CHAPTER - X

Sorption and Desorption of paraquat^{2+} on Na-Molecular Sieve - 13X System.

Molecular sieves are found to be most versatile, selective and universally applicable adsorbents available to industry. So the study of the use of molecular sieve in adsorption and catalysis is of great significance in industry and has deservedly received a great deal of interest in recent years. Zeolites as synthesized or formed in nature, are crystalline, hydrated alumino silicates of group I and II elements. Structurally they comprise a framework based on an infinitely extending three-dimensional net work of SiO_4 and AlO_4 tetrahedra linked together through common oxygen atoms. The isomorphic substitution of silicon by aluminium gives rise to a net negative charge compensated by cations. Zeolites can be represented by the empirical formula,

$$M_{2/n}O \ . \ Al_2O_3 \ . \ x\,SiO_2 \ . \ y\,H_2O \ .$$

where M is the compensating cation with valency n.

In this oxide formula x is generally equal to or greater than 2 (207) since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra. The structural formula of a zeolite can be represented by its unit cell composition:

$$Mx/n\ \ (AlO_2)_x\ \ (SiO_2)_y\ \ z\,H_2O\ .$$

The ratio y/x usually has a value of 1-5 depending upon the structure. The framework structures of zeolites are composed of arrangements of tetrahedra in building units going from ring structures to polyhedra. Usually, zeolites are classified using common structural units. Zeolites A, X and Y consist of linked cubooctahedra (cages or 24-hedra). Such a polyhedron, also called a sodalite unit, has a central cage of diameter 0.65 nm, accessible through six membered rings of oxygen atoms with a free diameter of 0.22 nm. In the mineral faujacite and the synthetic faujasites (zeolites X and Y), the cubooctohedra are linked with bridging oxygen atoms but in a tetrahedral symmetry. The sodalite units connected along two six-membered rings give rise to hexagonal prism. In this way, the polyhedra enclose a supercage with an internal diameter of 1.25 nm and accessible through four twelve-membered rings of oxygen atoms with a free aperture of 0.75 nm.

Owing to the isomorphic substitution of Si by Al, the three dimensional oxygen framework carries an excess negative charge, compensated by cations. These cations can be exchanged by other cations of different nature and valency. Not only simple cations can be exchanged but also complexes of cations such as $Cu(NH_3)_4^{2+}$ and $Pt(NH_3)_4^{2+}$. The only limitation to the nature of the cations that can be introduced by ion exchange is the acid stability of the zeolite. Generally, zeolites with higher Si : Al ratio are more acid stable. Sieving of one type of molecule out of a few containing a mixture of molecules with different shapes and/or sizes, is possible because the free apertures of the zeolites have molecular dimensions.

The ion exchange behaviour of some transition metal ions in zeolite A was studied by Gal et al (262) and in zeolite X by Wolff et al (263, 264) and Maes et al (220). Although several studies on molecular sieve A and Y involving inorganic and organic ions (210, 211, 209, 217, 218) have been reported in literature, such study with the herbicide, paraquat, is still lacking. So, in this section, are presented the sorption characteristics of paraquat^{2+} on Linde Molecular Sieve - 13X (powder form supplied by B.D.H Chemical Ltd., England, as gift) and its desorption from the adsorbent complex by monovalent and bivalent inorganic and organic ions in line with similar studies reported earlier with clay and resin systems.

Before use, the molecular sieve - 13X was saturated with 1(M) NaCl solution and dialysed against distilled water until free of chloride (220).

They were then dried at 50°C, ground and stored at room temperature over saturated NH_4Cl solution in a desiccator for at least a week. Then it was used for the exchange of paraquat^{2+}. The Na-molecular sieve - 13X - paraquat complex was used for desorption studies. The experimental procedures for studying the exchange of paraquat^{2+} was almost similar to the clay minerals and resins. About 0.1 gm of NaX was weighed into pyrex bottles to which increasing amounts of standard paraquat aqueous solution were added. The total volume was kept constant (15 ml) in each case by adding the requisite amount of water. They were then shaken for four hours and kept overnight to attain equilibrium. The aliquots were then centrifuged for about 20 minutes and the amount exchanged was determined from absorbance of the supernatants using a DU-2 spectrophotometer.

Similarly, for desorption study, the dry Na-sieve X-paraquat complex was weighed accurately ($\approx$0.1 gm) in different pyrex bottles to which varying amounts of desorbing electrolytes were added. The volume was kept constant (15 ml) in each case by adding the necessary amount of deionised water. They were also shaken for about four hours and kept 48 hours to attain equilibrium and paraquat content of the supernatants was measured as above.

SECTION - A

Studies on the Sorption

Sorption of paraquat on Na-Molecular-Sieve - 13X

The exchange isotherm of paraquat^{2+} on Na-Sieve-13X is shown in Fig. 74, which is of the Langmuir type indicating a strong interaction between the herbicide cation and the adsorbent. The plot of C/X against C (Fig. 74) is, accordingly, linear. From the slope of the line, the value of V_m is found to be 116 me/100 gm which nearly corresponds to the maximum exchange from the isotherm (110 me/100 gm).

The value of V_m is, however, found to be much less than the total exchange capacity of the sieve - 13X i.e. 632 me/100 gm (263). Thus the isotherm shows maximum exchange of about ≈ 17% for paraquat^{2+}. Steric factors based on cation size relative to the zeolite aperture diameters may explain the partial ion-sieve effect and incomplete exchange observed with paraquat^{2+} ion in zeolite X. The observations of Vansant and Vanhoof (219) may be recalled here where for steric reasons, organic cations (alkanediammonium ions) could not effect a complete replacement of Na initially present in the zeolites, so that the exchange reactions were confined to the large cavities in the crystal.

SECTION - B

Studies on Desorption

Desorption of paraquat^{2+} from Na-molecular-Sieve-13X - paraquat :

The results of desorption of paraquat^{2+} from its Na-molecular-sieve-13X-paraquat-complex are shown in Figs. 75, 76, 77, 78, 79, 80. According to the Fig. 75 and the selectivity coefficients (Table 12) for the monovalent inorganic ions at low concentration may be placed in the order: $Li^+ < Na^+ < NH_4^+ < Cs^+ < K^+ < Rb^+$ while at higher concentration the sequence is $Li^+ < Na^+ < Cs^+ < NH_4^+ < Rb^+ < K^+$. For the bivalent inorganic cations (Fig. 76), both at low and high concentrations the order of desorption is $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. Barrer et al (209) observed that for a low degree of cross-linking of polystyrene sulphonate resin selectivity was in the order : $Na^+ > Cs^+ > K^+ > Li^+ > H^+$, while with a high degree of cross-linking, with limited swelling, the selectivity sequence was changed to $Na^+ > Li^+ > H^+ > Cs^+ > K^+$.

Table 12

Desorption characteristics of paraquat^{2+} with respect to different ions from Na-molecular-Sieve-13X-paraquat.

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
1:1 Electrolyte			
	0.05	6.673	0.2522
LiCl	0.10	3.986	0.1726
	0.20	2.318	0.1139
	0.30	1.681	0.0871
	0.40	1.322	0.0733
	0.50	1.079	0.0611
	0.05	8.930	0.4200
NaCl	0.10	5.192	0.2793
	0.20	2.784	0.1620
	0.30	1.909	0.1143
	0.40	1.435	0.0861
	0.50	1.146	0.0693

Contd..

Table 12 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
	0.05	10.931	0.6159
CsCl	0.10	5.319	0.3524
	0.20	2.984	0.1867
	0.30	1.986	0.1242
	0.40	1.488	0.0931
	0.50	1.190	0.0744
	0.05	10.475	0.5672
NH_4Cl	0.10	5.635	0.3300
	0.20	2.895	0.1753
	0.30	2.075	0.1347
	0.40	1.555	0.1019
	0.50	1.252	0.0828
	0.05	11.55	0.7117
RbCl	0.10	5.99	0.3752
	0.20	3.07	0.1976
	0.30	2.08	0.1367
	0.40	1.57	0.1042
	0.50	1.26	0.0862

Contd..

Table 12 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
KCl	0.05	11.29	0.6574
	0.10	5.95	0.3695
	0.20	3.11	0.2043
	0.30	2.15	0.1445
	0.40	1.61	0.1107
	0.50	1.30	0.0905
2:1 Electrolyte			
$MgCl_2$	0.05	4.611	0.2531
	0.10	3.365	0.1976
	0.20	2.403	0.1460
	0.30	1.974	0.1209
	0.40	1.709	0.1047
	0.50	1.523	0.0936
$CaCl_2$	0.05	14.759	0.2773
	0.10	3.431	0.2103
	0.20	2.465	0.1567
	0.30	2.011	0.1278
	0.40	1.741	0.1106
	0.50	1.557	0.0939

Contd..

Table 12 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
	0.05	4.946	0.3125
$SrCl_2$	0.10	3.559	0.2360
	0.20	2.532	0.1715
	0.30	2.066	0.1399
	0.40	1.788	0.1211
	0.50	1.599	0.1033
	0.05	5.106	0.3458
$BaCl_2$	0.10	3.653	0.2533
	0.20	2.596	0.1849
	0.30	2.110	0.1508
	0.40	1.826	0.1305
	0.50	1.633	0.1167
<u>Quaternary ammonium salt</u>			
	0.05	2.030	0.0372
$(CH_3)_4NBr$	0.10	1.765	0.0442
	0.20	1.411	0.0447
	0.30	1.276	0.0444
	0.40	1.005	0.0440

Contd..

Table 12 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
$(C_2H_5)_4NBr$	0.05	0.969	0.0119
	0.10	0.770	0.0121
	0.20	0.550	0.0108
	0.30	0.455	0.0098
	0.40	0.385	0.0089
$(C_3H_7)_4NBr$	0.05	0.528	0.0047
	0.10	0.440	0.0051
	0.20	0.352	0.0053
	0.30	0.304	0.0052
	0.40	0.264	0.0049
$(C_4H_9)_4NBr$	0.05	0.303	0.0021
	0.10	0.242	0.0020
	0.20	0.220	0.0025
	0.30	0.185	0.0024
	0.40	0.165	0.0024

Contd..

Table 12 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
	0.002	0.770	0.0016
DDTABr	0.004	0.655	0.0017
	0.006	0.513	0.0015
	0.008	0.440	0.0014
	0.010	0.374	0.0012
	0.012	0.321	0.0010
	0.002	1.101	0.0028
CTABr	0.004	0.838	0.0026
	0.006	0.679	0.0023
	0.008	0.556	0.0020
	0.010	0.467	0.0017
	0.012	0.403	0.0015
	0.002	25.32	1.1399
EDA	0.005	16.05	0.8657
	0.010	11.54	0.7292
	0.020	8.23	0.5533
	0.030	6.69	0.4636

Contd..

Table 12 (Contd..)

Electrolyte used	Concentration of the electrolyte (M)	Distribution Coefficient	Selectivity Coefficient
	0.002	21.33	0.8063
PrDA	0.005	14.67	0.7131
	0.010	11.13	0.6653
	0.020	7.90	0.4945
	0.030	6.42	0.4562
	0.002	16.65	0.4373
BuDA	0.005	13.39	0.5735
	0.010	10.57	0.5690
	0.020	7.59	0.4381
	0.030	6.14	0.3549

molecular sieve - 13X is to be regarded as an extremely high cross-linked condensation polymer, virtually non-swelling, but neither of the above sequences correlates with that observed in the case of the molecular sieve.

Both the hydrated ionic radius and the reciprocal of the Debye-Huckel parameter, a^o, for the bivalent inorganic ions when plotted against logarithm of selectivity coefficient (Fig. 80) give linear graphs while for the monovalent inorganic ions, only the latter plot is linear (Fig. 80) as observed in clays and resins.

The exchange isotherms with tetraalkylammonium ions are shown in Fig. 77. The percentages of the herbicide released by these ions are much smaller than the inorganic ions and the exchange is inversely related to the size of the ions. Because of its rigid three-dimensional framework enclosing cavities, which are entered through windows of definite dimensions, exchange in molecular sieve - 13X is greatly influenced by steric and space factors.

Thus, using concentrated solutions of various methyl and ethylammonium halides, Barrer et al (209) reported virtually complete exclusion of the tetraethylammonium ion whilst the methylammonium derivatives gave upper limits to exchange which decreased as the number of alkyl groups in the cation increased. Ion sieve action of this type is encountered in all members of the zeolite group of minerals (258). With the long-chain surface active ions (Fig. 78), however, the extent of exchange increases with the chain length of the ions, although the maximum desorption with CTA^+ did not exceed even one percent.

Compared to other organic ions, the upper limits of exchange with the alkanediammonium ions are much higher (Fig. 79), although an inverse relation was observed between the maximum exchange and the molecular weight as noticed earlier in Amberlite IR-120 (P-140). A similar observation has been made by Vansant and Vanhoof (219) and has been attributed to the space requirement of the ions and difficulty of packing of the organic ions in the rigid non-swelling zeolite matrix. 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 greater affinity of the alkanediammonium ions for the molecular sieve - 13X.

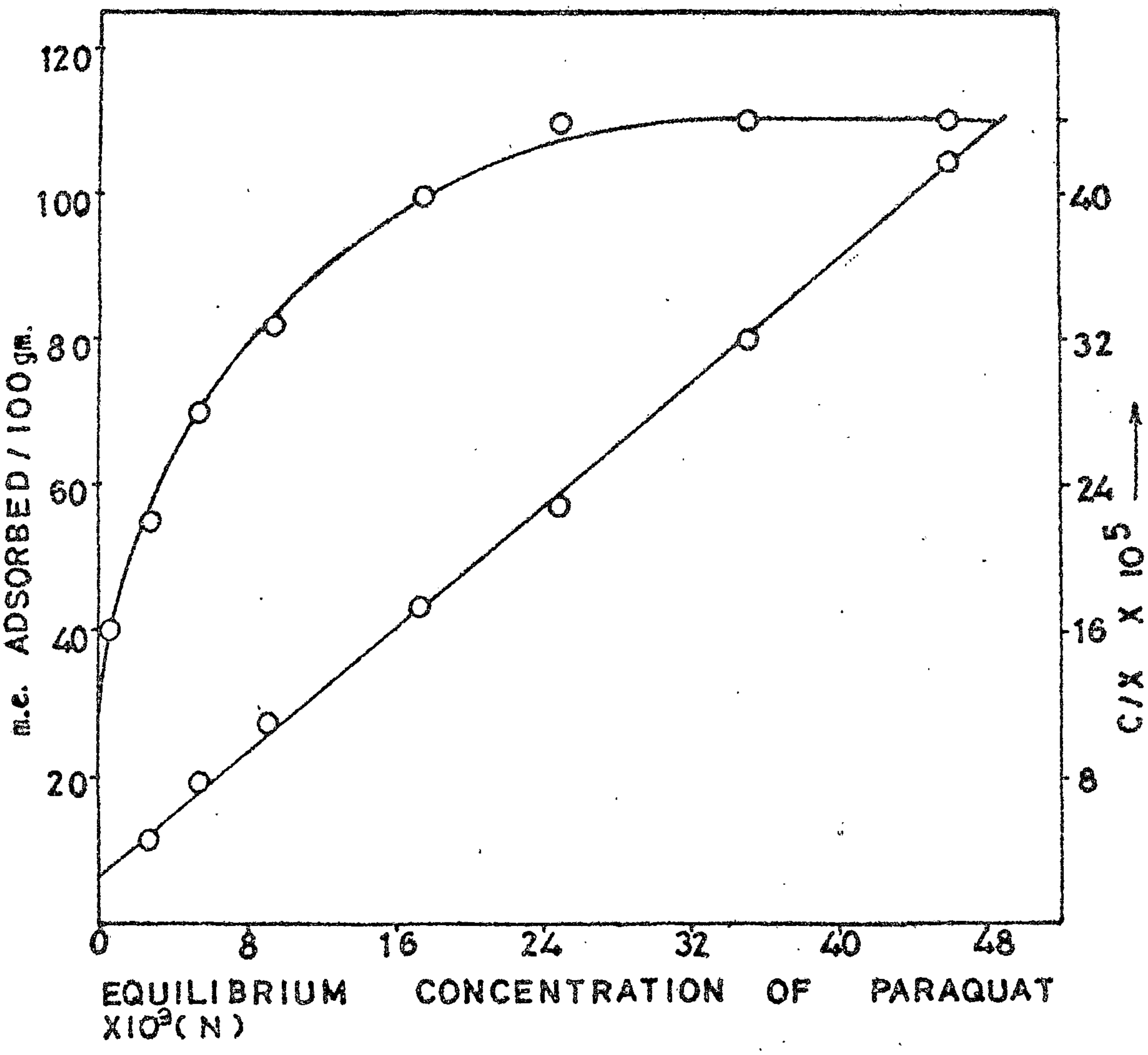

FIG. 74. EXCHANGE ISOTHERM OF PARAQUAT ON Na-MOLECULAR-SIEVE-13X.

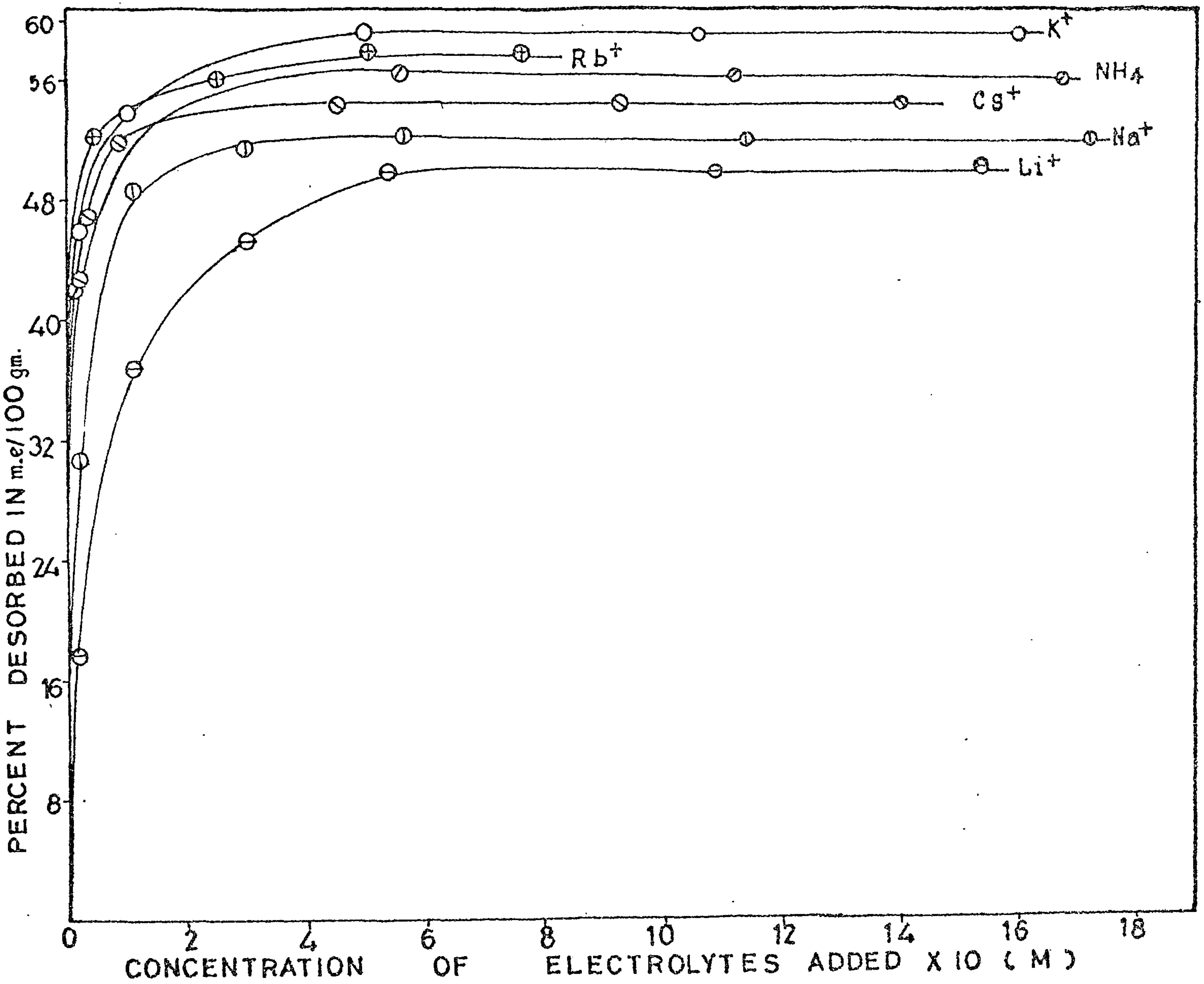

FIG. 75. DESORPTION ISOTHERMS OF PARAQUAT FROM Na-MOLECULAR-SIEVE-PARAQUAT BY MONOVALENT INORGANIC IONS.

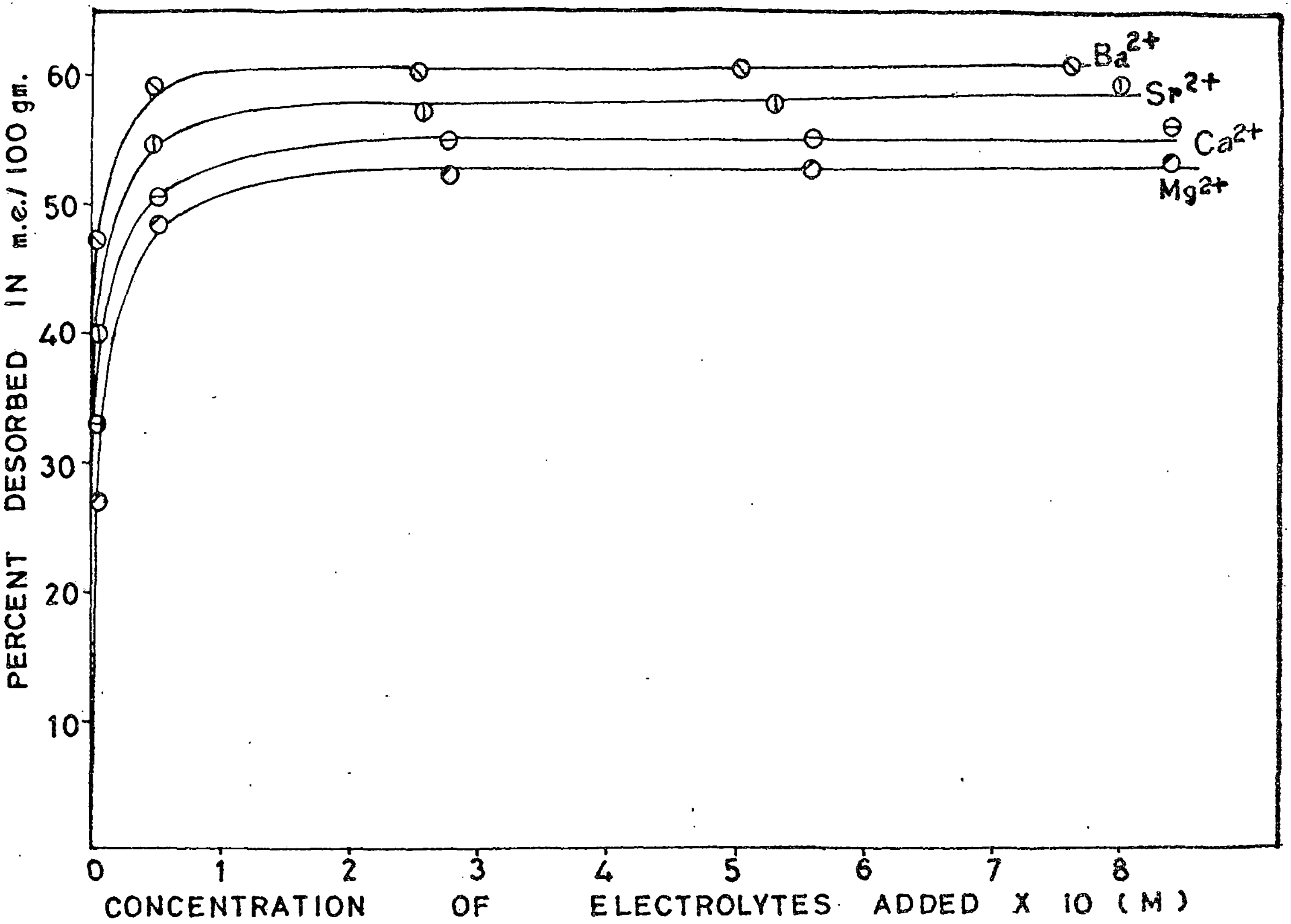

FIG. 76. DESORPTION ISOTHERMS OF PARAQUAT FROM Na-MOLECULAR-SIEVE-PARAQUAT BY BIVALENT INORGANIC IONS.

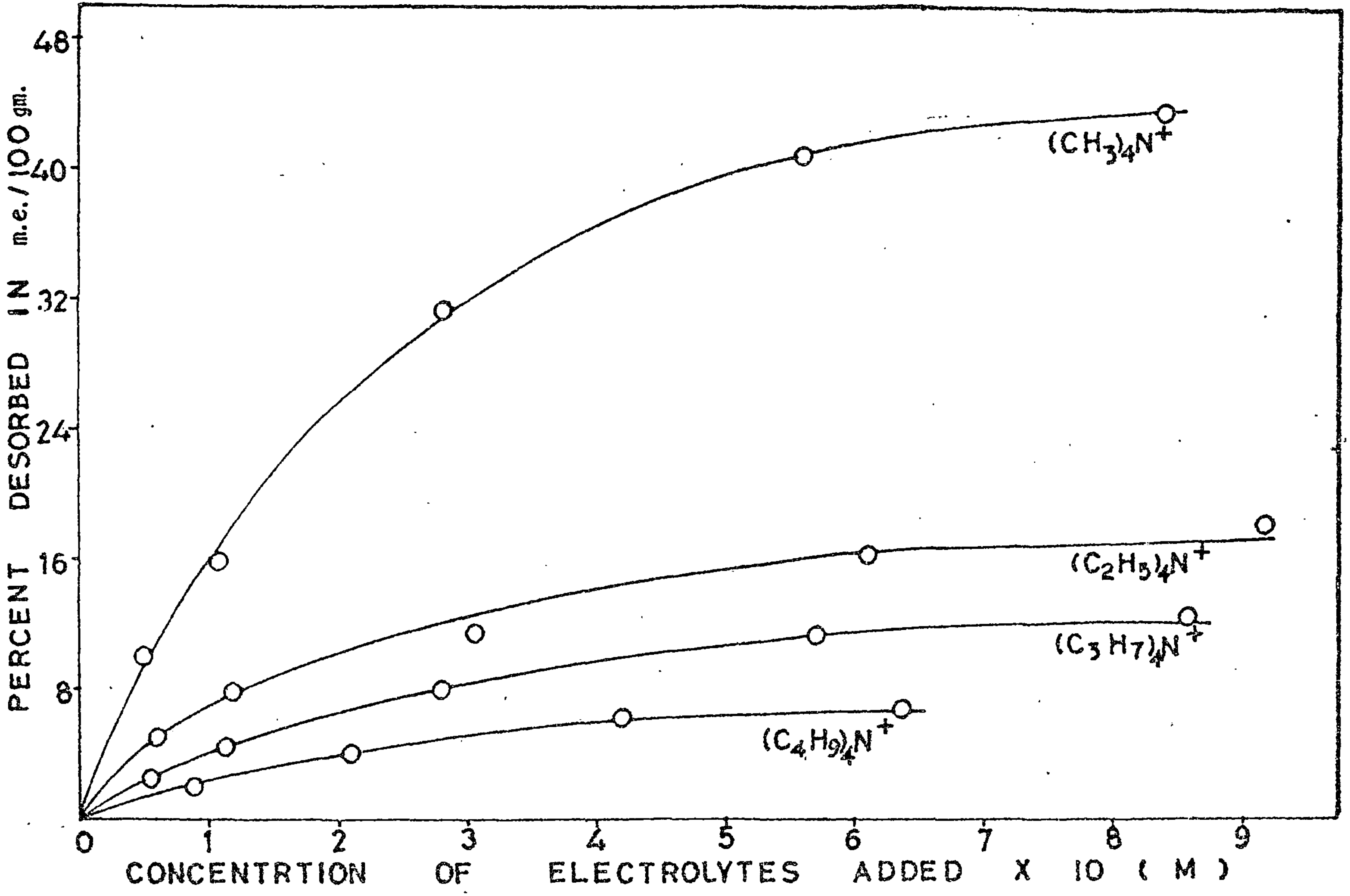

FIG. 77. DESORPTION ISOTHERMS OF PARAQUAT FROM Na-MOLECULAR-SIEVE-PARAQUAT BY TETRAALKYLAMMONIUM IONS.

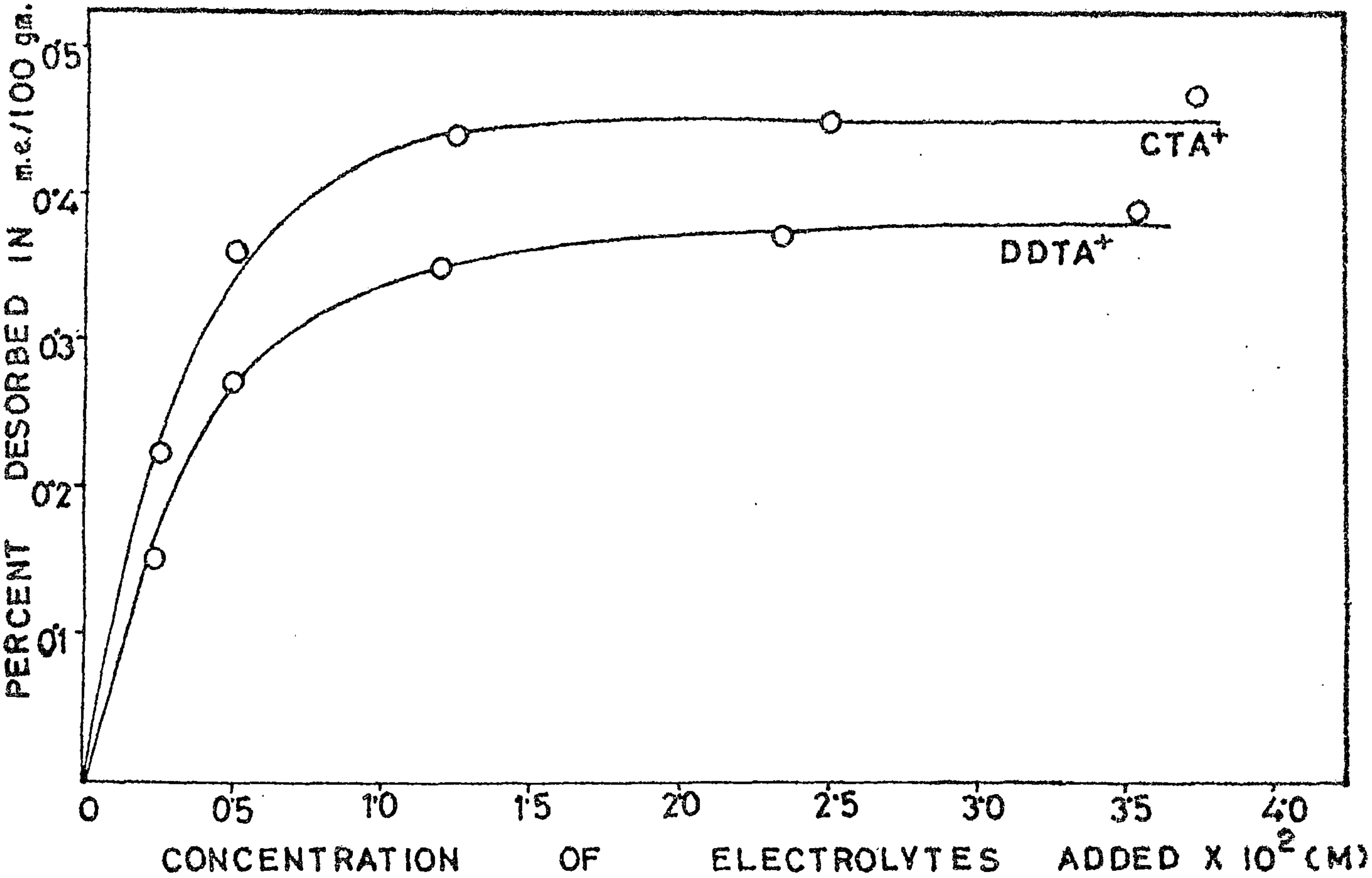

FIG. 78. DESORPTION ISOTHERMS OF PARAQUAT FROM Na-MOLECULAR-SIEVE-PARAQUAT BY LONG CHAIN SURFACE ACTIVE IONS.

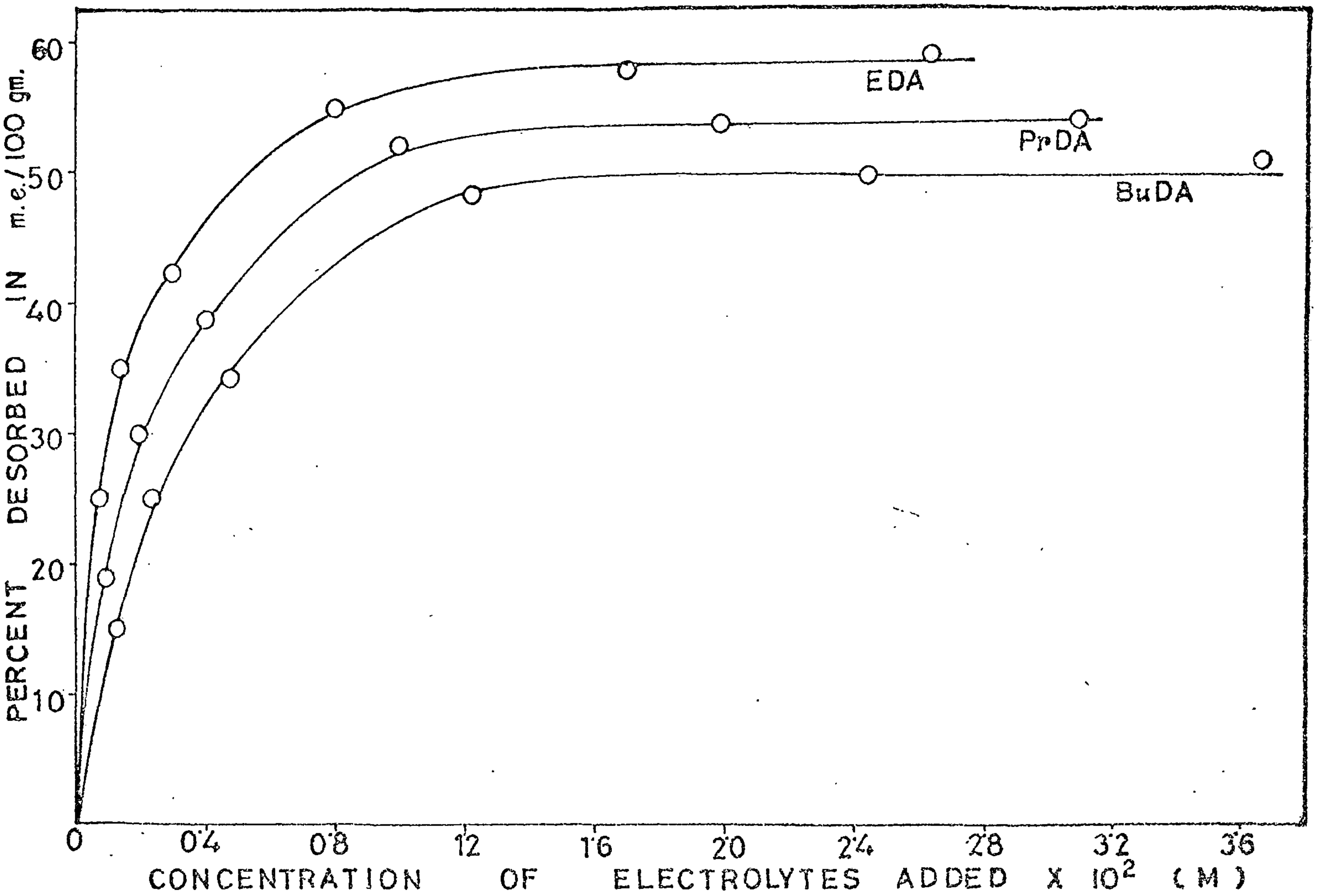

FIG. 79. DESORPTION ISOTHERMS OF PARAQUAT FROM Na-MOLECULAR-SIEVE-PARAQUAT BY ALKANE DIAMMONIUM IONS.

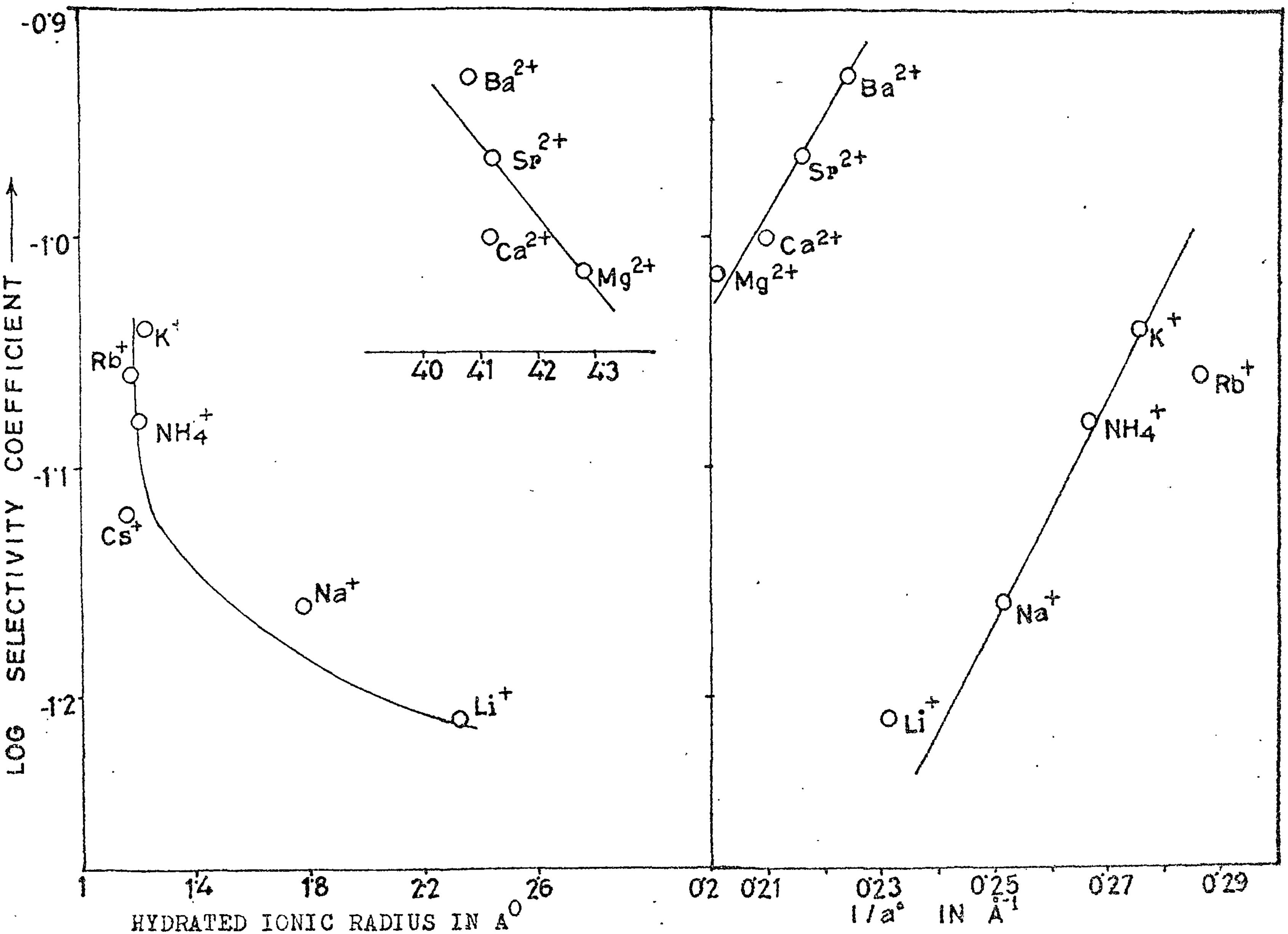

FIG. 80. CORRELATION OF SELECTIVITY COEFFICIENT WITH HYDRATED IONIC RADIUS AND DEBYE-HUCKEL PARAMETER a^{o} IN THE DESORPTION OF PARAQUAT FROM Na-MOLECULAR-SIEVE-PARAQUAT.