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Empirical Correlations Between Solvent Acidity and the Optical Characteristics of Solvated Electrons

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Correlations between essential characteristics of the optical absorption spectrum of the solvated electron (excitation energy, band-width) and the acceptor numbers of organic solvents are established.

Eine empirische Korrelation zwischen der Acidität von Lösungsmitteln und spektralen Charakteristika solvatisierter Elektronen

Es wird eine Korrelation zwischen den wesentlichen Charakteristika des optischen Absorptionsspektrums von solvatisierten Elektronen (Anregungsenergie und Bandenbreite) und den Acceptornummern organischer Lösungsmittel gefunden.

(Keywords: Solvated electron; Optical spectrum; Solvent effects)

Introduction

A knowledge on the spectral properties of the solvated electron is of interest in a number of areas of physical and chemical sciences. The importance of this problem ranges from the kinetics of radiochemical processes to that branch of spectroscopy which deals with the subject of the structure of liquids, and, more recently, to the problems of electrochemistry in organic solvents.

During the past decade, optical properties of excess electrons in liquids have been extensively studied, especially for solvent in which the maximum of e_{solv} absorption was found in the visible or in the near infrared region. Theoretical models for e_{solv} [1-3] share a limited success in the interpretation of these spectra, therefore some empirical correlations between the type of the solvent and the optical characteristics of the e_{solv} have been suggested.

Freeman[4] has proposed to compare the optical excitation energies (E_{max}) with the solvent structure and the polarizabilities of the solvating groups. The importance of solvent structure was illustrated through the use of the *Kirkwood* factor, which indicates the extent to which molecules align themselves with their neighbors to create short-range order. *Tremaine* and *Dixon*[5] related E_{max} to the classical semicontinuum charge-solvent interaction energy, calculated by assuming that the electron cavity radius is defined by the functional group of the solvent molecule. More recently, *Farhataziz*[6] has suggested that the E_{max} values should be a function of a distance between two hydrogen bonded atoms or negatively polar atoms, dielectric constant and density of the solvent. Another model was subsequently presented to describe the solvent effect on the width ($W_{1/2}$) of the e_{solv} spectrum[7].

Results and Discussion

In our opinion, the optical properties of solvated electrons may be considered in a simpler way. There is some evidence from data for the properties of ions that empirical parameters describing the solvating ability of individual solvent molecules are more important than bulk properties such as the dielectric constant[8]. Two such parameters introduced by *Gutmann's* school are the donor number DN[9] which measures solvent basicity and the acceptor number AN[10] which measures solvent acidity (in the sense of *Lewis*). Since we consider an excess electron, the parameter of interest is AN.

Table 1 lists AN, E_{max} and $W_{1/2}$ values for a number of organic solvents. Because the data for e_{solv} reported by various authors are sometimes inconsistent, the table records only results extracted from the most recent publications. Moreover, taking into account that E_{max} and $W_{1/2}$ values are dependent on temperature and pressure, corresponding data have been composed for the temperature 298 ± 5 K and for normal pressure.

On the basis of the data presented in Table 1 it is readily apparent that both E_{max} and $W_{1/2}$ vary considerably with solvent nature. The excitation energy displays a satisfactory correlation with AN (Fig. 1), yelding

$$E_{max} = 0.043\,(AN) + 0.210 \tag{1}$$

with a correlation coefficient of $r = 0.966$ for 16 solvents for which AN values are known[8]. Correlation is also obtained when $W_{1/2}$ values are plotted against AN (Fig. 2). Now we obtain

$$W_{1/2} = 0.033\,(AN) + 0.319 \tag{2}$$

with $r = 0.937$ for 12 experimental points.

Thus, it is clear that the donor-acceptor approach[11] is very attractive in the field of spectroscopy of the solvated electron. We imagine that the acceptor number is a supreme parameter influencing the values of E_{max}

Table 1. *Optical excitation energy and band-width of the solvated electron in various organic solvents*

No.	Solvent	AN^a	$E_{max}{}^b$	$W_{1/2}{}^c$	Ref.
1	Tetrahydrofuran	8.0	0.59	0.43	14
2	Diethyl ether	3.9	0.54	0.46	14
3	Diglyme	9.9	0.65	0.68	15
4	Hexamethylphosphoric-triamide	10.6	0.55	0.46	16
5	Methanol	41.3	1.97	1.40	17
6	Ethanol	37.1	1.82	1.59	17
7	2-Propanol	33.5	1.52	1.45	17
8	1-Butanol	36.8	1.95	1.57	17
9	2-Butanol	27.1	1.59	1.57	17
10	Ethylenediamine	20.9	0.92	0.88	18
11	Ethylamine	4.8	0.64	0.64	19
12	Diethylamine	9.4	0.61		20
13	1,2-Dimethoxyethane	10.2	0.61	0.65	15
14	*N,N*-Dimethylformamide	16.0	0.74		20
15	*N,N*-Dimethylacetamide	13.6	0.69		20
16	Dimethylsulfoxide	19.3	0.83		21

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[a] Acceptor number taken from Ref.[8].
[b] Excitation energy in eV.
[c] Band-width in eV.

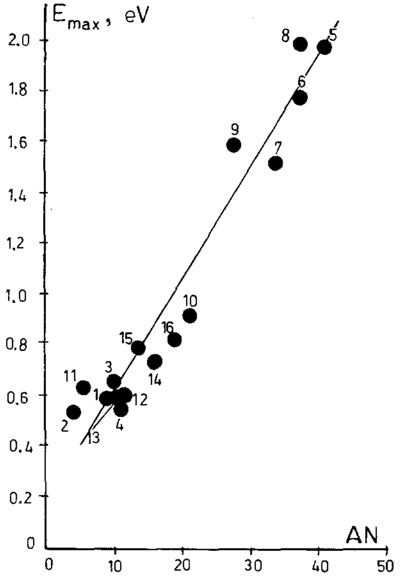

Fig. 1. Plot of the excitation energy of solvated electrons against the solvent acceptor number (for solvent numbers *cf.* Table 1)

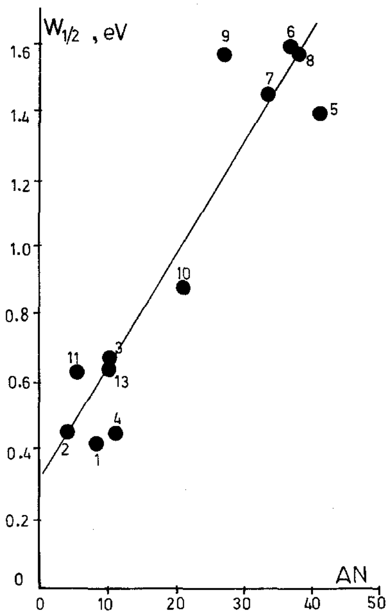

Fig. 2. Relationship between the band-width of the solvated electron and the solvent acceptor number (for solvent numbers *cf.* Table 1)

and $W_{1/2}$ in organic solvents, since it reflects both short-range and long-range interactions[8].

It should be added, however, that the data for e_{H_2O} fail the correlations represented by Eqns. (1) and (2). One possible reason for this behaviour might be a unique geometry of the hydrated electron. As it is known, the hydrated electron is surrounded octahedrally by six water molecules[12], whereas in alcoholic solutions four molecules of the solvent are oriented tetrahedrally towards the electron[13]. So, the reorganization of the solvent structure is especially dramatic during the creation of the hydrated electron. Deviation from the correlations may therefore be due to different entropy contributions.

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