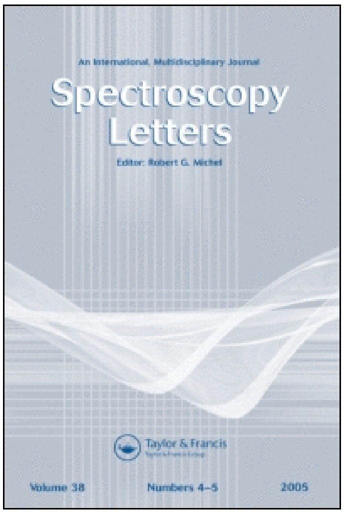

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Roles of the Acidity and Basicity of the Solvent in the Solvent Effect Observed in the Absorption Spectra of Certatn Types of Schiff Bases

Rozália Herzfeld[a]; Pál Nagy[a]
[a] Department of Chemistry, Juhász Gyula Teachers' Training College, Szeged, Hungary

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ROLES OF THE ACIDITY AND BASICITY OF THE SOLVENT IN THE SOLVENT EFFECT OBSERVED IN THE ABSORPTION SPECTRA OF CERTAIN TYPES OF SCHIFF BASES

Key words: Schiff bases, tautomerism, solvent effect, acidity and basicity parameters

Rozália Herzfeld and Pál Nagy

Department of Chemistry, Juhász Gyula Teachers' Training College,
P.O. Box 396, H-6701 Szeged, Hungary

ABSTRACT

A study was made of the solvent effects observed in the absorption spectra of N-(2-hydroxy-1-naphthylidene)anilines, N-(2-hydroxybenzylidene)amines and N-(4-hydroxybenzylidene)aniline in various solvents. It was established that the logarithm of the constant describing the equilibrium enol $\rightleftharpoons$ keto tautomer correlates closely with the parameters E_T^N and B_{KT} characteristic of the acidity or basicity of the solvents.

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INTRODUCTION

We earlier studied the enol $\rightleftharpoons$ keto tautomerism of N-(2-hydroxy-1-naphthylidene)anilines in solution in ethanol[1]. A simple method was described for determination of the concentration of the keto form and the equilibrium constant of the process. The effect of the basicity of the amine component was also examined.

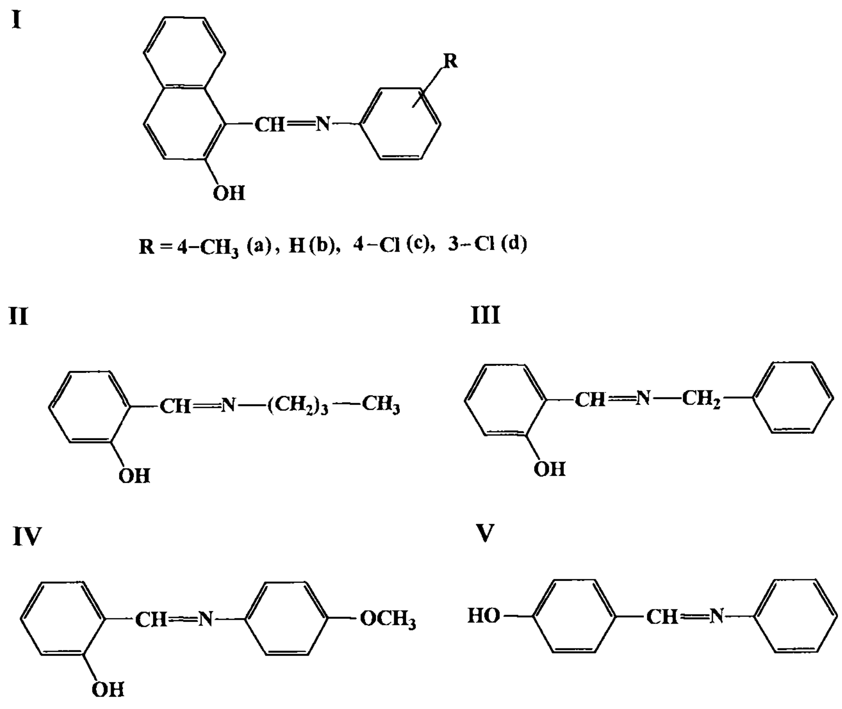
It is well known that the investigated tautomerism is to be observed as a solvent effect in the case of Schiff bases containing an OH group in the *o*- or *p*-position on the aldehyde ring. However, an appreciable quantity of the keto form is present only in solvents capable of hydrogen-bonding[2,3], and the solvent probably takes part in the process both as a proton donor and as a proton acceptor[4]. This was also concluded by Kamounach and Salman[5] from a comparison of the effects of various solvents. In other words, this means that the position of the enol $\rightleftharpoons$ keto equilibrium is influenced by both the acidity and the basicity of the solvents that give rise to this phenomenon (e. g. alcohols and water).

The present paper relates to a study of this process for several Schiff bases in various solvents and solvent mixtures, a connection being sought between the acidities and basicities of the solvents and the equilibrium constants. It is hoped that in this way we shall come closer to a better understanding of the mechanism of the solvent effect.

EXPERIMENTAL

The Schiff bases were prepared by condensation of the components in solution in ethanol. Following recrystallization, their purities were checked by melting point measurement. The solvents were of spectroscopic purity and anhydrous. Light absorption measurements were made on VSU-2P and Spektromom 195 spectrophotometers at 25 °C.

The following Schiff bases were investigated:



Scheme 1

The acidities of the solvents were characterized by the parameter E_T^N, introduced by Reichardt[6], and their basicities by modified Kamlett-Taft[7,8] parameter B_{KT}.

RESULTS AND DISCUSSION

Similarly as for compounds I and III[1,9], the absorption curves of compound II in various solvents exhibit well-defined isosbestic points (Figure 1), in accordance with the presumed enol $\rightleftharpoons$ keto equilibrium.

The equilibrium constant may be written as

$$K = \frac{[\text{keto}]}{[\text{enol}]} = \frac{\varepsilon - \varepsilon_e}{\varepsilon_k - \varepsilon} \qquad (1)$$

It may be calculated simply via measurement of the molar extinction (ε) at the maximum of the wavelength band ascribed to the keto form (ε_k). In this region, there is no significant absorption by the enol form ($\varepsilon_e \approx 0$) [2]; this may be confirmed by the method of Berstein[10]. The value of ε_k may be determined by the method described earlier[1], which involves measurement in ethanolic $CaCl_2$ solution.

The solvent effect is essentially less for compounds IV and V than for compounds I-III, i.e. the enol $\rightleftharpoons$ keto equilibrium is shifted strongly in the direction of the lower arrow. For this reason, the solvent-dependence is more significant in the region of the wavelength "pre-band" (Figures 2 and 3).

The values of ε_k for compounds of this type have not yet been determined, and the equilibrium constant (1) is therefore not known. Table 1 illustrates the variation in the equilibrium constants calculated as a function of solvent composition for compounds I-III in ethanol-hexane mixtures, while Table 2 lists ε data for compounds IV and V in the given solvent mixtures.

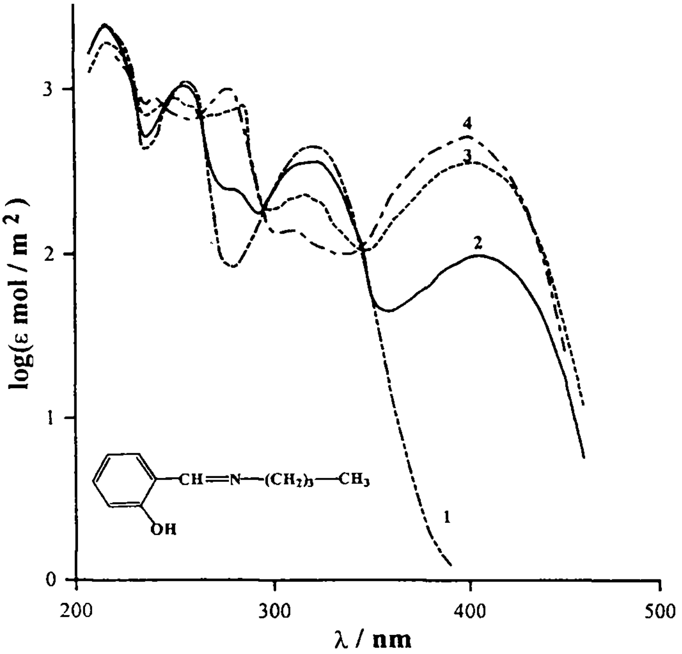


FIG. 1 Absorption curves of N-(2-hydroxybenzylidene)-n-butylamine in hexane (1), absolute ethanol (2), 40% water-ethanol (3), 60% water-ethanol (4) and absolute ethanol containing 1.425 mol dm^{-3} $CaCl_2$ (5).

Paired or multiparameter regression equations containing the solvent parameters can be applied effectively to various solvent-dependent rate and equilibrium processes[11-13]. For the processes involved in the present work, the following equations may be written with the E_T^N and B_{KT} values of the solvents:

$$\log K = b_1 E_T^N + a_1 \quad (2)$$

$$\log K = b_2 B_{KT} + a_2 \quad (3)$$

$$\log K = b_3' E_T^N + b_3'' B_{KT} + a_3 \quad (4)$$

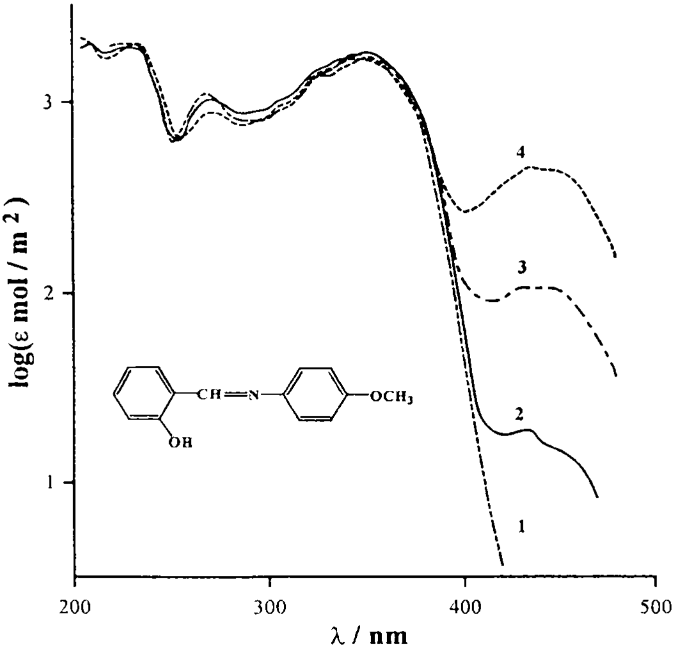


FIG. 2 Absorption curves of N-(2-hydroxybenzylidene)-4-methoxyaniline in cyclohexane (1), absolute ethanol (2), absolute ethanol containing 0.3 mol dm^{-3} $CaCl_2$ (3) and absolute ethanol containing 1.5 mol dm^{-3} $CaCl_2$ (4).

Since the solvent effect is very small for compounds IV and V, ε can be neglected relative to ε_k in Equation (1) (assuming that ε_k is similar in magnitude as for compounds I-III, so that $\varepsilon_k >> \varepsilon$). If this is taken into consideration, in the cases of compounds IV and V the above equations can be given in terms of log ε.

The values of E_T^N and B_{KT} for the solvents that were used were determined as reported previously[14], and are listed in Table 3. The maximum errors in the data are ± 0.005 for E_T^N, and ± 0.03 for B_{KT}.

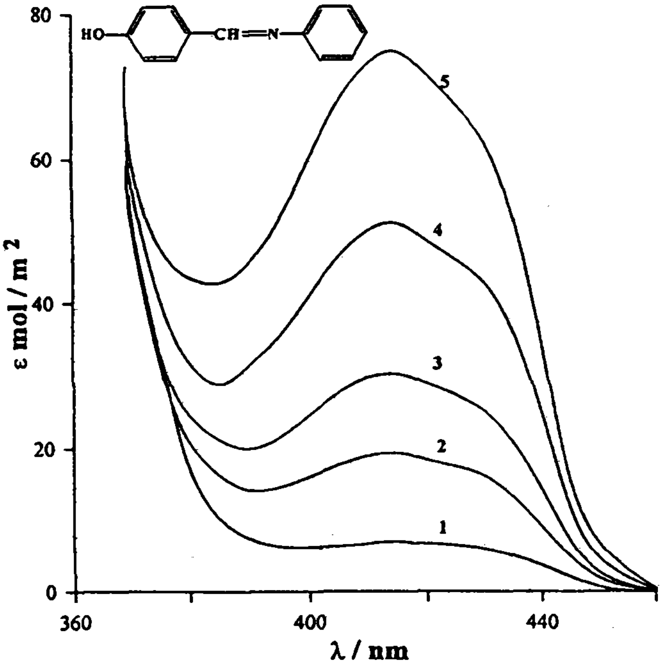


FIG. 3 "Pre-band" of N-(4-hydroxybenzylidene)aniline in absolute ethanol (1) or in absolute ethanol containing 0.05 (2), 0.1 (3), 0.2 (4) or 0.3 (5) mol dm^{-3} $CaCl_2$.

The data in Tables 1-3 were utilized to calculate the constants *a* and *b* in Equations (2)-(4), and also the correlation coefficients (r_1, r_2 and r_3) corresponding to the indices. In the interest of a better comparison of the effects of acidity and basicity, the coefficients b_3' and b_3'' were converted to "beta coefficients"; normalization of these led to the percentage distributions of the effects of acidity and basicity[15,16]. The results of the calculations are presented in Tables 4 and 5.

TABLE 1

Equilibrium constants calculated via Equation (1) for compounds I-III in ethanol-n-hexane solvent mixtures at 25 °C

Compound [ethanol] mol·dm^{-3}	K·10				K·10^2	
	I/a *	I/b *	I/c *	I/d *	II **	III ***
0	0.78	0.77	0.62	0.47	0.07	0.04
1.713	2.80	2.57	1.73	1.31	1.36	0.63
5.138	6.09	5.48	3.52	2.66	4.10	1.80
8.563	8.55	6.97	4.76	3.78	6.87	3.04
11.988	10.95	9.68	5.82	4.96	10.20	4.27
15.413	12.71	10.80	6.72	5.76	13.40	5.64
17.126	13.14	11.17	7.10	6.40	15.70	6.23

* ε_k values from reference 1.
** $\varepsilon_k = 715\ \mathrm{m^2\ mol^{-1}}$ (400 nm)
*** $\varepsilon_k = 818\ \mathrm{m^2\ mol^{-1}}$ (405 nm)

The equilibrium constant according to Equation (1) for compound III was also determined in eight pure solvents; the resulting data, together with the parameters E_T^N and B_{KT} [6,8], are to be seen in Table 6.

Use of these tabulated data to solve Equations (2)-(4) furnishes the correlation coefficients $r_1 = 0.962$, $r_2 = 0.855$ and $r_3 = 0.981$, with the beta values $\beta_{\mathrm{acid}} = 71.8\%$ and $\beta_{\mathrm{basic}} = 28.2\%$.

TABLE 2

Variation in the values of ε_{430} for compound IV and ε_{416} for compound V as a function of the ethanol concentration in ethanol-n-hexane, ethanol-benzene and ethanol-acetone solvent mixtures at 25 °C

$[\text{ethanol}]\,\frac{\text{dm}^3}{\text{mol}}$	$\frac{\varepsilon\cdot\text{mol}}{\text{m}^2}\cdot 10$					
	ethanol-hexane		ethanol-benzene		ethanol-acetone	
	IV	V	IV	V	IV	V
0	10.2	2.0	14.0	1.7	28.0	2.7
1.713	38.2	10.0	42.0	7.5	44.0	4.0
5.138	80.5	22.0	83.5	21.0	59.0	9.5
8.563	118.2	35.0	118.5	33.7	78.0	17.5
11.988	150.5	48.0	146.0	46.5	109.5	29.5
15.413	170.0	61.0	172.0	59.8	154.0	48.7
17.126	185.0	67.0	185.0	67.0	185.0	67.0

The data in Tables 4-6 reveal that the values of r_1 and r_2 for Equation (2) and particularly Equation (3) are rather poor (with the exception of the ethanol-benzene mixture), whereas a good correlation (r_3) is obtained with the multiparameter Equation (4) for every compound in all the solvent mixtures and in the pure solvents too (Table 6). This is a strong indication that both the acidity and the basicity of the solvent play a role in the formation of the keto form. This explains why the solvent effect is substantially higher in alcohols than in other solvents, because the alcohol molecules can participate in the process both as proton donors and as proton acceptors (in

TABLE 3

Values of E_T^N and B_{KT} for the solvent mixtures ethanol-n-hexane, ethanol-benzene and ethanol-acetone at 25 °C

[ethanol] dm^3 mol	ethanol-hexane		ethanol-benzene		ethanol-acetone	
	E_T^N	B_{KT}	E_T^N	B_{KT}	E_T^N	B_{KT}
0	0.074*	0 **	0.127*	0.08	0.355*	0.54
1.713	0.527	0.86	0.428	0.34	0.537	0.55
5.138	0.565	0.93	0.501	0.56	0.610	0.58
8.563	0.587	0.86	0.548	0.64	0.634	0.61
11.988	0.603	0.82	0.584	0.70	0.643	0.65
15.413	0.632	0.76	0.633	0.77	0.647	0.70
17.126	0.651	0.75	0.655	0.78	0.650	0.77

* from reference 6.

** from reference 8.

TABLE 4

Correlation coefficients (r_1, r_2 and r_3) obtained by solution of Equations (2)-(4), and the percentage distributions of the effects of acidity and basicity for compounds I-III in ethanol-n-hexane at 25 °C

Compound	r_1	r_2	r_3	β_{acid} %	β_{basic} %
I/a	0.940	0.773	0.977	69.2	30.8
I/b	0.936	0.769	0.973	69.1	30.9
I/c	0.928	0.754	0.971	68.1	31.9
I/d	0.916	0.726	0.974	66.2	33.8
II	0.966	0.813	0.986	73.6	26.4
III	0.928	0.739	0.977	67.8	32.2

TABLE 5

Correlation coefficients (r_1, r_2 and r_3) obtained by solution of Equations (2)-(4) (utilizing log ε), and the percentage distributions of the effects of acidity and basicity for compounds IV and V in various solvent mixtures at 25 °C

Solvent	Compound	r_1	r_2	r_3	β_{acid} %	β_{basic} %
ethanol-n-hexane	IV	0.938	0.770	0.976	69.0	31.0
	V	0.938	0.761	0.982	68.0	32.0
ethanol-benzene	IV	0.986	0.998	0.999	22.5	77.5
	V	0.983	0.999	0.999	14.3	85.7
ethanol-acetone	IV	0.833	0.958	0.990	31.8	68.2
	V	0.838	0.949	0.985	33.8	66.2

TABLE 6

Enol $\rightleftharpoons$ keto equilibrium constants of compound III in various solvents at 25 °C, determined as in Equation (1)

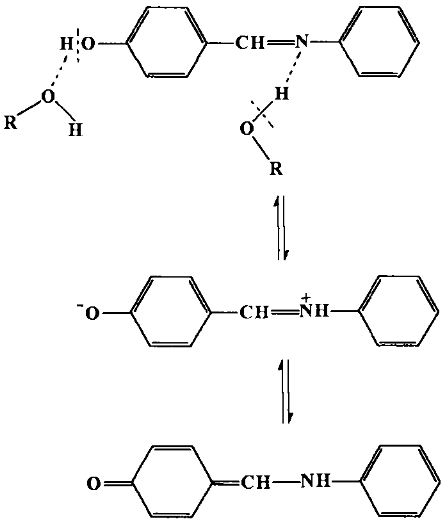
Solvent	$K\cdot10^3$	E_T^N *	B_{KT} **
n-hexane	0.4	0.074	0
benzene	1.8	0.127	0.08
acetone	4.5	0.355	0.54
tert.-butanol	26.6	0.407	0.95
sec.-butanol	38.0	0.506	0.90
n-butanol	53.0	0.602	0.85
ethanol	62.3	0.655	0.77
methanol	129.0	0.765	0.62

* from reference 6.

** from reference 8.

aqueous solution, there is even more extensive formation of the quinone form). However, a comparison of the data (especially those in Table 6) demonstrates that the acidity exerts a stronger effect than that of the basicity. The equilibrium constant may be seen to increase in parallel with E_T^N, in spite of the fact that the value of B_{KT} varies in the opposite direction in the series of alcohols.

On the basis of the results obtained, the interaction of the solvent and the Schiff base molecules conceivably proceeds as in the following process:



Scheme 2

For the *o*-hydroxy derivatives, of course, an additional role in the process is played by intramolecular hydrogen-bonding.

In contrast with the formation of the keto form, the possibility of formation of a zwitterionic structure has been proposed by a number of authors in their interpretations of the solvent effect[17,18], but this possibility has not been confirmed unambiguously. We consider that the two types of interpretation according to the above process do not exclude, but rather presuppose one another: the molecules pass from the enol form to the quinone form via a zwitterionic structure.

As concerns the positions of the above equilibria, it must also be taken into account that formation of the quinoid structure is inhibited by the conjugation of the Schiff base molecule. This too may play a part in the fact that the solvent effect is much smaller for compound IV, for example, than for compound II. The difference in stability of the naphthalene and benzene rings explains why, under otherwise identical conditions, much more of the quinone form is present in a solution of compound I than in solutions of compounds IV or V.

It should be added that the position of the enol $\rightleftharpoons$ keto equilibrium in the above solvent mixtures may be correlated directly with the activity coefficient of ethanol.

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