Formation constants of Schiff bases

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Abstract

The formation constants of the Schiff base between salicylaldehyde and aniline in water-methanol and water-dioxan mixtures of varying composition have been determined spectrophotometrically. The formation constants were found to vary with the mole fraction of water in both the solvent media.

Key words : Schiff base, formation constant, spectrophotometer, modified Job's method, aniline, salicylaldehyde, salicylidene aniline.

1. Introduction

The formation constants of Schiff bases have been determined by kinetic methods[1]. Only a few direct methods such as distribution method by Green et al[2] were employed to determine the formation constants at equilibrium conditions. The present paper describes the results obtained in the determination of formation constants of salicylidene aniline in aqueous methanol and aqueous dioxan mixtures by a modified Job's continuous variation method[3,4]. Dudek and Dudek[5] reported that the Schiff bases formed between substituted anilines and o-hydroxy aldehydes exist in two tautomeric (keto- and enol-) forms in solution and that the keto-enol equilibrium is solvent dependent, the keto form increasing with increase in the polarity of the solvent. Absorption maxima for the enol form and the keto form were reported by Dudek et al (loc. cit.) at 340 and 430 nm, respectively. Preliminary studies by the present authors indicated that the keto-enol equilibrium is not disturbed in the chosen solvent medium with change in concentration of the reactants. Absorption peak of the keto form is selected in the studies, since the absorption of the aldehyde or aniline or enol form is negligible at this wavelength.

2. Experimental

All the chemicals used were of the BDH quality. Methanol, dioxan, aniline and salicylaldehyde were purified by the standard methods reported in literature[6].

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ECIL(UV) spectrophotometer Model GS 865 A was used for absorbance measurements.

3. Procedure

Separate solutions of aniline and salicylaldehyde (each 0·005 M) were prepared in 100% methanol. 10 ml mixture of the two solutions in different ratios were prepared, the absorbance of each of these solutions was measured at 430 nm after equilibrating the mixture for 3 hr in a thermostat (at 303 ± 0·1° K) and plotted as a function of mole ratio. This experiment was repeated with 80 and 60% aqueous methanol and 60, 50, 40 and 30% dioxan. A similar experiment was repeated in 40% methanol using 0·0025 M aniline and salicylaldehyde solutions. The results are presented in Fig. 1.

4. Results and discussion

The absorption spectra of salicylaldehyde (0·0025 M) in methanol and 5 ml of aniline (0·005 M) + 5 ml of salicylaldehyde (0·005 M) in solution containing 100%, 80% and 60% of methanol by volume and 5 ml of 0·0025 M aniline + 5 ml of 0·0025 M salicylaldehyde in 40% methanol are presented in Fig. 2. The absorption curves for the stoichiometric (1 : 1) mixture of the two (each 5 ml of 0·005 M) in aqueous dioxan
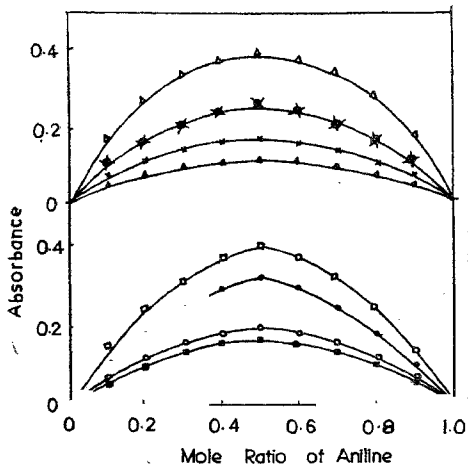

FIG. 1. Continuous variation curves for aniline-salicylaldehyde system in different compositions of methanol-water and water-dioxan mixtures: —○— 100% Methanol; —●— 80% Methanol; —□— 60% Methanol; —■— 40% Methanol; —△— 60% Dioxan; —×— 50% Dioxan; —⊗— 40% Dioxan; —△— 30% Dioxan.
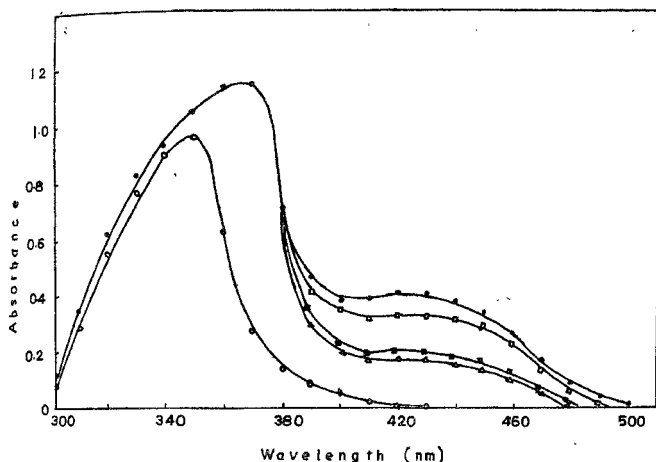
FIG. 2. Absorption curves for salicylaldehyde in methanol and for salicylidene aniline formed in different compositions of methanol-water mixtures : —○— Salicylaldehyde ; —■— Salicylidene aniline in 100% methanol ; —□— Salicylidene aniline in 80% methanol ; —●— Salicylidene aniline in 60% methanol ; —△— Salicylidene aniline in 40% methanol.

containing 60, 50, 40 and 30% of dioxan by volume are presented in Fig. 3: As there was little absorption for aniline, the optical absorption curve is not presented along with the above curves. It is clear from the absorption curves presented that there is no medium effect on the absorption maxima.

The absorption curves presented in Fig. 1 showed that one mole of the Schiff base salicylidene aniline is formed from one mole of each of the reactants. The absorbance values obtained in the Job's method showed deviation from those obtained in the presence of excess of the second component (Fig. 4). This is attributed to the low stability of the Schiff base in the absence of large excess of one of the components. Hence the absorbance, A_m, is determined by the procedure suggested by Al-Dilaimi et al[4]. In this procedure, one of the components (aniline or salicylaldehyde) is taken in a quantity which is the same as that present in the Job's method and the other in large excess. It is observed that a constant absorbance value is obtained if the second component is in 50 fold excess.
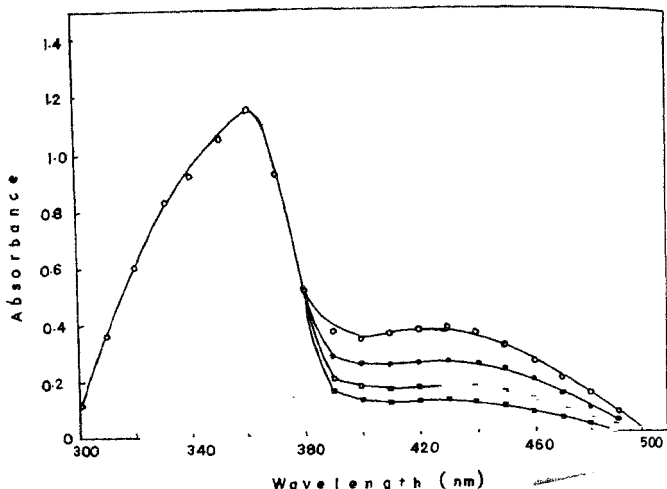
FIG. 3. Absorption curves for salicylidene aniline formed in different compositions of dioxan-water mixtures : ──■── Salicylidene aniline in 60% dioxan ; ──□── Salicylidene aniline in 50% dioxan ; ──●── Salicylidene aniline in 40% dioxan ; ──○── Salicylidene aniline in 30% dioxan.

Further at any concentration of the component (not present in excess) the A_m values increased with increase of polarity of the solvent.   This according to Dudek *et al* (*loc. cit.*) is due to the increase of the keto form.   In any solvent mixture the A_m value is obtained graphically from the absorbances measured on the solutions containing 1 to 5 ml of 0·005 M aniline or aldehyde and sufficient excess of the second component. The absorbance corresponding to the point of intersection of the linear plots (one obtained with the aniline and the other with the aldehyde) is taken as the value of A_m (Fig. 4).   The graphical method adopted for the evaluation of A_m showed that Beer's law is applicable to systems under investigation.   Since in 40% aqueous methanol a precipitate is observed, the studies were made with 0.0025 M solutions of aniline or aldehyde.

The formation constants (K_f) were obtained from the dissociation constant (K_d) calculated by Vosburgh and Cooper's[7] method using the equation
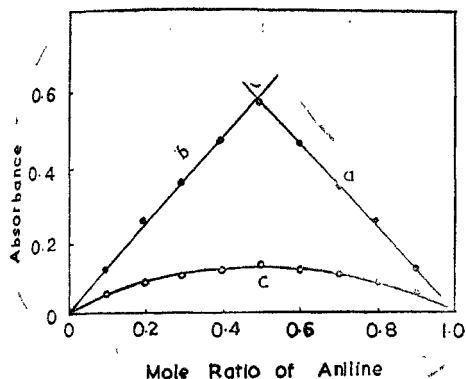
$$K_d = \alpha^2 c/(1 - \alpha)$$

FIG. 4. Plot of absorbance *vs* concentration of: (A) Aldehyde in presence of excess concentration of aniline; (B) Aniline in presence of excess concentration of aldehyde in 60% dioxan; and (C) Continuous variation curve for aniline—salicylaldehyde system in the same solvent mixture.

Table I

Formation constants of salicylidene aniline in different compositions of aqueous methanol and aqueous dioxan at 303·15°K

Solvent mixture % by volume	Mole fraction of water	A_x	A_m	Log K_f
100% Methanol	0·000	0·21	0·55	2·602
80% Methanol	0·361	0·33	1·10	2·389
60% Methanol	0·602	0·41	1·66	2·241
40% Methanol	0·773	0·19	1·48	2·130
60% Dioxan	0·761	0·125	0·56	2·170
50% Dioxan	0·827	0·18	0·85	2·134
40% Dioxan	0·877	0·26	1·27	2·114
30% Dioxan	0·917	0·38	1·94	2·083

where

$$a = (A_m - A_s)/A_m.$$

'a' is the degree of dissociation and 'c' is the concentration of salicylidene aniline formed, The measurements were repeated three or four times in each case and the

absorbances were found not to vary by more than $\pm 0 \cdot 01$ at the stoichiometric compo-sitions. This leads to an uncertainty of ± 5–10% in the computed values of the for-mation constants. The results presented in Table I show that formation of the Schiff base decreases linearly with increase in the mole fraction of water. Further $\log K$ values at any particular mole fraction of water are almost equal (within the experimental error) in the solvents studied. This suggests that the formation is dependent only on the mole fraction of water rather than on the nature of the solvent.

5. Acknowledgements

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