

EXAMINATIONS ON THE SOLVENT EFFECT OF ULTRAVIOLET ABSORPTION SPECTRA OF AROMATIC AZOMETHINES CONTAINING OH—GROUP

By J. HÍRES and L. HACKL

Institute for General and Physical Chemistry, The University, Szeged

To Professor Dr. Árpád Kiss on his 70th birthday

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In ultraviolet absorption spectrum of the aromatic azomethin derivatives containing OH-group in ortho- or para position on the aldehyde-ring, in ethanol, a band of low intensity appears between 400—450 m μ [1], [2]. In a previous paper we pointed out that this band can not be observed in solvents, the molecules of which contain no free electrons [3]. The aim of the present work was to investigate: what an effect the different solvents as well as the mixture of hexane-ethanol have on the absorption spectrum and to what an extent does it influence the intensity of the band appearing between 400—450 m μ .

In an earlier publication the absorption spectrum of N, N'-bis(salicylidene)ethylenediamine, N-salicylideneaniline and of N-salicylidenebenzylamine was determined in ethanol and hexane. It was stated that the band, observable in ethanol between 400—450 m μ ; does not appear in hexane in the absorption spectrum of these compounds. The intensity of this band was determined in such solvent mixture of hexane-ethanol wherein the concentration of ethanol changed. On the basis of the absorption curves the conclusion was drawn that an intermolecular hydrogen bonded complex is formed between the Schiff-basis present in solution and the molecules of the solvent. This assumption was based on, that the intensity of the band between 400—450 m μ increased if the concentration of the ethanol in the hexane-ethanol solvent mixture was increased. According to the data in the literature several authors proved that hydrogen bonded complex may be formed in a solvent if the solved molecule and the molecules of the solvent contain free electrons [4]—[7]. In their opinion an equilibrium is developed in the solution. The equilibrium constant can be calculated if the optical density is determined in the mixture of solvent containing also molecules with free electrons in different concentrations.

The concentration of ethanol in the solvents employed in the mixture of hexane-ethanol was higher than those used by earlier investigators. In our experiments the ethanol identical with the quantity of the solved Schiff-basis or its hundredfold quantity, produced no perceptible change of intensity.

Discussion

The spectra were examined in a mixture of hexane-ethanol wherein the concentration of the ethanol was increased as follows: 2M, 4M, 6M, 8M, 10M, 12M and 17,2M (pure ethanol). The spectra were determined also in methanol, propanol, buthanol, dioxane and ethyl ether. Absorption spectra determined in the solvent mixture are shown in Figs. 1, 2, 3 and 4.

The increase of the intensity of the band between 400—450 m μ could be observed as the concentration of the ethanol was increased in the mixture of the solvent. In pure ethanol the intensity of the band reached a limit value, and the value of the molar extinction coefficient did not change even if the quantity of the measured Schiff-basis was in- or decreased.

Table 1

	Compounds	λ m μ	Conc. of ethanol in hexane-ethanol solvent							
			2 M	4 M	6 M	8 M	10 M	12 M	17,2 M	
1.	N-salicylidenebenzylamine	410	log ϵ	1,70	2,05	2,24	2,36	2,47	2,56	2,67
			ϵ	50,6	110,7	171,8	229,1	295,2	363,1	467,8
2.	N, N'-bis (salicylidene)-ethylene-diamine	408	log ϵ	2,34	2,54	2,66	2,75	2,82	2,86	2,96
			ϵ	221,3	351,6	457,1	566,2	654,6	729,5	924,7
3.	N-salicylidene-p-toluidine	436	log ϵ	1,56	1,84	1,95	2,09	2,14	2,22	2,32
			ϵ	36,3	69,3	89,5	121,6	140,3	168	198,6
4.	N-salicylidene-i. propylamine	404	log ϵ	1,63	1,94	2,15	2,25	2,36	2,43	2,55
			ϵ	42,8	87,1	141,3	176,2	228,2	269,2	353,2

The values of the molar extinction coefficient determined in the mixture of the solvents are shown in Table 1. If the log ϵ values referring to the different concentrations of the ethanol, are compared with the logarithm of the concentration of the ethanol, a linear correlation can be noted (Fig. 5). On the basis of the figure the following correlation can be stated:

$$\log \epsilon = \log a + n \log [C_2H_5OH], \quad (1)$$

$$\epsilon = a[C_2H_5OH]^n. \quad (2)$$

In this formula the log ϵ is the molar extinction coefficient determined in the mixture of the solvent, $[C_2H_5OH]$ the concentration of the ethanol, a and n are constants depending upon the solved substance and the solvent. The slope of the plot n , and a a part of the log ϵ axis can be determined (Table 1 and Fig. 5).

This proportional change in the band intensity depending on the ethanol concentration shows that in this case a process takes place in which the

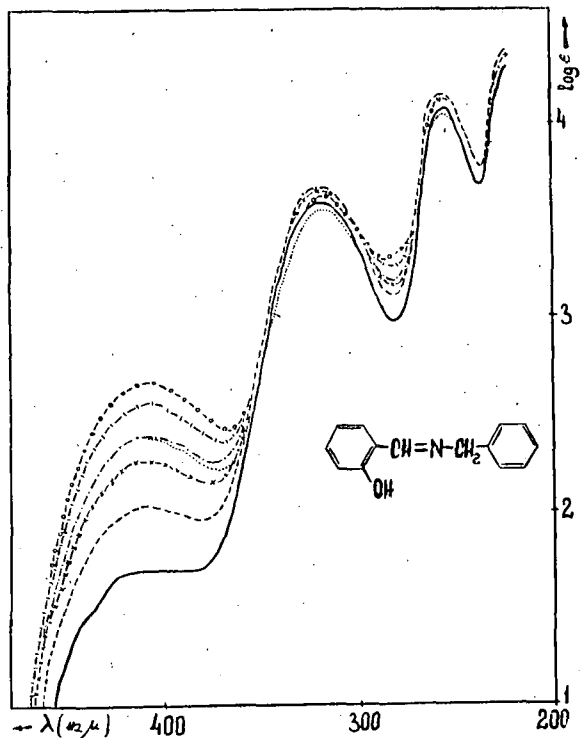


Fig. 1. The absorption spectrum of N-salicylidenebenzylamine in hexane-ethanol solvent mixture. Concentration of ethanol top to bottom: pure ethanol, 12 M, 10 M, 8 M, 6 M, 4 M, and 2 M.

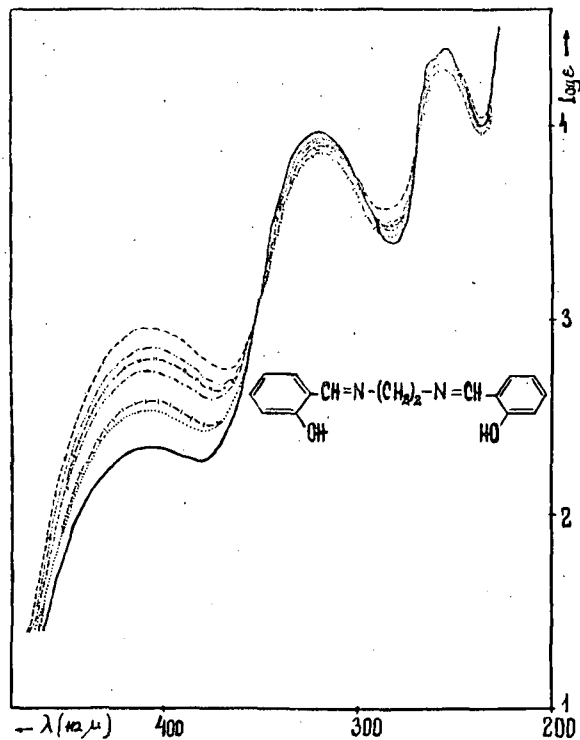


Fig. 2. The absorption spectrum of N,N'-bis(salicylidene)ethylenediamine in hexane-ethanol solvent mixture. Concentration of ethanol top to bottom: pure ethanol, 12 M, 10 M, 8 M, 6 M, 4 M, and 2 M.

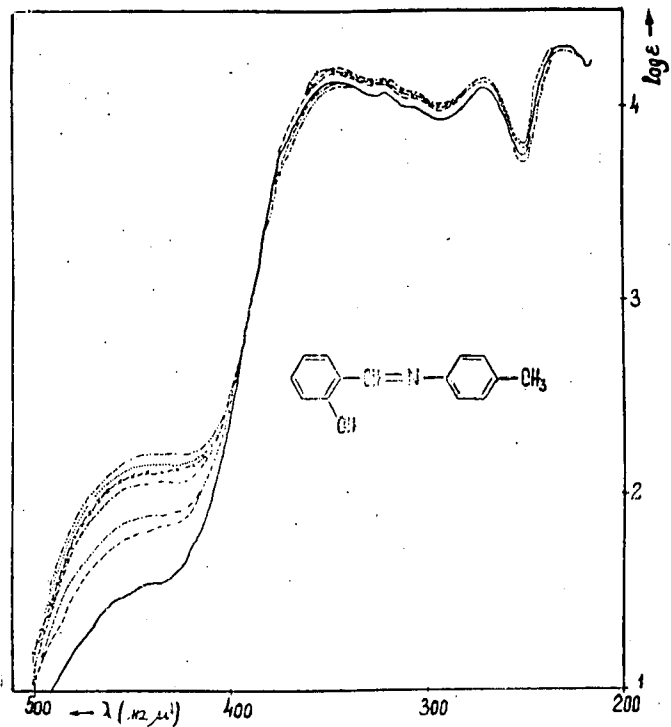


Fig. 3. The absorption spectrum of N-salicylidene-p-toluidine in hexane-ethanol solvent mixture. Concentration of ethanol top to bottom: pure ethanol, 12 M, 10 M, 8 M, 6 M, 4 M, and 2 M.

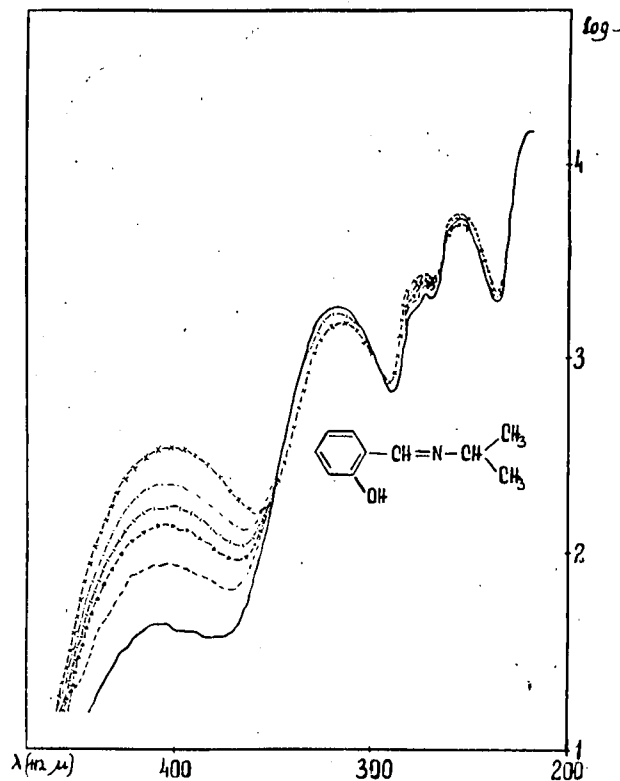


Fig. 4. The absorption spectrum of N-salicylidene-i-propylamine in hexane-ethanol solvent mixture. Concentration of ethanol top to bottom: pure ethanol, 12 M, 10 M, 8 M, 6 M, 4 M, and 2 M.

quantity of ethanol is significant. It is also probable that an equilibrium system develops since the absorption curves have almost identical points of intersection. In the case of determinations of absorption spectra the initial concentration of Schiff-bases was always the same. If the extinction determined in the solvent mixture is proportional to the concentration of associate produced then the equations 1 and 2 are similar to the adsorption isotherm. Therefore it is probable that in the solvent mixture hydrogen bonding associate is produced between the Schiff-base solved and the molecules of the solvent, in which the number of ethanol molecules changes depending on the ethanol

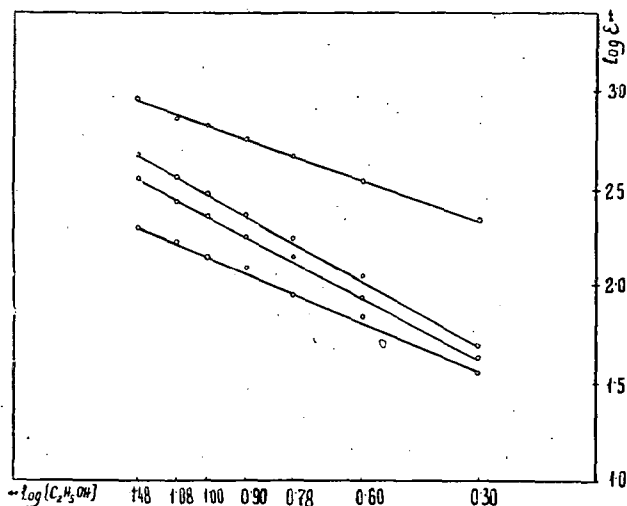
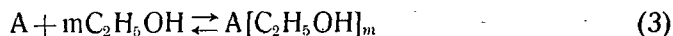


Fig. 5

concentration of the solvent mixture. The given equilibrium state can be reached in such manner too if the Schiff-base is dissolved first in ethanol and after this an appropriate quantity of hexane is added. By changing the quantity of ethanol in the solvent mixture the equilibrium optionally pushed.

At different ethanol concentration of the solvent mixture calculations were made in connection with the equilibrium constants. Considering the conditions and relations given by BABA and NAGAKURA [4], [6] the values of equilibrium constants are increasing, probably because at the formation of the associate one molecule Schiff-base reacts with m ethanol molecule.

In a given interval of the ethanol concentration of the solvent mixture (0,5M—6,0M) well agreeing equilibrium constants were gained on the base of the following considerations:



$$K = \frac{A[C_2H_5OH]_m}{[A][C_2H_5OH]^m} \quad (4)$$

If a is the initial concentration of the Schiff-base in the solvent mixture, C_{12} is the equilibrium concentration of the associate produced, b is the concentration of ethanol and supposed that $C_{12} \ll b$, then:

$$K = \frac{C_{12}}{(a - C_{12})b^m} \quad (5)$$

$$C_{12} = \frac{Kab^m}{1 + Kb^m} \quad (6)$$

Since the band intensity between 400–450 $m\mu$ in hexane is zero:

$$C_{12} = \frac{a\varepsilon}{\varepsilon_{12}} \quad (7)$$

In equation (7) ε and ε_{12} respectively are the molar extinction coefficients determined in the solvent mixture and in pure ethanol. On the base of (6) and (7) the value of K can be calculated:

$$K = \frac{\varepsilon}{(\varepsilon_{12} - \varepsilon)b^m} \quad (8)$$

Table 2

Conc. of EtOH	C_{12}	$a - C_{12}$	$\frac{C_{12}}{a - C_{12}}$	K
N-salicylidenebenzylamine				$m = 1,500$
2 molar	10,56	89,44	0,118	$4,44 \cdot 10^{-2}$
4 "	23,66	76,34	0,310	$4,16 \cdot 10^{-2}$
6 "	36,72	63,28	0,580	$4,48 \cdot 10^{-2}$
N, N'-bis (salicylidene)ethylenediamine				$m = 1,164$
2 molar	23,93	76,07	0,315	$1,40 \cdot 10^{-1}$
4 "	38,02	61,98	0,613	$1,22 \cdot 10^{-1}$
6 "	49,43	50,57	0,977	$1,21 \cdot 10^{-1}$
N-salicylidene-p-toluidine				$m = 1,120$
2 molar	18,27	81,73	0,224	$1,03 \cdot 10^{-1}$
4 "	34,89	65,11	0,536	$1,13 \cdot 10^{-1}$
6 "	45,06	54,94	0,820	$1,10 \cdot 10^{-1}$
N-salicylidene-i-propylamine				$m = 1,426$
2 molar	12,11	87,89	0,138	$5,13 \cdot 10^{-2}$
4 "	24,66	75,34	0,327	$4,53 \cdot 10^{-2}$
6 "	40,00	60,00	0,666	$3,19 \cdot 10^{-2}$
8 "	49,88	50,12	0,995	$5,13 \cdot 10^{-2}$

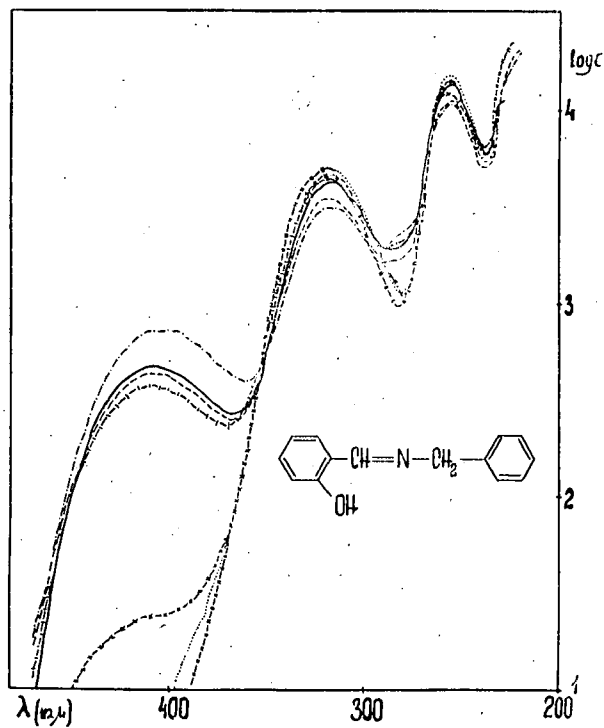


Fig. 6. The absorption spectrum of N-salicylidenebenzylamine in various solvents. The solvents top to bottom: methanol, ethanol, propanol, butanol, dioxane, ethyl ether and hexane.

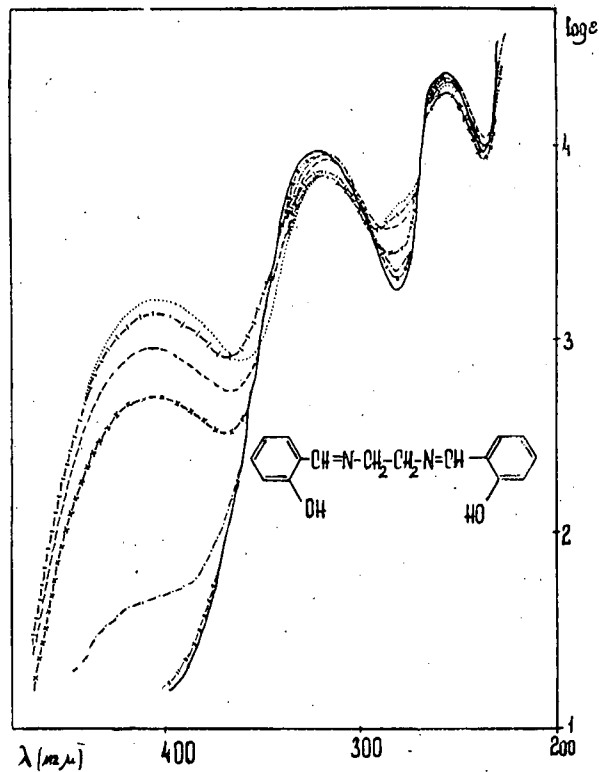


Fig. 7. The absorption spectrum of N,N'-bis(salicylidene)ethylenediamine in various solvents. The solvents top to bottom: methanol, ethanol, propanol, butanol, dioxane, ethyl ether and hexane.

The value of m in the equations was determined by plotting the logarithm of ethanol concentration of the solvent mixture against logarithm of concentration ratio of the associated (C_{12}) and free ($a-C_{12}$) Schiff-base molecules. A linear correlation was observed between 0,5M—6,0M ethanol concentration. The slope of the plot gives the values of m .

The values of constants calculated on the base of equation (8) are shown in Table 2.

Table 3

	Solvent	D	Fig. 6.	Fig. 7.
			log ϵ 410 m μ	log ϵ 408 m μ
1.	Methanol	31,2	2,86	3,21
2.	Ethanol	25,8	2,67	2,96
3.	Propanol	22,2	2,63	2,92
4.	Butanol	19,2	2,58	2,72
5.	Dioxane	3,0	1,37	1,67
6.	Ethyl Ether	4,4	—	—
7.	Hexane	2,0	—	—

The absorption spectra of the compounds were determined in methanol, propanol, butanol, dioxane and ethyl ether. On the base of the absorption spectra it is proved that, the change of the dielectric constant of the medium exerts a strong influence on the intensity of the 400—450 m μ band (Figs. 6, 7). The value of intensity of the band is relatively greatest in methanol — according to the medium having the greatest dielectric constant — the intensity is gradually decreased with decreasing of the dielectric constant of the solvent. On the base of data given in Table 3 established that the logarithm of extinction changed linearly with the dielectric constant.

Experimental

The absorption spectra have been determined by Beckman DU spectrophotometer using cell-thickness $d=1$ cm and $d=0,1$ cm. The solvents were purified and dried by the usual methods.

N-salicylidenebenzylamine: Molar quantity of salicylaldehyde and benzylamine was mixed without solvent. On cooling the mixture yellowish-green crystals were precipitated. Crystallized from ethanol m. p.: 30—31°.

N,N'-bis(salicylidene)ethylenediamine: 2 mols salicylaldehyde and 1 mol ethylenediamine were mixed in ethanol. Shortly greenish-yellow crystals were precipitated. Crystallized from ethanol m. p.: 124,5°.

N-salicylidene-p-toluidine: Easily obtained from salicylaldehyde and p-toluidine in ethanol. Crystallized from ethanol m. p.: 99,5°.

N-salicylidene-i.propylamine: A mol quantity of i.propylamine is added to one mol salicylaldehyde on cooling. The water from the reaction mixture was removed with Na_2CO_3 . After drying in vacuum it was distilled. b. p.: $80^\circ/1-2$ mm.

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