It has been shown that two simple mechanisms, one ionic and the other free radical, can be devised to explain partially the thermal decomposition of nitric acid. Neither mechanism will explain the observed effect of added nitrates upon the rate. Both mechanisms will explain the rate behavior for the decomposition of the pure acid and of dilute solutions of water in nitric acid. Only the free radical mechanism is consistent with the observed absence of an ionic strength effect. The free radical mechanism can be modified to explain the effect of added nitronium ion. The activation energy for the initial rate of the liquid phase decomposition can be predicted, on the basis of the free radical mechanism, from gas phase kinetic data. This prediction is upheld. Further study concerning the nature and the amounts of the species present in liquid nitric acid is necessary if the kinetic data are to be evaluated more thoroughly.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR STUDIES, CORNELL UNIVERSITY]

The Activity Coefficients of Strong Electrolytes. The Halide Salts[1]

BY R. M. DIAMOND

RECEIVED MAY 28, 1958

The idea of "localized hydrolysis," suggested by Robinson and Harned to explain the order of the activity coefficients of the alkali metal hydroxides, fluorides, formates and acetates,[2] is extended to the consideration of other alkali and alkaline earth salts and is shown to give a reasonable explanation for certain anomalies in the order of the activity coefficients of the halides, in particular, for the usual order $Cl < Br < I > ClO_4$. The water structure-breaking and structure-tightening properties of ions are also considered to explain and to predict various other features of the orders of the activity coefficients of large relatively unhydrated ions.

There have been numerous attempts to modify or to extend by means of additional terms the Debye–Hückel expression[3] for the mean activity coefficient of a strong electrolyte so as to obtain an expression usable from the very dilute solution range to concentrations above one molal.[2,4–9] These have resulted in qualitative or quantitative expressions for handling the necessary ion–ion and ion-solvent interactions. (With the latter can also be included the changes in the solvent–solvent interactions caused by the presence of the ions.) The former category obviously includes the electrostatic interaction of an ion with its ion atmosphere[3] and also the possibility of association of an ion with oppositely charged neighbors.[4] The latter category involves particularly the hydration of the ions[8,10] but also the effects of hydration on the dielectric constant[5] and structure of the water solution.[11] However, in spite of the considerable progress made (some in a more or less empirical fashion), there are still difficulties in explaining, even qualitatively, the complete behavior of the activity coefficients of such a simple group of salts as the alkali halides. Such a qualitative explanation is the purpose of this paper.

The alkali metal chlorides, bromides and iodides have activity coefficients which, for a particular halide, decrease in the order Li>Na>K>Rb>Cs at any fixed concentration. The coefficient for a particular salt initially decreases, passes through a minimum and then increases (Fig. 1 and Table I). Both of these features usually are ascribed to the effects of hydration of the cations. The (crystallographically) smaller ions are the more highly hydrated, giving the opposite order for the size of the hydrated alkali cations and for their distance of closest approach to the halide ion, $\mathring{a}$. In dilute solution, the observed activity coefficient order for these alkali halides is correctly given by the Debye–Hückel expression using the above mentioned order

TABLE I

ACTIVITY COEFFICIENTS FOR 1.0 m SOLUTIONS[12] AT 25°[13]

	OH	$C_2H_3O_2$	F	Cl	Br	I	ClO_4
H				0.809	0.871	0.963	0.823
Li	0.554	0.689		.774	.803	.910	.887
Na	.678	.757	0.573	.657	.687	.736	.629
K	.756	.783	.645	.604	.617	.645	
Rb		.792		.583	.578	.575	
Cs	.771	.802		.544	.538	.533	
Mg		.307		.570	.723	.892	.946
Ca				.500	.597	.741	.754
Sr				.461	.535	.680	.643
Ba		.325		.395	.469	.649	.512

	Formate	Acetate	Propionate	Butyrate
Na	0.661	0.757	0.808	0.868

$$\ln \gamma_{\pm} = -\frac{A|Z_1Z_2|\sqrt{I}}{1 + B\mathring{a}\sqrt{I}}$$

of $\mathring{a}$ for the alkali ions, that is, by the limitation on how close the oppositely charged ion atmosphere can approach the central ion. But the increasing magnitude of the differences in the values of $\gamma_{\pm}$ for the different alkalies and the occurrence of a minimum and then a rise in the value of the activity coefficient with increasing concentration (the great-

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[1] This work was supported in part by the U. S. Atomic Energy Commission.

[2] R. A. Robinson and H. S. Harned, *Chem. Revs.*, **28**, 419 (1941).

[3] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

[4] N. Bjerrum, *K. danske vidensk. Selsk.*, **7**, No. 9 (1926); "Selected Papers," Einar Munksgaard, Copenhagen, 1949.

[5] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

[6] G. Scatchard, *Chem. Revs.*, **19**, 309 (1936).

[7] H. S. Frank, THIS JOURNAL, **63**, 1789 (1941).

[8] R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948).

[9] E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

[10] N. Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

[11] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[12] It should be noted that for all other concentrations for which data are available, *i.e.*, 0.1 to several molal, see reference 13, the same orders of the activity coefficients hold.

[13] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," appendix 8.10, Butterworths Scientific Publications, London, 1955.

est rise occurs with lithium halides, with a progressively smaller effect for the heavier cations; cesium halides have barely reached their minima at saturation, Fig. 2) show that other factors are involved, although their origin may also be due to effects of ion hydration. One way is through changing the dielectric constant of the solution. The more highly hydrated ions tie-up more water molecules in their solvation shell, decreasing the number of orientable water dipoles left free and thus decreasing the dielectric constant of the solution.[14] This decrease in the dielectric constant increases the electrical free energy of the ions and "salts them out," causing an increase in their activity coefficients.[5]

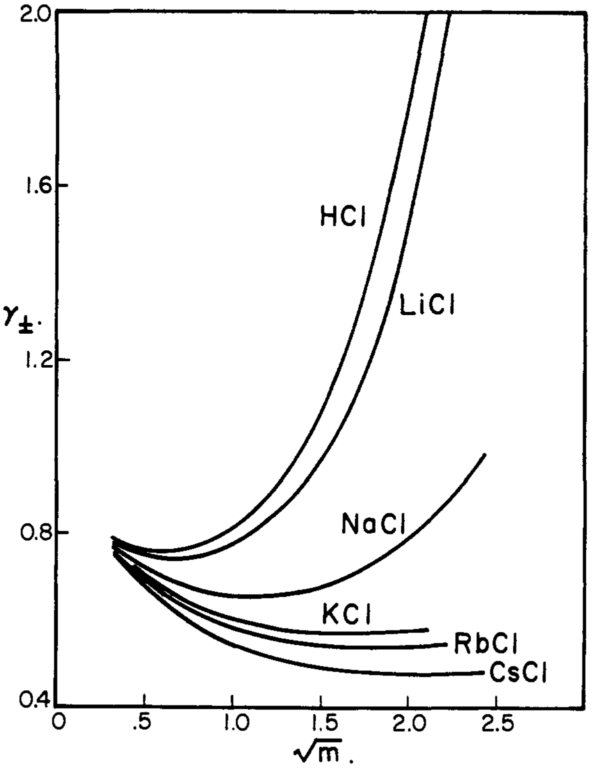

Fig. 1.—The activity coefficients of the alkali and hydrogen chlorides as a function of $\sqrt{\text{molality}}$. Data taken from ref. 13.

But probably the most important effect of ion hydration on the activity coefficient is that first suggested by Bjerrum.[10] He showed that considering the hydrated ion, rather than the unsolvated ion, as the solute species led to a positive correction term to the logarithm of the activity coefficient calculated without regard to ion hydration, and that this correction depends upon the hydration number of the ions and upon the water activity. These two factors are related and they both cause the positive correction term to ln $\gamma_{\pm}$ to increase from cesium to lithium, giving the experimentally observed order of the activity coefficients. Stokes and Robinson have added such a correction term to the Debye–Hückel expression, and using only the empirical parameters $\mathring{a}$ and n, the ion hydration number, and the experimental values of the water activity, have been able to fit remarkably well the experimental values of ln $\gamma_{\pm}$ for strong 1-1 electrolytes up to concentrations of about 2 m.[8] But it should be noted that the values of $\mathring{a}$ and n used are empirical quantities and should not be taken too literally. They are not, in fact, always completely self-consistent, or even reasonable, as is described below, and this is because all other types of ion–water, ion–ion and water–water interactions have been neglected.

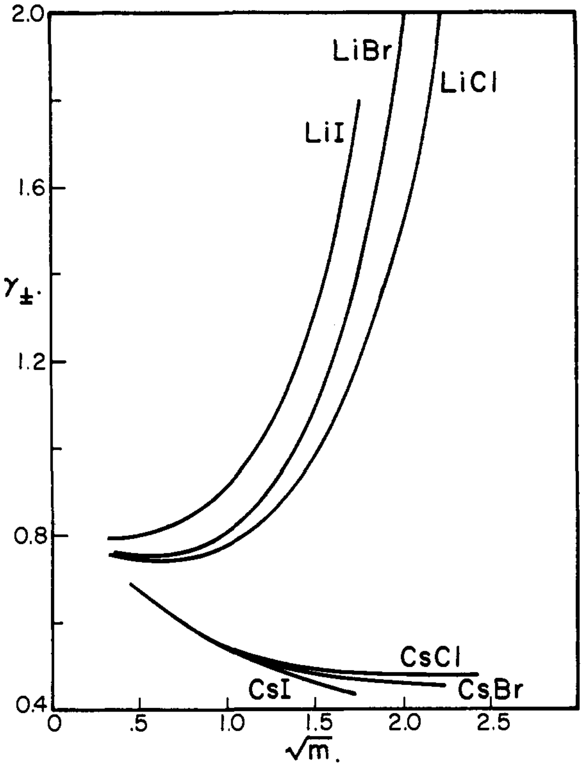

Fig. 2.—The activity coefficients of the halides of lithium and of cesium as a function of $\sqrt{\text{molality}}$. Data taken from ref. 13.

Glueckauf[9] has improved the Stokes–Robinson treatment by also taking into account the difference in the sizes of the water molecule and the (hydrated) ions by using volume fractions instead of mole fractions in calculating the ideal entropy contribution to the total free energy of the solution. If the hydrated ions are larger, or smaller, than a water molecule, the result is a positive contribution to the value of ln $\gamma_{\pm}$. That is, when the species of different size mix, the sum of the entropy increases for the large and small species, due to the greater volume available to them in the solution, is always greater than the corresponding entropy of mixing of two species of the same volume. The corresponding increase in the value of ln $\gamma_{\pm}$ is directly proportional to the molality for not too concentrated solutions. In the range of concentration where $0.018mr << 1$, m being the molality and $r = \phi_V / V_w^0$, with ϕ_V the apparent molar volume of the (unhydrated) electrolyte and V_w^0 the molar volume of pure water, the additional volume frac-

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[14] (a) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952); (b) F. E. Harris and C. T. O'Konski, *J. Phys. Chem.*, **61**, 310 (1957).

tion contribution to the Stokes–Robinson expression can be approximated

$$\Delta \ln \gamma_{\pm} = \frac{0.018m}{\nu} [(r + n) - \nu]^2$$

where ν is the total number of ions produced by one molecule of electrolyte. Glueckauf's treatment leads to more reasonable (smaller) values for the hydration number n and is certainly an improvement, although it requires an additional piece of information, the value of the apparent molar volume of the electrolyte. But it still leaves unexplained the difficulties to be described in the second paragraph below, and for large ions there is another factor acting in the opposite direction. This is the breaking of the water structure by the ions, the formation of a "thawed" zone of water molecules around the ion.[11] A water molecule near an ion tends to be oriented by two influences, the field of the ion and the hydrogen-bonded coördination with the structure of the surrounding water molecules. There is a competition between these two influences and the "thawed" zone is where they are of comparable magnitude.[15] Closer in toward the ion, the water molecules are increasingly rigidly oriented by the field of the ion, forming the primary hydration shell of the ion. Farther away from the ion, beyond the "thawed" zone, the water molecules are coördinated into the hydrogen-bonded short-range structure of ordinary water. In the intermediate "thawed" zone, the water molecules may switch back and forth between orientation into the neighboring water structure or toward the ion, and so have more possible rotational freedom. This leads to some "extra" entropy for the solution, as pointed out by Frank and Evans, but more importantly in the present case, also to a higher energy content, by the amount of energy necessary to break the water hydrogen bonds in the "thawed" zone. The effect is larger, the larger the size of the ion, up to the point where the field at the surface of the ion is too weak to pull the nearest water molecule around against the orientation imposed by the local water structure. Since with an increase in concentration, less water structure-breaking will occur per ion (due to overlapping between the ions), the "extra" energy content per ion will decrease and this leads to a negative correction term to ln $\gamma_{\pm}$. The correction term should be more negative the larger the size of the ion and, in actual fact, this feature enters into the value of the empirical parameter $\mathring{a}$, requiring a somewhat smaller value for it for large relatively unhydrated ions than would be necessary if the effect were explicitly taken into account. This is more likely the cause of the observation that such ions tend to have values of $\mathring{a}$ which may be too small to be physically acceptable than the second-order effect suggested by Glueckauf,[9] especially since, for large relatively unhydrated ions, the use of volume fractions instead of mole fractions makes the situation with respect to the values of $\mathring{a}$ even worse.

But a certain amount of care must be exercised when considering this water structure-breaking effect. In the sense used above it arises from a roughly even competition between the ion and the surrounding water structure to orient and bind the particular water molecules under consideration. If the charge of the ion is not distributed over the entire surface, or if the ion is very large, or has hydrophobic groups, very different results may occur. Consider the case of the salts of the homologous series of normal fatty acids, *i.e.*, formate, acetate, propionate, etc. In this series the charge is localized in the carboxylate group at the end of a hydrocarbon chain. With formate, there is no significant problem but as the chain gets longer, its interaction with the water becomes increasingly important relative to the attractive interaction of the carboxylate group. The uncharged hydrocarbon segments do not attract their surrounding water molecules as strongly as do the water molecules still farther out and so do not lead to the thawing effect. In fact just the reverse occurs, the water structure is tightened. The water molecules next to the hydrocarbon are pulled back more tightly into the water structure and away from the hydrocarbon by the unbalanced attraction of the water molecules on one side and the hydrocarbons on the other. This tightening of the water structure[16] resembles a type of surface tension effect and the larger the hydrocarbon chain, the greater the effect. With an increase in concentration, it becomes more and more difficult to force additional ions into the increasingly tightened water structure, and so leads to a positive correction term to ln $\gamma_{\pm}$, the magnitude of the correction increasing with increasing size of the uncharged portion of the ion. This factor, as well as the term added by the use of volume fractions, probably accounts for the fact that the activity coefficients of the sodium salts go in the order formate<acetate<propionate<butyrate,[17] Table I, and leads to the expectation that the tetra-substituted ammonium halides will similarly show, at a given concentration, an increase in $\gamma_{\pm}$ with an increase in size of the cation.

From what has been said, one might expect that the activity coefficients of a particular alkali chloride, bromide and iodide should show a dependence on the hydrated size and hydration number of the halide ion similar to the way that the activity coefficients of the alkali salts of a particular halide so depend upon the alkali cation. As the smaller chloride ion is certainly more hydrated than the iodide ion, this would lead to the order Cl > Br>I for the activity coefficients of the halide salts. But, in actuality, the activity coefficients increase in the unexpected sequence Cl < Br < I for the lithium, sodium and potassium salts, with the difference between chloride and iodide becoming smaller in going from lithium to potassium. At rubidium the order reverses and the cesium salts

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(15) Equating the energy of breaking one or two hydrogen bonds in water (ΔE = 5–10 kcal.) to the potential energy between an ion and a dipole (assuming a value of ϵ = 4–5 for the local dielectric constant around the ion) yields the crude estimate of 3–4 Å. for the separation of univalent ion and water dipole in the thawed region, certainly a reasonable magnitude.

(16) This effect leads to an extra decrease in the entropy of the solution, an effect which is especially pronounced for neutral molecules in water compared to in a normal structureless solvent, as pointed out by Frank and Evans, ref. 11.

(17) But with sodium valerate a critical concentration is reached at which micelle formation occurs with a great lowering in the activity coefficient. With the still larger carboxylate anions this occurs at lower concentrations.

continue this trend and show activity coefficients decreasing still more markedly than those of rubidium in the originally expected order, $Cl > Br > I$. The relative orders hold at any given concentration of the salts (Fig. 2 and Table I). These experimental results require Stokes and Robinson to make the unlikely assignment of greater hydration numbers for $I>Br>Cl$ for the lithium, sodium and potassium salts, and leave them with the unhappy necessity for variable values of the hydration number for an ion depending upon its co-ion.[8] These difficulties are not as marked in Glueckauf's treatment[9] but are nevertheless still there.

An explanation for this situation, a purpose of this paper, is suggested by the behavior of the alkali fluorides, hydroxides, formates and acetates, the "second group" of alkali salts in the classification of Robinson and Harned.[2] With these salts, the activity coefficients increase in the order $Li < Na<K<Rb<Cs$, which is the reverse of that of the halides other than fluoride. Robinson and Harned suggest that this is due to an association of the ions through an intervening water molecule, that is, to a "localized hydrolysis."[2] Because of the field of the cation, the water molecules around it are oriented with their protons pointing out, and the molecules are polarized, with their protons more positive than in an ordinary water molecule. The smaller the cation, the more highly polarized are the water molecules and the greater the repulsive force acting upon the water protons. (With polyvalent cations such as Fe(III), Al(III), etc., the repulsion becomes so great as to cause the transfer of the proton to the next water molecule and actual hydrolysis takes place.) The anions of the second group of salts are all anions of weak acids, that is, they are all proton acceptors. They, too, interact more or less strongly with their surrounding water molecules and polarize the molecules but in this case the protons are pointing in to the anion, tending to bond to these proton acceptors. (They all show some actual hydrolysis.) Such an interaction is greatly enhanced if it is with the already polarized water molecule of the cation, and this leads to a type of ion-pairing through the agency of the water molecule. Schematically

$$C^{+}\text{---}\overset{H}{O}H\text{---}A^{-}$$

Such an interaction corresponds thermodynamically to a reduction in the number of ions, *i.e.*, to true association, and leads to a lowered activity coefficient. The effect will be greater the smaller and more highly polarizing, the cation, and so should decrease from lithium to cesium, yielding activity coefficients for these salts which should increase from Li to Cs as is observed (Table I).

But the effect should also depend upon the basicity of the anion. Hydroxide ion might be expected to cause the greatest decrease in the activity coefficient, as it does, and formate, acetate and fluoride might be expected to show a smaller but similar effect as the fragmentary data assembled in Table I so indicate.

Although this localized hydrolysis can be treated thermodynamically as a true association, this does not really imply or require any such definite ion-pairing. Any, even very small, increased interaction between the oppositely charged ions through the medium of a polarized water molecule (or through more than one, which would weaken the individual interaction, but increase the number of ion interactions) will reduce the partial molal free energy of the ions and lower the activity coefficient. It seems reasonable to suggest that the effect has no sharp cut-off; it is large with the hydroxides, smaller with the fluorides, formates and acetates, and would be still smaller, but still present, with the anions of yet stronger acids, such as Cl^-, Br^-, I^-. The corresponding hydrohalic acids are all strong acids in water solution, but in a differentiating solvent of lower dielectric constant, such as glacial acetic acid,[18,19] they become associated, *i.e.*, weak acids, with strengths in the order $(HF)<HCl<HBr<HI$. Even in water the halides must show their different basic strengths by decreased interaction with water, and more particularly with the protons of the water molecules, in the order $F>Cl>Br>I$. So although the effect will be small, such ion–solvent interactions will decrease slightly the activity coefficients of the halide salts, and the magnitude of the decrease will fall from $F>Cl>Br>I$. Just as with the fluorides, the effect falls off with the decrease in polarizing power of the alkali metal cations from lithium to cesium. But in contra-distinction to the fluorides, the effect with the other halides is always so small as to be unable to change the order of the activity coefficients of the alkalies as determined by the degree of hydration of the cations, so that $\gamma_\pm$ for the chlorides, bromides and iodides decreases in the order $Li>Na>K>Rb>Cs$. But the author wishes to suggest that, in fact, the coöperative ion–water interaction represented by "localized hydrolysis" reduces the activity coefficient of LiCl more than that of LiBr which, in turn, is reduced more than that of LiI and so is the cause of the inverted order for the activity coefficients, $LiCl < LiBr < LiI$. The effect should be smaller with the less polarizing sodium ion, and still smaller with the potassium salts, and this is as observed (Table I). With the weakly hydrated rubidium salts the effect is so small that the "normal" halide order appears, and with the still less hydrated cesium salts the order of $\gamma_\pm$ as $Cl>Br>I$ is well marked.

It also should be noted that the hydrogen halides themselves fit into the sequence as comparable to the lithium salts. This is as expected, for although the H_3O^+ ion is larger than the Li^+ ion, its unique structure enables it to (hydrogen)-bond to water molecules better than its size alone would indicate, so that its hydration is comparable to that of lithium ion,[9,20] as is also its participation in localized hydrolysis.

If the previous discussion is correct, the activity coefficients of perchlorate ion, the symmetric anion of a still stronger acid, should be predictable. Perchlorate salts, in general, should have activity coefficients lower than those of the corresponding iodide salt (because of lesser hydra-

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[18] S. Bruckenstein and I. M. Kolthoff, This Journal, **78**, 1 (1956).

[19] J. C. McCoubrey, *Trans. Faraday Soc.*, **51**, 743 (1955).

[20] D. G. Tuck and R. M. Diamond, to be published.

tion and greater water structure-breaking), unless the cation is so small and highly charged as to cause appreciable interaction with the iodide ion (through a water molecule) and so lower significantly the activity coefficient of the iodide salt. Among the alkali metals this would be most important with LiI and least with CsI, and so, the activity coefficients of LiI and $LiClO_4$ should be most similar, that of NaI should be significantly greater than that of $NaClO_4$ and as one descends the alkali family to the cesium salts, where localized hydrolysis effects are negligible, the predicted order of activity coefficients should become more markedly that determined by hydration and water structure-breaking effects alone, namely, $F > Cl > Br > I > ClO_4$. Experimental data are available only for the acids and the lithium and sodium salts, but they do show the predicted behavior (Table I).

Since the dipositive alkaline earth ions as a group are more highly hydrated than the unipositive alkali metal cations, the rise in activity coefficients with increasing concentration should be more marked, and, experimentally, this is so with a larger spread in the values of the activity coefficients of a particular halide from Mg to Ba than from Na to Cs. But the localized hydrolysis effect should also be enhanced due to the greater fields of the alkaline earth cations, and so the activity coefficient order $I>Br>Cl$ should also be more marked; and it is, see Table I. As with the alkalies, this effect should decrease as one descends the family to the larger and less polarizing cations, but with the highly polarizing dipositive ions, no reversal to the order expected of independent halide ions in solution occurs, even at barium, although there is a trend in that direction. This trend toward the order $F>Cl>Br>I>ClO_4$ is more obvious if one compares the iodide and perchlorate salts. With magnesium, the localized hydrolysis effect is so important, even with the iodide, that the activity coefficients of MgI_2 are below those of $Mg(ClO_4)_2$. With calcium the decrease in the activity coefficients of the iodide salt due to this effect is smaller and $\gamma_{\pm}$ for CaI_2 and $Ca(ClO_4)_2$ are similar. With strontium and barium iodides the effect becomes unimportant, and the order $I > ClO_4$ becomes increasingly marked.

The effect of localized hydrolysis should be still more important with small tripositive cations, and so, if no actual complex ion formation occurs, the order $I>Br>Cl$ should be expected there, too, with the activity coefficients of the perchlorates becoming perhaps larger than those of the iodides, at least for small cations. There are few experimental data with which to compare, but in the case of the rare earth chlorides and bromides whose activity coefficients have been measured up to about $0.03m$,[21] the order $Br>Cl$ is apparent.

In summary it is seen that the idea of an interaction between oppositely charged ions through the intermediary of a water molecule is a reasonable one even for the anions of acids normally considered strong, and this leads to a decrease in the mean activity coefficient of the ions. This effect, which depends upon the polarizing power of the cation on the water molecule (proton repulsion) and upon the proton accepting ability of the anion, can explain, then, the anomalous anion order of the activity coefficients of the alkaline earth and of most of the alkali metal halides, and the reversal of this order with the rubidium and cesium halides. The activity coefficients of the perchlorate salts (and presumably of other large, relatively unhydrated and non-associating ions) are in agreement with what would be expected from the effects discussed in this paper of water structure-breaking (a decrease in $\gamma_{\pm}$ with an increase in the size of the ion), and those ions where the charge is localized at one part of a hydrophobic structure, as with the normal carboxylate anions, will show the opposite behavior because of their water structure-tightening effect.

[21] F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2781 (1952); F. H. Spedding and I. S. Yaffe, *ibid.*, **74**, 4751 (1952).

ITHACA, N. Y.

[CONTRIBUTION FROM THE NICHOLS LABORATORY, NEW YORK UNIVERSITY]

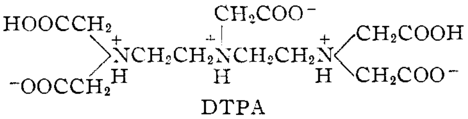
The Acid Dissociation Constants of Diethylenetriaminepentaacetic Acid and the Stability Constants of Some of its Metal Chelates[1]

BY EDWARD J. DURHAM AND DANIEL P. RYSKIEWICH[2]

RECEIVED MARCH 26, 1958

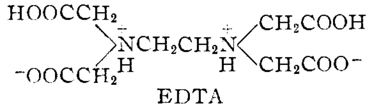
The acid dissociation constants of diethylenetriaminepentaacetic acid, H_5Y, and the stability constants of its chelates with Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2} and Cd^{+2} were determined at 20° and an ionic strength of 0.10. The existence of a stable monohydrogen chelate species, MHY^{-2}, and the usual chelate, MY^{-3}, is illustrated. No bimetallic chelate is formed. The *p*H dependence of chelate formation is quantitatively described by means of *p*M, % MHY^{-2} and % MY^{-3} *versus* *p*H plots.

The chelating properties of diethylenetriaminepentaacetic acid, DTPA, are of interest in view of its structural relationship to the well known chelating agent ethylenediaminetetraacetic acid, EDTA.



$$\mathrm{(HOOCCH_2)(^{-}OOCCH_2)}\overset{+}{\underset{H}{N}}\mathrm{CH_2CH_2}\overset{+}{\underset{H}{N}}\mathrm{(CH_2COO^-)CH_2CH_2}\overset{+}{\underset{H}{N}}\mathrm{(CH_2COOH)(CH_2COO^-)}$$

DTPA



$$\mathrm{(HOOCCH_2)(^{-}OOCCH_2)}\overset{+}{\underset{H}{N}}\mathrm{CH_2CH_2}\overset{+}{\underset{H}{N}}\mathrm{(CH_2COOH)(CH_2COO^-)}$$

EDTA

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[1] Abstracted from a dissertation submitted by Daniel P. Ryskiewich to the Faculty of New York University in partial fulfillment of requirements for the degree of Doctor of Philosophy.

[2] Geigy Chemical Corp., Ardsley, N. Y.