

CCA-1050

YU ISSN 0011-1643

541.122.3:541.45

Original Scientific Paper

Spectrophotometric Study of Acid-Base Equilibria in Non-Aqueous Solvents

T. Jasinski, A. A. El-Harakany, A. A. Taha, and H. Sadek

Research Centre for Advancement of Post Graduate Science Studies, Alexandria
University, Alexandria, A.R.E.

Received August 22, 1977

The equilibrium constants for the reaction of 2,6-dichloro-4-nitrophenol, 2,6-dinitrophenol, 2,5-dinitrophenol and 2,4-dinitrophenol with some aliphatic amines of different structures have been determined spectrophotometrically in chlorobenzene, ethyl acetate and carbon tetrachloride as solvents. The data show that such reactions in inert solvents lead essentially to ion-pairs of the type $BH^+ \dots A^-$ where, HA and B represent the phenol and amine molecule, respectively. This conclusion was found to be in agreement with that obtained by other workers. In chlorobenzene as a solvent, the basic strengths fall in the order mono- < di- < tri-*n*-butyl amine, while in ethyl acetate the order of basic strengths becomes: mono- > di- > tri-*n*-butyl amine. These results are discussed from the point of view of solvation as an important role in the determination of the relative strengths of butylamines, as well as the extent to which dinitrophenols are affected by chelation between the phenolic OH and ortho-nitro group. However, in chlorobenzene and ethyl acetate as solvents, the relative basic strengths of pyridine and aniline derivatives remain independent of the solvent when bromophenol blue is used as a reference acid. The of $K_{BH^+A^-}$ values for aniline derivatives proved to be more suitable for judging the effect of the substituent than the basic strength in aqueous solution.

INTRODUCTION

The use of indicators for the purpose of defining and measuring acid-base equilibria in different non-aqueous solvent systems has been reviewed by several authors¹⁻³. There is, however, little information on the acid-base properties of some organic bases, e. g. pyridine and aniline derivatives in non-aqueous solvents⁴⁻⁶. Studies of infrared absorption spectra⁷ in inert solvents having low dielectric constant showed that such reactions lead essentially to ion-pair formation, in which protons are transferred according to the reaction:



This reaction has been adopted as a quantitative expression for the reactivity of a base towards a reference acid (or vice versa).

This paper is concerned with the spectrophotometric study of the relative strengths of some aliphatic amines in ethyl acetate and chlorobenzene as inert solvents. This technique has also been extended to the study of pyridine and aniline derivatives with bromophenol-blue as a reference acid.

EXPERIMENTAL

Materials

All materials used were either BDH or Fisher grade reagents.

Chlorobenzene was purified by double fractional distillation and collected at 132 °C.

Ethyl acetate was purified according to the method of Gillo⁸; the main fraction was collected at 77.1 °C.

n-Butylamine (b. p. 77 °C), di-*n*-butylamine (b. p. 158—159 °C), and Tri-*n*-butylamine (b. p. 210—212 °C), were dried over KOH pellets and fractionally distilled from CaH₂ immediately before use. Small constant boiling centre cuts were taken at their boiling points. Quinoline, quinaldine, β-picoline, γ-picoline, 2,6-lutidine, 2,4,6-collidine, *N*-methyl aniline, *N,N*-dimethyl aniline, *o*-toluidine and *p*-toluidine were purified as described elsewhere⁹. The liquid amines were dried over KOH and redistilled under reduced pressure immediately before use.

2,4-, 2,5-, and 2,6-dinitrophenols were purified according to the method of Pearson and Vogelsong². Chemically pure 2,6-dichloro-4-nitrophenol was used without further purification. Bromophenol Blue was recrystallized from benzene; (m. p. 270 °C).

Apparatus

The absorbances of the solutions were measured in stoppered 10 mm wide silica cells by means of a SP 1800 PYE UNICAM spectrophotometer. The cell compartment was thermostated at (25 ± 0.1) °C. The glassware and cells were always heated for 2 hours at 100 °C and cooled in a desiccator over CaCl₂, before use.

Preparation of Solutions

10⁻³ mol/dm³ stock solution of the appropriate acid was prepared in the proper solvent and used for all measurements. Similarly a stock solution of 10⁻¹ mol/dm³ of the base was prepared in the same solvent. Different aliquots of the base were added to 0.5 ml of the stock acid and diluted with the same solvent to 10 ml, in stan-

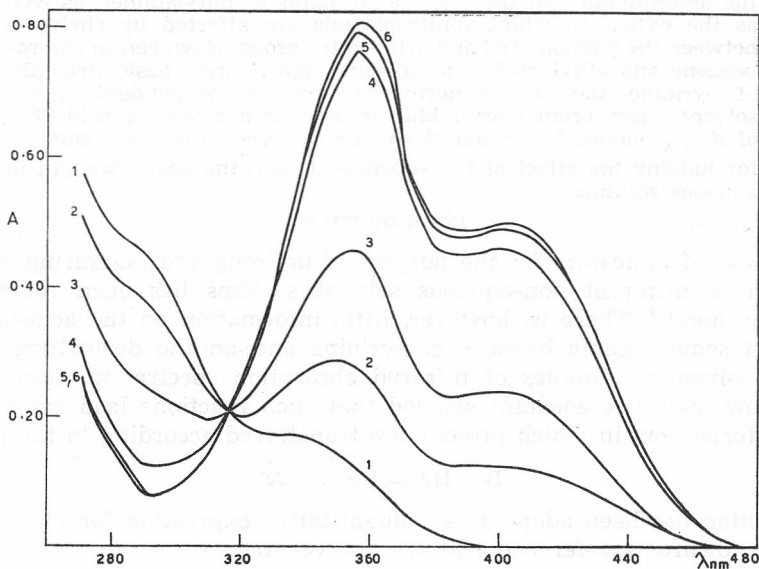


Figure 1. Absorption spectra of 5×10^{-5} mol dm⁻³ 2,4-dinitrophenol in ethyl acetate in the presence of *n*-butylamine

- 1) no base added
- 2) 0.5×10^{-4} mol dm⁻³
- 3) 1.0×10^{-4} mol dm⁻³
- 4) 2.5×10^{-4} mol dm⁻³
- 5) 5×10^{-4} mol dm⁻³
- 6) 50×10^{-4} mol dm⁻³

standard measuring flasks, in order to obtain 5×10^{-5} mol/dm³ acid concentration. The absorbances were measured at the selected wavelength using the pure solvent as a reference. It must be noticed that, within this base concentration range, the association of the base can be neglected¹⁰. In the meantime, instead of forming intermolecular hydrogen bonds, the indicator acids they probably form weak chelate bonds because of the small magnitude of the entropy change accompanying their formation¹¹.

Spectra of Acid and Ion-Pairs

2,4-Dinitrophenol in solution gives rise to two well defined absorption bands in the presence of either an acidic or basic component³. Figure 1. represents the spectra of 2,4-dinitrophenol with *n*-butylamine in ethyl acetate as solvent. A considerable absorption at 400 nm is observed which corresponds to ion-pair formation. At this wavelength the free acid and base do not absorb. It can be noticed that this absorption increases with increasing the base concentration till it reaches a maximum.

At this limiting absorbance it can be assumed that the reaction is complete, i. e., the ion-pair concentration will be equal to the initial acid concentration.

Calculation of Equilibrium Constants

The values of equilibrium constants $K_{\text{BH}^+\text{A}^-}$ were calculated using the equation¹²:

$$K_{\text{BH}^+\text{A}^-} = \frac{A}{\varepsilon_{\text{BH}^+\text{A}^-} \left(C'_{\text{HA}} - \frac{A}{\varepsilon_{\text{BH}^+\text{A}^-}} \right) \left(C'_B - \frac{A}{\varepsilon_{\text{BH}^+\text{A}^-}} \right)}$$

where A is the molar absorption of the solution, $\varepsilon_{\text{BH}^+\text{A}^-}$ the absorption coefficient of the ion-pair, and C'_{HA} and C'_B are the initial molar concentrations of the acid and base respectively.

By applying the Bent-French method¹³, the composition of the reaction product was determined. Figure 2. represents a typical example of the variation of $\log \frac{A}{A_0 - A}$ against $\log [B]$ where A_0 is the limiting absorbance of the solution, at which complete conversion of the acid to ion-pair occurs. A straight line with unit slope was obtained which showed that the molar acid to base ratio was 1 : 1. This indicates that $\text{BH}^+ \dots \text{A}^-$ was the only possible product.

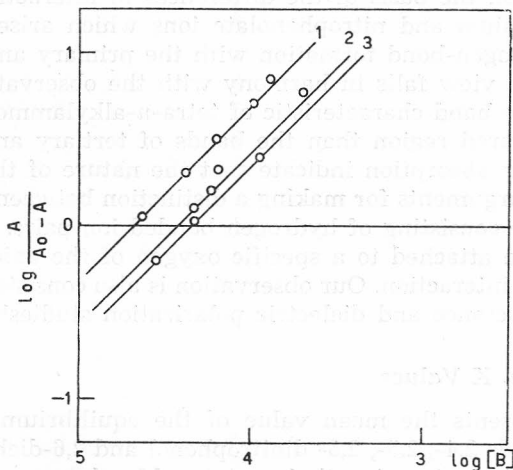


Figure 2a. Conformance of acid-base equilibria in mixtures of 2,6-dinitrophenol (HA) with (1)-*n*-butyl(2)di-*n*-butyl(3)tri-*n*-butylamin(B) in ethyl acetate to the assumed pattern of reaction (1)

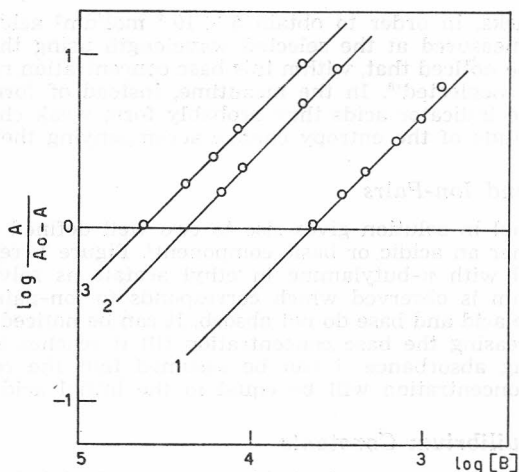


Figure 2b. Conformance of acid base equilibria in mixtures of 2,6-dinitrophenol (HA) with (1)-*n*-butyl (2)-*n*-butyl (3) tri-*n*-butylamine (B) in chlorobenzene to the assumed pattern of reaction (1).

RESULTS AND DISCUSSION

Determination of the Equilibrium Constants for the Systems of Isomeric Dinitrophenols-aliphatic Amines in Inert Solvents Analysis of Absorption Curves

The spectral absorption curves for pure 2,6-dinitrophenol with *n*-butyl, di-*n*-butyl and tri-*n*-butyl amines in ethyl acetate and chlorobenzene were measured. It has been found that upon addition of the amine the absorption band intensity of the free acid in both solvents decreases and simultaneously a new band with a maximum shifted towards the red region, characteristic of the reaction product (ion-pair) appears. These maxima are shifted slightly towards longer wavelength in the order primary < secondary < tertiary. This behaviour can be explained on the basis of the differences in interaction energies of the substituted ammonium and nitrophenolate ions which arise from the greater possibility of hydrogen-bond formation with the primary amine than with the other amines. This view falls in harmony with the observation of Davis¹ who has shown that the band characteristic of tetra-*n*-alkylammonium salt is much nearer to the infrared region than the bands of tertiary and secondary salts. These variations in absorption indicate that the nature of the cation furnishes one of the strong arguments for making a distinction between salts consisting of ionpairs and those consisting of hydrogen bonded ion-pairs. In the latter type, the cation must be attached to a specific oxygen of the anion and not merely held by coulombic interaction. Our observation is also consistent with the results obtained by conductance and dielectric polarization studies^{14,15}.

Medium Effects on K Values

Table I represents the mean value of the equilibrium constants for the reaction of the acids 2,4-, 2,5-, 2,6- dinitrophenol and 2,6-dichloro-4-nitrophenol with some aliphatic amines in ethyl acetate, chlorobenzene and carbon tetrachloride at 25 °C. In carbon tetrachloride and chlorobenzene, *n*-butylamine

appears to behave as a very weak base, so that no reliable results can be reported for its reaction with 2,4- and 2,5- dinitrophenols. This observation is also supported by the results of Pearson and Vogelsson².

Taking $K_{BH^+A^-}$ as a measure of the relative basicity of amines with a selected reference acid, it can be noticed from Table I that, generally, the tertiary amine is the strongest base in chlorobenzene irrespective of the reference acid. In the case of 2,6-dinitrophenol with *n*-, di-*n*-, and tri-*n*-butylamine in chlorobenzene, one can see that the base strength increases rapidly from primary (4800), secondary (25500), to tertiary amine (44400). Comparison of these basic strength data with those obtained in water shows that these values are considerably higher than those obtained in aqueous media. This may be due to the difference in the degree of solvation for these solvents. This behaviour is also consistent with the findings of Pearson and Vogelsson².

In ethyl acetate as a solvent, which contains a basic oxygen atom, the effect of solvation on $K_{BH^+A^-}$ values is considerably larger than that obtained in chlorobenzene or carbon tetrachloride as solvent. Table I shows that primary and secondary amines, irrespective of the reference acid, are the stronger bases in ethyl acetate ($D = 6.3$). However, in chlorobenzene ($D = 5.6$), which has about the same dielectric constant but lacking the basic oxygen atom, the $K_{BH^+A^-}$ are relatively low. This may be due to the presence of electron rich areas in the ethyl acetate system which stabilize the ion-pair through hydrogen bonding. In the case of tertiary amines, hydrogen bonding cannot operate, since the single hydrogen atom at the nitrogen atom is hydrogen bonded to the oxygen atom of the nitrophenolate anion.

Medium Effects on Acid Strength

Considering Table I, the values of $K_{BH^+A^-}$ for the reaction of, 2,4-dinitrophenol with the given selected amines decreases in the order ethyl acetate $>$ chlorobenzene $>$ carbon tetrachloride, which is consistent with the order of decreasing dielectric constant and the solvation power of the solvent. This trend can be explained in the case of ethyl acetate and chlorobenzene as due to the difference in solvation power, which decreases the chelation effect of the acid. This leads to the increase in the acid strength of 2,4-dinitrophenol. The same explanation can also be applied to the reaction of the remaining dinitrophenols with aliphatic amines in both ethyl acetate and chlorobenzene.

On the other hand, when carbon tetrachloride is used as a solvent, although the molecule as a whole has no dipole moment, it may associate with a phenolic OH group due to partial polarization of the $Cl^- - C^+$ bond, and such association could compete with the association of 2,4-dinitrophenol with the amines leading to a lower value of $K_{BH^+A^-}$ in carbon tetrachloride than in ethyl acetate and chlorobenzene.

Medium Effects on Basic Strength

In Table I comparison of the data obtained on the basic strength of aliphatic amines in non-aqueous media with that obtained in H_2O ³, show a marked contrast in their behaviour. In chlorobenzene solvent the basic strength increases in the order primary $<$ secondary $<$ tertiary, which can be easily explained as being due to the inductive effect of the alkyl group which increases the electron density on the nitrogen atom. One must take into consideration that

TABLE I
 Mean Equilibrium Constant Values for the Reaction $B + HA \rightleftharpoons BH^+ \dots A^-$ (B-Aliphatic Amines, HA-Dinitrophenols) in Ethyl Acetate, Chlorobenzene and Carbon Tetrachloride.

Nitrophenol pK _a (H ₂ O)	Amine pK _b	Ethyl acetate			Chlorobenzene			Carbon tetrachloride		
		K ₂₅ °C	λ	ε	K ₂₅ °C	λ	ε	K ₂₅ °C	λ	ε
2,4-Dinitrophenol (4.00)	n-Butylamine (3.39)	9000	400	11900	—	—	—	—	—	—
	Di-n-Butylamine (2.69)	7400	400	10700	3800	400	8000	1100	395	6000
	Tri-n-Butylamine (3.17)	6100	400	8700	5500	405	9500	(858)* 650 (417)*	400	8300
2,5-Dinitrophenol (5.15)	n-Butylamine	3600	450	5000	—	—	—	—	—	—
	Di-n-Butylamine	3500	455	4800	594	450	5100	(270)*	—	—
	Tri-n-Butylamine	250	460	3700	599	455	5100	(50.8)*	—	—
2,6-Dinitrophenol (3.76)	n-Butylamine	49700	430	8400	4800	425	8000	(6250)*	—	—
	Di-n-Butylamine	29700	435	8200	25500	435	8500	(35900)*	—	—
	Tri-n-Butylamine	22900	440	7800	44400	435	8800	(9340)*	—	—
2,6-dichloro-4-nitrophenol (3.68)	n-Butylamine	44400	390	19100	11300	375	15600	(—)*	—	—
	Di-n-Butylamine	41500	390	18800	84200	385	17900	(52500)*	—	—
	Tri-n-Butylamine	26000	390	18200	—	—	—	(9640)*	—	—

pK_b values in H₂O from PEARSON and VOGELSONG (ref. 2).

* values in carbon tetrachloride solvent were taken from Jasinski et al. (ref. 20).

the steric effects cannot play a role in this system, otherwise the effect should be greater in chlorobenzene, where there is a greater association with dinitrophenol than in H_2O where dissociation takes places.

In ethyl acetate, the order of increasing basicity is: primary > secondary > tertiary amines which is in agreement with Dikension's theory¹⁶.

From the above discussion one can conclude that the solvation effects are more important than the simple inductive effect accompanying the exchange of a hydrogen atom by an alkyl group on a nitrogen atom. These findings are also consistent with those obtained by Bayles and Cheiwyne³.

Acid-Base Equilibria of Bromophenol-Blue with Some Aniline and Pyridine Derivatives

The phenomenon of the colour changes of the acid indicator bromophenol blue was studied using aniline and pyridine derivatives in ethyl acetate and chlorobenzene solvents. The titration of this indicator acid with aromatic amines in both solvents shows a maximum at 405 nm which corresponds to the complete conversion of bromophenol blue to its yellow basic form. On the other hand, following the addition of a strong base (e. g. tri-*n*-butylamine) to the acid indicator in the same solvents, when the base to acid concentration ratio exceeds

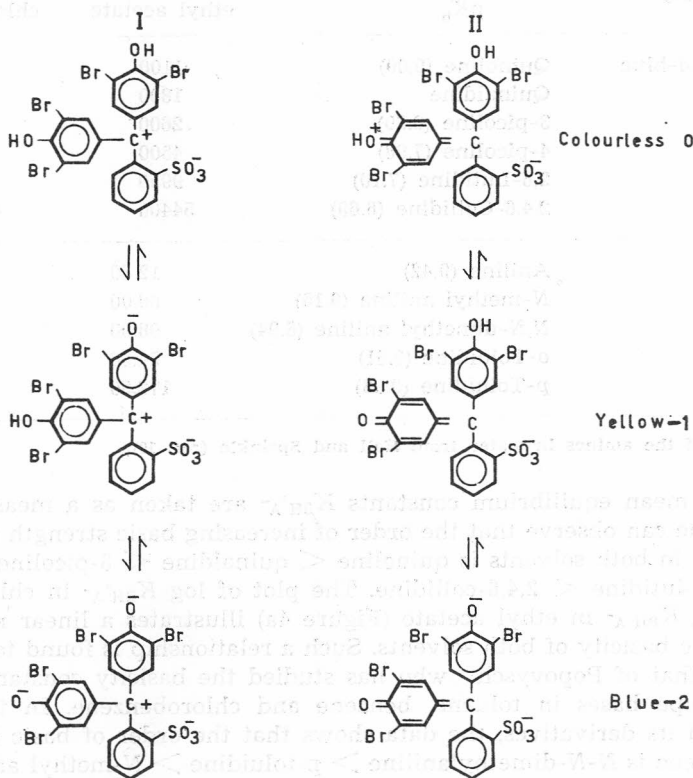


Figure 3.

1,6, a blue color is produced, which is characterized at a new band by a maximum at 570 nm. This shows that bromophenol blue exists in three forms in the presence of strong bases. These forms can be represented by three alternative formulae (Figure 3). Because of the precipitation of the blue form in ethyl acetate and chlorobenzene on standing, measurements of the relative strengths of bromophenol blue were restricted to the yellow form with the shorter wavelength region, namely at 405 nm. Davis¹ and Bell and Bayles¹⁷ have studied such an indicator structure and proved that this yellow compound is the sultone formation of bromosulfonphthalein.

Medium Effects on $K_{BH^+A^-}$ Values

The calculated values of the acid-base equilibrium constants for the reaction of bromophenol blue with α -, β -, γ -picilines, 2,6-lutidine, 2,4,6-collidine, aniline, *N*-methyl, *N,N*-dimethyl aniline, *o*-toluidine, and *p*-toluidine in ethyl acetate and chlorobenzene are given in Table II.

TABLE II

Mean Equilibrium Constant Values for the Reaction of Bromophenol-blue with some Pyridine and Aniline Derivatives in Ethyl Acetate and Chlorobenzene at 25 °C

Reference acid	Base pK_b	K in ethyl acetate	K in chlorobenzene
Bromophenol-blue	Quinoline (9.00)	1100	6400
	Quinaldine	1800	16500
	3-picoline (8.20)	2600	35200
	4-picoline (7.98)	4500	36600
	2,6-Lutidine (7.10)	9950	93900
	2,4,6-Collidine (6.69)	54400	483500
	Aniline (9.42)	12.80	16.3
	<i>N</i> -methyl aniline (9.15)	60.00	87.0
	<i>N,N</i> -dimethyl aniline (8.94)	98.00	382.0
	<i>o</i> -Toluidine (9.61)	54.50	25.6
	<i>p</i> -Toluidine (8.93)	172.50	117.5

pK_b values of the amines in water from Hall and Sprinkle (ref. 19).

If the mean equilibrium constants $K_{BH^+A^-}$ are taken as a measure of the basicity, one can observe that the order of increasing basic strength of pyridine derivatives in both solvents is quinoline < quinaldine < 3-picoline < 4-picoline < 2,6-lutidine < 2,4,6-collidine. The plot of $\log K_{BH^+A^-}$ in chlorobenzene against $\log K_{BH^+A^-}$ in ethyl acetate (Figure 4a) illustrates a linear relationship between the basicity of both solvents. Such a relationship is found to be consistent with that of Popovysch¹⁸ who has studied the basicity constants of some pyridine type bases in toluene, benzene and chlorobenzene. In the case of aniline and its derivatives, the data shows that the order of basic strength in chlorobenzene is *N,N*-dimethylaniline > *p*-toluidine > *N*-methyl aniline > *o*-toluidine > aniline, while in ethyl acetate it is *p*-toluidine > *N,N*-dimethyl

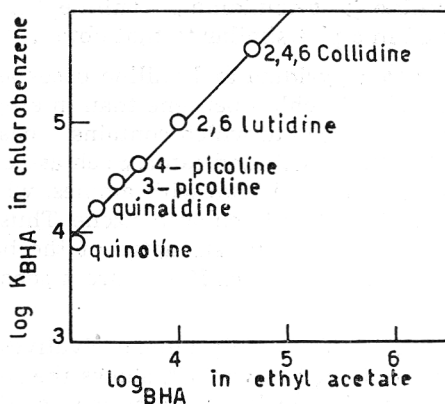


Figure 4a. Relationship between the basicity constants of pyridine derivatives in chlorobenzene and ethyl acetate.

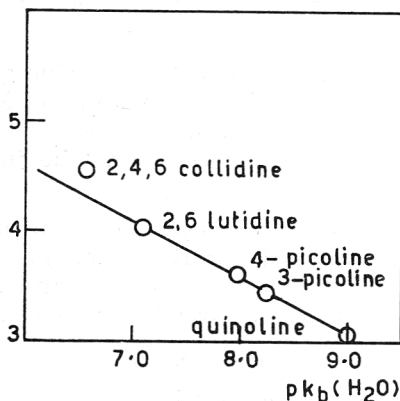


Figure 4b. The relationship of equilibrium constant logarithms for bromophenol-blue-pyridine system in ethyl acetate and the pK_b values of the amines in water.

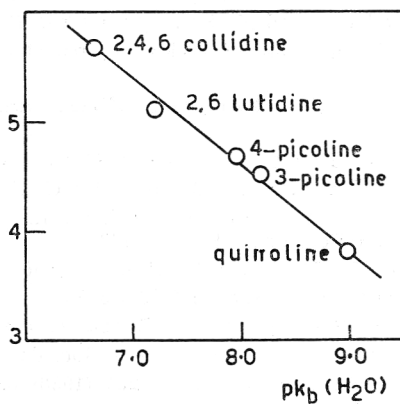


Figure 4c. The relationship of equilibrium constant logarithms for bromophenol-blue-pyridine system in chlorobenzene and the pK_b values of the amines in water.

aniline $>$ *N*-methyl aniline $>$ *o*-toluidine $>$ aniline. Therefore, a non linear relationship was observed in a plot similar to that obtained in pyridine systems.

These findings show that pyridine and aniline bases associate more extensively with bromophenol blue in chlorobenzene than in ethyl acetate. A reasonable explanation is that ethyl acetate which contains a basic oxygen atom, can associate to some extent with the acid indicator. Such association could compete with the association of bromophenol blue with amines, which leads to a lower value of $K_{BH^+A^-}$ in ethyl acetate than in chlorobenzene. Thus, it can be concluded that although the order of the relative strengths of the bases is the same for different solvents, the absolute values of $K_{BH^+A^-}$ are a sensitive function of the medium.

Comparison of the $K_{BH^+A^-}$ values of pyridine derivatives in ethyl acetate and chlorobenzene with those obtained in water¹⁹, shows the same order of basicity as shown in Figure 4b and 4c. The order of the basic strengths of aniline derivatives in both solvents can be explained as being due to the substituent effect. Successive substitution of the NH_2 group by the alkyl group (+ I effect) in the aniline molecules increases the basic strength in both solvents as shown in Table II.

A methyl group in the ring *o*- or *p*- to the amino group also increases the basic strength though the effect is smaller than that of *N*-substitution. Comparing these data with the values obtained in water, one can say that the basic strength of aniline derivatives in water cannot be judged simply from the nature of the substituents.

From the above findings it can be concluded that the data for the reaction of bromophenol blue with aniline derivatives in ethyl acetate and chlorobenzene are more suitable for judging the effect of the substituents than those obtained in aqueous solution, where abnormal trends are frequently observed.

REFERENCES

1. M. M. Davis, *Acid-Base Behaviour in Aprotic Organic Solvents*, Natl. Bur. Stand., Monograph 105 Washington D. C., 1968.
2. R. C. Pearson and D. C. Vogelsong, *J. Amer. Chem. Soc.* **80** (1958) 1038.
3. J. W. Bayles, and A. Chetwyn, *J. Chem. Soc.* (2328) 1958.
4. T. Jasinski, Z. Kokot, and H. Smagowski, *Roczn. Chem.* **39** (1965) 455.
5. T. Jasinski, T. Misiak, and T. Skarzynaska, *Roczn. Chem.* **39** (1965) 1485.
6. T. Widernikowa and T. Jasinski, *ZESZ. Nauk WSP G Dansk, Med. Fiz. Chem.* **10** (1970) 115.
7. G. M. Barrow, E. A. Yerger, *J. Amer. Chem. Soc.* **77** (1956) 4474.
8. L. Gillo, *Bull. Soc. Chim. Belges* **48** (1939) 34; *C. A.* **34** (1940) 2221.
9. D. D. Perrin, W. L. F. Armarego, and Dawn, R. Perrin. *Purification of Laboratory Chemicals* Pergamon Press, 1966.
10. M. M. Davis and H. B. Hetzer, *J. Res. NBS* **60**, (1958) 569.
11. M. M. Davis, *J. Amer. Chem. Soc.* **84** (1962) 3623.
12. T. Jasinski and H. Smagowski, *Roczn. Chem.* **41** (1967) 363.
13. H. Bent and C. French, *J. Amer. Chem. Soc.* **63** (1941) 568.
14. C. A. Kraus and J. Franklin, *Inst.* **225** (1938) 687.
15. A. A. Maryott and T. Res, *NBS*, **41** (1948) 1.
16. A. F. Trotman and Dikenson, *J. Chem. Soc.* (1949) 1293.

17. R. P. Bell and J. W. Bayler, *J. Chem. Soc.* (1952) 1518.
18. O. Popovysch, *J. Phys. Chem.* **66** (1962) 915.
19. N. F. Hall and M. R. Sprinkle, *J. Amer. Chem. Soc.* **54** (1932) 3469.
20. T. Jasinski, and T. Widernikowa, *Roczn. Chem.* **43** (1969) 1253.

SAŽETAK

Spektrofotometrijski studij kiselinsko-bazne ravnoteže u bezvodnim otapalima

T. Jasinski, A. A. El-Harakany, A. A. Taha i H. Sadak

Određene su konstante ravnoteže za reakcije 2,6-diklor-4-nitrofenol, 2,6-dinitrofenol, 2,5-dinitrofenol i 2,4-dinitrofenol s raznim alifatskim aminima u klorbenzenu, etil acetatu i ugljik-tetrakloridu.

Diskutirani su različiti faktori koji utječu na bazičnost alifatskih amina.

RESEARCH CENTRE FOR ADVANCEMENT
OF POST GRADUATE SCIENCE STUDIES
ALEXANDRI UNIVERSITY
ALEXANDRIA, A.R.E.

Prispjelo 22. kolovoza 1977.