

CHAPTER VIII

Adsorption and Desorption of diquat on Amberlite IR-120 (Strong Cation Exchange Resin) System.

Amberlite IR-120 (Rohm & Haas Co., Philadelphia, U.S.A.), a styrene base sulphonic acid cation exchange resin, is commercially available as spherical, brown particles with 30+ mesh having an insoluble, high molecular weight polymeric and tightly cross-linked structural character. The resin consists of an enormous non diffusible anionic part and a simple small diffusible cationic part. The exchange of ions with resins take place throughout the whole gel structure of the resin and is not limited merely to surface effects (107, 264).

This strong cation exchanger was converted into its H-form by leaching the exchanger with 1.0(N) HCl until the leachate composition was constant. It was then washed with deionised water to free the chloride ions and air dried. The resin was then kept in a desiccator over saturated NH_4Cl solution (r.h. 79.5%). The ion exchange capacity of the resin was determined by direct titration of its acid form with standard KOH and was found to be 468. me/ per 100 gm of the dry resin (dried at 80°C).

For exchange study it was converted into the Na-form by adding an equivalent amount of NaOH. The Na-resin was then

air dried and placed in a desiccator over saturated NH_4Cl . After seven days, it was used for the exchange of diquat²⁺. A known weight of the resin was dried overnight in an air oven at 80°C and after drying, its weight was recorded. The difference gave the moisture content per gm. of the resin. The calculations were done on the basis of this dried resin at 80°C . The Na-IR-120 diquat resin complex was used for desorption studies.

The experimental procedures for studying adsorption of diquat was almost alike as in the case of clay minerals. About 0.1 gm of Na-IR-120 resin was taken into pyrex bottles to which increasing amount of diquat (of known concentration) was added. The total volume was kept constant (15 ml) in each case by adding requisite amount of water. The systems were allowed to equilibrate overnight after occasional shaking. After centrifugation, for about 15 minutes, the diquat contents of the supernatant liquids were estimated by a Beckman DU-2 Spectrophotometer at 307 nm as before.

To study desorption, the Na-IR-120-diquat resin * complex was weighed accurately (~ 0.1 gm) in pyrex bottles to which varying amounts of desorbing electrolytes were added. The volume was kept constant (15 ml.) in each case by adding requisite amount of deionised water. They were shaken for

about four hours and kept overnight to attain equilibrium (48 hours for organic electrolytes) and the diquat content of the solutions was estimated spectrophotometrically as above.

SECTION A

Sorption Studies

Sorption of diquat²⁺ on Na-IR-120 resin

Fig. 71 shows the exchange isotherm of diquat²⁺ on Na-IR-120 which belongs to the high affinity class in the classification of Giles et al (68). The plot of Q/x against Q (Fig. 71) is linear showing obedience to the Langmuir equation. From the slope of this straight line, the value of V_m is found to be 388 me/100 gm which agrees well with the maximum exchange i.e. 390 me/100 gm obtained from the flat portion of the sorption isotherm, but less than the exchange capacity (468 me/100 gm) of the resin. The lower value may be caused by the physical inaccessibility of the resin to the large-sized diquat²⁺ ions. The herbicide cations at low concentrations are found (Fig. 71) to be attached on the resin surface so strongly that the equilibrium concentration becomes negligible upto the exchange of about 315 me/100 gm as can be seen from the initial steep rise of the exchange isotherm.

SECTION B

Desorption studies

Desorption of diquat²⁺ from Na-IR-120-diquat

The results of the desorption of diquat²⁺ from its resin complex are shown in Figs. 72, 73, 74, 75, 76, 77 and in Table 13. The desorption isotherms with the monovalent and bivalent cations (Fig. 72, 73) show typical features as in the cases of clay minerals. On the basis of the extent of exchange as well as distribution and selectivity coefficients (Table 13), the cations can be arranged in the following order: $\text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ for the monovalent and $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ for the bivalent, maintaining almost the general lyotropic series. In the order of selectivities of monovalent cations for resin, it has often been observed that H^+ behaves anomalously (265, 266, 267) as noted here. It is interesting to note that the percentages of diquat²⁺ desorption from this resin by monovalent and bivalent inorganic ions are much higher than in the case of clay minerals excepting chlorite. This is probably due to the fact that the herbicide cation is less strongly held by the Amberlite IR-120 resin matrix than in the clay minerals studied in the present work.

In order to ascertain the role of ionic hydration (161, 263) in the exchange reactions, the desorption experiments have also been carried out in 50% aqueous-ethanolic

Table - 13

Description characteristics of diquat²⁺ with respect to different ions from Na-IR-120 Resin-diquat.

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
<u>1:1 Electrolyte</u>			
LiCl	0.1	2.34	0.0316
	0.3	2.54	0.0667
	0.5	2.21	0.0741
	1.0	1.83	0.0922
	2.0	1.23	0.0856
NaCl	0.1	4.71	0.0926
	0.3	4.44	0.1701
	0.5	3.76	0.1927
	1.0	2.54	0.1847
	1.5	1.82	0.1485
KCl	0.1	7.49	0.1932
	0.3	5.90	0.2843
	0.5	4.79	0.3192
	1.0	2.91	0.2657
	1.5	2.03	0.2040

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
NH ₄ Cl	0.1	6.29	0.1464
	0.3	5.23	0.2269
	0.5	4.23	0.2446
	1.0	2.72	0.2188
	1.5	1.92	0.1734
HCl	0.1	3.92	0.0696
	0.3	3.06	0.0906
	0.5	2.58	0.0966
	1.0	1.97	0.1063
	2.0	1.28	0.0956
RbCl	0.1	7.88	0.2101
	0.3	6.82	0.3785
	0.5	4.98	0.3505
	1.0	2.97	0.2822
	1.5	2.08	0.2223

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
CsCl	0.1	8.28	0.2276
	0.3	7.09	0.4094
	0.5	5.10	0.3708
	1.0	3.05	0.3065
	1.5	2.11	0.2323
<u>2:1 Electrolyte</u>			
MgCl ₂	0.025	8.59	0.2466
	0.05	6.95	0.2426
	0.1	5.46	0.2256
	0.2	4.44	0.2369
	0.4	3.55	0.2513
CaCl ₂	0.025	9.95	0.3449
	0.05	7.75	0.3166
	0.1	6.03	0.2937
	0.2	4.83	0.3091
	0.4	3.74	0.3118

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
SrCl ₂	0.025	10.53	0.3942
	0.05	8.28	0.3757
	0.1	6.46	0.3583
	0.2	5.14	0.3858
	0.4	3.91	0.3865
BaCl ₂	0.025	13.09	0.6839
	0.05	9.65	0.5801
	0.1	7.36	0.5593
	0.2	5.61	0.5801
	0.4	4.09	0.5192
<u>Quaternary ammonium salt</u>			
(CH ₃) ₄ NBr	0.1	3.80	0.0664
	0.2	4.61	0.1362
	0.3	4.51	0.1754
	0.4	4.16	0.1909
	0.6	3.59	0.2116

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
$(C_2H_5)_4NBr$	0.1	1.56	0.0211
	0.2	2.34	0.0462
	0.3	2.47	0.0639
	0.4	2.24	0.0655
	0.6	1.66	0.0517
$(C_3H_7)_4NBr$	0.1	0.93	0.0078
	0.2	0.78	0.0084
	0.3	0.80	0.0110
	0.4	0.82	0.0134
	0.6	0.74	0.0143
$(C_4H_9)_4NBr$	0.1	0.27	0.0012
	0.2	0.25	0.0015
	0.3	0.35	0.0032
	0.4	0.39	0.0042
	0.6	0.27	0.0030

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
DTABr	0.004	10.89	0.0612
	0.006	14.24	0.1125
	0.010	15.34	0.1635
	0.012	15.27	0.2091
	0.016	13.66	0.1757
DDTABr	0.004	5.40	0.0214
	0.006	6.56	0.0351
	0.010	6.69	0.0469
	0.012	6.22	0.0462
	0.016	4.90	0.0373
CTABr	0.004	2.93	0.0085
	0.006	3.26	0.0123
	0.010	2.93	0.0136
	0.012	2.93	0.0149
	0.016	2.56	0.0141

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
	0.004	1.46	0.0030
CPOL	0.006	1.62	0.0043
	0.010	1.36	0.0043
	0.012	1.30	0.0044
	0.016	1.22	0.0046
<u>Alkane diammonium salt</u>			
	0.01	18.56	0.7340
EDA	0.03	12.09	0.6578
	0.05	10.01	0.6535
	0.07	8.73	0.6346
	0.1	7.64	0.6535
	0.01	17.58	0.6502
PrDA	0.03	11.76	0.6086
	0.05	9.74	0.5977
	0.07	8.55	0.5889
	0.1	7.36	0.5594

Contd..

Table - 13 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
BaDA	0.01	16.75	0.5844
	0.03	11.56	0.5804
	0.05	9.46	0.5465
	0.07	8.30	0.5309
	0.1	7.25	0.5267

medium (Fig. 72, 73) with Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . It is observed that higher amount of diquat²⁺ is released from the resin matrix in 50% ethanolic medium than in pure aqueous medium for each of these desorbing ions. The order of preference is $\text{Li}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ for monovalent and $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ for bivalent inorganic ions, which is same as in the pure aqueous medium except in the position of NH_4^+ . According to Athavale et al (206), this anomalous behaviour of NH_4^+ may be due to its non spherical nature.

However the general characteristics of the exchange in the resin may be attributed to the altered solvation of

these ions, the resulting ionic sizes, their activities and the dielectric properties of the solvent mixture on the coulombic interactions. From the studies of monovalent cations on sulphonic acid type of resin in aqueous and mixed solvent media it has been inferred by Athavale et al (206) that the order of selectivities of the cations is governed by their capacities to form contact type of ion-pairs with the resin-sulphonate, both in the aqueous and in the mixed solvents. Similar assumptions may be made here to explain the experimental results. In this connection, Reichenberg's (232) discussion on the basic interactions underlying ion exchange selectivities of alkali metal ions as due to "a balance between (i) Coulomb interactions between the mobile counterions (in various states of hydration) and the fixed groups of the exchanger, and (ii) ion-dipole and ion-induced dipole interactions between the counterions and water molecules (ionic hydration)", may be recalled.

As noted in the case of clay minerals, here also the plots of hydrated ionic radius as well as the reciprocal of the Debye-Hückel parameter, a^0 , against logarithm of the selectivity coefficient (Fig. 77) are linear for bivalent inorganic ions while for the monovalent inorganic ions, linearity is obtained only with $1/a^0$ in aqueous medium. This implies that in the case of monovalent ions, a^0 is a better

parameter than hydrated ionic radius to correlate and predict the relative affinities of the ions for the resin whereas for the bivalent ions, both the parameters may be used to this end.

The exchange isotherms with organic ions are shown in Figs. 74, 75, 76. It can be seen that the amounts of diquat²⁺ released by DDTA⁺, CTA⁺, CP⁺, (C₂H₅)₄N⁺, (C₃H₇)₄N⁺ and (C₄H₉)₄N⁺ are much smaller than the inorganic ions and the exchange is inversely related to the size of the ions. The size of the organic ions may be too big to pass another ion into the narrow cavities of the rigid non-swelling resin structure and the results can be interpreted in terms of the space requirements as shown by Barrer, Buser and Grutter (221). This is a classic example of selectivity vis-a-vis ion-sieve action imposed by the structure of the adsorbent and observed in all members of the Zeolite group of minerals (272). Interestingly, the isotherms with (CH₃)₄N⁺, (C₂H₅)₄N⁺, DTA⁺ and DDTA⁺ are S-shaped and may be placed in the S-group of curves of Giles et al (211). The curves are initially convex towards the concentration axis, tending to change the curvature to that of a concave one at the latter stages. The S-type of isotherms indicate cooperative adsorption i.e. adsorption occurs with increasing ease as the solute concentration increases in the initial part of the isotherm,

suggesting that adsorbed molecules encourage the retention of additional like-molecules at adjacent sites. Recent theoretical treatment^{by}/Giles et al (211), however, shows that this type of curve occurs when the activation energy for desorption of the solute is concentration dependent, and/or is markedly reduced by large negative contributions of the solvent or a second solute.

The desorption by alkanediammonium ions i.e. EDA, PrDA and BuDA (Fig. 76), however, presents a higher exchange of diquat²⁺ from the resin matrix compared with the other organic ions studied, although an inverse relation was observed between the maximum exchange and the molecular weight. Due to their short-chain structure, possibly these ions experience less steric hindrance and also owing to their double charge sites in the structure, probably an important contribution of van der Waals interaction causes the higher affinity of the alkanediammonium ions for the resin surface. A similar decrease in the maximum exchange with increasing molecular weight of the alkanediammonium ions was observed in the Zeolite -X by Vansant and Vanhoof (224) and has been attributed to the space requirement of the ions and the difficulties of packing of these organic ions in the Zeolite framework.

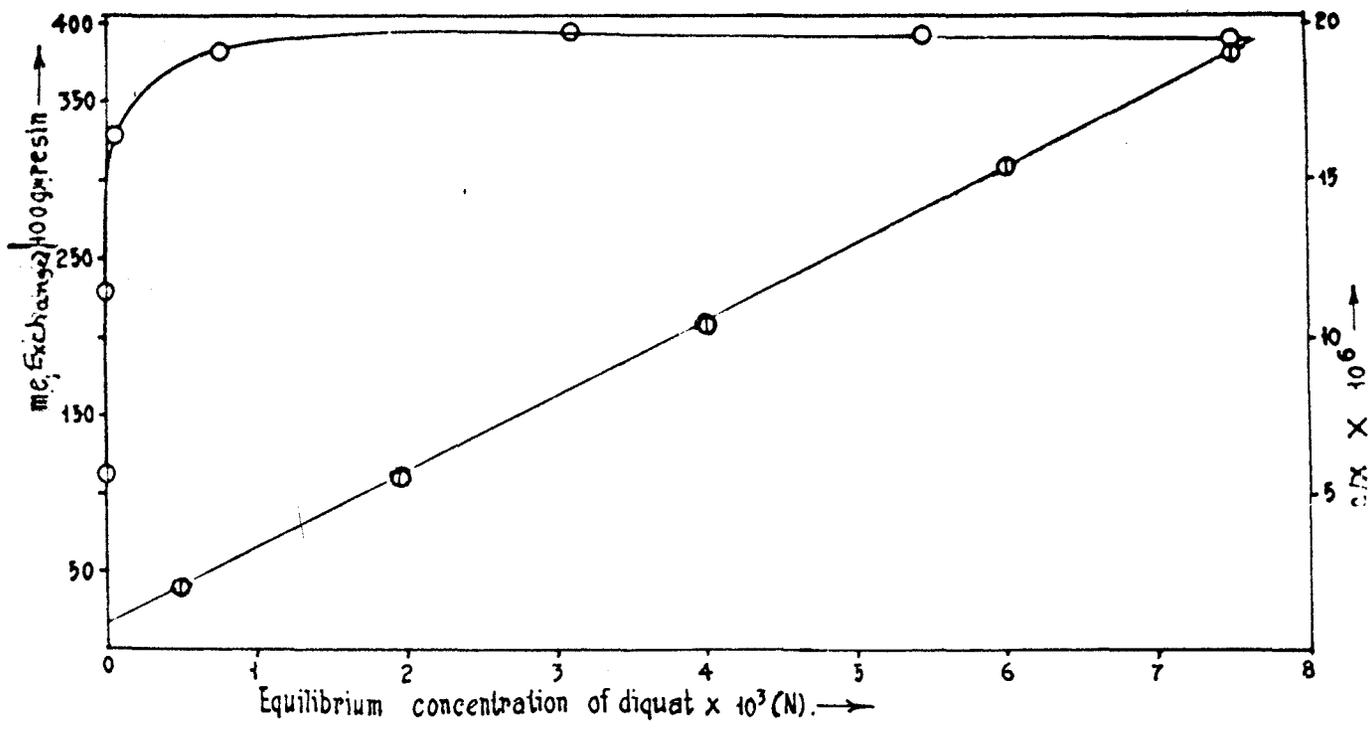


Fig. 71. Exchange isotherm of diquat on Na-9R-120, strong Cation Exchange resin.

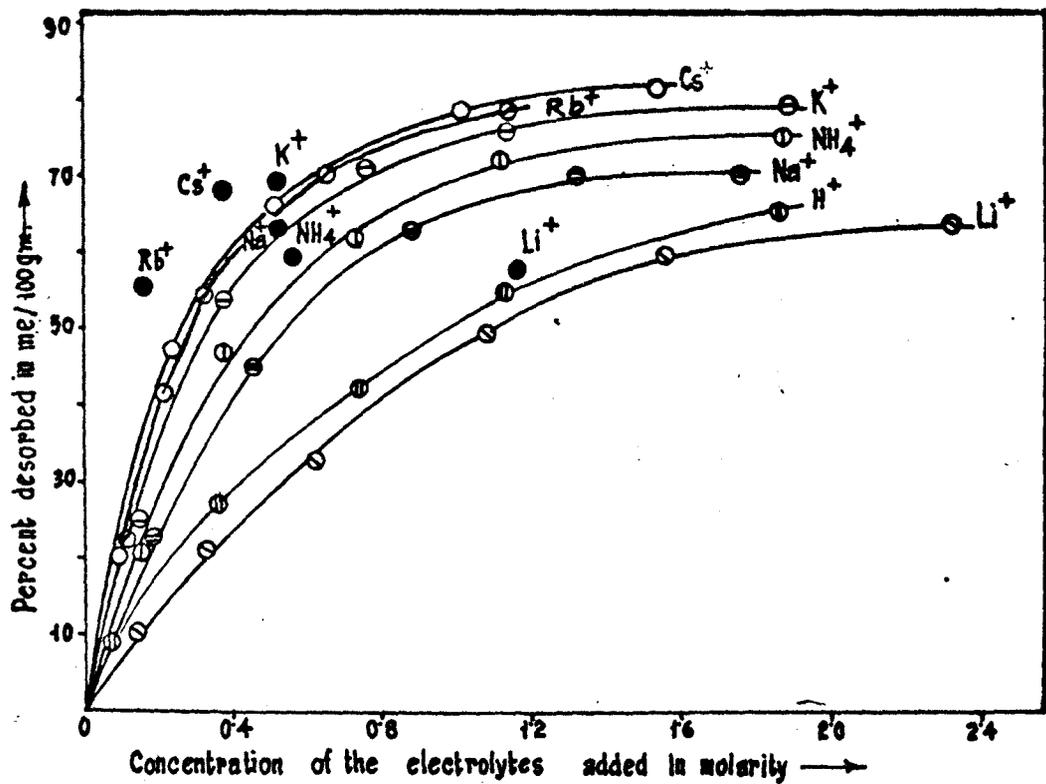


Fig. 72. Desorption isotherms of diquat from Na-IR-120-resin-diquat by monovalent inorganic ions.

● Desorption in 50% ethanol medium.

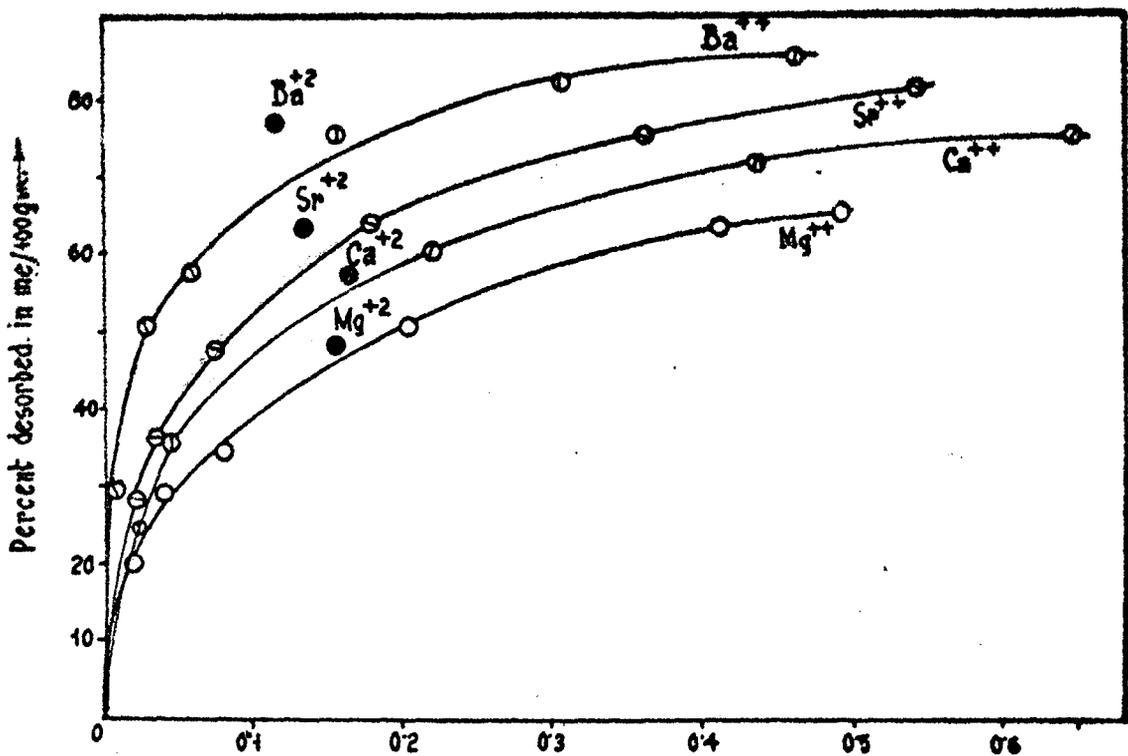


Fig. 7.3 Desorption isotherms of diquat from Na-IR-120-resin-diquat by bivalent inorganic ions
 ● Desorption in 50% ethanol medium.

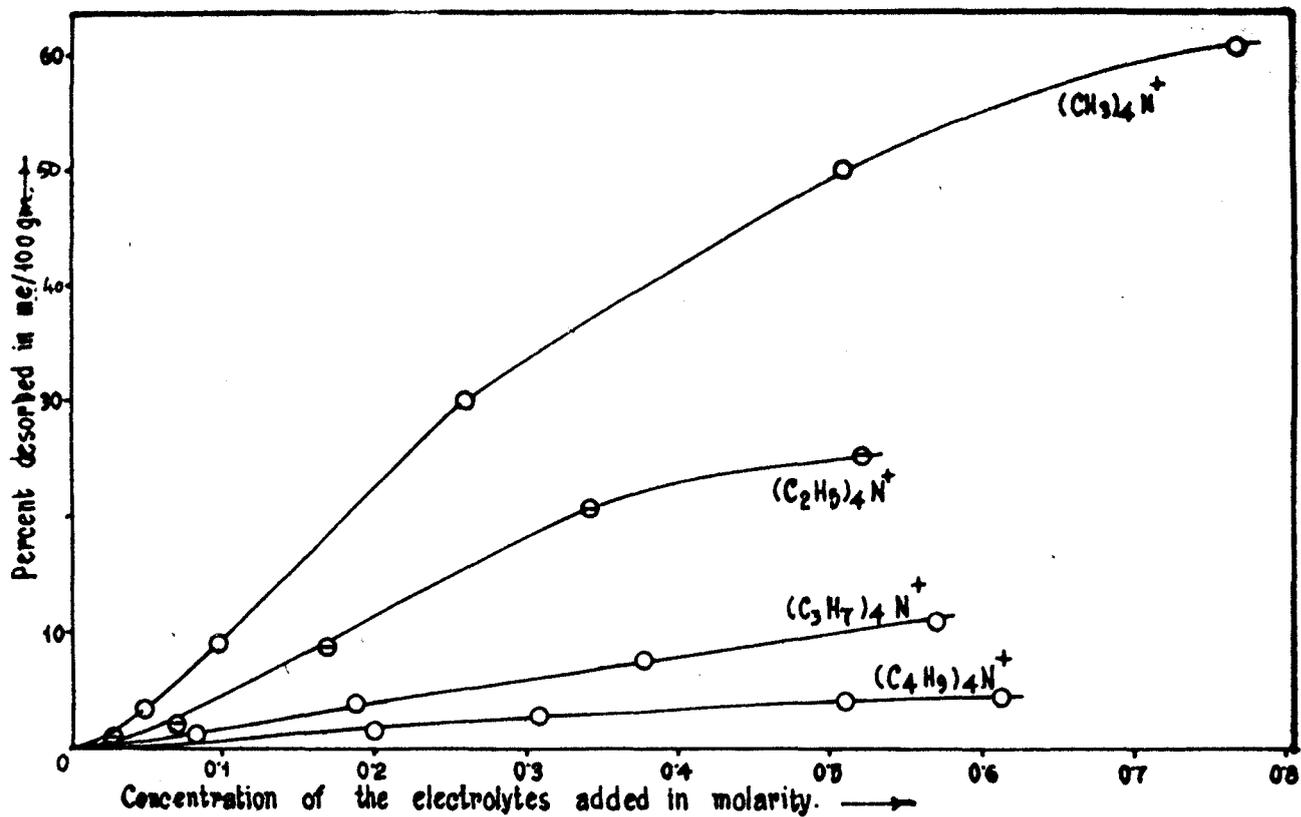


Fig. 74. Desorption isotherms of diquat from Na-IR-120-resin-diquat by monovalent organic ions.

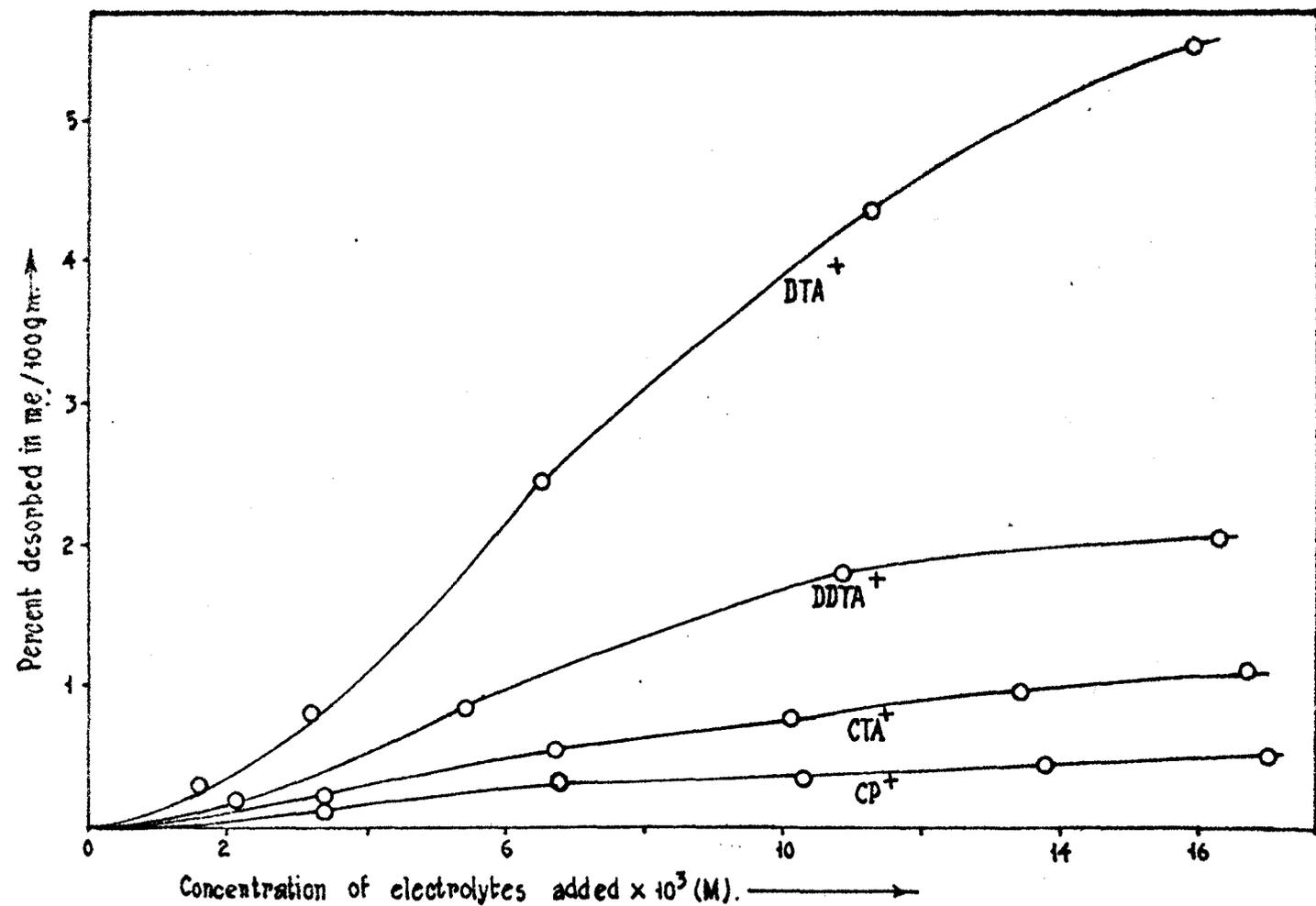


Fig. 75. Desorption isotherms of diquat from Na-IR-120 resin-diquat by monovalent organic ions.

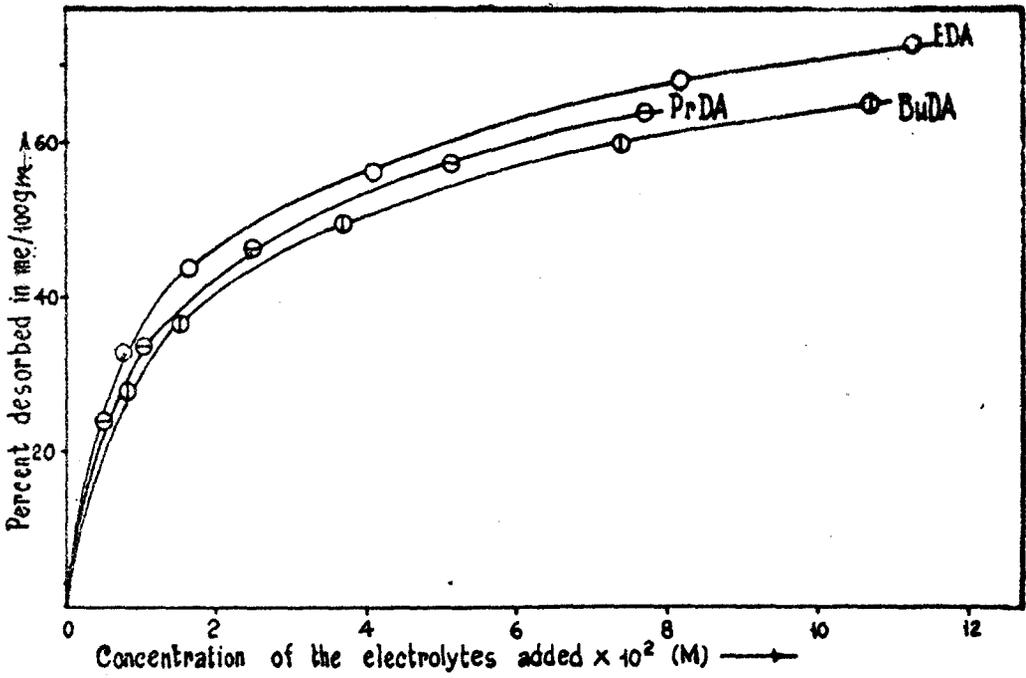


Fig. 76. Desorption isotherms of diquat from Na-IR-120-resin-diquat - by bivalent organic ions.

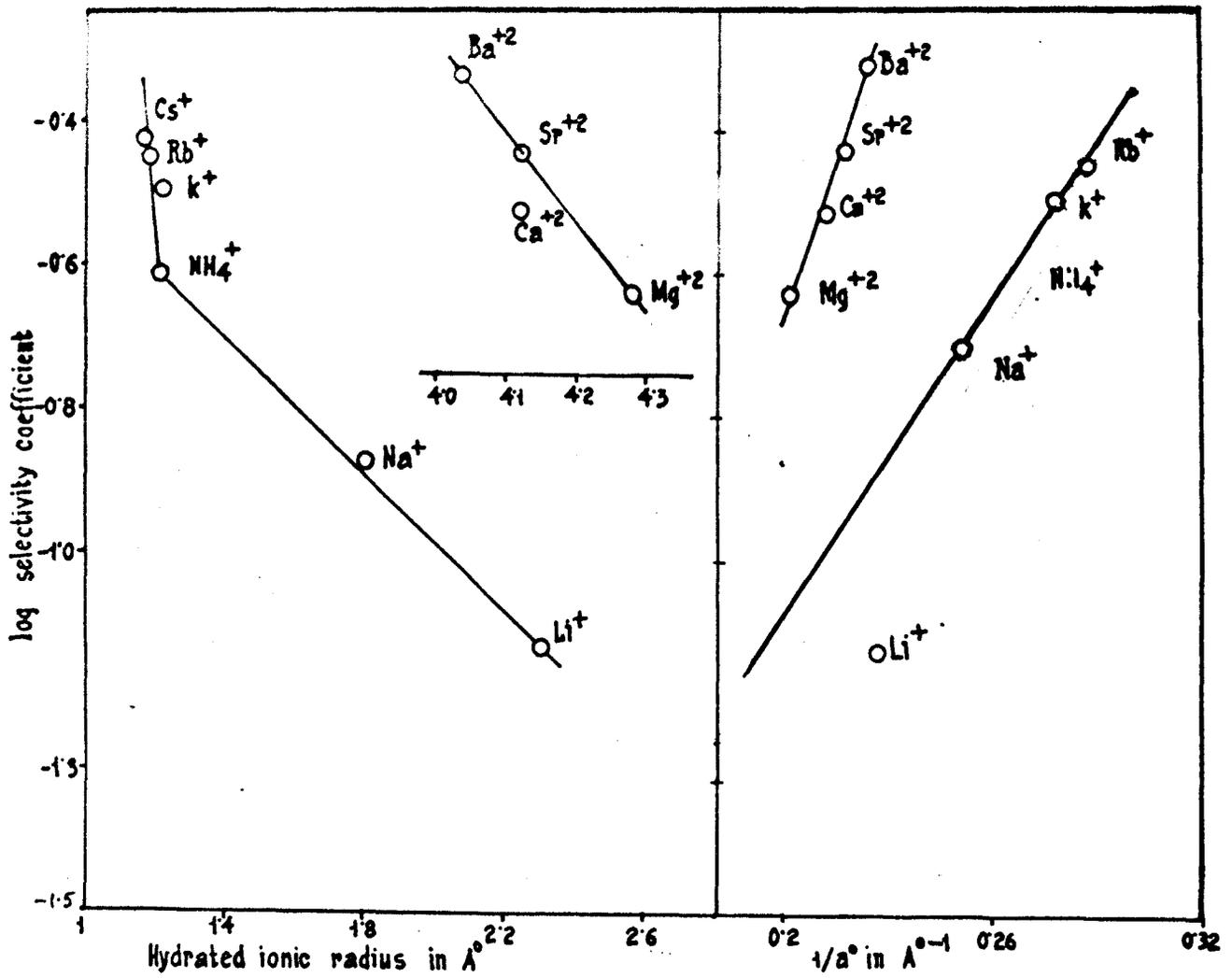


Fig. 77. Correlation of selectivity Coefficient with hydrated ionic radius and Debye-Hückel parameter a° in the desorption of diquat from Na-IR-120-resin-diquat.