

## RELATIONSHIPS BETWEEN DIFFUSION COEFFICIENT, GIBBS ENERGY OF SOLVATION, AND KINETICS OF ION TRANSFER IN LIQUID/LIQUID SYSTEMS

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**ABSTRACT.** Linear relationships are reported between  $\ln D$  (diffusion coefficient) and the Gibbs energy of solvation, as well as between the Gibbs energy of solvation in one solvent and that in another, with correlation coefficients of 0.998 and 0.999, respectively. Also, further evidence is given of the linear relationship between diffusion coefficient and the rate constant for ion transfer across liquid/liquid systems.

### INTRODUCTION

In two recent papers Qureshi et. al. [1,2] have tried to correlate the Gibbs energy of solvation of monovalent cations to the corresponding cationic electronegativities ( $E_N$ ) using Sanderson's values for the latter [3]. These correlations were tested for a variety of solvent systems. As stated by Qureshi et. al. [1], no pretense was made to derive such relationships, but rather, they were presented as useful guides to predict Gibbs energies of solvation for different monovalent cations in a given solvent. However, regardless of its predictive power, it still remains to explain how or why, from a physical standpoint, ionic electronegativities influence, in some way, the Gibbs energies of solvation of ions.

In connection with studies of the Gibbs energy of transfer of ions across immiscible electrolyte solutions, linear Gibbs energy relationships (LGER) were recently proposed [4], thereby correlating Gibbs energies of solvation to a physical property of the ions in the solvent - namely the diffusion coefficient. The proposed LGER's satisfactorily explained the experimental observations of Shao and Girault [5]. The purpose of this communication is to test further the recent proposal by presenting further data from the literature, thereby proving that the proposed LGER's are more general in nature, and not isolated instances that hold true only for limited cases.

### THEORY

The diffusion of an ion in a given solvent may be regarded as a process whereby the degree of solvation of the ion changes from one position to another [6]. Hence, since diffusion is an activated process it was proposed [4] that

$$\Delta G_{\text{act,diff}} = b \Delta G_{\text{solv}} + \text{const} \quad (1)$$

This equation automatically lays the foundation for a physical model of ion solvation since the Gibbs energy of solvation of given ion can then be related to the diffusion coefficient of the ion in the given solvent in view of the transition

state theory expression connecting  $\Delta G_{\text{act,diff}}$  to  $\ln D$ . Thus,

$$\ln D = A \Delta G_{\text{solv}} + \text{const} \quad (2)$$

where  $A$  is a constant.

Similarly, for the transfer of an ion from one solvent to another, say from water ( $w$ ) to an oil ( $o$ ) phase, since: [1] as in Eq. [1], the Gibbs energy of transfer (which is the difference in the Gibbs energy of solvation of the ion in the two solvents) is linearly related to the Gibbs energy of activation for ion transfer, and [2] the latter is related to the rate constant for ion transfer through the transition state theory expression, it follows that [4]:

$$\ln k^{w \rightarrow o} = B \Delta G_{\ddagger} + \text{const} \quad (3)$$

where  $B$  is a constant.

It can be seen that a consequence of Eqs. (2) and (3) is:

$$D = (\text{const}) k^{w \rightarrow o} \quad (4)$$

## RESULTS AND DISCUSSIONS

The above linear relation between  $\ln D$  and  $\Delta G_{\text{solv}}$  (Eq. (2)) has been tested for a series of related ions in different solvents using data from the literature [8,9], and Fig. 1 is a representative example for the Group I metal ions in ethanol (eth). A straight line is obtained, with a correlation coefficient of  $r = 0.998$ .

Furthermore, it is observed that there is a linear relationship, with a slope equal to unity, between  $\Delta G_{\text{solv}}$  of a series of related ions in a given solvent (say, solvent 1) and  $\Delta G_{\text{solv}}$  of the the same series in another solvent (say, solvent 2), this relationship often taking the form

$$\Delta G_{\text{solv},1} = \Delta G_{\text{solv},2} + \text{constant} \quad (5)$$

This is shown in Fig. 2 below taking, as example, data from the literature [9] for the solvents acetonitrile (ac) and formamide (form). The linear plot has a correlation coefficient of  $r = 0.999$ .

It follows from the above that if Walden's rule is valid for the series of ion, then the linear relationship observed in solvent 1 between  $\ln D$  and  $\Delta G_{\text{solv}}$  will also be valid for the same series in solvent 2. However, it must be remarked that Walden's rule is not always a correct assumption. Although generally valid for large ions, deviations are observed in many instances. Stewart et. al. [10] have recently given the example of the tetraphenylborate ion, for which  $D^w/D^{\text{dce}} = 6.44$ , whereas  $\eta^{\text{dce}}/\eta^w = 0.87$  (where  $\text{dce} = 1,2\text{-dichloroethane}$ ). Thus the above generalization should hold only if Walden's rule is applicable for the same series of ions in different solvents.

In both Figs. 1 and 2 the alkali metal ions were taken as examples, and although the linear relationships observed between  $\ln D$  and  $\Delta G_{\text{solv}}$  as well as between  $\Delta G_{\text{solv},1}$  and  $\Delta G_{\text{solv},2}$  hold well for these similar ions, it has recently been observed [11, 12] that Eq. [5] holds also for dissimilar ions, and even for cations and anions in the same systems. The observation is thus more general than at first thought.

Regarding Eq. (2), however, the same has so far not been observed for dissimilar ions. The data presently reported, and those so far tested, concern series of

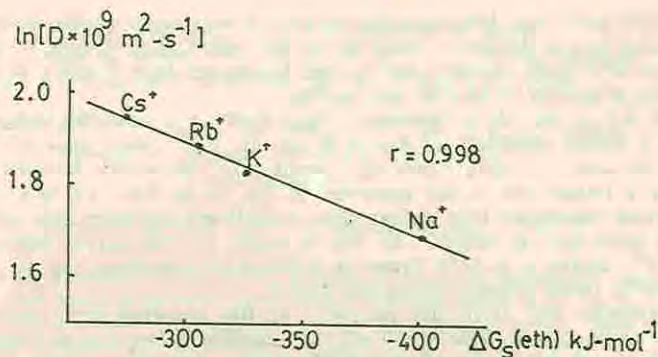


Fig. 1.  $\ln D$  versus  $\Delta G_{\text{Solv}}$  (ethanol) for Group I metal ions.

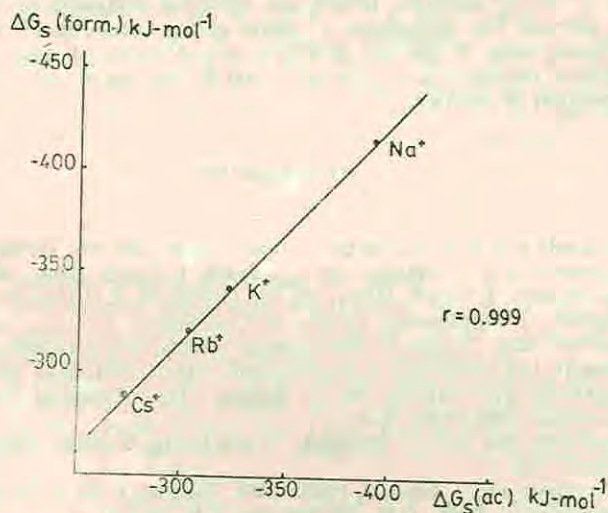


Fig. 2.  $\Delta G_{\text{Solv}}$  (formamide) versus  $\Delta G_{\text{Solv}}$  (acetonitrile) for Group I metal ions.

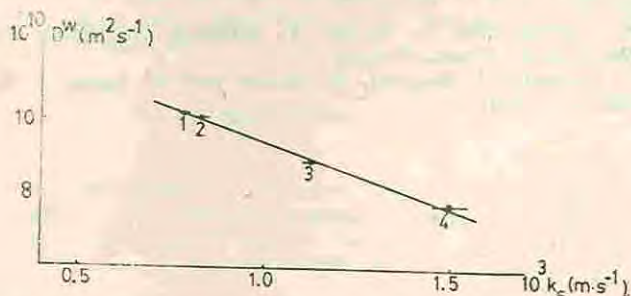


Fig. 3.  $D^{\text{W}}$  versus  $k^{\text{W}+\text{nb}}$  for (1)  $\text{EtMe}_3\text{N}^+$ , (2)  $\text{Et}_2\text{Me}_2\text{N}^+$ , (3)  $\text{Et}_3\text{MeN}^+$ , (4)  $\text{Et}_4\text{N}^+$ . (nb = nitrobenzene).

related ions, e.g. ions in a homologous series, such as the tetraalkylammonium ions, or ions in the same Group of the Periodic Table. This is not surprising since it is well documented in the literature that LGER's in general hold for series of similar or related substances.

As far as Eq. (4) is concerned, Fig. 3 shows a linearity between  $D^W$  and  $k^{W+O}$  for a series reported by Kakiuchi et. al. [13]. Note that Fig. 10 of ref. [13] can be converted into a plot of  $D$  versus  $k$  in view of the Nernst-Einstein relation. That a linear plot is not apparent in Fig. 10 of ref. [13] is solely the result of plotting dissimilar ions rather than selectively plotting related or similar ions. The same plot is redrawn in Fig. 3 below for the series  $\text{EtMe}_3\text{N}^+$ ,  $\text{Et}_2\text{Me}_2\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ , where a methyl group is successively replaced by an ethyl group, the linearity found thereby validating Eq. (4).

Unfortunately, both the accuracy of the reported data, as well as the lack of a systematic kinetic study of, for example, a homologous series of ion, remain handicaps preventing a wider test of the proposed relationships.

Nevertheless it is hoped that the LGER's proposed will prove to be useful guides to help predict  $\Delta G_{\text{solv}}$  of ions in a variety of solvents as well as in estimating  $k^{W+O}$ . In addition, unlike the relations proposed by Qureshi et. al. [1,2], Eq. (2) has the advantage of being easily reconcilable with a physical model - namely that of viewing solvation and diffusion as activated processes, with the latter regarded as a process in which the degree of solvation changes from one position to another.

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