CHAPTER -I

INTRODUCTION

Section-A

Introduction
and
A Review of Previous Work.

The organic matter in soils plays an important role in the formation of fertile soils, the base for plant production. The interaction of the organic matters with the soil constituents like metal ions, clay minerals and hydrous metal oxides largely determines the physical, physico-chemical and biological properties of soils. The total organic matter in soil is usually divided into two parts —— that which is recognizable as fragmentary materi from living organisms and that which is unorganised, darke in colour, and gel-like in its properties. The latter is called humic matter or humus. The humus substances are essentially large polymers called bio-polymers, mostly made by aggregation of a large number of atoms through chemical bond rather than colloidal assemblage of smaller molecules. They may carry both the positive and negative charges and behave like polymers and polyelectrolytes as well[1].

Formation of Humus:

Certain biological activities are believed to be accountable for formation of soil humus. The degradation of polymeric substances like poly-saccharides, lignins and proteins incorporated in plants and animals yield simple compounds which in turn, are utilised by soil micro-organisms in their metabolic pathways or sustain enzymatic or chemical condensation to be transformed into new polymers. Some of the polymers constitute an important part of the soil by forming resistant complexes with metal ions and clays[2,3,4]. The intensity of microbiological activity in soils depends to a great extent upon temperature and moisture. Besides, the mechanism of formation of humus molecules is also dependent upon the moisture condition of the soil medium. The rate at which the condensation by-products (water) preventing the growth of molecules are removed largely determines the size of the molecules of humus, as in the case of high molecular weight compounds. So, the formation of humus substances with a smaller size of molecule is more favoured in the zone of excessive moisture, for example, podzolic soils than in soils experiencing a periodic moisture deficit (e.g. chernozem) ensuring the removal of condensation product (water). Similar views about the effect of climatic condition on humus formation were also shared by Bachelier[5] and Duchaufour[6]. They pointed out that the alternate wetting and drying contributed to the condensation and polymerisation of humus substances.

Chemical nature of Humus:

The chemical nature of humus has not been definitely ascertained as yet and is believed to be a mixture of several groups of chemical complexes defined by certain common and characteristic properties. From each group a large number of different well-defined organic compounds have been isolated by various workers. According to Oden[7] the soil humus can be separated into four groups of organic complexes:

(i) Humic acid: Insoluble in alcohol, readily soluble in dilute alkalies and reprecipitated by acids.

(ii) Hymatomelanic acid: Soluble in alkalies, precipitated by acids but the precipitate is soluble in alcohol.

(iii) Fulvic acid: Soluble in alkalies and not precipitated by acids.

(iv) Humins: Insoluble in alkalies and alcohol. This fraction mainly contains undecomposed plant materials.

Investigations on chemical nature of humus reveal that hexosamines, polycyclic aromatics and oxygen containing functional groups are contained in about 50 - 55% of the total humic acids so far identified. The remaining unknown fraction is supposed to be formed by easily oxidisable heterocyclic components with higher degree of unsaturation resulting in the dark colour, a characteristic for all types of humus substances. The E.S.R. signals obtained by Haworth[8] in case of humic acids suggest the presence of aromatic core contained in such substances, to which are attached a number of chemical units like proteins, polysaccharides and simple phenols, although the nature of linkage is not certain. In case of metal-humic acid interactions, the ion exchange and sequistration properties of humic acids in particular indicate that the anion formation by chelation with phenolic groups poses quite an interesting alternative to the assumption that the metals are present as salts of carboxylic acid groups. The above noted assumption for the chemical structure of natural humic matter is strongly supported by the analogy of humus like substances prepared by various chemical condensation of different quinones with amino acids[9,10,11]. The fact that the natural humic substances are formed by condensation of different quinones and amino acids taking place in soils in a complex physico-chemical way is amply suggested by the different physical studies and chemical properties like metal retention and complex forming tendencies of synthetic humic acids[12].

Variation in the humus content of soils

The humus content varies from soil to soil ranging between 0.2% ~~to~~ and about 20%. Further, humus concentration also varies with soil depth - its concentration usually decreases with increasing depth of a soil and the highest concentration is found in the upper 20 - 30 cm of the soil. The concentration of humus is, however, practically negligible below the 15 cm. in the brown forest, red, and yellow soils. Accumulation of humic matter may be found in the B_1 - horizon of well-marked humus podzol, 75-78% of the humus being extractable as humic acids.

State of Soil Humus

Humus is not found to remain as free compounds in any significant amount in normal soils. Nor can they be extracted from soil by water. However, they can be extracted by means of chemical reagents capable of displacing polyvalent cations and by complexing agents. Complete removal of inorganic constituents like clay, silica, etc. from extracted humic acids is not possible[13,14]. However, the content of this material can be reduced to a minimum level by exhaustive treatment with strong H-resins. Humic substances form soluble salts with sodium, potassium and other alkali metals while the solubility of free acids largely depends on average molecular weights. Solubility of salts formed by polyvalent cations depends on the type of unsaturation. The state of aggregation of soil humus can be predicted by the differential extraction technique.

Extraction of soil Humus.

Although different reagents like acidic solvents, weakly basic solvents, chelating reagents as solvents and basic solvents with reducing properties are usually applied for extraction of humic matters, the most extensively used solvent is dilute NaOH, because it effects the dissolution of substantial amount of organic matter.

Some objections have been mooted against the use of NaOH as extracting solvents, for it might bring about a deep - seated change in the physicochemical properties of organic matter. However, Schnitzer and Skinner[15] did not observe any modification caused by alkali extraction of organic matter in podzol soil in B_h horizon with 0.5M NaOH.

Any way, to avoid the possibility of any alteration in the structure of humus, some other solvents like $Na_4P_2O_7$, $(NH_4)_2CO_3$, Na_2CO_3, $NaHCO_3$ and their suitable combinations have been tried. But they have proved much less effective in their extracting capacity than NaOH. This apart, the chief demerit of ammoniacal solutions is that they react with lignin and other phenolic components and probably with carbohydrate compounds[16] while $Na_2P_4O_7$ suffers from the drawback that it extracts metal complexes from soils.

Martin and Reeve[17] successfully removed a large portion of organic matter from podzolic soils by using a number of complex forming reagents like Na_2EDTA, oximes, acetyl acetone, etc. The mechanism involved in such extraction is that these complex-forming reagents form strong bond with polyvalent metal ions and thereby liberate humus from soils.

Levesque and Schnitzer[18] have recently tried Dowex - 1 resin in the extraction of organic matter and compared its efficacy with that of NaOH-extraction. They have concluded that NaOH extraction procedure is still by far the best method.

Fractionation of Humus substances.

Fractionation of humic matter has been effected by various methods. The techniques incorporate fractional precipitation at different pH's, chromatographic separation, electrophoresis and gel filtration etc.

Studies on the influence of electric field on humic acids by Sheffer[19] et al. indicate that the use of higher potential and longer time may effect separation of humus substances into a large number of fractions. Waldron and Mortensen[20] used paper electrophoresis in presence of 0.22 M borate buffer at pH 9 for fractionation of humic matter.

Ziechmann[21] was successful in separating three fractions of humic acids by use of low voltage electrophoresis. Partition paper chromatography helped Kononova and Belchikova[22] to fractionate humic and fulvic acids. Schnitzer and Skinner[23] harnessed the sephadex gel technique and successfully prepared seven fractions of podzol fulvic acids differing in number average molecular weights, nitrogen, -COOH and phenolic -OH contents, as well as in I.R. and N.M.R. spectra. Recently, Dorado Bernel[24] has tried sephadex G-25 gel to separate humic acids.

Purification of Humus.

Usually an appropriate combination of several techniques namely, electrodialysis, reprecipitation, centrifugation, redissolving and finally repeated treatment with H-resins is used to purify humic matter from different impurities e.g. salts, clays, sesquioxides etc. This process ensures production of almost ash free humic acids[25,26].

Molecular Weight of Humic matter.

It is an established fact that humic matter is a heterogeneous assembly of chemically allied substances and as such, determination of molecular weight of a single humic acid component is not possible. So, what is, in fact, obtained is an average molecular weight. Again, the values of molecular weight of humic matter so far reported are fo to largely depend on their origins, methods of extraction, fractionation procedures as well as the techniques applied for the determination of their molecular weights.

Methods, hitherto, used to assess the molecular weigh of humus substances include diffusion technique, cryoscopi and ebullioscopic measurements, ultra-centrifuge technique light scattering process, vapour pressure osmometry, viscometry etc. It may be noted that cryoscopic methods usually yield much lower values of molecular weight than those determined by osmometric or ultra centrifuge technique in case of high molecular weight substances.

By means of diffusion technique Zeil[27] obtained mol cular weight for humic acid fractions as 1060 and 1650. Ebullioscopic measurement of some acetone-soluble oxidatio products of humic acids yielded to Fuchs et al.[28] their mol cular weights around 1400. For the same fulvic acid extrac from B_h horizon of podzol soil fractionated by gel filtrati Schnitzer and Skinner[23] obtained molecular weights as 5813 and 5819 by ultracentrifuge measurement and vapour pressure osmometry respectively. Flaig and Beutelstacher[29] used the ultra-centrifuge technique and found molecular weights as high as ranging between 30,000 and 50,000. Schnitzer and Desjardins[30] found the molecular weight of soil organic matter within 1690 and 669 for podzol A_0 and B_h horizon respectively by freezing point depression method. Posner[31] estimated the molecular weight of soil humic matter fractions at 70,000 and 200,000 - the difference is quite notable. Filkov[32] fractionated humic acids from Moldavion soil groups on the various grades of sephadex and obtained two fractions from each humic acids with their molecular weights remarkably differing - one having molecular weight less than 5,000 while the other showing values between 50,000 and 100,000. Orlov and Gorskova[33] determined the molecular weight by light scattering method and found it to be 63,300 for humic acid from sod. podzolic soil and 88, 200 for humic acid extracted from chernozem. Recently, Gaberman and Litovko[34] recommended electrometric method for molecular weight determination of humic acids.

Complexing properties of humic matter with metal ions.

Investigations on interaction between soil organic matter and different metal ions by a number of workers[35,36,37] revealed that humus substances are capable of forming complex linkages of various kinds with metals. Based on different types of linkages between functional groups of humic acids and soil organic constituents, categorisation of metal - organic matter derivatives in three main types has been attempted[38], though such a clear-cut distinction is not always tenable:

(i) Ionic type - Salt types of compounds formed by participation of phenolic OH and COOH groups.

(ii) Semi-polar type - Complex chelate type of compounds formed by co-ordination linkages with amino, imino and thio-ether groups.

(iii) Adsorption type of compounds formed by polarisation effect and hydrogen bridge linkages with special participation of terminal groups.

It may be pointed out that each of polyfunctional groups contained in humic acids is affected differently under different sets of conditions. So, measurement and prediction of reactivity of any one group pose a very difficult problem unless it is known to be specifically affected by the conditions in the reaction medium.

Ion exchange properties of humic matter.

Unlike clay minerals, soil humus is found to have no well-defined capacity for binding with exchangeable cations reversibly. According to Bartelett and Norman[39], the charge of exchanging cations influences their complexing with humic matter; for example, more barium is exchanged than potassium at the same concentration of hydrogen ions. The exchange mechanism generally follows the lyotropic order and that means it is dependent on the charge as well as on the hydrated size of the exchanging ions.

In the exchange process, ions are replaced in equivalent quantities by other ions and the equilibrium state depends on concentrations and activities of all ions present in the system. Again, the nature of the surface and the amount of solid phase as well greatly influence the exchange capacity. The Schulze-Hardy rule[40] is well applicable to the exchange process involving humus substances.

pH dependence of ion exchange process

The pH of exchange solutions exerts a remarkable effect on the exchange capacity of humic matter as seen in case of other polyfunctional exchangers, cation exchange capacity increasing with the increase in pH values[41,42]. This is traced to the change in the degree of dissociation of phenolic-OH and -COOH groups in humic acids with pH. Lewis and Broadbent[43] demonstrated by an experiment with model substances that there was limiting pH value below which exchange of cations did not occur. In the use of adsorption of copper and uranyl cation by carboxyl groups it was found that the limiting pH value of each ion was independent of the activity of exchange sites of the exchangers, while the limiting pH value for barium was lowered proportionately to the increase of exchange acidity.

Nature of exchange sites in humus

Different investigators have arrived at different conclusions while characterising the exchange sites accountable for exchange properties of soil humus.

The observed relationship between the contents of lignin-like materials of the soil organic fractions and the exchange capacity led to the idea that the active sites were of phenolic character, phenolic H-atoms being the most acidic sites in lignin. On the other hand, only a low decrease observed in the exchange capacities for the cations following the blocking of active sites with lower acidity than pK = 6 by dimethyl sulphate led Gillam[44] to conclude that the active groups must be carboxylic. However, Broadbent and Bradford[42] studied the effect of selective blocking of the exchange sites with dimethyl sulphate and diazomethane on the exchang capacities of organic matter and suggested the participation of both phenolic-OH and COOH groups in the exchange mechanis Again, based on the elimination of whole exchange capacity of sandy loam for Zn by treatment with dimethyl sulphate, Himes and Barber showed[45] the predominance of phenolic-OH group in determining the exchange properties of soil humic matter while Broadbent[46] claimed with the help of ion exchange Chromatography that the dominant role was played by COOH group in the ion exchange process.

Studies of Schnitzer and Skinner[47] on the mechanism of metal-humus interactions by specific blocking of phenolic-OH and COOH groups indicate two types of interactions:

(a) A main reaction involving simultaneous participation of COOH and phenolic-OH groups.

(b) A subsidiary reaction involving only COOH groups.

However, according to these authors, the possibility of participation of carbonyl groups in the exchange reaction between metal and humic matter could not be ruled out though no evidence to this effect is yet obtained.

Metal retention in Humus by ion exchange process

Detailed studies on the exchange properties of humic matter have been provided by Zadmard[40] and Schachtchabel[48]. Earlier workers, notably Hissink and Gedroiz, had firmly established the importance of the exchange properties of humus in the over-all picture of soil-fertility[82].

Studies of Zadmard on the exchange properties of peat in K-, Ca-forms showed the order of entry of monovalent cations in both the systems as H > Cs > Rb > K > Na > Li. For divalent cations it was Sr > Ba > Ca > Mg with K- peat and Ba > Sr > Mg with Ca- peat. However, the comparison of exchange isotherms for K- and Ca- peats is rendered uncertain by the fact that K-peat contained not the whole peat but the residue after much of K-humate had been removed by decantation. In comparing monovalent and divalent cations, a peculiar and distinctive behaviour was found. With K-humate monovalent cations entered some what more rapidly than divalent cations of comparable size, especially at higher concentrations. In Ca-humus the divalent cations entered much more strongly than the monovalent system. Hydrogen entered by exchange very energetically but could be quantitatively displaced by continued washing with the calcium acetate solution.

Investigations of Baver and Hall[49] on the exchange behaviour of crude humic acids indicated the order of entry of alkali and alkaline earth metals: Ba > Ca > Mg > Sr > K > Na > Li.

Comparison of several clay minerals with soft coal and humic matter in calcium - ammonium exchanges in the solution of equivalent amounts of Ca^{2+} and NH_4^+ by Schachtschabel[48] revealed that all the cation exchangers showed a strongly predominant uptake of Ca^{2+} as compared with NH_4^+ while under the same conditions kaolinite and montmorillonite took up about equal quantity of calcium and ammonium.

Recent studies on the ion exchange equilibria in Florida and Indiana histosols by Baligar et al.[50] have reveale that they have a greater fraction of the Ca in the exchange phase than in solution whereas with Mg, Na, K, Rb the reverse has occurred.

Investigations on ionic binding properties of Cu and Ca by Broadbent[46] using chromatography column led to the assumption that in the Cu-fixation some functional groups participated, which showed no interaction with Ca^{2+}.

The comparative determination of the exchange capacity of soil organic matter for Cu and Ba by Lewis and Broadbent[51] with the help of ion exchange chromatography pointed out the association of the exchange capacity with phenolic and carboxylic functional groups.

The studies on the interaction of Cu with humic and fulvic acids by Manskaya et al.[52] showed that maximum Cu was fixed by humic acid at pH 2.5 to 3.5 while fulvic acid showed the fixation of most Cu at pH values near 6.

The exchange studies by Basu et al.[53] with crude humic acids and some trace element cations indicated that adsorption followed the order $Zn^{2+} > Mn^{2+} > Ni^{2+} > Cu^{2+}$ while the order of release from the respective humates for H^{+} and Mg^{2+} was $Mn^{2+} > Ni^{2+} > Cu^{2+}$; the actual amounts released by H^{+} was much greater than those by Mg^{2+}. The studies further demonstrated that the adsorption isotherms were in each case some what higher than the release isotherms, seemingly indicative of formation of mixed bond type of complexes.

The investigations on the adsorption of mixture of Mg and some trace element cations in different proportions on crude humic acids by Mukherjee[54] indicated the order of adsorption as $Ni^{2+} > Co^{2+} > Mn^{2+}$.

The exchange mechanism is also found operative in case of interaction between humic matter and hydroxides of Al and Fe. According to Deb[55] a simultaneous reaction of coagulation and peptisation occurred when the extracts of soil organic substances were mixed with iron oxides and the peptised amounts of iron oxides varied depending on the nature of organic matter, pH and concentration of sols. However, Alexandrova[56] found the metal-organic compounds of humic acids, metals, including Fe and Al, largely dependent on the hydration state of sesquioxides, no reaction taking place in case of strongly dehydrated or crystalline forms of sesquioxides. She[57] further observed some undefined functional groups were not affected in the reaction of organic substances with metal hydroxides leaving a small residual exchange capacity. Schnitzer and Skinner[58], on the other hand, obtained stable complex compounds with iron and aluminium compounds and extracts from podzolic soils by the application of goethite (FeOOH), Gibbsite (AlOOH) and iron- or aluminium -saturated ion exchangers and soils, respectively. Again, according to Levashkevich[59] investigations with freshly precipitated iron and aluminium hydroxides in pH range 3 to 5 indicated strong adsorption of humic acids by aluminium hydroxides and occurrence of slow adsorption in case of precipitated iron hydroxides.

The soluble metal-soil organic matter complexes and their stability.

A number of publications have been made by different workers on the stability of various metal-humus complexes soluble in a certain range of pH and concentration. The stability constant values are found dependent on pH. The order of such constants reported by Schnitzer and Skinner[60] in case of certain metal ions forming complexes with fulvic acids was $Cu^{2+} > Fe^{2+} > Pb^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+}$ at pH 3.5 and at pH 5 the order was $Cu^{2+} > Pb^{2+} > Ni^{2+} > Mn^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+}$. But the sequence does not tally with that obtained by Irving and William[61] : $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Ca^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$, which is, however, in agreement with the result of the investigations made by Beckwith[62], and Khanna and Stevenson[63].

Section-B

Ion exchange Formulation

A number of approaches[64], both qualitative and quantitative, have been embarked upon to make a break-through in the understanding of equilibrium between the ions in the exchange phase and those in solutions. To this effect experiments were performed with the variation in the concentrations of ions and the results indicated an exponential relationship between the ions exchanged and the concentrations of exchanging ions. However, in most of the mathematical representations in connection with the ion exchange reactions some limitations have been tacitly accepted. These limitations include, for example, (i) ignoring of the simultaneous presence of the cation and the anion exchange reactions in a system, (ii) the assumption that the exchange capacity of an exchanger is constant, though in some cases, the exchange capacity is found to considerably vary with pH and the nature of the exchanging ions as well, (iii) consideration that the simple stoichiometric equivalence between the ions taken up and released is present, the deviation being explained away as simultaneous adsorption of molecules or formation of complex ions, (iv) the postulate that the perfect reversibility exists in an exchange process under consideration.

On this basis, the Freundlich and Langmuir adsorption equations were proposed. The original form of the Freundlich equation is:

$$x/m = kc^{1/p}$$

where x is the amount adsorbed, m, the weight of the material taken and c, the equilibrium concentration of the electrolyte; k and 1/p are the constants. This equation was used by Wiegner[65] in 1912. This equation has two shortcomings: (a) it does not flatten out at higher values of c as expected in case of a system with fixed exchange capacity (b) it shows that the exchange varies with the variation of the total volume whereas Wiegner showed that the position of equilibrium was independent of volume. Jenny[82], however, in 1926 overcame the second objection by suggesting the equation:

$$\frac{x}{m} = K\left(\frac{c}{a-c}\right)^{\frac{1}{p}}$$

With the variable character of two constants incorporated in this equation, a good agreement is often obtained with experimental data over a limited range. However, according to Marshal[66], the equation was satisfactory in respect of k, but 1/p varied most irregularly. Vageler[82] proposed a similar equation with only one constant, but it could not explain the variability of the equilibrium with volume.

The law of mass action in formulating the ion exchange as a completely reversible reaction was first harnessed by Ganssen[67]. Kerr[68] suggested the specific mass action for uni-univalent and uni-bivalent exchanges. They were of the forms:

$$\frac{(\bar{X})(Y^{+})}{(\bar{Y})(X^{+})} = k_1$$

$$\frac{(\bar{X})^2(Y^{+2})}{(\bar{Y})\,(X^{+2})} = k_2$$

The ions in the exchange phase is indicated by a bar; the constants k_1 and k_2 are termed as selectivity coefficients and the ionic terms represent concentrations in equilibrium solutions. But, inasmuchas the activities of the ions in the exchange phase are not known, only the qualitative or emperical equilibrium constants can be obtained. Bauman[69] and Gregor[70] opined that the equilibrium constant values are rendered further uncertain because of swelling and volume change of the exchanger, particularly in case of resins. The model suggested by Gregor, though thermodynamically less well-defined, helped to bring out clearly ~~the~~ the physical action of swelling pressure. However, Boyd[71] et al. made a more vigorous application of the law of mass action, in which they assumed that ion exchange was a solid solution process based on the solid-solution idea of Vanselow[72].

In the above formulation all the exchange sites were implicitly assumed to be of equal value. However, Wiegner et al.[73] first pointed this tacit assumption and with a view to interpreting some of their experimental observations, they resorted to the idea of loosely and firmly bound ions on the surface of the exchange substrate. He had also to assume the existence of micropores and cleavages in the face of necessary information being not available on the surface characteristics of silicates with which he worked.

Jenny[74] visualised a kinetic condition on the surface and derived a mass action equation representing the exchange process of univalent ions. Davis[75], later, developed the idea to multiply the charged ions. Krishnamoorthy and Overseet[76] applied the statistical method as was used by Fowler[77] and Guggenheim[78] in the case of gas adsorptions on solid surfaces. Mukherjee[79] attempted to interprete the ion exchange processes on the basis of electrical double layer. His concept consisted in the assumption of exchangeable ions: the osmotically active and osmotically inactive ions forming the mobile and the immobile part of the double layer respectively. True, the concept led to only qualitative results, but in some respect it yielded better agreement to the experimental observations.

In the present thesis an attempt has been made to fit the data, obtained from the exchange reactions between a particular complex cation in the exchanger phase like humic, hymatomelanic and fulvic acids, both natural and synthetic, and some inorganic and organic cations in the solution phase in the models like (i) Kielland's[80] and (ii) Pauley's[81]. So, a short review of these models is furnished below.

Kielland's model:

The first attempt to describe the ion exchange equilibrium by theoretical equation which deviates from the regular pattern was made by Kielland. He introduced the soli phase activity coefficients and followed Vanselow[72] in treating the hetero-ionic form of the ion exchanger as a solid solution of the components $\bar{A}$ and $\bar{B}$, the bars referrin to the exchanger phase.

For the exchange of ions of any valency according to the reaction:

$$m\bar{A}^{n+} + nB^{m+} = mA^{n+} + n\bar{B}^{m+}$$

Kielland's equation takes the general form as

$$\log K_C = \log K + C\left[n - 2n\bar{x}_B + (n-m)\bar{x}_B^2\right] \quad .. \qquad (1)$$

where K = thermodynamic equilibrium constant.

k_c = selectivity coefficient including corrections for activities of ions in solution, hence call corrected selectivity coefficient.

and X_B = equivalent ionic fractions of B in the exchang phase.

It may be pointed out that for uni-univalent system m = n when the above equation becomes:

$$\log K_c = \log K + C\,(1 - 2\bar{x}_B) \quad .. \qquad (2)$$

which is identical with Barrer's[83]. Barrer, in fact, deduce this equation on a sounder theoretical basis.

Pauley's model

The essential feature of Pauley's model is the electrostatic attraction between counter ions and the fixed ionic groups. It is assumed that all counter ions in the ion exchanger are found at their distance of closest appro to the fixed ionic groups. Writing AR and BR for the pairs of fixed ionic groups and counter ions at the distance of closest approach, the exchange of A for B into two process can be split,

$$AR \longrightarrow A + R \qquad .. \qquad (3)$$

$$R + B \longrightarrow BR \qquad .. \qquad (4)$$

Coulomb's law (without any correction) leads to the following results for the above processes:

$$\Delta G_1^0 = \int_{a_A^0}^{\infty} \frac{e^2}{r^2 \epsilon}\, dr = \frac{e^2}{a_A^0 \epsilon} \qquad .. \qquad (5)$$

and $$\Delta G_2^0 = \int_{\infty}^{a_B^0} \frac{e^2}{r^2 \epsilon}\, dr = - \frac{e^2}{a_B^0 \epsilon} \qquad .. \qquad (6)$$

where ΔG_1^0 and ΔG_2^0 are the free energy changes for the process (3) and (4) e = electronic charge, ϵ = dielectric constant, r = distance from centre of fixed charge, a_i^0 = distance of closest approach between ion i and fixed ionic group. Hence, the over-all free energy change is

$$\Delta G_0 = \Delta G_1^0 + \Delta G_2^0 = \frac{e^2}{\epsilon}\left(\frac{1}{a_A^0} - \frac{1}{a_B^0}\right) \qquad .. \qquad (7)$$

and the thermodynamic equilibrium constant K_A^B is

$$\ln K_A^B = -\frac{\Delta G^o}{kT} = \frac{e^2}{RT\epsilon}\left(\frac{1}{a_B^o} - \frac{1}{a_A^o}\right) \qquad \ldots (8)$$

Therefore, a linear relationship should exist between $\ln K_A^i$ and $\frac{1}{a^o}$. The model leads qualitatively to preference of counter ion with the smaller a^o value and ion of higher valency.