SCHIFF BASE EQUILIBRIA

VII.* FORMATION AND DISTRIBUTION OF N-(β-HYDROXYETHYL)SALICYLIDENEIMINE

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Summary

The formation constant and pK of the Schiff base N-(β-hydroxyethyl)salicylideneimine in aqueous solution at 25° have been determined spectrophotometrically to be $5 \cdot 01 \times 10^3$ and $11 \cdot 4$ respectively. These equilibrium constants have been used to account for the distribution of the imine between water and chloroform.

INTRODUCTION

It has already been shown[1] that the length of the alkyl chain has little influence on the formation constants of the N-alkylsalicylideneimines. We report here the significant effect of a β-hydroxy group in the alkyl chain.

EXPERIMENTAL

Ethanolamine, obtained as a colourless liquid from British Drug Houses, was purified by distillation (b.p. 171°). Its solutions were kept under nitrogen and standardized by acidification with a known excess of perchloric acid followed by back titration.

N-(β-Hydroxyethyl)salicylideneimine was prepared by mixing equimolar proportions of ethanolamine and salicylaldehyde in ethanol. After the ethanol and water had been distilled off, the Schiff base was distilled twice under reduced pressure (b.p. 180°/14 mm); yield 60% (Found: C, $65 \cdot 3$; H, $6 \cdot 7$; N, $8 \cdot 6$. Calc. for $C_9H_{11}NO_2$: C, $65 \cdot 4$; H, $6 \cdot 7$; N, $8 \cdot 5\%$).

Chloroform, laboratory reagent grade, was purified by first shaking with concentrated sulphuric acid and then washing with water. It was stored in the dark.

Other experimental details have been described previously.[2]

RESULTS AND DISCUSSION

The notation of previous papers[2] is retained here, HA representing salicylaldehyde, B representing ethanolamine, and HBA the neutral form of the imine. The values of pK_1, the pK of salicylaldehyde, as it varies with ionic strength, are also taken from the earlier work.[2] Throughout the calculations, the pK of ethanolamine, pK_2, was taken as $9 \cdot 40$, the value found by pH titration of an acidified $2 \cdot 3 \times 10^{-3}$M solution.

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[1] Green, R. W., and Sleet, R. J., *Aust. J. Chem.*, 1966, **19**, 2101.

[2] Green, R. W., and Alexander, P. W., *Aust. J. Chem.*, 1965, **18**, 329.

Formation and Acid Dissociation of the Schiff Base

The spectrophotometric data used to calculate K_F and pK_3 are summarized in Figure 1. As before, the mean molar extinction coefficient of salicylaldehyde is given as a function of a_H and [B] by the expression

$$E = \frac{E_A K_1/a_H + E_{HBA} K_F[B] + E_{BA} K_F K_3[B]/a_H}{1 + K_1/a_H + K_F[B] + K_F K_3[B]/a_H} \qquad (1)$$

However, in comparison with the behaviour of ethylamine solutions,[1] the plateau region of Figure 1 was less clearly defined; and even above pH 10 the observed optical density continued to change with ethanolamine concentration up to 2M. Calculation confirmed that the formation and acid dissociation equilibria of the Schiff base overlapped significantly, and exact values of E_{HBA} and E_{BA} could not be read directly from the curves.

To determine K_F, therefore, the terms representing BA^- were first neglected and (1) was rearranged in the form:

$$E/[B] + (E - E_A)K_1/a_H[B] = E_{HBA}K_F - EK_F \qquad (2)$$

Below pH 9, the left side of (2) was a linear function of E from whose slope and intercept K_F and E_{HBA} could be derived. With these values known, a similar rearrangement of (1) applied to the high-pH region yielded K_3 and E_{BA}. The results are presented in Table 1, and the treatment is confirmed by the good fit between calculated curves and experimental points in Figure 1.

TABLE 1

MOLAR EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS OF SALICYLIDENEIMINES AT 25°

Constant	Ethanolamine	Ethylamine[a]	Constant	Ethanolamine	Ethylamine[a]
$\log K_F$	3·70	4·44	E_{HBA}	$6·03 \times 10^3$	$6·15 \times 10^3$
Standard error	0·01	0·01	E_{BA}	0	$0·79 \times 10^3$
pK_3	11·4	11·8	d_1	330 (CHCl$_3$)	140 (toluene)
			d_3	5·6 (CHCl$_3$)	160 (toluene)

[a] Ref. 1 for comparison.

The low value of K_F compared with that of the ethylamine derivative is probably attributable to intramolecular hydrogen bonding between the amine and hydroxyl groups of ethanolamine, with a resultant reduction in the tendency of the amine group to condense with aldehyde.

Ethanolamine (pK 9·4) is a much weaker base than ethylamine (pK 10·6), no doubt because of hydrogen bonding and the inductive effect of the hydroxyl group. In the Schiff bases the pK is under the additional influence of tautomerism and resonance, common to both imines, so that the smaller difference (0·4) in pK_3 is not surprising.

Distribution Equilibrium of the Schiff Base

In contrast to the salicylideneimines of methylamine,[3] ethylamine,[2] and n-butylamine,[1] the N-(β-hydroxyethyl)imine did not distribute measurably into toluene from aqueous solution, no doubt because of the strongly hydrophilic character of the aliphatic hydroxyl group. This also made its appearance in the negligible distribution ($d_2 = 0$) of ethanolamine into both toluene and chloroform. However, chloroform was found to extract the hydroxyethylimine to a measurable extent, and this solvent was used throughout the distribution studies, the results of which are summarized in Figure 2.
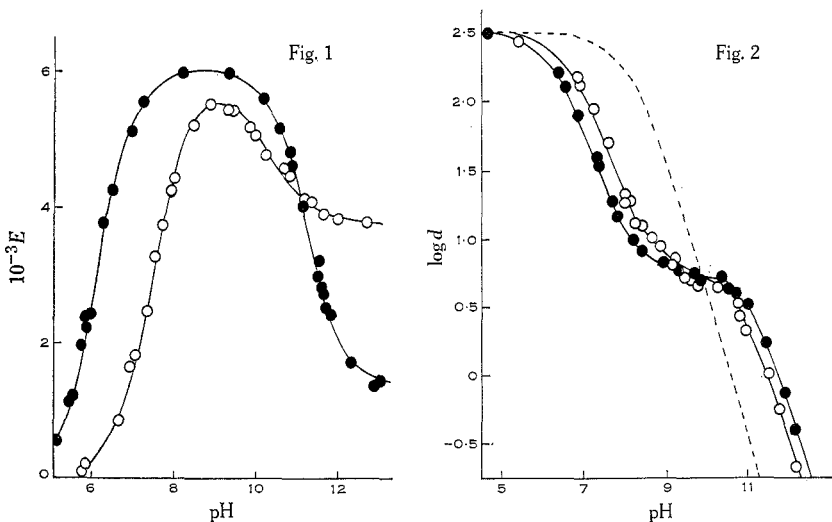

Fig. 1.—Molar extinction coefficient of salicylaldehyde at 400 mμ in the presence of excess ethanolamine. A_T $1 \cdot 66 \times 10^{-4}$M; B_T $1 \cdot 64 \times 10^{-2}$M ($\bigcirc$), $0 \cdot 393$M ($\bullet$). Continuous curves are calculated from the constants of Table 1.

Fig. 2.—Distribution of salicylaldehyde between water and chloroform in the presence of ethanolamine. A_T 10^{-2}M; B_T $9 \cdot 90 \times 10^{-2}$M ($\bigcirc$), $2 \cdot 51 \times 10^{-1}$M ($\bullet$). Continuous curves are calculated from the constants of Table 1. Broken curve represents distribution in the absence of amine.

Below pH 4 there was no detectable Schiff base formation and $d = d_1$, the distribution coefficient of HA determined in a separate experiment. The observed distribution coefficient then decreased with increasing pH. That this was not simply due to the formation of A$^-$ was obvious from the appearance of the yellow Schiff base colour in the chloroform phase and from the divergent courses of the d against pH curves. Near pH 9, where Schiff base formation was strongly favoured, d had a fairly constant value, which was taken as a first approximation to the distribution coefficient, d_3, of the imine. A curve-fitting programme written in Fortran and run on the CDC computer operated by CSIRO in Canberra then made only a very small change in d_3 to produce the continuous curves plotted in Figure 2. The good fit further confirms our spectrophotometric estimates of the equilibrium constants. The values of d_1 and d_3 are recorded in Table 1.

[3] Green, R. W., and Le Mesurier, E. L., *Aust. J. Chem.*, 1966, **19**, 229.