Short Communication

Solvent and substituent effects in the formation of Schiff bases

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Abstract

The formation constants of the Schiff bases formed between salicylaldehyde and substituted anilines in water–methanol and water–dioxan mixutres of varying composition have been determined spectrophotometrically. The formation constants of the bases except those formed with ortho-substituted anilines were found to decrease with the mole fraction of water in both the solvent media. A linear relationship was found between the log formation constants and the log dissociation constants of the conjugate acids of aniline studied. Here also the ortho-substituted anilines were found to be exceptions.

1. Introduction

In our earlier paper[1], we have described a modified Job's method of continuous variation for the determination of formation constants of Schiff base, salicylidene aniline, formed between salicylaldehyde and aniline in water–methanol and water–dioxan mixtures of varying composition. Here we are presenting the formation constant of Schiff bases formed between salicylaldehyde and the substituted anilines. The introduction of a substituent in the phenyl-ring of the aniline changes the electron density at nitrogen and alters the formation constant. Hence a parallelism is expected between the formation constants of the Schiff bases and the pK_a of the corresponding aniline or the substituent constants (σ, σ°, σ^+) of the substituted aniline.

2. Experimental

All the chemicals used are of BDH make. Methanol, dioxan, salicylaldehyde, o-toluidine, m-toluidine, p-toluidine, o-chloroaniline, m-chloroaniline, and p-chloroaniline were purified by the standard methods described in literature[2,3]. ECIL (UV) spectrophotometer model GS 865 A was used for absorbance measurements.

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Table I

Formation constants of N-salicylidene anilines formed between salicylaldehyde and substituted anilines in methanol water and dioxan water mixture of varying composition

| Solvent mixture	Mole fraction of water	H	o-CH$_3$	Log K_f of o-HOC$_6$H$_4$C $=$ NC$_6$H$_4$R, where R is				
				m-MCH$_3$	p-CH$_3$	o-Cl	m-Cl	p-Cl
100% Methanol	0·000	2·602	1·734	2·655	2·906	1·347	1·817	2·301
80% Methanol	0·361	2·389	2·006	2·434	2·704	1·540	1·589	2·066
60% Methanol	0·602	2·241	2·116	2·279	2·568	1·645	1·450	1·919
40% Methanol	0·773	2·130	2·221	...	...	1·743	...	...
60% Dioxan	0·761	2·170	2·252	2·241	2·528	1·808	1·400	1·848
50% Dioxan	0·827	2·134	2·287	2·195	2·495	1·830	1·360	1·818
40% Dioxan	0·877	2·114	2·306	2·162	2·475	1·869	1·326	1·778
30% Dioxan	0·917	2·083	2·331	2·126	2·447	1·896	...	1·758
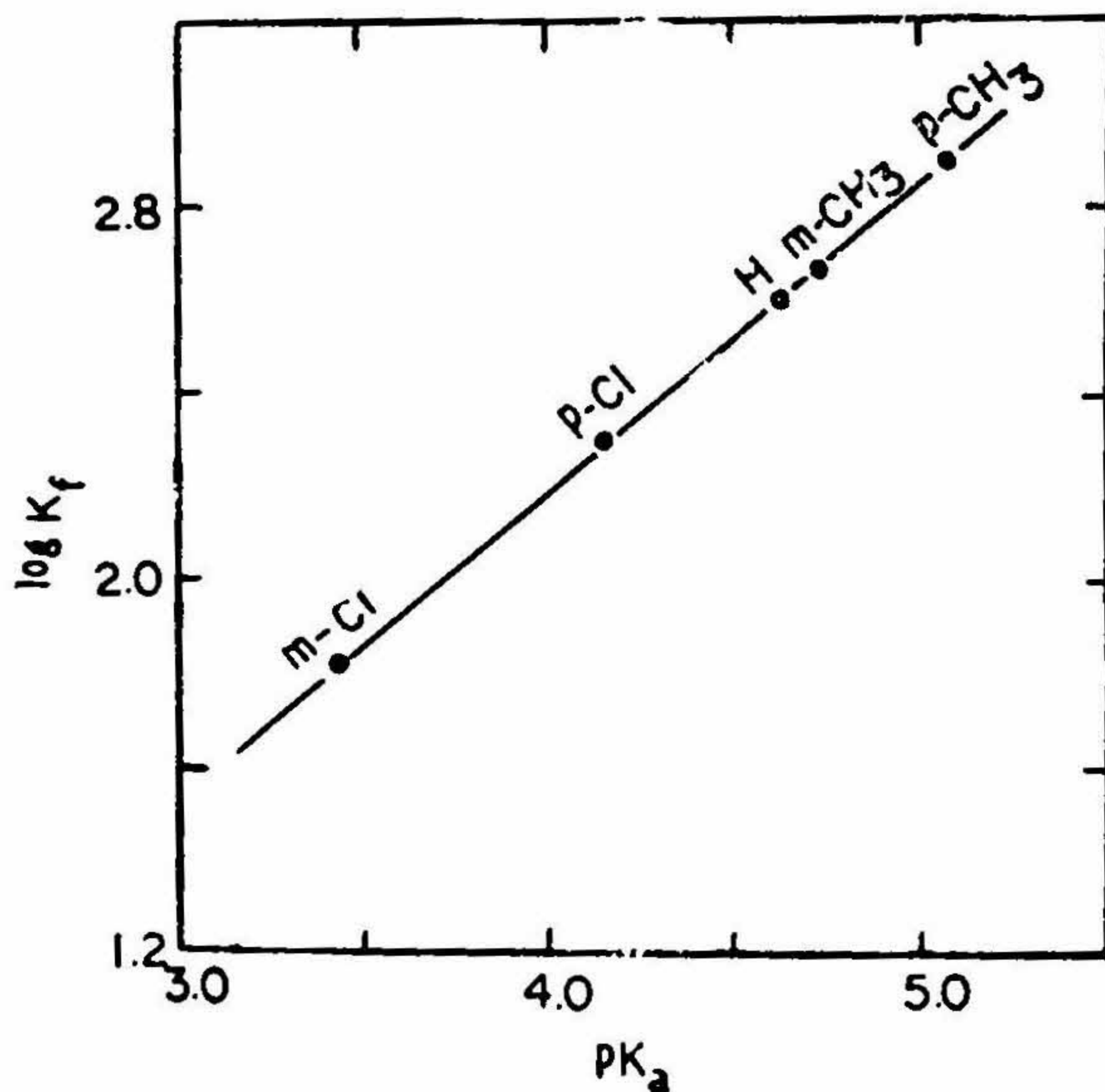
FIG. 1. Plot of log K_f of N-salicylidene anilines *vs* pK$_a$ of the corresponding substituted anilines in 100% methanol.

3. Procedure

The procedures adopted for the preparation of the solutions, the measurement of the absorbance and the determination of formation constants are similar to those described in our earlier paper. The concentrations of anilines and salicylaldehyde in the chosen
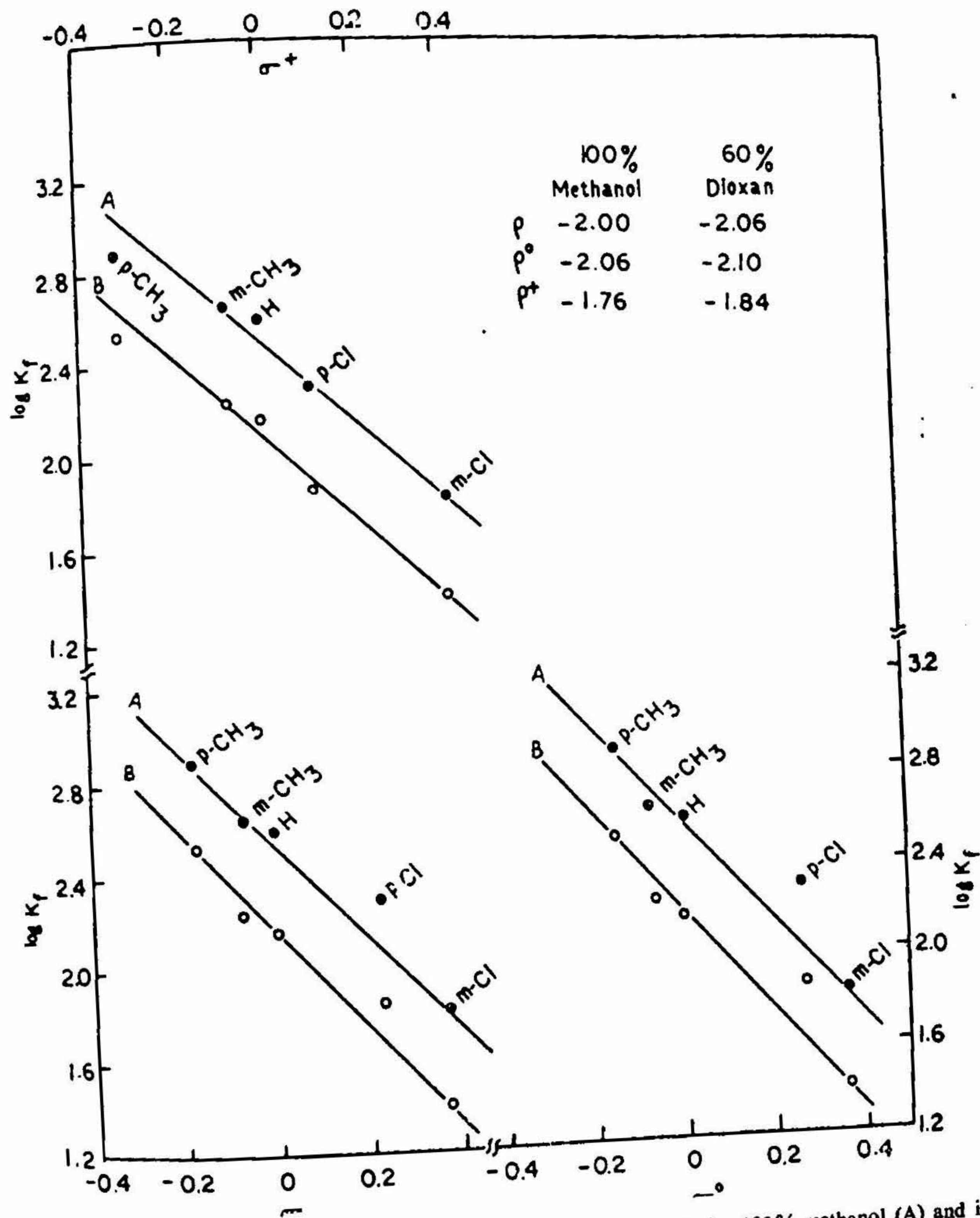
FIG. 2. Plots of log K_f of N-salicylidene anilines *vs* sigma constants in 100% methanol (A) and in 60% dioxan (B).

solvent mixture were selected depending on the magnitude of the absorbance of the keto-form (at 430 nm) and the solubility of the Schiff base.

4. Results and discussion

The formation constants in different compositions of aqueous methanol and aqueous dioxan are presented in Table I. The log formation constant of Schiff bases of m- and p-bases decreased with mole fraction of water while that of ortho-bases increased. Log K_f values of the Schiff bases at any particular mole fraction of water are almost equal (within the experimental error) in the two solvents. This suggests that the formation is dependent only on the mole fraction of water rather than on the nature of the solvent. A linear relationship was observed between the log formation constants and pK_a's[4] of anilines at all solvent compositions investigated. Ortho-substituted Schiff bases were found exceptional. A representative plot of log K_f vs pK_a is presented in fig. 1 in 100% methanol. The behaviour of the ortho-compounds could be traced to the steric hindrance caused by CH_3 or Cl group to the formation of the intermediate addition compound.

It is observed that good linear 'rho-sigma' plots are obtained in both the media studied. Representative plots in 100% methanol and 60% dioxan are presented in fig. 2. ρ-Value obtained in the former plots agreed well with that reported ($-2 \cdot 004$) by Pratt et al[5]. However, it is not possible to confirm this unequivocally in view of the limited data available. The ρ-value is independent of the nature of the medium.

References

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