SCHIFF BASE EQUILIBRIA

III.* N-METHYLSALICYLIDENEIMINE

By R. W. GREEN† and E. L. LE MESURIER†

Summary

At 25° the formation constant of the Schiff base of salicylaldehyde and methyl-amine is $3 \cdot 72 \times 10^4$; and the pK of the phenolic group of the Schiff base is $11 \cdot 7$. The neutral form of the imine has distribution coefficients of $23 \cdot 5$ between water and toluene and $9 \cdot 0$ between water and cyclohexane.

INTRODUCTION

The formation and acid dissociation of *N*-n-butylsalicylideneimine have recently been examined spectrophotometrically,[1] and the distribution of the system into toluene has been explained in terms of the measured equilibrium constants. The Schiff base examined here differs from the above only in the length of the *N*-alkyl chain, a difference which has little effect on the aqueous equilibria but markedly influences the distribution behaviour.

EXPERIMENTAL

Methylamine hydrochloride was recrystallized from 95% ethanol and dried and stored in the dark in a desiccator. Chloride determination showed it to be more than $99 \cdot 5\%$ pure. Solutions were prepared by direct weighing and their concentrations checked by gravimetric chloride determination.

Cyclohexane, Laboratory Reagent grade, was used without further purification. Other reagents were as previously described.[1]

Experimental methods have also been described previously.[1] In distribution work, wherever justified by low values of the distribution coefficient, both phases were analysed.

RESULTS AND DISCUSSION

Potentiometric titration of methylamine hydrochloride (6×10^{-3}M at 25°) gave pK $10 \cdot 51$, which may be compared with $10 \cdot 62$ interpolated from the data of Everett and Wynne-Jones.[2]

The optical densities at 400 mμ of salicylaldehyde solutions (2×10^{-4}M) were measured in the presence of 50, 150, 2000, and 4000-fold excess of methylamine over the pH range 5–13. The variation of optical density with amine concentration and pH closely resembled that for n-butylamine, and analysis of the curves led to the constants shown in Table 1. The formation constant, K_F, was evaluated between pH 4 and

* Part II, *Aust. J. Chem.*, 1965, **18**, 659.

† School of Chemistry, University of Sydney.

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

[2] Everett, D. H., and Wynne-Jones, W. F. K., *Proc. R. Soc.* A, 1941, **177**, 499.

pH 7, and the acid dissociation constant pK_3, between $10 \cdot 7$ and $12 \cdot 6$. As before, the experimental points could be accurately fitted over the whole range by curves calculated from the constants of Table 1, together with previously measured values for the aldehyde.

TABLE 1

MOLAR EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS AT $25°$

	Methylamine	n-Butylamine[1]
$E_{HBA}(400 \text{ m}\mu)$	$5 \cdot 6 \times 10^3$	$6 \cdot 6 \times 10^3$
$\log K_F$	$4 \cdot 57 \pm 0 \cdot 01$	$4 \cdot 75$
pK_3	$11 \cdot 7$	$12 \cdot 0$
Distribution coeff. of HBA		
into toluene	59	$1 \cdot 9 \times 10^3$
into cyclohexane	$9 \cdot 0$	—

Fig. 1.—Distribution of salicylaldehyde between water and toluene in the presence of methylamine. $A_T = 0 \cdot 05$M. $B_T = 0 \cdot 10$M. Continuous curve is calculated from the constants of Table 1.
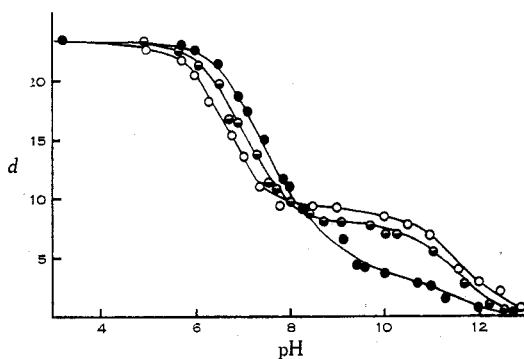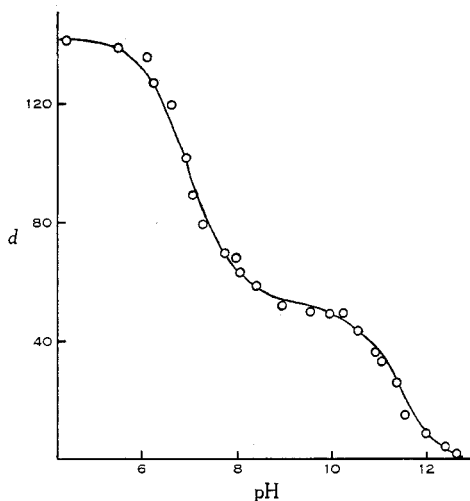

Fig. 2.—Distribution of salicylaldehyde between water and cyclohexane in the presence of methylamine. $A_T = 0 \cdot 05$M. $B_T = \bullet, 0 \cdot 05$M; $\ominus, 0 \cdot 10$M; $\bigcirc, 0 \cdot 20$M. Continuous curves are calculated from the constants of Table 1.

The effect of methylamine on the distribution of salicylaldehyde into toluene and cyclohexane is shown in Figures 1 and 2. The different shape of the curves from

those obtained with n-butylamine[1] derives solely from the fact that the distribution coefficient of the Schiff base HBA is now lower than that of the free aldehyde. The same mathematical treatment as before still accounts for the experimental results, as demonstrated by the continuous calculated curves in the Figures.