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Correlation of Solvation Free Energy of Electron with Empirical Parameters of Solvents. A Criterion for Electrophilic Effects of Solvents

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The solvation free energy of electrons in *N,N*-dimethylformamide, methanol, and water was estimated by means of electron photoemission into solution, and the data were compared with empirical parameters such as thermodynamic quantities, structural and kinetic parameters of solvents. It was confirmed that the interaction of an electron with solvent molecules is purely electrostatic and that the solvation free energy can be used as a tentative criterion of electrophilic properties of solvents.

The empirical parameters of solvents have been proposed as a measure of polarity or nucleophilic and electrophilic properties of solvents. These parameters were deduced from the solvent effects on the band shift of optical absorption spectra of particular solutes, NMR solvent shift, thermodynamic quantities of solvation, or kinetic parameters of solvent dependent processes.

The interaction of a solute with solvent molecules has been conceptualized from various points of view. Stengle *et al.*[1] proposed a three-region model: (1) the region of ordering effect of a solute on its immediate neighborhood, (2) the region of disordering of solvent structure, and (3) the bulk region where solvent structure is unperturbed. Cox *et al.*[2] classified the interaction into five types: (1) electrostatic interactions (either Born type or its modifications), (2) different hydrogen-bonding donor or acceptor properties of ions and solvents, (3) different types and extent of solvent structure, (4) dispersion force interactions, and (5) different Lewis acidity and basicity of ions and solvents. Some of these interactions are interrelated, *e.g.*, influence of hydrogen-bonding properties of solvents on their structure. The solvation effect would be more involved in kinetic processes where the structure of the activated complex plays an important role.

A solvent molecule and the usual solute are, in general, of dipolar character, so that the nucleophilic interaction occurs simultaneously with electrophilic interaction at different sites of a molecule depending the structural characteristics of the solute and solvent. However, a solvated electron is known to be the simplest entity with a unit negative charge held in a cavity created by dilated solvent molecules, so that the interaction of an electron with solvent molecules gives information on the simple electrostatic interaction.

The solvation free energy of an electron in polar solvents has been estimated by means of electron photoemission (EPE) into solution.[3] In this paper a discussion is given on how the solvation free energies of electrons in various polar solvents correlate with the empirical parameters of solvents and how these values can be used as a tentative criterion of electrophilic solvent effects.

Results and Discussion

Solvation Free Energy of Electron. The solvation free energy of a photoemitted electron was estimated by the EPE method. The photoemission current was measured in a cell equipped with a three-electrode system where the working electrode (mercury pool electrode) was illuminated by ultraviolet light (365 nm wavelength) under a controlled potential. The cell contained a highly concentrated supporting electrolyte solution saturated with dinitrogen oxide as an electron scavenger. The photoemission current, I_p, is expressed by the law of five-halves[4]

$$I_p = A(h\nu - h\nu_0 - e\phi)^{5/2}, \tag{1}$$

where A is a constant, $h\nu$ the energy of incident light, ν_0 the threshold frequency, and ϕ the electrode potential. The plot of $I_p^{0.4}$ *versus* ϕ gives a straight line, and extrapolation of the plot to $I_p=0$ gives the threshold potential, ϕ_0. Thus, we have $h\nu_0 = h\nu - e\phi_0$. The difference in energies required for the photoemission from mercury into vacuum and from mercury into solution gives the solvation free energy of the eletron ($\Delta G_s(e^-)$):

$$\begin{aligned} -\Delta G_s(e^-) &= W_{m-v} - h\nu_0 + e\Phi \\ &= W_{m-v} - h\nu + e(\phi_0 + \Phi), \end{aligned} \tag{2}$$

where W_{m-v} is the work function of electron photoemission from mercury into vacuum, Φ the Volta potential difference between mercury and solution.

The values of $\Delta G_s(e^-)$ thus obtained are the energy difference between electrons *in vacuo* and in solution, corresponding to those of the solvation free energy of ions estimated by Born-Haber cycle. It is noteworthy that the hydration energy of the fully hydrated electron was estimated to be 161[5] or 165[6] kJ mol^{-1} by radiation chemical studies, while our result is 108 kJ mol^{-1}. Our value presumably corresponds to the so-called damp or unlocalized electron, which is assumed to exist in solution only for a few tens picoseconds[7] before being fully solvated.

We had difficulty in estimating the values of ΔG_s-(e^-) in various solutions due to the absence of information on the values of Volta potential difference for non-aqueous solutions. Only three data on *N,N*-

Table 1. Values of solvation free energy of electron, $\Delta G_s(e^-)$, and donor number (DN)

Solvent	DMF	MeOH	H_2O
$-\Delta G_s(e^-)$/kJ mol^{-1}	62	98	108
DN[a]	26.6	19.0	18.0

a) The values of DN are given in kcal mol^{-1} (1 cal = 4.184 J.

dimethylformamide (DMF), methanol (MeOH), and water (H_2O) are available (Table 1), which do not seem sufficient for a discussion of the general features of solvent effects. However, they are in line with the values estimated by a modified Born equation for fully solvated electrons in polar solvents.[8]

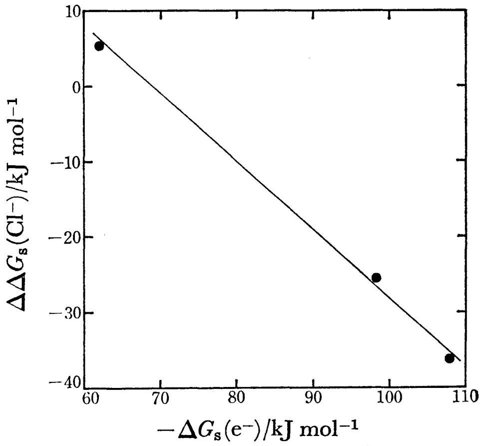

Fig. 1. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and solvation free energy of chloride ion, $\Delta\Delta G_s(Cl^-)$ (reference solvent: acetonitrile).

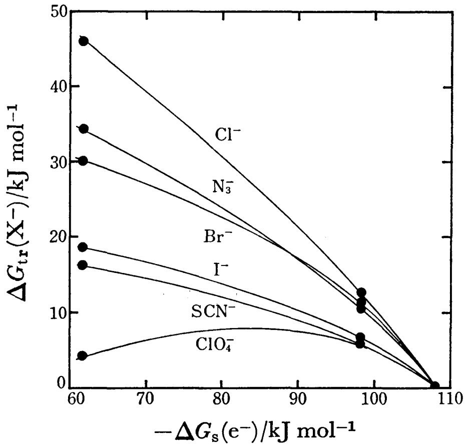

Fig. 2. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and free energy of transfer of anions, $\Delta G_{tr}(X^-)$ (reference solvent: water).

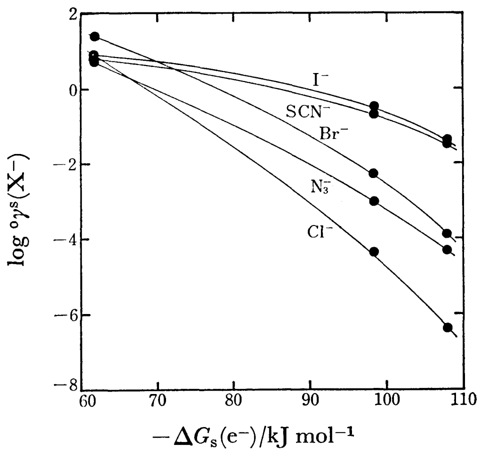

Fig. 3. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and logarithm of solvent activity coefficient of anions, log $^o\gamma^s(X^-)$ (reference solvent; acetonitrile).

Correlation of $\Delta G_s(e^-)$ with Solvation Free Energy of Halide Ions. The values of $-\Delta G_s(e^-)$ are plotted against the solvation free energies of chloride ion in DMF, MeOH, and H_2O in Fig. 1, where $\Delta\Delta G_s(Cl^-)$ denotes the difference between the solvation free energy of Cl^- in a given solvent and that in acetonitrile.[9] The plot gives a straight line. When we plot the values of $-\Delta G_s(e^-)$ against the free energy of transfer, $\Delta G_{tr}(X^-)$, for several anions,[2] the plot of Cl^- is closest to a straight line, the deviation from linearity being pronounced in the order $Cl^- < N_3^- < Br^- < I^- < SCN^- < ClO_4^-$ (Fig. 2). The logarithm of the solvent activity coefficient, log $^o\gamma^s$, shows a similar trend (Fig. 3), where $^o\gamma^s$ is given in molar scale at 25 °C with acetonitrile as a reference solvent.[10] The order of deviation from linearity among the anions is the same as in the case of the free energy of transfer of anions, as can be predicted from the relation, $\Delta G_{tr} = -RT \ln {^o\gamma^s}$ and also from the valence-bond description. If we assume that chloride ion is the least polarizable anion among the anions considered and that the solvated electron is a simple entity with a unit negative charge in solution, the close correlation between the solvation free energy of chloride ion and that of electron is understandable.

The solvent shift of a halogen nucleus such as ^{35}Cl, ^{79}Br, or ^{127}I in respective halide ion[1] and also of ^{19}F in hexafluorophosphate ion, PF_6^-,[11] shows no trend of correlation with $\Delta G_s(e^-)$. Hall[12] suggested the origin of the NMR solvent shift as follows: (1) molecular volume and packing geometry, (2) hydrogen-bonding interactions, (3) charge transfer to solvent interactions, (4) orbital overlap with large atoms in solvent, and (5) charge distributions in solvent molecule. Stengle *et al.*[1] emphasized the prevailing effect of charge transfer interactions. It seems that the solvent shift depends primarily on short-range interactions, the solvent shift thus showing a considerable discrepancy from the trend of $\Delta G_s(e^-)$.

Correlation of $\Delta G_s(e^-)$ with AN-, E_T-, and Z-Values. The value of $\Delta G_s(e^-)$ will be discussed as a criterion of electrophilic properties of solvents in relation to several empirical parameters of solvents.

The acceptor number (*AN*) was proposed by Mayer *et al.*[13] as a measure of electrophilic property of solvents. The value is based on the measurement of NMR solvent shift of ^{31}P nucleus in triethylphosphine oxide, $(C_2H_5)_3PO$. The oxygen atom in $(C_2H_5)_3PO$ is attacked by solvent molecules, and the π-bonding character of the P–O bond is reduced. The effect, coupled with possible polarization of σ-bonding of the P–O bond, results in the decrease of the electron density of ^{31}P nucleus, causing NMR chemical shift. In order to standardize the *AN*-values, the chemical shift was extrapolated to null concentration of the substrate, the value of 1:1 adduct of $(C_2H_5)_3PO$ and $SbCl_5$ in 1,2-dichloroethane being taken as 100. The values of $-\Delta G_s(e^-)$ are plotted against *AN*-values (Fig. 4), the plot showing a straight line with only a slight deviation. The deviation can be attributed either to the hydrogen-bonding of hydroxyl solvent or to the change in solvent structure caused by the nucleophilic substrate. It seems that the remaining coordination sites of phosphorus atom in $(C_2H_5)_3PO$ is almost completely blocked from the solvent attack. This effect is quite different from the case of carbonyl compounds. When we plot the values of $-\Delta G_s(e^-)$ against the chemical shift of ^{13}C or ^{17}O nucleus in acetone,[14–16] linearity is no longer observed (Fig. 5). Maciel and Ruben[14] attributed the predominant effect of hydroxyl solvents to the dipolar or Lewis base interaction coupled with intermolecular hydrogen-bonding. However, it is more likely that the coordination sites of the carbon atom in the carbonyl group are poorly shielded toward the nucleophilic attack of solvent molecules.

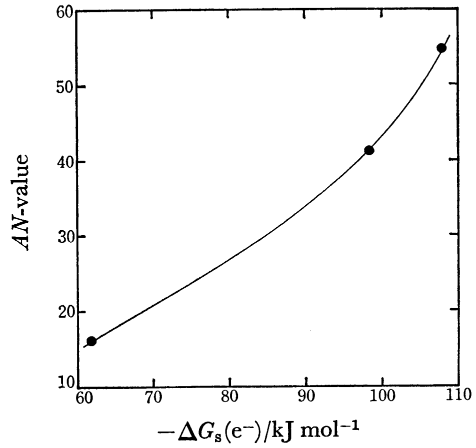

Fig. 4. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and Mayer-Gutmann-Gerger's acceptor number (*AN*).

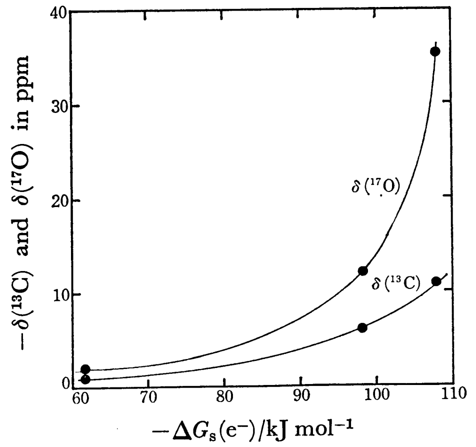

Fig. 5. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and NMR solvent shift of ^{13}C and ^{17}O nuclei in acetone, $\delta(^{13}C)$ and $\delta(^{17}O)$.

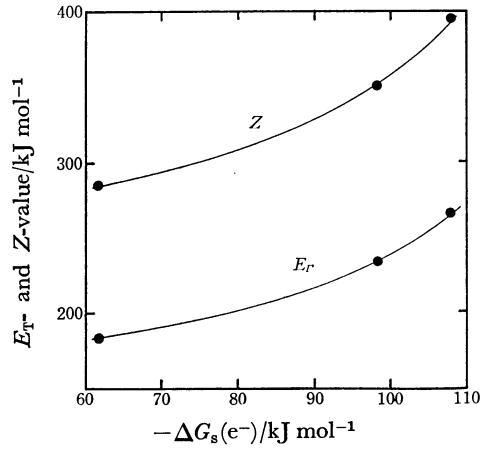

Fig. 6. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and Dimroth-Reichardt-Siepmann-Bohlmann's E_T-value or Kosower's *Z*-value.

A similar correlation to the case of *AN*-value can be seen in the plot of $-\Delta G_s(e^-)$ *versus* E_T- or *Z*-value (Fig. 6). The E_T-value was proposed by Dimroth *et al.*,[17] the value representing the energy of the lowest electronic transition of *p*-(1-pyridinio)-phenolate in various solvents. The oxygen atom of the solute is highly basic and sterically accessible for solvent molecules. The *Z*-value, proposed by Kosower[18] as a measure of solvent polarity, is the energy of charge transfer band of 1-ethyl-4-(methoxycarbonyl) piridinium iodide, the iodide ion of which is attacked by solvent molecules. Both E_T- and *Z*-values primarily represent the electrophilic properties of solvents, but from the curvilinear plots in Fig. 6 the effect of donicity or hydrogen-bonding of solvents seems to exist.

Correlation of $\Delta G_s(e^-)$ *with Kinetic Parameters of Solvent Dependent Processes.* A typical solvent parameter for a kinetic process is the *Y*-value proposed by Grunwald and Winstein[19] as a series of the ionizing power of solvents. This is defined as $Y = \log(k/k_0)$, where k and k_0 represent the first order solvolysis rate constant of *t*-butyl chloride at 25 °C in a given solvent and in a reference solvent (80% ethanol and 20% water), respectively. The plot of $-\Delta G_s(e^-)$ *versus* Y is shown in Fig. 7, where the datum of DMF is taken from the work of Mayer *et al.*[13] A set of data on the ionization rate constant, k_1, of 2-methyl-2-(*p*-methoxyphenyl)propyl *p*-toluenesulfonate is given by Smith *et al.*[20] The plot of $-\Delta G_s(e^-)$ *versus* $\log k_1$ is also shown in Fig. 7. Both plots show a remarkably

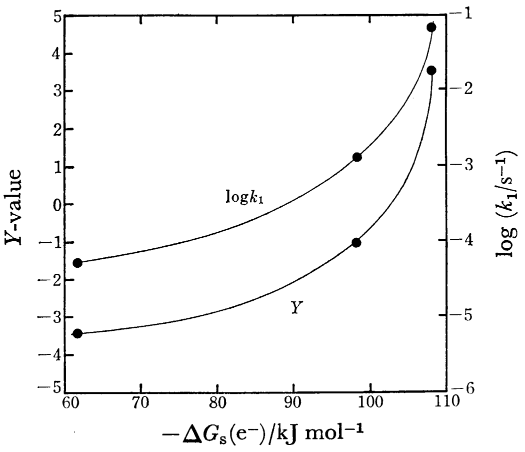

Fig. 7. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and Grunwald-Winstein's *Y*-value or Smith-Fainberg-Winstein's log k_1-value.

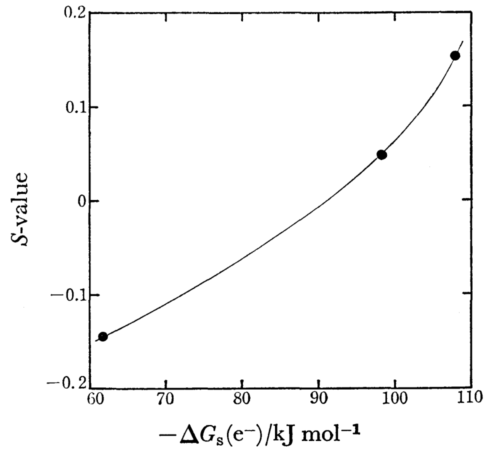

Fig. 8. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and Brownstein's S-value.

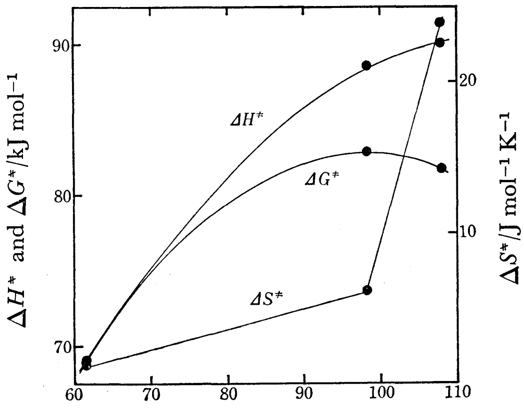

Fig. 9. Relationship between solvation free energy of electron, $\Delta G_s(e^-)$, and Arrhenius energy, ΔH^*, free energy of activation, ΔG^*, and entropy of activation, ΔS^*, for reaction, n-$C_4H_9Br + N_3^- = n$-$C_4H_9N_3 + Br^-$.

curvilinear correlation, the effect of hydroxyl solvents being enhanced.

The S-value proposed by Brownstein[21)] as a solvent dependent parameter was defined by the relation, $\log(k_{\text{solvent}}/k_{\text{EtOH}}) = SR$, where k is a reaction rate constant, equilibrium constant or a function of spectral shift, and R a constant characteristic of the sensitivity of a given reaction. The plot of $-\Delta G_s(e^-)$ *versus* S-values also show a similar curvilinear trend to that of Y-values and log k_1-values (Fig. 8). The curvilinear correlation can be interpreted by taking the concerted effect of nucleophilic and electrophilic interactions into consideration. The nucleophilic attack of solvent is more pronounced in DMF (DN=26.6) than in MeOH or H_2O, while the electrophilic interaction is more enhanced in H_2O than DMF, MeOH being the intermediate (Table 1).

Delpuech[22)] reported the Arrhenius energy for a substitution reaction, n-$C_4H_9Br + N_3^- = n$-$C_4H_9N_3 +$ Br^-, in various solvents. The plot of $-\Delta G_s(e^-)$ *versus* ΔH^*, ΔG^*, and ΔS^* is shown in Fig. 9. In this reaction the solvent attack on the anion seems to play a predominant role, stronger solvation requiring higher Arrhenius energy. It is noteworthy that the entropy of activation is fairly negative in the case of water. Thus, the free energy of activation is smaller in the case of water than in that of methanol. A possible hydrogen bonding of water molecule may increase the orderliness of the activated complex.

In view of the results obtained the solvent parameter can be expressed in terms of three effects: (1) nucleophilic effect represented by the donor number (2) electrophilic effect represented by the solvation free energy of electron, and (3) hydrogen-bonding energy. The three terms have the same dimension and can be expressed in the same unit, *e.g.* J mol^{-1}. Thus, we can estimate the overall solvent effect by the linear combination of the three terms provided the appropriate coefficients for each term are determined experimentally.

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References

1) T. R. Stengle, Y-C. E. Pan, and C. H. Langford, *J. Am. Chem. Soc.*, **94**, 9037 (1972).
2) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).
3) K. Yamashita and H. Imai, *Bull. Chem. Soc. Jpn.*, **50**, 1066 (1977).
4) A. M. Brodsky and Yu. Ya. Gurevich, *Electrochim. Acta*, **13**, 1245 (1968).
5) J. Baxendale, *Radiat. Res. Suppl.*, **4**, 139 (1964).
6) J. Jortner and R. M. Noyes, *J. Phys. Chem.*, **70**, 770 (1966).
7) J. E. Aldrich, M. J. Bronskill, R. K. Wolf, and J. W. Hunt, *J. Chem. Phys.*, **55**, 530 (1971).
8) K. Yamashita, M. Kitamura, and H. Imai, *Chem. Lett.*, **1976** 1363.
9) U. Mayer, *Coord. Chem. Rev.*, **21**, 159 (1976).
10) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Am. Chem. Soc.*, **94**, 1148 (1972).
11) W. J. DeWitte and A. I. Popov, *J. Solution Chem.*, **5**, 231 (1976).
12) C. Hall, *Quart. Rev., Chem. Soc.*, **25**, 87 (1971).
13) U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).
14) G. E. Maciel and G. C. Ruben, *J. Am. Chem. Soc.*, **85**, 3903 (1963).
15) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2752 (1965).
16) H. A. Christ and P. Diel, *Helv. Phys. Acta*, **36**, 170 (1963).
17) K. Dimroth, Ch. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963).
18) E. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).
19) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
20) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).
21) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).
22) J-J. Delpuech, *Tetrahedron Lett.*, **25**, 2111 (1965).