of electrolyte by the resin due to the Donnan membrane effect.

Effect of $\overline{X}_M$:

Figures (2.2.1.1 to 2.2.1.3) indicate that for lithium-hydrogen exchange in sulfate solution, the selectivity coefficient, for resins X1 and X2 sharply decreases with increase in $\overline{X}_M$; for resins X4 and X8, it first sharply decreases and then somewhat increases with increase in $\overline{X}_M$; for resins X12 and X16, it first sharply and then slowly decreases with increase in $\overline{X}_M$. For lithium-hydrogen exchange in chloride solution, the selectivity coefficient, for resins X1,X2,X12 and X16 decreases with increase in $\overline{X}_M$ and for resins X4 and X8 it first decreases with increase in $\overline{X}_M$ over some range and is then practically constant over some range. For sodium-hydrogen exchange in chloride solution, the selectivity coefficient decreases with increase in $\overline{X}_M$. The behaviour for lithium-hydrogen exchange in sulfate solution is different from that of sodium-hydrogen and potassium-hydrogen exchange in sulfate solution with these resins (30). For a resin of perticular X, this effect is to be attributed to the changes in the first two terms of equation (2.10). 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, perticularly of higher X, may be, to some extent, micro-heterogeneous (19A), containing regions of somewhat different X. The competing counter ions M^+, would be taken up by the different regions to different extents.

Fig. 2.2.1.6 Variation of the selectivity coefficient with X at definate values of $\bar{X}_M$ in lithium sulfate solution.

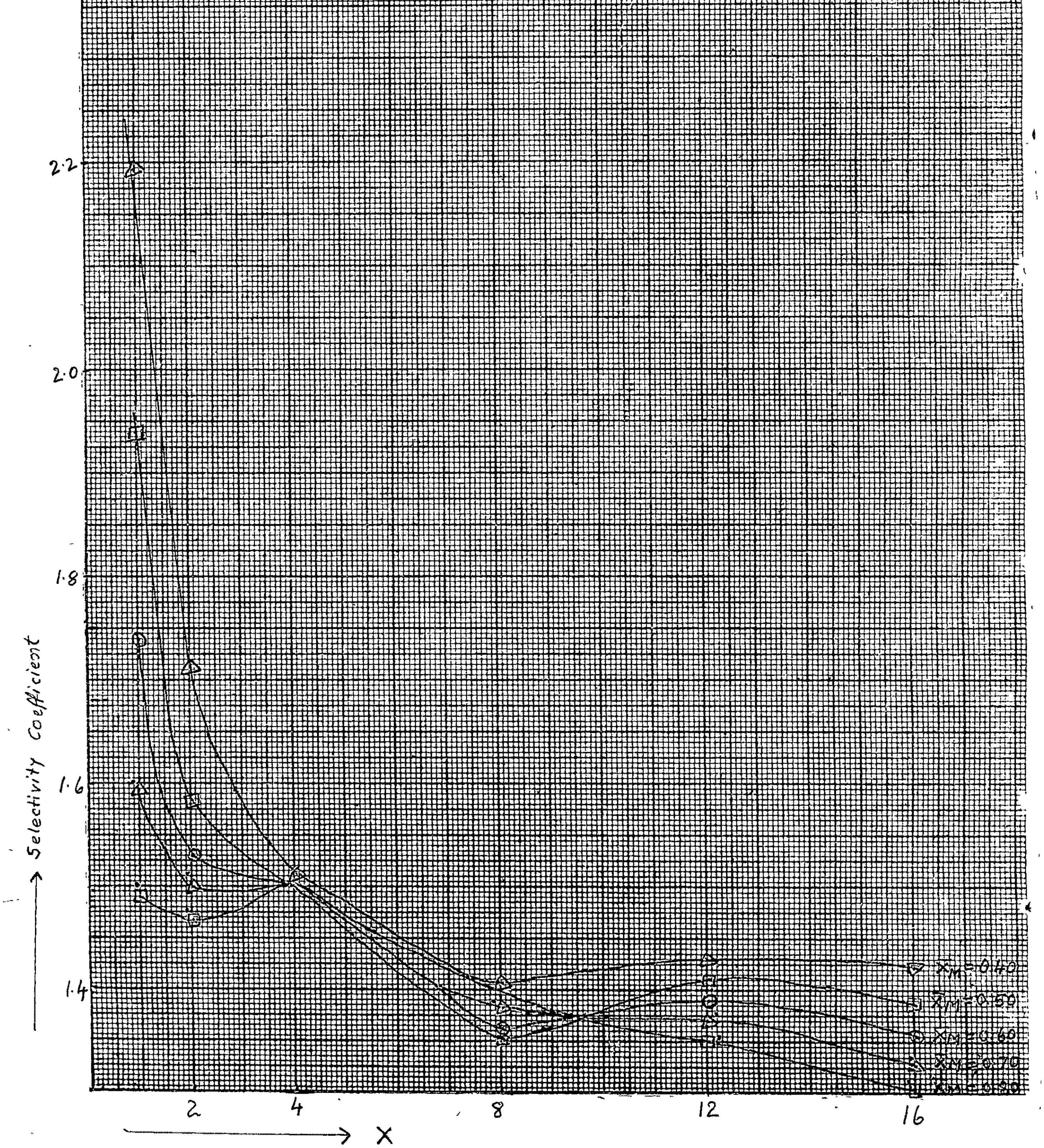

Table 2.2.1.09

Values of selectivity coefficients obtained from figure 2.2.1.1 for lithium-hydrogen exchange in sulfate solution, for resins X1 to X16, at definate values of $\overline{X}_M$

$\overline{X}_M$	Values of K_H^M for					
	X1	X2	X4	X8	X12	X16
0.40	2.195	1.715	1.510	1.405	1.430	1.420
0.50	1.940	1.585	1.500	1.350	1.410	1.385
0.60	1.740	1.530	1.510	1.360	1.390	1.355
0.70	1.595	1.500	1.515	1.380	1.370	1.325
0.80	1.490	1.470	1.520	1.400	1.350	1.295

Table 2.2.1.10

Values of X for resins IR-120 and IR-200 obtained from figure 2.2.1.6

$\overline{X}_M$	Resin IR-120		Resin IR-200	
	K_H^M	X	K_H^M	X
0.40	1.40	-	1.55	3.4
0.50	1.35	8.0	1.50	4.0
0.60	1.36	8.0	1.45	5.5
0.70	1.38	8.0	1.40	7.0
0.80	1.40	8.0	1.35	12.0

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 figure (2.2.1.1) the values of the selectivity coefficients for lithium-hydrogen exchange in sulfate solution were obtained for definate values of $\overline{X}_M$ (table 2.2.1.09) for resins of different X. In figure (2.2.1.6) the selectivity coefficients are plotted against X, for definate 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 definate $\overline{X}_M$, the selectivity coefficient first decreases, then somewhat increases and again decreases slowly with increase in X. These variations in selectivity coefficients with X, at definate $\overline{X}_M$, should be attributed to changes in the second and third terms of equation (2.10).

Effect of a and structure :

Figure (2.2.1.4a) indicates that for resin IR-120 the selectivity coefficient is essentially independent of a . From figure (2.2.1.4a) the values of the selectivity coefficients were obtained at definate values of $\overline{X}_M$, and then from figure (2.2.1.6), the values of X were read for lithium-hydrogen exchange in sulfate solution. The values (table 2.2.1.10) indicate that X is fairly constant ($\sim$ 8.0). Same pattern was also obtained in sodium-hydrogen exchange and potassium-hydrogen exchange in sulphate solution (30). This is in agreement with the fact that the resin IR-120 is of the same type structurally, as resins X1 to X16 and of X about 8.

For resin IR-200 also, figures (2.2.1.4b and 2.2.1.5) the selectivity coefficients are essentially independent of a . From figure (2.2.1.4b), the values of selectivity coefficients for lithium-hydrogen exchange in sulfate solution were obtained for definate values of $\overline{X}_M$ and then from figure (2.2.1.6), the values of X were read for lithium-hydrogen exchange in sulfate solution. It is observed (table 2.2.1.10) that the values of 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 divinylbenzene, and presumably of X about 8. This may be so because of the change in the polymerisation technique. The changes in the structure are considered to have given better stability to attrition and temperature.

2.2.2 Ion exchange equilibrium studies with weak acid-strong base type salts :

2.2.2.a Introduction :

In the earlier section, ion exchange equilibrium studies of strong acid-strong base type salts with styrene-divinylbenzene copolymer based sulfonic acid cation exchange resins of different relative degree of crosslinking (% nominal divinylbenzene content) have been described. In this section, the study of ion exchange equilibria of some weak acid- strong base type salts (sodium formate and sodium acetate) is described.

2.2.2.b Experimental :

Resins : The resins used were from the same samples used in the earlier work.

Chemicals : Sodium acetate, sodium hydroxide and oxalic acid were of A.R.(B.D.H.) quality. Formic acid was of C.P.quality. Distilled water was used.

Solutions : All the solutions were prepared in distilled water. Sodium acetate was made anhydrous and then known weight was dissolved in known volume of water. For sodium formate, standard solutions of formic acid and base containing equivalent quantities were mixed. The solutions were then suitably diluted.

Procedure : The procedure for the study of exchange equilibria was similar to that given in the earlier work.

2.2.2.c Nomenclature :

$[AH]_e$ = the concentration of titratable acid in gm. equivalents per liter at equilibrium,

P.E. = percent exchange of the maximum possible =

$$100 \cdot \frac{[AH]_e}{[M^+]_i} \text{ or } 100 \cdot \frac{[AH]_e}{[\bar{H}^+]_i}$$

whichever is more,

$$1/R = \frac{[M^+]_i}{[\bar{H}^+]_i}$$

and

other symbols used are the same as given earlier.

2.2.2.d Results :

Tables (2.2.2.1 and 2.2.2.2) give the results obtained for sodium formate and sodium acetate for exchange with resins of different degree of crosslinking used.

Table 2.2.2.1

Exchange equilibrium of cation exchange resins with sodium formate : $10^2[M^+]_i = 3.985$

Resin	$10^2[\overline{H^+}]_i$	$10^2[\overline{M^+}]_e$	R	P.E.
X 1	2.575	2.478	0.6463	96.23
	4.154	3.430	1.042	86.08
	5.876	3.718	1.476	93.30
	8.332	3.848	2.090	96.56
	11.74	3.890	2.946	97.61
X 2	2.399	2.334	0.6022	97.27
	3.936	3.387	0.9879	86.04
	5.431	3.675	1.363	92.23
	7.800	3.789	1.957	95.08
	10.88	3.862	2.730	96.92
X 4	2.370	2.349	0.5947	99.12
	3.910	3.416	0.9823	87.38
	5.421	3.675	1.360	92.23
	7.767	3.776	1.948	94.75
	10.87	3.877	2.728	97.27
X 8	2.264	2.248	0.5682	99.26
	3.753	3.364	0.9417	89.56
	5.243	3.689	1.315	92.58
	7.570	3.833	1.900	96.18
	10.47	3.862	2.628	96.92

Table 2.2.2.1 (Continued)

Resin	$10^2\left[\overline{H^+}\right]_i$	$10^2\left[\overline{M^+}\right]_e$	R	P.E.
X 12	2.387	2.334	0.5991	97.73
	3.771	3.358	0.9462	89.04
	5.306	3.703	1.331	92.92
	7.567	3.833	1.899	95.83
	10.70	3.848	2.685	97.97
X 16	2.170	2.170	0.5446	100.0
	3.582	3.286	0.8989	91.75
	5.041	3.703	1.289	92.92
	7.219	3.819	1.811	95.83
	10.07	3.904	2.527	97.97
IR-200 a = 0.58	2.240	2.205	0.5620	98.44
	3.645	3.242	0.9147	88.94
	5.029	3.660	1.263	91.85
	7.274	3.848	1.825	96.56
	10.10	3.877	2.534	97.29

Table 2.2.2.2

Exchange equilibrium of cation exchange resins with sodium acetate : $10^2 \left[M^+\right]_i = 4.000$

Resin	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[\overline{M^+}\right]_e$	R	P.E.
X 1	2.530	2.498	0.6324	98.35
	4.092	3.758	1.023	92.93
	5.826	3.923	1.446	98.21
	7.551	3.967	1.888	99.17
	10.16	3.981	2.532	99.51
X 2	2.335	2.316	0.5837	99.17
	3.895	3.663	0.9736	94.06
	5.494	3.908	1.372	97.70
	7.002	3.938	1.750	98.44
	9.290	3.952	2.323	98.79
X 4	2.389	2.389	0.5973	100.0
	3.867	3.663	0.9668	99.91
	5.396	3.880	1.349	97.43
	6.977	3.952	1.744	98.79
	9.399	3.952	2.350	98.79
X 8	2.305	2.305	0.5761	100.0
	3.766	3.619	0.9414	96.10
	5.217	3.894	1.304	97.34
	6.711	3.938	1.688	98.44
	9.080	3.967	2.270	99.17

Table 2.2.2.2 (Continued)

Resin	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[\overline{M^+}\right]_e$	R	P.E.
X 12	2.300	2.288	0.5749	99.40
	3.785	3.619	0.9462	95.61
	5.357	3.923	1.340	98.01
	6.789	3.967	1.697	99.17
	9.149	3.967	2.287	99.17
X 16	2.191	2.191	0.5476	100.0
	3.601	3.519	0.9001	97.72
	5.002	3.894	1.250	97.34
	6.419	3.952	1.604	98.79
	8.527	3.952	2.131	98.79
IR-200	2.176	2.176	0.5441	100.0
a =	3.632	3.503	0.9078	96.47
0.58	5.060	3.866	1.265	96.65
	6.521	3.952	1.630	98.79
	8.660	4.000	2.165	100.0

2.2.2.e Discussion :

When a cation exchange resin is placed in an aqueous solution of a weak monobasic acid-strong base salt, MA, the following equilibria exist.

$$\overline{H^+} + M^+ \rightleftharpoons H^+ + \overline{M^+} \qquad (2.18)$$

$$H^+ + A^+ \rightleftharpoons HA \qquad (2.19)$$

Hence when AH is a weak acid, $\left[\overline{M^+}\right]_e$ is relatively much greater than $\left[H^+\right]_e$ and this is more so, the higher the pK value of the weak acid. Hence the value of P.E. at a perticular value of R is much higher than it would be if the salt were strong acid-strong base type under similar conditions. This is so as indicated by the results given in tables (2.2.2.1 and 2.2.2.2). The value of P.E. is high and reaches almost completion for lower and higher values of R. This is of interest, in that for the conversion of a resin in a perticular cation form, the use of weak acid - strong base salts may need a smallar volume of solution and hence a faster complete conversion may be achieved. It is, however, to be seen that molecular sorption (31) of weak acid on the resin should be low, as then, that would be eliminated in the usual washing of the resin in the perticular cation form. It is also to be noted that the effect of the degree of crosslinking as well as cations (Na^+ or K^+) (32) on the value of P.E. (which is high) is not marked.

2.2.3 Ion exchange equilibrium studies with strong acid - weak base type salts :

2.2.3.a Introduction :

In the earlier sections, ion exchange equilibrium studies of strong acid- strong base type salts and of weak acid - strong base type salts with styrene divinylbenzene copolymer based sulfonic acid cation exchange resins of different degree of crosslinking have been described. In this section, the study of ion exchange equilibria of a strong acid - weak base type salt (aniline hydrochloride) is described.

2.2.3. b Experimental :

Resins : The resins used were from the same samples used in the earlier work.

Chemicals : Aniline and sodium hydroxide used were of A.R. quality. For the preparation of aniline hydrochloride, dry gaseous hydrochloric acid was passed in a solution of distilled aniline in ether and the precipitated aniline hydrochloride was filtered, washed with ether and then vacuum-dried at room temperature, in a desiccator. The solutions were prepared with freshly prepared salt with known weight in known volume of distilled water and were rechecked by titration (bromination method). The agreement of the strength of the salt solution by two methods is illustrated by the following ;

Strength	
by weight	by titration
0.03929 N	0.03940 N

Procedure : The procedure for the study of exchange equilibria and the evaluation of the selectivity coefficients was same as given earlier,

2.2.3. c Nomenclature :

The symbols used are same as given in earlier work.

2.2.3.d Results :

Table (2.2.3.1) and figure (2.2.3.1) give the results for the variation of the selectivity coefficients for anilinium-hydrogen exchange with $\overline{X}_M$, for resins of different degree of crosslinking used.

Table (2.2.3.2) gives the selectivity coefficients obtained from figure (2.2.3.1) for anilinium-hydrogen exchange for resins X1 to X20 at definate values of $\overline{X}_M$ and figure (2.2.3.2) gives the plots of these selectivity coefficients at definate values of $\overline{X}_M$,against X, for anilinium-hydrogen exchange.

Table (2.2.3.3) gives the values of the selectivity coefficients and X for maxima in the plots of the figure (2.2.3.2) and figure (2.2.3.3) gives the plots of X and K against $\overline{X}_M$.

Table (2.2.3.4) gives the values of X for the resin IR-200, obtained from figure (2.2.3.2).

Table 2.2.3.1

Exchange equilibrium of cation exchange resins with aniline hydrochloride

Resin	$10^2[M^+]_i$	$10^2[\overline{H}^+]_i$	$10^2[H^+]_e$	$\overline{X}_M$	K^M_H
X1	4.041	2.509	1.766	0.7039	1.846
	4.041	4.200	2.433	0.5794	2.084
	4.041	5.906	2.816	0.4768	2.095
	4.041	7.551	3.066	0.4156	2.152
	4.041	9.228	3.225	0.3494	2.122
	3.940	10.90	3.291	0.3018	2.193
X2	4.027	2.332	1.805	0.7738	2.781
	4.027	3.889	2.502	0.6446	2.961
	4.027	5.405	2.896	0.5338	2.956
	4.027	6.949	3.145	0.4526	2.947
	4.027	8.563	3.298	0.3851	2.831
	4.119	10.97	3.489	0.3181	2.584
	4.119	14.05	3.592	0.2557	2.340

Table 2.2.3.1 (Continued)

Resin	$10^2 [M^+]_i$	$10^2 [\overline{H}^+]_i$	$10^2 [H^+]_e$	$\overline{X}_M$	K^M_H
X4	4.027	2.357	1.932	0.8204	4.198
	4.027	3.899	2.704	0.6933	4.617
	4.027	5.425	3.088	0.5693	4.345
	4.027	6.977	3.306	0.4737	4.128
	4.027	8.572	3.418	0.3989	3.721
	4.119	10.83	3.592	0.3314	3.383
	4.119	13.95	3.694	0.2588	3.166
X8	4.027	2.249	1.949	0.8668	6.095
	4.027	3.727	2.775	0.7447	6.463
	4.027	5.253	3.225	0.6139	6.393
	4.027	6.769	3.426	0.5060	5.839
	4.027	8.303	3.546	0.4271	5.754
	4.119	10.46	3.694	0.3531	4.745
	4.119	13.61	3.773	0.2771	4.172

Table 2.2.3.1 (Continued)

Resin	$10^2\left[M^+\right]_i$	$10^2\left[\overline{H}^+\right]_i$	$10^2\left[H^+\right]_e$	$\overline{X}_M$	K^M_H
X12	3.940	2.279	1.923	0.8439	5.151
	3.940	3.844	2.820	0.7336	6.936
	3.940	5.289	3.286	0.6212	8.241
	3.940	6.841	3.486	0.5095	7.977
	3.940	8.311	3.567	0.4290	7.186
	3.940	9.795	3.621	0.3698	6.659
	4.119	13.58	3.788	0.2789	4.429
	4.119	16.76	3.796	0.2266	3.443
X16	3.940	2.138	1.782	0.8318	4.119
	3.940	3.552	2.636	0.7422	5.687
	3.940	5.064	3.157	0.6279	6.805
	3.940	6.413	3.414	0.5322	7.386
	3.940	7.843	3.542	0.4515	7.326
	3.940	9.239	3.613	0.3911	7.124
	4.119	12.86	3.813	0.2970	5.400
	4.119	15.66	3.844	0.2455	4.546

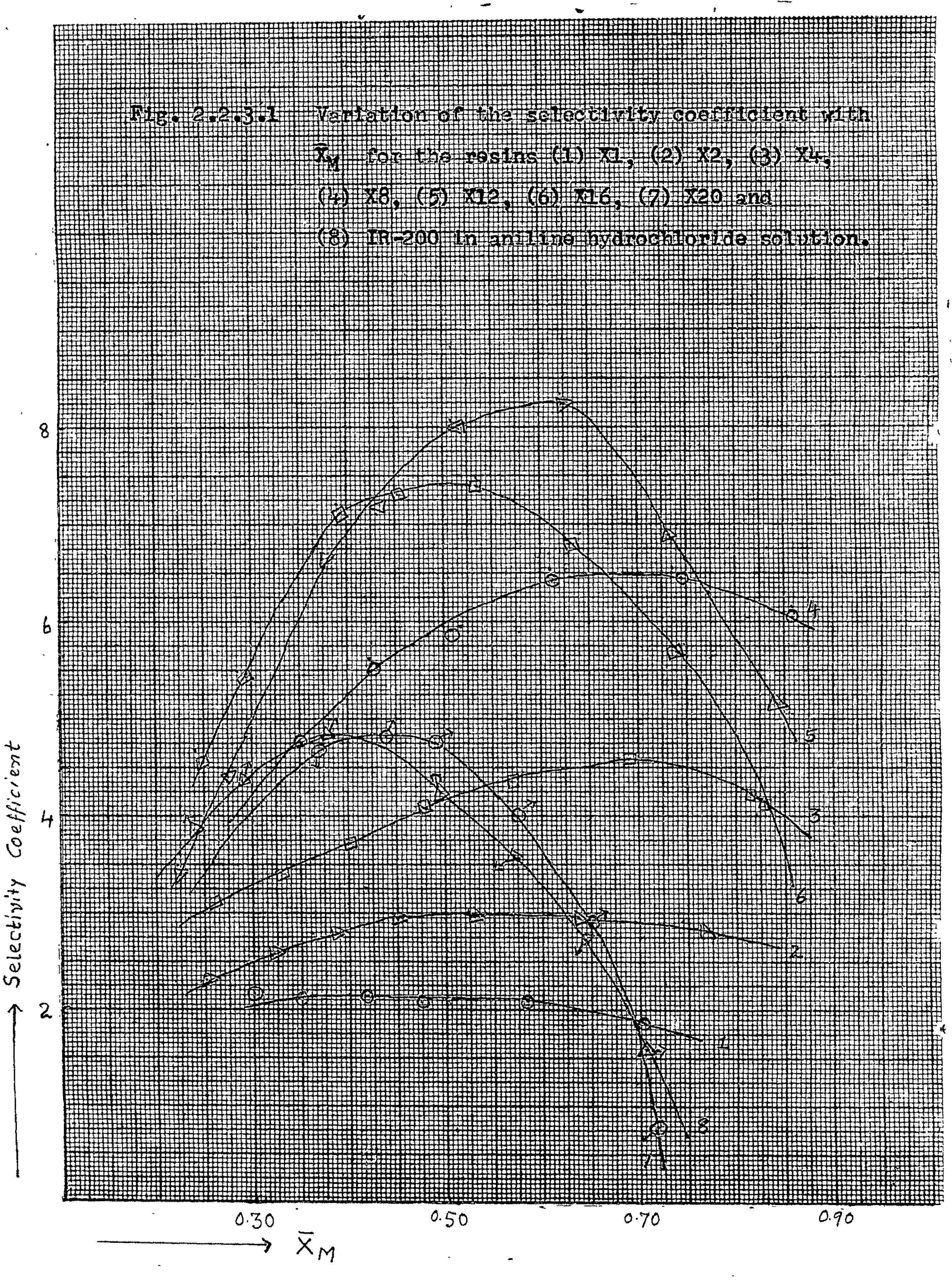

Fig. 2.2.3.1 Variation of the selectivity coefficient with $\bar{X}_M$ for the resins (1) X1, (2) X2, (3) X4, (4) X8, (5) X12, (6) X16, (7) X20 and (8) IR-200 in aniline hydrochloride solution.

Table 2.2.3.1 (Continued)

Resin	$10^2 \left[M^+ \right]_i$	$10^2 \left[\bar{H}^+ \right]_i$	$10^2 \left[H^+ \right]_e$	$\bar{X}_M$	K_H^M
X20	3.940	2.227	1.603	0.7196	1.761
	3.940	3.697	2.404	0.6503	2.912
	3.940	5.100	2.941	0.5766	4.011
	3.940	6.637	3.269	0.4925	4.730
	3.940	7.803	3.389	0.4343	4.805
	3.940	9.607	3.510	0.3653	4.697
IR-200 a = 0.58	3.940	2.179	1.546	0.7098	1.578
	3.940	3.678	2.372	0.6449	2.748
	3.940	5.063	2.885	0.5698	3.621
	3.940	6.506	3.205	0.4926	4.234
	3.940	7.916	3.382	0.4272	4.520
	3.940	9.393	3.510	0.3736	4.867
	4.119	13.07	3.773	0.2886	4.426
	4.119	15.84	3.805	0.2401	3.832

2.2.3.e Discussion :

Effect of $\overline{X}_M$

Table (2.2.3.1) and figure (2.2.3.1) indicate that the selectivity coefficient first increases and then decreases with increase in $\overline{X}_M$ in all cases studied. This behaviour is different from that studied for the strong acid- strong base type salts and weak acid - strong base type salts in the previous sections. This implies that the changes in the first two terms of the equation (2.10) dealing with the activity coefficients are of different type than those for strong acid - strong base type salts studied. Small contribution to the decrease in the selectivity coefficient at higher values of $\overline{X}_M$, may be attributed to some volume changes in the resin particle and another contributary reason may be that the resin may be, to some extent, microheterogenus (19A).

Effect of X

From figure (2.2.3.1) the values of the selectivity coefficients are obtained for definate values of $\overline{X}_M$ for resins of different X and are given in table (2.2.3.2). In figure (2.2.3.2) the selectivity coefficients are plotted against X, for constant values of $\overline{X}_M$. With increase in X, at constant values of $\overline{X}_M$, the selectivity coefficient increases and then decreases. This behaviour which is due to change in the second and third terms of equation(2.10) is again rather different from that for strong acid-strong base salts given earlier.

Fig. 2.2.3.2 Variation of the selectivity coefficient with X at definate values of $\bar{X}_M$ in aniline hydrochloride solution.

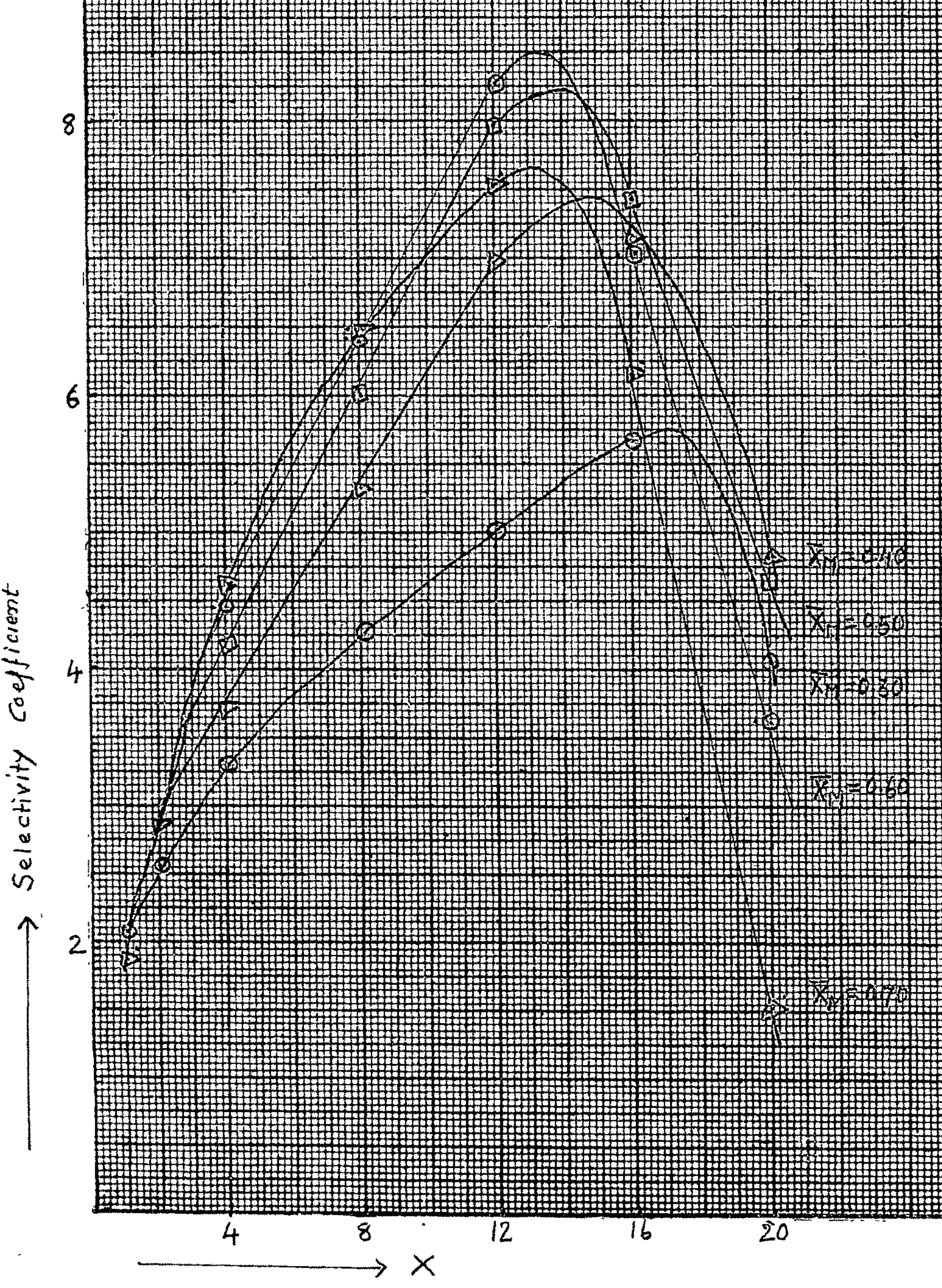

Table 2.2.3.2

Values of the selectivity coefficients obtained from figure 2.2.3.1 for anilinium-hydrogen exchange, for resins X1 to X20, at definate values of $\bar{X}_M$

$\bar{X}_M$	Values of K_H^M for						
	X1	X2	X4	X8	X12	X16	X20
0.30	2.075	2.55	3.30	4.25	5.00	5.65	4.05
0.40	2.15	2.85	3.70	5.30	6.95	7.15	4.80
0.50	2.10	3.00	4.15	6.00	7.95	7.40	4.65
0.60	2.05	2.95	4.45	6.40	8.25	7.05	3.60
0.70	1.85	2.90	4.60	6.45	7.50	6.15	1.50

Fig. 2.2.3.3 Variation of K and X with $\overline{X}_M$ for maxima in figure 2.2.3.2.

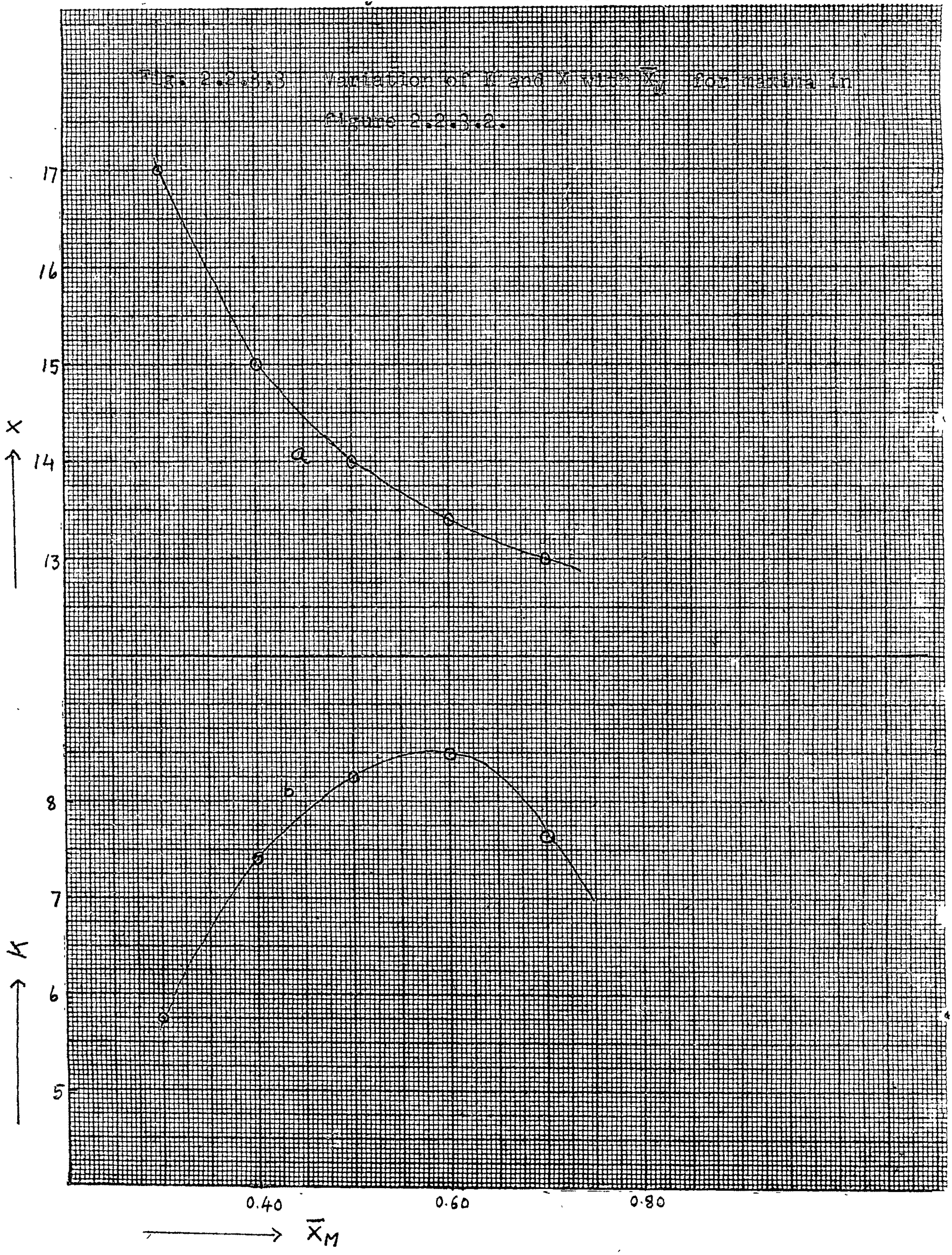

Table 2.2.3.3

Values of the selectivity coefficients and X for maxima in the plots of figure 2.2.3.2

$\overline{X}_M$	K_H^M	X
0.30	5.75	17.0
0.40	7.4	15.0
0.50	8.25	14.0
0.60	8.5	13.4
0.70	7.65	13.0

Table 2.2.3.4

Values of X for resin IR-200, obtained from figure 2.2.3.2

$\overline{X}_M$	K_H^M	X
0.30	4.50	9.2
0.40	4.85	7.0
0.50	4.15	4.2
0.60	3.25	2.2
0.70	1.70	0.8

Table (2.2.3.3) gives the selectivity coefficients and X for maxima in figure (2.2.3.2). It is observed that as $\overline{X}_M$ increases for the maximum selectivity coefficient, the values of X decreases (figure 2.2.3.3a) and the value of the maximum selectivity coefficient first increases and then decreases (figure 2.2.3.3b).

Effect of structure of the resin :

For resin IR-200, the values of the selectivity coefficients were obtained from figure (2.2.3.1) at definate values of $\overline{X}_M$ and then from figure (2.2.3.2) the values of X were read out for anilinium-hydrogen exchange. The values given in table (2.2.3.4) indicate that the values of X vary significantly with $\overline{X}_M$. This supports the conclusion that resin IR-200 is structurally of different type than other resins used, though it is also styrene-divinylbenzene copolymer based sulfonic acid cation exchange resin.

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