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A GENERAL EMPIRICAL EQUATION FOR SALT EFFECTS

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Summary: A general quantitative treatment for salt effects by means of an empirical relationship between the observed rates k and the concentrations of added electrolyte is presented. The proposed equation has been successfully tested for a variety of processes in the literature.

It has long been known that the addition of electrolytes to a reaction medium may alter the rates of chemical processes quite significantly. Attempts to correlate rates with the amount of added electrolyte have met with limited success. Debye-Hueckel equation[1], for example,which relates reaction rates with the ionic strength of the medium, applies only to dilute solutions. Occasionally, simple expressions have been derived which fit the observed data for particular reactions. This is the case of the linear dependance of the rates of solvolysis of some esters on the concentration of added sodium perchlorate.[2a,b] This observation, described by Winstein as a "normal" salt effect, is unfortunately not universal. For low electrolyte concentrations, rates for many reactions deviate significantly from this "normal" behaviour, forcing a second, "special" salt effect to be invoked.[2c,d]

It was recently shown[3] that the polarity of binary liquid mixtures can be effectively described as a function of the molar concentration of the more polar component. The general equation (1), where P_G and P_G^o are polarity values for the mixture and the pure less polar component , respectively, c_p is the molar concentration of the more polar component, and E_D and c* are adjustable constants, was found to apply for a wide range of solvent mixtures.

$$P_G = P_G^o + E_D \cdot \ln (c_p/c^* + 1) \qquad (1)$$

If a linear dependance of the free activation energy of a chemical process on the polarity of the medium is assumed, as for example in the well known Grunwald-Winstein relationship[4], equation (2) can be written for a two-component solvent mixture.

$$\ln k = \ln k_o + A \cdot \ln (c/c^* + 1) \qquad (2)$$

Equation (2) provides a means of predicting changes of reaction rates in solvent mixtures with the variation of the proportion of the components. In particular, in the case of salt solutions, we may treat the added salt as a more polar "co-solvent" and obtain a relationship between the rate of a reaction and the concentration of the added electrolyte. The constant A is a measure of the susceptibility of the reaction to the addition of a particular salt to the medium, c is the molar concentration of the added salt, c* is a threshold concentration value which divides curves of ln k vs. ln c into a linear and a logarithmic part,[3] and k_o is the observed rate in the absence of the salt.

Equation (2) has been successfully tested for a variety of processes from the literature and appears to be of general applicability.[2,5-7] Three particular cases of (2) are worth considering. Firstly, when the range of concentrations c is well above the threshold value c*, (2) reduces to equation (3) and a straight line is obtained when ln k is plotted against ln c.[5]

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

Secondly, when c* is much greater than the concentration range of salt employed, equation (2) may be expanded to a Mac Laurin series and equation (4) results.[6]

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

Finally, when A = 1, equation (5) is obtained, and a linear dependance of the rates on the concentration of added electrolyte is observed. This is the "normal" salt effect described by Winstein and co-workers.[2]

$$k = k_o + k_o . c/c^* \qquad (5)$$

Equation (2) should prove rather useful for reactions in mixed solvents and in particular in the presence of electrolytes. Besides the merit of being very simple, this empirical relationship unifies a wealth of data under a coherent picture, describing "special" or "specific" effects as particular cases of a general behaviour.

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References:

1. R.A.Y.Jones, "Physical and Mechanistic Organic Chemistry",Cambridge University Press, Cambridge, 1979, p. 95.
2. (a) A.H.Fainberg and S.Winstein,J.Amer.Chem.Soc.,1956,78,2763;(b) Idem,ibid.,1956,78,2780; (c) S. Winstein and E.Clippinger,ibid.,1956,78,2784;(d) A.H.Fainberg ,G.C.Robinson and S.Winstein, ibid., 1956,78,2777.
3. H.Langhals, Angew.Chem.Int.Ed.Engl., 1982,21,724.
4. E. Grunwald and S. Winstein, J.Amer.Chem.Soc., 1948, 70, 846.
5. For examples, see J.N.Broensted and C.E.Teeter, J.Phys.Chem., 1924,28,579; R.W.Chlebek and M.W.Lister, Can.J.Chem., 1966, 44, 437; W.A.Eaton,P.George and G.I.Hanania,J.Phys.Chem., 1967, 71, 2016.
6. See, for examples of (4), J.F.J. Engbersen and J.B.F.N. Engberts, J.Amer.Chem.Soc.,1975,97, 1563; B.G.Cox and H.Maskill, J.Chem.Soc.Perkin 2, 1983, 1901; E. Kalatzis and C.Mastrokalos, ibid.,1983, 53.
7. A. Jensen, F. Basolo and H.M.Neumann, J.Amer.Chem.Soc., 1958, 80, 2354; M.Lahti and A. Kankaanperä, Acta Chem.Scand., 1970, 24, 706.

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