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POLARITY AND SALT EFFECTS:
A GENERAL EMPIRICAL RELATIONSHIP

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Abstract - An empirical expression for salt effects arising from variations of the polarity of the medium is presented. The equation correlates the rate of a chemical process in solution with the molar concentration of an added electrolyte. Several examples from the literature are shown to obey this empirical relationship.

The addition of electrolytes to a reaction medium has long been known to alter, often quite significantly, the rates of reactions in solution. These salt effects are generally rationalized as arising from changes in the polarity of the medium by the addition of ionic species. Attempts to quantify these changes by relating the reaction rates to the amount of added salt have met with limited success. The well-known Debye-Hueckel equation, for example, applies only to dilute solutions.[1] Other semi-empirical expressions for higher salt concentrations, which correlate the observed rates with the ionic strength of the medium, have proved to be of restricted validity.[2] On the other hand, a theoretical approach to the problem yields equations which are of little practical use, because of a number of not easily accessible variables involved.[3] Simple empirical relationships have been found to apply to particular cases, but these equations lack generality. An example of these relationships is the linear dependance of the rate constants on the concentration of added salt, which Winstein and co-workers characterized as a "normal" salt effect.[4,5]

We have recently reported[6] that an empirical equation, originally employed by Langhals[7] to express the polarity of a binary liquid mixture as a function of the concentration of the more polar component, may be successfully applied to electrolyte solutions. The rate constants of many reactions in the presence of salts were reported to vary with the salt concentrations in accord with the proposed equation. The present work analyses in more details the applications of this relationship to data gathered from the literature for a variety of chemical processes, demonstrating the usefulness of this equation in quantifying salt effects.

RESULTS AND DISCUSSION

For a reaction rate dependent on the addition of an inert electrolyte , equation (1) relates the rate constant k to the molar concentration c of the added salt.[6]

$$\ln k = \ln k_o + A.\ln(c/c^* + 1) \qquad (1)$$

The constant k_o is the reaction rate constant in the absence of electrolyte, A and c* are adjustable parameters.

Equation (1) was derived with the implicit assumption that the addition of an electrolyte changes the polarity of a solvent, thereby affecting the rate of a reaction in this medium. The requirement of a non-specific interaction between the electrolyte and reactants eliminates beforehand, from the range of reactions to be tested, all of those examples where the added salt plays a specific role in the kinetics(*).

The constant A in equation (1) is a measure of the susceptibility of the reaction to the addition of a particular electrolyte to the medium. The parameter c* is a threshold concentration of salt, which defines a transition between two regions or ranges of electrolyte concentration (see below , Figure 1).

When $c^* \gg c$, equation (2) is a good approximation to (1).[6,7]

$$\ln k = \ln k_o + A.c/c^* \qquad (2)$$

For $c^* \ll c$, equation (1) can be written as

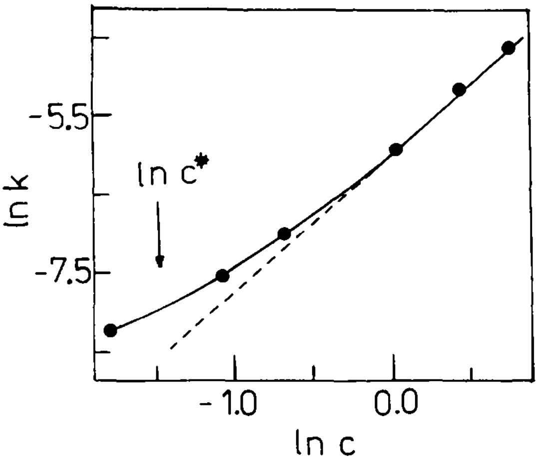
$$\ln k = \ln k_o + A.\ln(c/c^*) \qquad (3)$$

Finally, when A = 1, one obtains relationship (4) which describes the "normal" salt effect mentioned previously.[4,5]

$$k = k_o + k_o.c/c^* \qquad (4)$$

The applicability of equation (1) is best visualized with a graphical example taken from the literature. A plot of ln k vs ln c for the hydrolysis of ethyl orthoformate in water-dioxane at 25°C in the presence of $LiClO_4$

(*)- Although in many cases the above distinction is evident (for example, nucleophilic substitutions involving salts as reactants or as counterion leaving groups are clearly not expected to follow (1)), a clearcut separation between specific and non-specific salt-reactant interactions is not always easy to draw. In fact, it is not unreasonable to suggest some sort of specific interaction between a salt and reactants/transition states for any process where salt effects are observed. These interactions however , just as in the case of solvent-reactant interactions, are often not explicitly taken into account in the general kinetic equations, and the added electrolyte treated as part of a non-specific "medium" and not as a reactant or catalyst.



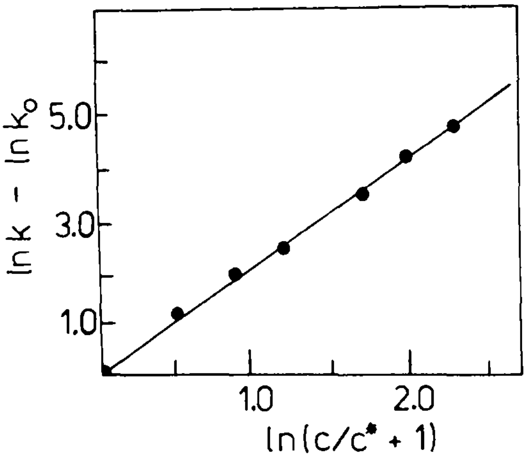


Figure 1 - Hydrolysis of ethyl orthoformate in water-dioxane in the presence of $LiClO_4$ (see ref. 9). Variation of the logarithm of the rate constant k with the logarithm of the molar concentration c of added salt.

Figure 2 - Data of Fig. 1 plotted according to equation (1) (see entry (a) of Table 1) .

is shown in Figure 1. For high concentrations of salt a linear plot is obtained but a significant deviation from linearity is observed for more dilute salt solutions. Figure 2 is a plot of the same data according to equation (1), for a value of $c^* = 0.22$ M . A straight line with a correlation coefficient of 0.9997 is obtained for the whole range of salt concentrations. Notice that c* is a threshold value which defines a transition between two regions. For low concentrations of salt ($c^* \gg c$), values of ln k increase linearly with the concentration of added salt (equation (2)). For more concentrated solutions ($c^* \ll c$), values of ln k vary linearly with the logarithm of the concentration of added electrolyte (equation (3)). Depending on the concentration range employed, kinetic data from the literature are found to obey equation (1) or the particular cases (2) - (4). Table 1 lists a variety of processes which illustrate this behaviour, together with the values of A and c*, the number of data points and the corresponding correlation coefficient for each case. The variety of chemical processes and the good correlations obtained demonstrate the general validity of this empirical treatment.

Special Cases: For sufficiently large range of salt concentrations , discontinuities in the curves of ln k vs ln (c/c* + 1) are sometimes observed (see entries (o) , (p) and (q) in Table 1). A similar phenomenon was observed by Langhals when measuring the polarity of binary liquid mixtures.[7] Such discontinuities were shown to be an intrinsic property of the mixture under study, irrespective of the polarity scale employed. In the case of some electrolyte solutions, this amounts to saying that the same salt affects the polarity and the reaction rates in a medium in two qualitatively different ways, whether it is present in very dilute or more concentrated

TABLE 1 - Application of equation (1) to examples from the literature

Chemical Process	Electrolyte	Range of Salt Concentration, M	A	c*	Number of Points	Correlation Coefficient	Ref.
(a) Hydrolysis of ethyl orthoformate in H_2O-dioxane at 25°C	$LiClO_4$	0.16-1.95	2.13	$2.2x10^{-1}$	7	0.9997	9
(b) Decomposition of diazoacetates in HOAc at 15°C	KNO_3	0.005-0.1	0.04	$3.5x10^{-3}$	6	0.9975	10
(c) Acetolysis of cyclohexyl tosylate at 50°C	$LiClO_4$	0.01-0.3	1.21	$3.5x10^{-2}$	6	0.9999	5
(d) Acetolysis of erythro-3-p-anisyl-2-butyl brosylate at 25°C	$LiClO_4$	0.001-0.1	0.47	$9.7x10^{-4}$	7	0.9976	8
(e) Acetolysis of 2-(2,4-dimethoxyphenyl)ethyl brosylate at 50°C	$LiClO_4$	0.001-0.3	1.20	10^{-1}	7	0.9998	11
(f) Equilibrium of aniline, trinitrobenzene and DABCO in DMSO	Et_4NCl	0.01-1.16	1.14	$9.3x10^{-3}$	10	0.9958	12
(g) Hydrolysis of p-nitrophenyldichloroacetate at 25°C	n-Bu_4NBr	0.1-1.0	-2.07	$5x10^{2}$	7	0.9989	13
(h) Diazotization of 1-methyl-4-aminopyridinium perchlorate	$NaClO_4$	0.5-3.5	0.80	$8x10^{2}$	8	0.9968	14
(i) Dissociation of tris-(1,10-phenanthroline)iron(II) at 25°C	Quinine.HCl	0.25-0.3	0.40	$1.6x10^{-2}$	6	0.9951	15
(j) Racemization of tris-(1,10-phenanthroline)iron(II) at 25°C	Na Camphorsulfonate	0.05-0.6	0.70	$2.6x10^{-1}$	8	0.9888	15
(k) Reaction between $K_4Fe(CN)_6$ and $K_2S_2O_8$ at 40°C	KNO_3	0.033-0.15	1.17	$2.6x10^{-2}$	13	0.9987	16
(l) Ionization of t- butyl chloride in ether at 25°C	$LiClO_4$	0.06-5.46	3.25	10^{-1}	13	0.9937	17
(m) Isomerization of 1-phenylallyl chloride in ether at 25°C	$LiClO_4$	0.02-2.83	2.00	$2.2x10^{-2}$	12	0.9980	17
(n) Decomposition of diazobenzene-2-sulfonic acid at 10°C	KCl	0.01-0.49	-1.37	$7.5x10^{-1}$	6	0.9951	18
(o) Acetolysis of cholesteryl tosylate at 50°C [a]	$LiClO_4$	10^{-6}-$6x10^{-4}$	0.16	$2.4x10^{-6}$	8	0.9861	11
		0.001-0.3	0.97	$3.3x10^{-2}$	8	0.9999	11
(p) Acetolysis of cholesteryl tosylate at 50°C [b]	Diphenylguanidinium perchlorate	10^{-6}-10^{-4}	0.10	$1.4x10^{-6}$	5	0.9945	11
		0.001-0.1	0.32	$2.6x10^{-3}$	5	0.9963	11
(q) Dissociation of benzoic acid at 25°C [c]	NaCl	0.05-0.5	0.12	$2.6x10^{-3}$	7	0.9994	19
		0.7-3.0	-0.27	$4.8x10^{2}$	7	0.9890	19

a) $c_b = 10^{-3}$ M, $k_{c_b} = 3.09 \times 10^{-4}\ s^{-1}$; b) $c_b = 10^{-4}$ M, $k_{c_b} = 2.0 \times 10^{-4}\ s^{-1}$; c) $c_b = 0.7$ M, $K_{c_b} = 11.8 \times 10^{-5}$ M solutions. These special cases are conveniently handled by dealing separately with each of these two concentration ranges, the more dilute "salt (I)" and the more concentrated "salt (II)" regions. Both regions follow an equation of the form (1). For the dilute "salt (I)" region, just as in all other cases described previously, the salt effect is regarded as a perturbation of the chemical rate in the pure solvent, by the addition of the electrolyte to the medium. At the breakpoint concentration c_b , a different salt behaviour sets in. This "salt (II)" region, which commences at c_b, is now regarded as arising from a perturbation of the chemical rate in the "pure" solvent where the electrolyte concentration is c_b. Accordingly, in this region, equation (1) is slightly modified to (5)

$$\ln k = \ln k_{c_b} + A.\ln\left(\frac{c-c_b}{c^*} + 1\right) \qquad (5)$$

where k_{c_b} refers to the rate constant at the breakpoint concentration of the salt.

As an example of this special behaviour, consider the acetolysis of cholesteryl tosylate at 50°C in the presence of diphenylguanidinium perchlorate (entry (p) in Table 1).[11] Reaction rates were measured for salt concentrations which ranged from 10^{-6} to 10^{-1} M. Up to a concentration of 10^{-4} M, equation (1) is verified for $c^* = 1.4 \times 10^{-6}$ M and $A = 0.1$. Beyond this breakpoint concentration, equation (5), with $k_{c_b} = 2 \times 10^{-4}$ s^{-1}, $c_b=10^{-4}$M, $c^* = 2.6 \times 10^{-3}$ M and $A = 0.32$,fits the experimental data very well.

Another interesting example is the variation of the dissociation constant of benzoic acid at 25°C in the presence of NaCl (entry (q) in Table 1).[19] Up to a concentration of about 0.7 M NaCl, K values increase with the addition of electrolyte and equation (1) is obeyed for $c^* = 2.6 \times 10^{-3}$ M. For higher concentrations of sodium chloride, however, values of the dissociation constant decrease with the addition of salt, Equation (5), with a large value of c* (c* = 4800 M), then applies. This behaviour parallels the interesting findings of Langhals of a "synergistic" effect in some binary mixtures, which are more polar than either of the two pure components.[7]

Conclusions: The variety of examples cited indicates that equation (1) is a valuable empirical relationship, capable of unifying a wealth of data under a simple, quantitative framework. It should prove very useful in comparing the influence of different salts on the reaction rates of chemical processes. As a tool for predicting rates by simple extrapolation, this equation may also find considerable application. Thus, for example, in electrochemical studies, the addition of an electrolyte, required in the solution for adequate conductivity, changes the polarity of the medium over that of the pure solvent.[20] This effect is often overlooked, in spite of the fact that the rates of electrochemical processes may be fairly dependent on the polarity of the medium. Equation (1) may be used to estimate rates in organic solutions of salts at various dilutions and as a common basis for comparison of different supporting electrolytes. Finally, it is hoped that this empirical relationship may spur the investigations on salt-reactant interactions, and shed more light onto the dim field of salt effects in physical organic chemistry.

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