FURTHER DATA RELATING TO THE INTERPRETATION OF SOLVENT EFFECTS OBSERVED IN THE ABSORPTION SPECTRA OF SCHIFF BASES

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The solvent effects observed in the absorption spectra of N-(2-hydroxy-benzylidene)amine and N-(4-hydroxybenzylidene)amine were studied in various solvent mixtures. Good correlations were found between the intensity of the band at around 400 nm and the E_T^N and B_{KT} values of the solvents.

Introduction

It is known that, in the case of Schiff bases in which the aldehyde component contains an OH group in the o- or p-position, a characteristic solvent effect can be observed in the absorption spectra. For instance, on the addition of alcohol or water a new band (the "fore-band") appears at around 400 nm, which cannot be detected in an apolar solvent. Since this phenomenon was first observed [1-4], many different suggestions have been put forward concerning its investigation and interpretation. The phenomenon has been linked with an intramolecular and with an intermolecular

hydrogen-bond [5-10].

Dudek [11] and Ledbetter [12] interpreted the phenomenon in terms of the development of a benzoid-quinoid tautomeric equilibrium depending on the solvent. The effects of substituents [13] and various salts on the solvent effect [14] are in agreement with this supposition. The equilibrium constant of the process can be calculated for the solvent mixtures [15-17], as can the concentration of the quinoid form in some cases [18].

However, recent investigations have led some research workers to discount the formation of the quinoid form; instead, they presume a twin-ionic structure [19-21]. On the other hand, other authors consistently interpret the solvent effect in terms of the benzoid-quinoid equilibrium [23].

Thus, though it has been widely investigated, the problem is not yet solved. The present paper reports on a study of the correlation between the solvent effect and the acidity and basicity parameters of the solvent. The results provide further data promoting a better understanding of the solvent effect observed in the absorption spectra of Schiff bases.

Experimental

The Schiff bases were prepared by mixing ethanolic solutions of the components. Their purities were checked via melting point measurements after recrystallization. The solvents were purified by means of the methods customary in spectroscopy, and carefully dried. VSU-2P and Spektromom 195

Spectrophotometers were used to determine the absorption
curves. The values of the acidity parameter (E_T^N) and the
basicity parameter, (B_{KT}) [23-25] of the solvents were meas-
ured and calculated as described earlier [26]. The measure-
ments were carried out at 25 $^{\circ}$C.

Results and discussion

The experiments revealed that the solvent effect ob-
served for the above Schiff bases can be characterized by an
A ⇌ B equilibrium process, which is dependent on the temper-
ature. The position of the equilibrium varies with the
examined compound and the solvent used. This is demonstrated
by the well-defined isosbestic points of the absorption
curves determined in different solvents, which can be seen
in Figures 1. and 2. (The Figures clearly show that $CaCl_2$,
similarly to the solvent, but more significantly, influences
the A ⇌ B equilibrium.) The structure of form B is debatable.
Either the quinoid (B_1) or the twin-ionic (B_2) structure can
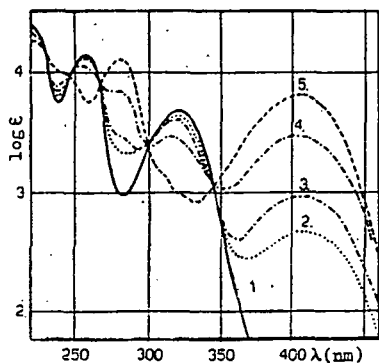be supposed:
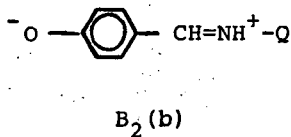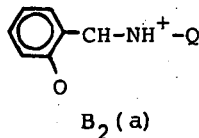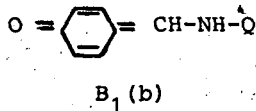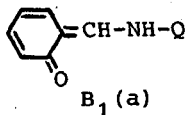
Figure 1.: Absorption curves
of N-(2-hydroxybenzylidene)
benzylamine in different
solvents. Solvents: 95 %
hexane-ethanol (1); ethanol
(2); methanol (3); 40 %
water-methanol (4); 1.5
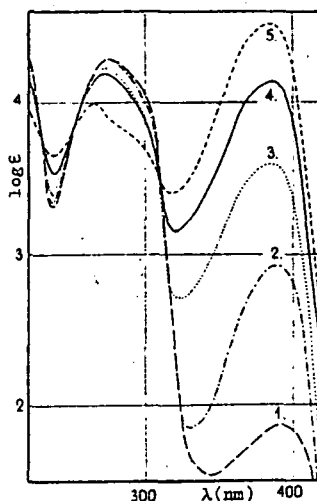mol/dm³ CaCl₂ in ethanol
(5).

Figure 2.: Absorption curves
of N-(4-hydroxybenzylidene)
benzylamine in different
solvents. Solvents: 95 %
hexane-ethanol (1); ethanol
(2); 40 % water-ethanol (3);
0.3 mol/dm³ CaCl₂ in ethanol
(4); 1.5 mol/dm³ CaCl₂ in
ethanol (5).

The equilibrium constant for the A ⇌ B process is:

$$K = \frac{\varepsilon - \varepsilon_A}{\varepsilon_B - \varepsilon} \quad ; \quad \log K = \log \frac{\varepsilon - \varepsilon_A}{\varepsilon_B - \varepsilon} \qquad (1)$$

where ε_A and ε_B are the molar absorption coefficients of
forms A and B, and ε is the molar absorption coefficient of
the equilibrium mixture at the wavelength corresponding to
the band maximum at around 400 nm. Thus, the solvent ap-
plied influences the equilibrium constant value.

The two or multiple-parameter regression equations [27-29] involving the solvent parameters can be well applied for different kinds of solvent-dependent equilibrium processes. If this method is applied for the examined equilibrium, using the E_T^N and B_{KT} values:

$$\log K = b_1 E_T^N + b_2 B_{KT} + a' \tag{2}$$

and taking (1) into consideration:

$$\log \frac{\varepsilon - \varepsilon_A}{\varepsilon_B - \varepsilon} = b_1 E_T^N + b_2 B_{KT} + a' \tag{3}$$

can be determined directly in various solvents. However, ε_A is nearly zero, since these compounds do not exhibit appreciable absorption in the region of the "fore-band" in apolar solvents. This was confirmed by the method of Berstein and Kaminckij [30] and is illustrated in Figures 3 and 4. These Figures present the absorption measured in the region of the "fore-band" in different solvents (characteristic of form B) in comparison with the absorption measured at the maximum of the band characteristic of form A. It can be seen that the resulting straight lines cross the x-axis at one point, which means that only form A absorbs in the region of the "fore--band", i.e. $\varepsilon_A = 0$ in Eq. (3). For the Schiff bases of 2- and 4-hydroxybenzaldehyde with aliphatic amine and benzylamine, we have determined the values of ε_B as well [31], applying the salt effect which influences the position of the A ⇌ B equilibrium. However, in the case of aromatic Schiff bases the equilibrium is strongly shifted in the direction of the bottom arrow.

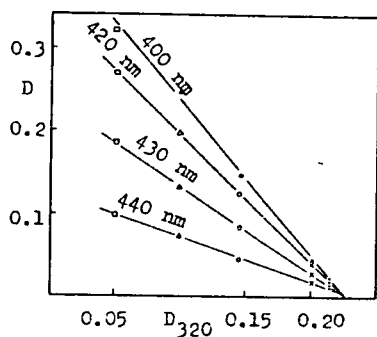Therefore, this method cannot be used, though it is probable

Figure 3.: Change in absorption measured in the region of the fore-band as a function of the absorption at 320 nm in solutions of N-(2-hydroxybenzylidene)benzylamine in different solvents.
$c=5.10^{-4}$ mol/dm^3, l=0.1 cm.
Solvents: ethanol (.); methanol (x); 40%= water-ethanol (O); 2 mol/dm^3 CaCl$_2$ in methanol (Δ); 1.5 mol/dm^3 CaCl$_2$ in ethanol (□)
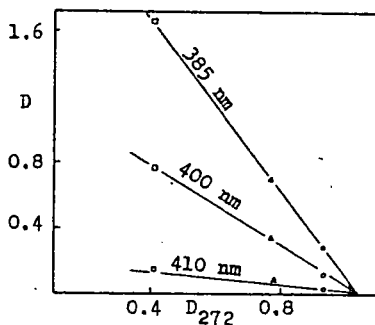
Figure 4.: Change in absorption measured in the region of the fore-band as a function of the absorption at 272 nm in solutions of N-(4-hydroxybenzylidene) benzylamine in different solvents.
$c=5.10^{-4}$ mol/dm^3, l=0,1 cm.
Solvents: ethanol (,); 40 % water-ethanol (o); 0.3 mol/dm^3 CaCl$_2$ in ethanol (Δ); 1.5 mol/dm^3 CaCl$_2$ in ethanol (□).

that the ε_B values of these compounds are at least as high as they are for the compounds of the corresponding aldehyde with aliphatic amines. Thus, for the examined Schiff bases and solvents ε_B, and therefore Eq. (3) can be applied as

$$\log \varepsilon = b_1 E_T^N + b_2 B_{KT} + a \qquad (4)$$

where $a = a' + \log \varepsilon_B$.

In the case of Schiff bases, we have measured the values of ϵ, E_T^N and B_{KT} in different solvent mixtures. They are collected in part in our earlier papers [26, 32] and in part in Tables I and II.

Table I

Molar absorption coefficients of N-(2-hydroxybenzylidene)-benzylamine *at 405 nm and those of* N-(4-hydroxybenzylidene)benzylamine *at 385 nm in different solvent mixtures* /t=25°C/

$$\epsilon_B(405) = 8180 \qquad \epsilon_B(385) = 55930$$

[ethanol] mol/dm³	ethanol-hexane		ethanol-benzene		ethanol-acetone	
	ϵ_{405}	ϵ_{385}	ϵ_{405}	ϵ_{385}	ϵ_{405}	ϵ_{385}
0.000	3.3	2*	14.4	5.0	36.8	9.2
1.704	51.2	80	76	54.4	69.6	29.6
3.409	104.8	144	130	103.2	100	62.4
6.817	196	268	216	222.4	170	144
10.226	292	400	320	374	252	276
13.635	380	566	412	568	356	484
17.044	480	820	480	820	480	820

*extrapolated value

We have used the data obtained to calculate the constans of Eq. (4) and the multiple correlation coefficients for various types of Schiff bases by applying the least squares method. In order to make a better comparison of the effects of E_T^N and B_{KT}, the regression coefficients were calculated for the

Table II

E_T^N and B_{KT} values ($t=25$ ^oC) of ethanol-acetone mixtures

[ethanol] mol/dm^3	E_T^N	B_{KT}	[ethanol] mol/dm^3	E_T^N	B_{KT}
0.000	0.355*	0.54	10.226	0.640	0.63
1.704	0.537	0.55	11.931	0.643	0.65
3.409	0.580	0.56	13.635	0.648	0.68
5.113	0.610	0.58	15.340	0.647	0.70
6.817	0.625	0.59	17.044	0.650	0.77
8.522	0.634	0.61			

* literature data [23]

"beta coefficients" [33]. By normalizing β_1 and β_2, we have obtained in percentages the distribution of the effects of acidity and basicity in relationship (4). The calculated data are listed in Table III.
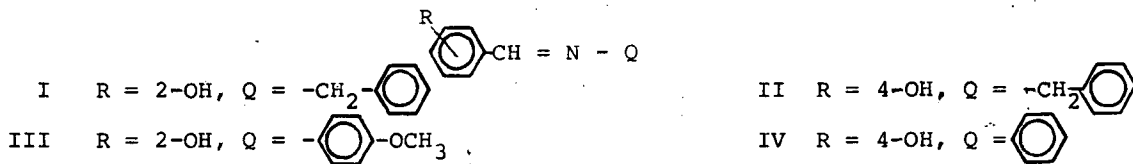
From the data in Table III, it can be seen that, for the compounds examined, according to Eq. (4) there are good correlations between the "fore-band" intensity and the E_T^N and B_{KT} values of the solvents.

The correlations between the E_T^N and B_{KT} values for the three solvent mixtures in Table III are as follows: good in the ethanol-benzene mixture (r=0.980), weak in the ethanol-hexane misture (r=0.922), and very bad in the ethanol-acetone mixture (r=0.653). Accordingly, in the ethanol-benzene mixture there is a good correlation:

$$\log \epsilon = b_E E_T^N + a_E \qquad (5)$$

Table III

Solution of regression equation (4) for the following Schiff bases in different solvent mixtures:

R

$\bigcirc$CH = N - Q

I   R = 2-OH, Q = -CH$_2$$\bigcirc$

II   R = 4-OH, Q = -CH$_2$$\bigcirc$

III R = 2-OH, Q = -$\bigcirc$-OCH$_3$

IV   R = 4-OH, Q = $\bigcirc$

Compound	Solvent	b_1	b_2	a	β_1 (%)	β_2 (%)	n	R
I		5.460	-1.191	0.098	73.64	26.36	7	0.9860
II	ethanol-hexane	6.092	-1.124	-0.160	76.76	23.24	7	0.9946
III		3.732	-1.079	0.723	67.82	32.18	7	0.9769
IV		4.582	-1.380	0.048	66.92	33.08	7	0.9832
I		1.308	1.227	0.897	42.89	57.11	7	0.9994
II	ethanol-benzene	2.048	1.616	0.295	47.17	52.83	7	0.9993
III		0.483	1.243	0.985	21.49	78.51	7	0.9992
IV		0.485	1.902	0.010	15.09	84.91	7	0.9996
I		2.012	2.663	-0.622	48.95	51.05	7	0.9899
II	ethanol-acetone	3.706	4.350	-2.760	51.95	48.05	7	0.9912
III		0.940	2.626	-0.316	31.82	68.18	7	0.9889
IV		1.796	4.194	-2.489	35.83	64.17	7	0.9912

and

$$\log \varepsilon = b_B B_{KT} + a_B \tag{6}$$

which is slightly worse than that in Eq. (4). However, in
the ethanol-hexane, and especially the ethanol-acetone mix-
tures, the correlation according to regression equations
(5) and (6) is considerably worse than that based on rela-
tionship (4). Figures 5 and 6 illustrate the measured log ε
values and those calculated via the regression equations
for N-(4-hydroxybenzylidene)butylamine solutions. Thus, it
is to be expected that the position of the A $\rightleftharpoons$ B equilib-
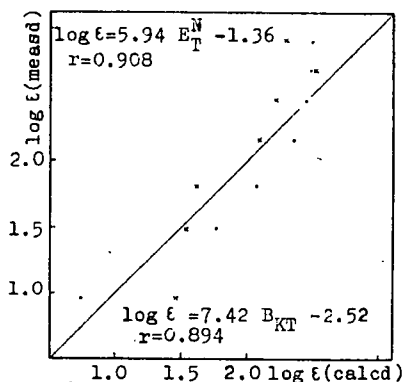rium characteristic of the solvent effects of the Schiff

Figure 5.: Measured log ε and
values calculated from Eq.
(5) (.) and Eq. (6) (x) in
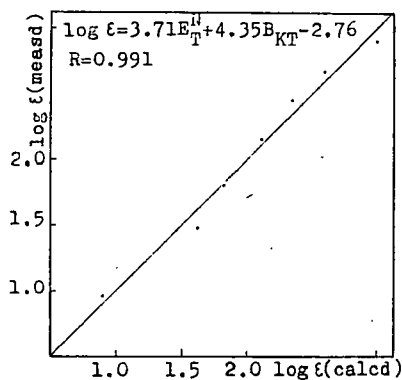ethanol-acetone solution of
N-(4-hydroxybenzylidene)ben-
zylamine

Figure 6.: Measured log ε
and values calculated
from Eq. (4) in ethanol-
-acetone solution of
N-(4-hydroxy-benzylidene)
benzylamine

bases studied is influenced by both the acidity and the basicity parameters. This is valid for both the 2- and the 4-hydroxy derivatives, i.e. the possible intramolecular hydrogen-bond in the case of the 2-hydroxy derivatives does not cause any significant change in the phenomenon described. In Table III there is no significant difference between the data on compounds I and II and those on compounds III and IV. Slight differences can be seen between the Schiff bases formed with benzylamine and those with the aromatic amine (I, II and III, IV, respectively). In the latter case, the effect of the basicity (β_2') is higher for every solvent mixture, while the effect of the acidity (β_1') on the process is lower. This is presumably connected with the lower electron density of the azomethine-nitrogen of the aromatic derivatives. It is noteworthy that in these compounds the A $\rightleftharpoons$ B equilibrium is generally shifted strongly in the direction of the bottom arrow in every solution.

We have investigated the applicability of relationship (4) in pure solvents as well. The results are summarized in Table IV.

From use of the data in the Table, the regression equations (5), (6) and (4) are as follows:

$$\log \varepsilon = 3.376 \ E_T^N + 0.566 \qquad\qquad r = 0.9623$$

$$\log \varepsilon = 2.029 \ B_{KT} + 0.845 \qquad\qquad r = 0.8616$$

$$\log \varepsilon = 2.556 \ E_T^N + 0.723 \ B_{KT} + 0.498$$

$$R = 0.9827$$

It can be seen that the correlations with E_T^N or with B_{KT} are worse than with the multiple-parameter equation.

Table IV

Molar absorption coefficients of N-(2-hydroxybenzylidene)-
benzylamine *at 405 nm in different solvents at 25 ^{O}C*

ε_B = 8150 [31]

Solvent	ε	E_T^N [23]	B_{KT} [25]
n-hexane	3.3	0.074	0.00
benzene	14.4	0.127	0.08
acetone	36.8	0.355	0.54
terc. buthanol	212	0.407	0.95
sec. buthanol	300	0.506	0.90
n-buthanol	412	0.602	0.85
ethanol	480	0.654	0.77
methanol	940	0.765	0.62

This also indicates that both the acidity and basicity of
the solvents play roles in the examined process.

We earlier [14, 18, 31] reported that some salts
(CaCl$_2$, NaI, LiCl) in ethanolic solution exert a consider-
able influence on the solvent effect in the absorption
spectra of N-(2-hydroxybenzylidene)amine and N-(4-hydroxy-
benzylidene)amine. Depending on the salt concentration,
the A $\rightleftharpoons$ B equilibrium is shifted markedly in the direction
of the upper arrow. These observations led us to investi-
gate whether there is any salt effect during the determina-
tion of E_T^N values. Figure 7 illustrates the increase in the
E_T^N value of ethanol on the action of NaI. The ε values [14]
of the "fore-band" maxima of N-(2-hydroxybenzylidene)amine
and N-(4-hydroxybenzylidene)amine are shown in the Figure,

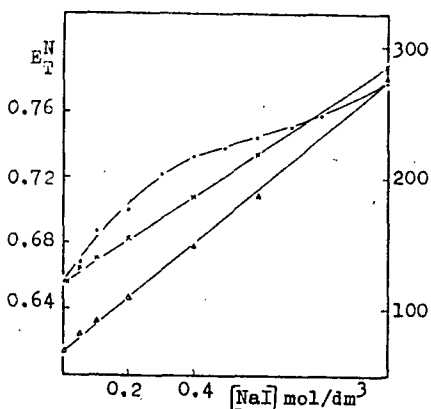*Figure 7.*: Changes in the E_T^N value of ethanol (.), the ε_{436} (x) value of N-(2-hydroxybenzylidene) aniline and the ε_{420} (Δ) value of N-(4-hydroxy-benzylidene)aniline as functions of the NaI concentration (t=25 ^{O}C)

too. Equation (5) indicates a good correlation between the corresponding data for both N-(2-hydroxybenzylidene)aniline (r=0.9869) and N-(4-hydroxybenzylidene)aniline (r=0.9947). It is very likely that there is a certain degree of simi-larity between the Schiff bases examined and the mechanism of the solvent effect of the betaine dye used to measure E_T^N. Further investigations are required to clarify this problem.

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НОВЫЕ ДАННЫЕ К ПОНИМАНИЮ ВЛИЯНИЯ РАСТВОРИТЕЛЯ
В АБСОРЦИОННЫХ СПЕКТРАХ ОСНОВАНИЙ ШИФФА

П. Надь и Р. Герцфельд

Авторы исследовали влияние растворителя в абсорционных спектрах N-/2-гидрокси-бензилиден/амина и N-/4-гидрокси-бензилиден/амина. Нашли хорошую корреляцию между данными интенсивности полосы около 400 нм и E_T^N растворителей а также B_{KT} .