Linear Solvation Energy Relationship of the Energy of the Absorption Maximum of the Solvated Electron with the Solvatochromic Parameter Alpha

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Abstract

A linear free energy relationship was found between $\bar{\nu}_{\mathrm{max}}$, the energy of the absorption maximum of the solvated electron in various solvents, and the alpha solvatochromic parameter which is a measure of the hydrogen bond donor ability of the solvent. The relationship is $\bar{\nu}_{\mathrm{max}} = 9470\alpha + 5590$ cm^{-1} with a correlation coefficient of 0.926 and a standard deviation of 1800 for 16 solvents. This is significantly better than a correlation based on the $E_T(30)$ parameter of Dimroth. There is a considerable similarity between the solvent, temperature, and pressure dependence of $\bar{\nu}_{\mathrm{max}}$ and the absorption spectra of halide ions which are known to be due to a charge transfer to solvent process.

Introduction

Several efforts have been made to find linear free energy relationships (LFER) between the absorption maximum of the solvated electron in various solvents and theoretical calculations or empirical parameters [1–8]. Most involve only a limited number of solvents or have poor correlations. Fox and Hayon collected a large number of values of the absorption maximum of the solvated electron in various solvents from the literature and demonstrated that the energy of the absorption maximum of iodide ion gives a significant correlation with the energy of the absorption maximum of the solvated electron in a variety of solvents (although a correlation coefficient was not given) [4].

This correlation had been indicated with a few solvents earlier [1]. Burrows pointed out some limitations of this approach and carried out a correlation of the energy of the absorption of the solvated electron with the $E_T(30)$ scale of Dimroth which has been widely used for LFER [8,9]. A correlation coefficient of 0.944 (but no standard deviation) was reported for 12 solvents and 12 solvent mixtures although 5 other solvents were discarded because it was considered that their deviations were excessive.

Over the years a number of one parameter and multiple parameter systems have been proposed to correlate solvation behavior [9–25]. The solvatochromic parameters of Taft and co-workers appear to have a pleasing combination of applying to a wide variety of solvents and relationships as well as some connection with fundamental solvent properties such as dipole moment and pK in water. The Taft group has given strong arguments that their parameters have advantages over other approaches [23–30]. Therefore, this study to correlate the energy of the absorption maximum of the solvated electron with the solvatochromic parameters was carried out.

Results and Discussion

Of the solvents and solvent mixtures considered in the study of Burrows [8], there are 16 for which solvatochromic parameters are available [24]. A standard regression analysis of the absorption maximum of the solvated electron, $\bar{\nu}_{\mathrm{max}}$, *versus* the alpha acidity solvatochromic parameter, α, gave $\bar{\nu}_{\mathrm{max}} = 9470\alpha + 5590$ with a correlation coefficient of 0.926 and a standard deviation of 1800 (see Fig. 1). This compares favorably with the approach of Burrows [8] which gave a correlation coefficient of 0.875 and a standard deviation of 2320 for the same group of 16 solvents. Burrows had to omit 5 solvents in order to improve his correlation coefficient to 0.944. However, since none of these were in error by more than two standard deviations, the usual standards of statistical analysis do not sanction the arbitrary removal of any of these solvents from the correlation, let alone five [31]. It is puzzling why the result for dioxane (which does not appear to be included in his Fig. 1) was not also questioned by Burrows since it has a larger deviation than the result for 1-butanol which he discarded.

The correlation with the solvatochromic parameter alpha also shows relatively large deviations for several

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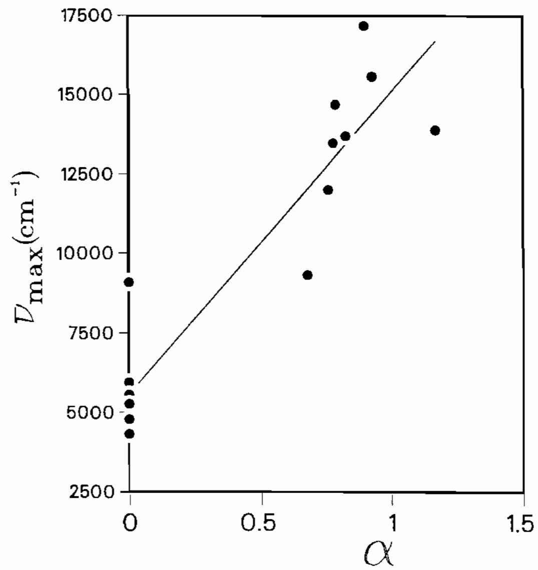

Fig. 1. Plot of the absorption maxima of the solvated electron, $\bar{\nu}_{max}$, against the alpha solvatochromic parameter.

solvents, but none deviate by as much as two standard deviations. Therefore, there is no statistical justification for discarding them. An attempt to improve the correlation by addition of the Hildebrand solubility parameter, δ_H, and the dipolarity/polarizability parameter, π^* [23], did not improve the correlation coefficient or standard deviation significantly.

The remarkable result of this LFER was the dependence solely on the acidity parameter alpha with no significant dependence on the polarity/polarizability parameter pi*. It has been shown that $E_T(30)$ is correlated with both alpha and pi* with a ratio of coefficients close to unity [23]. Thus, it is not surprising that something which is correlated with alpha alone would be correlated better by using alpha alone rather than by using a function which depends almost equally on alpha and pi*. In a LFER study concerning the free energy of solvation of halide ions [25], it was found that the dependence on alpha was greater the smaller the size of the halide ion for chloride, bromide, and iodide ions. The fluoride ion would be expected to have a much greater dependence on alpha if the measurements could be made [4]. It has been stated that for many purposes, the solvated electron may be considered to be the zeroth halide [32]. This study shows that the hydrogen bond donor strength of the solvent does have a great effect on the energy levels of the solvated electron in addition to the effect of the size of the cavity. This has been suggested before only occasionally [33, 34].

The similarity of the dependence of $\bar{\nu}_{max}$ of the solvated electron and the $\bar{\nu}_{max}$ of halide ions upon the solvatochromic parameters [35] confirms the earlier suggestions [1, 4, 36, 37] that the electronic transition of the solvated electron is more similar to a charge transfer to solvent process than to a $1s \rightarrow 2p$ type transition. The electronic transitions of the halide ions in solution are generally considered to be due to a charge transfer to solvent process [32]. Measurements of the pressure and temperature dependence of $\bar{\nu}_{max}$ of the solvated electron made more recently [38] also support this suggestion.

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