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Electronic absorption spectroscopic studies of enolimine-ketoamine equilibria in Schiff bases

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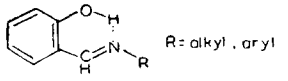
Abstract. The enolimine-ketoamine equilibria in a variety of alkyl and arylsalicylaldimines have been studied in 1,2-dichloroethane, methanol, ethanol, *iso*-propanol and *t*-butanol by electronic absorption spectroscopy. The equilibrium depends on the nature of the alcohol and the strength of hydrogen bond formed with the ketoamine. In arylsalicylaldimines, the equilibrium is sensitive to the nature of the substituents.

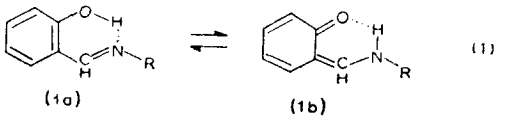
Keywords. Schiff base equilibria; electronic absorption spectra.

1. Introduction

The Schiff bases derived from the condensation of salicylaldehyde with alkyl and arylamines, known as *N*-alkyl or arylsalicylaldimines, are considered as suitable models for pyridoxal and, in general, B_6 vitamins. The salicylaldimines are planar intramolecularly hydrogen bonded structures. Proton tautomerism can occur in such structures leading to an equilibrium between the neutral intramolecularly



hydrogen bonded form (enolimine tautomer, Ia) and the proton transferred



(ketoamine tautomer, Ib) structure. Evidence in favour of such a tautomerism in selected solvents has been shown by electronic absorption (Ledbetter 1966), infrared (Ledbetter 1977) and NMR (Dudek and Dudek 1966) spectroscopy. The effect of solvents on the electronic absorption spectra of Schiff bases has received

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considerable attention in recent years. Alexander and Sleet (1970) have examined the ultraviolet absorption spectra of monosalicylaldimines of ethylamine, ethanolamine and *n*-butylamine in various solvents like water, absolute ethanol, dioxan and cyclohexane. In cyclohexane, two maxima around 255 and 320 nm were observed. In ethanol, in addition to these, new bands at ~280 and ~400 nm were noticed. A comparison with the spectra of N-methylamines of *m*- and *p*-hydroxy benzaldehydes in the same solvents has shown that *o*- and *p*-hydroxybenzylideneimines exist mainly as dipolar ketoamines in polar, hydrogen bonding solvents and *m*-isomers exist mainly as the enolimine tautomeric form in all the solvents. The former set of bands in cyclohexane have been assigned to enolimine tautomer and the latter to the ketoamine tautomer of Schiff bases. Polar hydrogen bond forming solvents thus seem to favour the formation of ketoamine form. Charette *et al* (1964) have also examined a series of N-alkyl Schiff bases by ultraviolet absorption spectroscopy in different solvents. The changes in the spectra when inert solvents are replaced by hydrogen bond forming solvents have been interpreted in terms of solvation equilibria. The interaction of enolimine with a hydrogen bond forming solvent (alcohol) would presumably reduce the O-H bond strength and facilitates proton transfer to the nitrogen centre. Seliskar (1977) has demonstrated that the ratio of enolimine to ketoamine forms of N-ethylsalicylaldimine varies roughly linearly with the number of aliphatic carbon atoms of a series of straight chain alcohols used as solvents ; obviously, this is related to the proton donating ability of alcohols.

Thus, the data so far reported in the literature presents only a qualitative picture of the nature of Schiff bases in various solvents. No attempt has so far been made to obtain thermodynamic data for the equilibrium (1). It would be interesting to determine the specific role of an alcohol in determining the relative amounts of tautomers in the equilibrium. More interesting would be to determine the amount of ketoamine as a function of the concentration of alcohol in a ternary system. The influence of the structure of alcohol could easily be rationalized from such a study. In this paper, we report our results on the electronic absorption spectra of the following Schiff bases in 1,2-dichloroethane, methanol, ethanol, *iso*-propanol and *t*-butanol.

(i) N-Salicylideneethylamine (SE) ; R = C_2H_5
(ii) N-Salicylidene *n*-butylamine (SB) ; R = n-C_4H_9
(iii) N-Salicylideneaniline (SA) ; R = C_6H_5-
(iv) N-Salicylidene *p*-toluidine (SPT) ; R = CH_3 C_6H_5-
(v) N-Salicylidene *p*-nitroaniline (SPNA) ; R = NO_2 C_6H_4-
(vi) *Bis* (N-Salicylidene)-1,2-diaminoethane (BSE) ; R = CH_2 CH_2 NH_2

2. Experimental

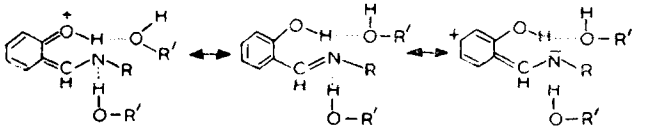
All the Schiff bases were prepared by methods described in the literature (Alexander and Sleet 1970 ; Selisker 1977 ; Decoene and Teyssie 1962). SE was prepared by refluxing equimolar amounts of salicylaldehyde and anhydrous ethylamine in methanol for two hours. After evaporating the residual ethylamine and methanol, the yellow liquid product was dried over anhydrous sodium sulphate and vacuum

distilled (B.P. 87–88° C/5 mm). SB was prepared by condensing equimolar amounts of salicylaldehyde and *n*-butylamine in dry methanol at room temperature. Excess methanol was removed by vacuum evaporation and water by treatment with anhydrous sodium sulphate. The residue was fractionally distilled (B.P. 140° C/1 mm). SA was prepared by refluxing equimolar amounts of salicylaldehyde and aniline in dry methanol for about 1½ h. The solid SA was filtered and recrystallized twice from methanol (M.P. 47° C). SPT and SPNA were prepared in a manner similar to that of SA and the solids recrystallized from methanol (M.P. 98° C and 152° C respectively). BSE was prepared by the condensation of salicylaldehyde (0·2 mol) with ethylenediamine (0·1 mol). A yellow solid separated out and was recrystallized from methanol (M.P. 123° C).

All the solvents were purified by standard methods (Riddick and Burger 1970). Electronic absorption spectra were recorded by a Pye-Unicam SP700 spectrophotometer fitted with a SP770 constant temperature cell holder and SP 775 electrical controller. The equilibrium constants (K) were evaluated by the method of Baba and Suzuki (1961). The enthalpies ($\triangle H°$) were obtained by determining K at two or more temperatures.

3. Results and discussion

The electronic absorption spectrum of SB in 1,2-dichloroethane and methanol are shown in figure 1 (a). The spectra in 1,2-dichloroethane show intense bands at 256 and 314 nm. Following Seliskar (1977) the 256 and 314 nm bands may be assigned to $3\,'A' \leftarrow 1\,'A'$ and $2\,'A' \leftarrow 1\,'A'$ transitions ($\pi \rightarrow \pi^*$) respectively. The 256 nm band undergoes a small blue shift and the 314 nm band either remains the same or undergoes a small red shift in methanol. The intensity, however, increases appreciably. On the other hand, the 254 and 325 nm bands in arylsalicylaldimines undergo large red shifts in alcohols. This is probably due to the weak intramolecular hydrogen bond present in arylsalicylaldimines. On solvation, the red shift can be attributed to the major contributions of polar



(II a) (II) (R = aryl) (II b)

structures (IIa and IIb) to the excited state. These structures are stabilized by solvent polarity, resulting in a red shift of the bands. The progressive addition of methanol in the concentration range 1·72–7·35 mol. dm^{-3} to a dichloroethane solution of SB has an interesting effect. While in 1,2-dichloroethane, SB has no absorption at $\sim$ 400 nm, the progressive addition of methanol causes a band to appear in the 400 nm region, whose intensity increases with increase in the concentration of methanol. At high methanol concentrations, noticeable but smaller shifts of the $\sim$ 400 nm band to lower wavelengths has been observed. Similar changes occur in the spectra of arylsalicylaldimines in presence of various alcohols. Following Ledbetter (1966) and Alexander and Sleet (1970), the $\sim$ 400 nm band

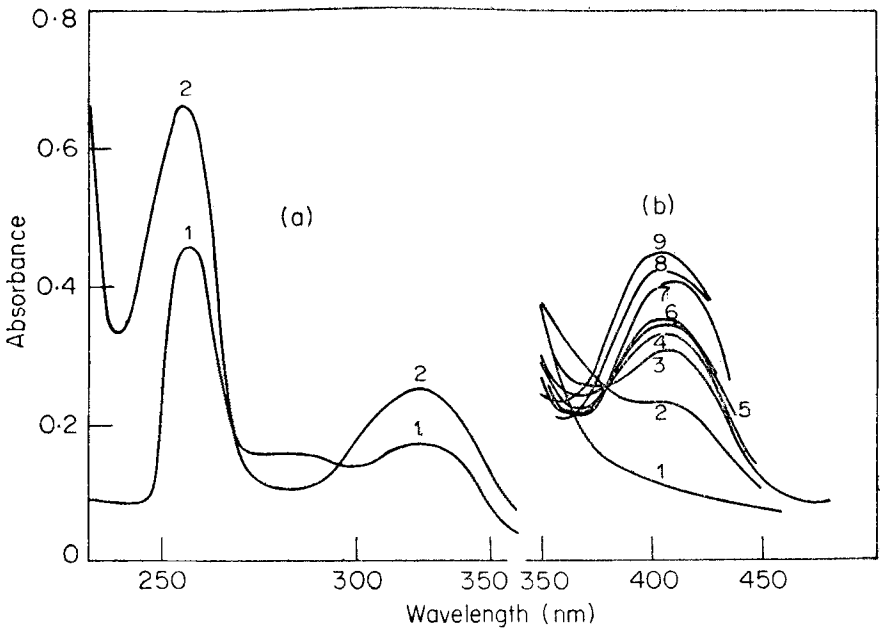


Figure 1. (a) The electronic absorption spectrum of N-salicylidene-*n*-butylamine (SB) in, 1 ; 1,2-dichloroethane and 2 ; methanol. (b) Effect of methanol on the electronic absorption spectra of SB in 1,2-dichloroethane in the 350–450 nm range 1 ; $1{\cdot}90 \times 10^{-4}$ mol dm^{-3} of SB ; 2 to 9 correspond to $1{\cdot}90 \times 10^{-4}$ mol dm^{-3} of SB in 1,2-dichloroethane plus 1·69, 3·0, 3·7, 4·2, 4·5, 5·9, 6·6 and 7·35 mol dm^{-3} of methanol.

was assigned to the ketoamine form. The formation of the ketoamine is probably due to solvation and resonance stabilization. The formation of (Ib) requires the loss of a large amount of resonance energy (Dudek 1963), which is only possible if the ground state is stabilized by extensive contribution of polar reso-

nance structures, such as (Ic). The structure (Ic) gets stabilized in polar solvents thereby increasing the concentration of the ketoamine tautomer. The dependence of ketoamine formation on the concentration of alcohol and the presence of isobestic points around 380 nm indicates that there is a definite equilibrium between enolimine and ketoamine forms and that alcohol molecules are involved in this equilibrium as in

$$\text{Enolimine} + \text{R OH} \rightleftharpoons \text{ketoamine}. \qquad (2)$$

The 400 nm band was not, however, observed in acetonitrile. This clearly means that a polar hydrogen bonding solvent is necessarily involved in this equilibrium process. The spectral band positions are shown in table 1. The variation in intensity of the 400 nm band with the concentration of alcohols in 1,2-dichloro-

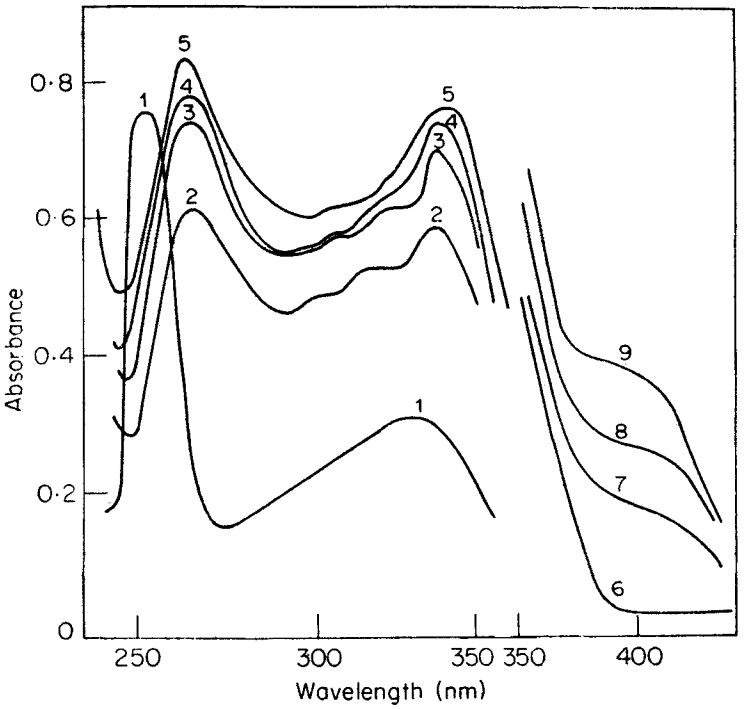


Figure 2. The electronic absorption spectrum of N-salicylidene-aniline (SA, 7·36 $\times 10^{-5}$ mol cm^{-3}) in 1 ; 1,2-dichloroethane, 2 ; cyclohexane, 3 ; *t*-butanol, 4 ; ethanol and 5 ; methanol. 6–9 correspond to 1·47 $\times 10^{-3}$ mol dm^{-3} of SA in 1,2 dichloroethane, *t*-butanol, ethanol and methanol respectively.

Table 1. Electronic absorption spectral data of Schiff bases.

Schiff base	Absorption maxima (nm) in			
	1,2-Dichloro-ethane	Methanol	Ethanol	*t*-Butanol
SE	256	254	254	255
	315	315	315	315
	..	402	403	405
SB	256	254	254	255
	314	316	316	315
	..	400	401	402
SA	254	270	270	270
	325	338	337	335
	..	430	435	437
SPT	267	270	..	270
	335	335	..	335
	..	428	..	437
SPNA	268	270 (Sh)	..	270 (Sh)
	335	355	..	358
	..	442 (VW)	..	445 (VW)

Sh : Shoulder VW : Very weak

Table 2. Thermodynamic data of enolimine-ketoamine equilibria of Schiff bases in various alcohols.

Sl. No.	Schiff base	Solvent	K $dm^3\ mol^{-1}$	$-\Delta H^\circ$ $kJ\ mol^{-1}$
1	SE	Methanol	0·247	21·8
		Ethanol	0·217	21·4
		t-butanol	0·165	17·9
2	SB	Methanol	0·36	27·7
		t-butanol	0·195	18·1
3	SA	Methanol	0·124	18·4
		t-butanol	0·067	13·4
4	SPT	Methanol	0·152	20·1
		Ethanol	0·132	19·4
		t-butanol	0·074	15·0
5	SPNA	Methanol	0·067	12·6
		Ethanol	0·060	11·7
6	BSE	Methanol	0·184	33·4
		iso-propanol	0·154	29·3
		t-butanol	0·103	21·3

ethane has been quantitatively treated and equilibrium data obtained as shown in table 2. A typical plot for the calculation of equilibrium constant is shown in figure 3. It is interesting to examine the effect of varying R in R **OH** on the equilibrium (2). For **SB**, while the equilibrium constant and enthalpy with methanol are 0·36 $dm^3\ mol^{-1}$ and 27·7 $kJ\ mol^{-1}$ respectively, they are 0·195 $dm^3\ mol^{-1}$ and 18·1 $kJ\ mol^{-1}$ respectively with *t*-butanol. For Schiff bases under investigation, the equilibrium constants and enthalpies vary in the order : methanol > ethanol > *iso*-propanol > *t*-butanol. Methanol is a better proton donor than *t*-butanol (Murthy and Rao 1968 ; Joesten and Schaad 1974) and so one would expect the former to favour the ketoamine than the latter. With methanol, the equilibrium constants and enthalpies for Schiff bases **SB** and SE vary in the order **SB** > SE. This trend is consistent with the fact that the nitrogen atom becomes more basic when R = n-C_4H_9 than when R = C_2H_5. Interesting substituent effects can be seen in the spectral and equilibrium data of arylamine Schiff basis. In the spectra of *para*-sustituted arylsalicylaldimines in various alcohols (figure 4), the 400 nm band is more intense in **SPT** and less intense in SPNA than SA ; in *t*-butanol, the 400 nm band in SPNA could hardly be seen. In SA, **SPT** and SPNA where the substituents in the *para* position of aniline ring are **H**, CH_3 and NO_2 respectively, the equilibrium constants and enthalpies with any alcohol are in the order SPT > SA > SPNA. Thus, while the electron donating CH_3 group

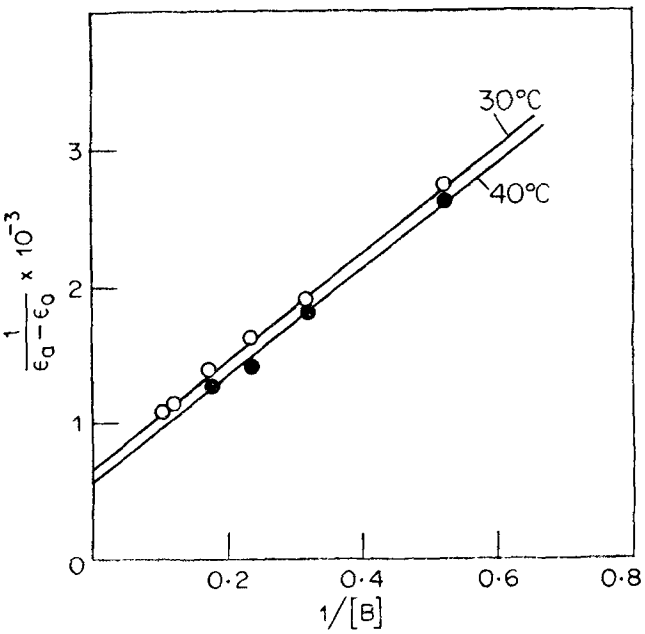


Figure 3. Typical plot on the calculation of equilibrium constant for the N-salicylideneethylamine-methanol system in 1,2-dichloroethane.

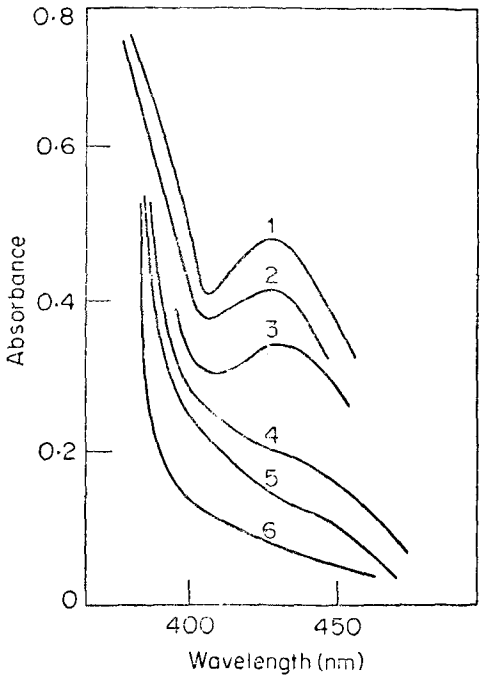


Figure 4. The electronic absorption spectra of *para*-substituted arylsalicylaldimines in different alcohols. Spectral curves 1–3 correspond to N-salicylidene *p*-toluidine in methanol, ehthanol and *t*-butanol and curves 4–6 correspond to that of N-salicylidene *p*-nitroaniline in methanol, ethanol and *t*-butanol respectively.

favours ketoamine form, the electron withdrawing NO_2 group does not. In case of BSE, although the equilibrium constants are not larger than the remaining Schiff bases, the enthalpies of tautomerism are largest. This is probably due to the fact that two enolimine moieties per mole of BSE are involved in the equilibrium.

The results obtained in this study indicate that alcohol molecules break the intramolecular hydrogen bond and weaken the O-H bond of enolimine thereby facilitating proton transfer to the nitrogen atom. At the same time alcohol molecules also form hydrogen bond with the oxygen atom of the ketoamine form, thereby shifting the equilibrium to the right. Methanol forms a stronger hydrogen bond than *t*-butanol and hence the formation of ketoamine is more favourable in the former solvent than in the latter. The differing strength of hydrogen bonds also explains why the characteristic band of ketoamine occurs at a longer wavelength in *t*-butanol than in methanol (table 1). Thus, hydrogen bonding plays a major role in determining the relative amounts of enolimine and ketoamine forms in the Schiff base equilibria in alcohol solvents. Similar conclusions have been arrived at in the keto-enol equilibria in other systems (Murthy *et al* 1962).

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References

Alexander P W and Sleet R J 1970 *Aust. J. Chem.* **23** 1183
Baba H and Suzuki S 1961 *J. Chem. Phys.* **35** 1118
Charette J J, Falthanal G and Teyssie P 1964 *Spectrochim. Acta* **20** 597
Decoenne C and Teys ie P 1962 *J. Polym. Sci.* **57** 121
Dudek G O 1963 *J. Am. Chem. Soc.* **85** 695
Dudek G O and Dudek E P 1966 *J. Am. Chem. Soc.* **88** 2407
Joesten M D and Schaaq L J 1974 *Hydrogen bonding* (New York : Marcel Dekker)
Ledbetter J W 1966 *J. Phys. Chem.* **70** 2245
Ledbetter J W 1977 *J. Phys. Chem.* **81** 54
Murthy A S N and Rao C N R 1968 *Appl. Spectry. Revs.* **2** 69
Murthy A S N, Balasubramanian A, Kasturi T R and Rao C N R 1962 *Can. J. Chem.* **40** 2267
Riddick J A and Burger W B 1970 *Technique of chemistry. Organic solvents* (New York : Wiley, Interscience) Vol. 2
Seliskar C J 1977 *J. Phys. Chem.* **81** 1331