CROATICA CHEMICA ACTA CCACAA **51** (1) 1—10 (1978)

CCA-1093

YU ISSN 0011-1643
541.13:541.45
Original Scientific Paper

Potentiometric Study of Acid-Base Interactions in Acetonitrile

T. Jasinski, A. A. El-Harakany, F. G. Halaka, and H. Sadek

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

Received October 8, 1976

The potentiometric titration curves of acids of different types were studied using piperidine and tetra-*n*-butylammonium hydroxide, (Bu_4NOH), as titrants in acetonitrile (AN) as solvent. The effect of methanol addition on the shape of the potentiometric curves was discussed.

The dissociation constants, K_{HA}, and homoconjugation constants, $K_{HA_2^-}$, of some acids were potentiometrically determined in AN. No exact correlation was found between K_{HA} of the studied acids in AN and the corresponding values in water. It was concluded that the acid characteristics, its anion properties, and the solvent type are the most important factors determining $K_{HA_2^-}$.

The heteroconjugation constants, $K_{AHA_1^-}$ of some anions with different acids were also determined. $K_{AHA_1^-}$ values for some substituted benzoic acids with reference to acetate ion were found to follow a linear free energy relationship with Hammett substituent constants.

INTRODUCTION

A great attention has been recently paid to the study of acid-base interactions in non aqueous solvents, specially in inert aprotic and dipolar aprotic solvents[1-5]. In amphiprotic solvents, like water and alcohols, both cations and anions can be solvated. However, in inert aprotic and dipolar aprotic solvents, solvation can only occur to one kind of ions, particularly cations. An anion with localized charge can only be stabilized by hydrogen bonding to a proton donor. In this connection, Kolthoff[6] recognized two distinct reactions (a) homoconjugation in which the anion (A^-) and its conjugated acid (HA) form the stable structure (HA_2^-) through hydrogen bonding, and (b) heteroconjugation where the anion (A^-) is hydrogen bonded to a different acid (HA_1) to form the structure (AHA_1).

This paper is concerned with the potentiometric study of the homoconjugation constants $K_{HA_2^-}$, and the heteroconjugation constants $K_{AHA_1^-}$, of acids of different types using piperidine and tetra-*n*-butylammonium hydroxide (Bu_4NOH) as titrants.

EXPERIMENTAL

Chemicals

All materials used were either BDH or Fisher grade reagents.

Solvents. — Acetonitrile (AN), was purified according to the method of Coetzee and McGuire[7]. Methanol: Specially dried reagent (99.9%) was fractionally distilled.

Acids. — Acetic (b. p. 118 °C), chloroacetic (m. p. 63 °C), dichloroacetic (assay 99%), trichloroacetic (m. p. 59.5 °C), trifluoroacetic (b. p. 72.4 °C), *p*-toluensulfonic, benzoic (m. p. 123 °C), *p*-nitrobenzoic (m. p. 242 °C), nitrobenzoic (m. p. 148 °C), *m*-nitrobenzoic (m. p. 143 °C), 3,5-dinitrobenzoic (m. p. 205 °C), *m*-chlorobenzoic (m. p. 158 °C), *p*-chlorobenzoic (m. p. 238 °C), m-bromobenzoic (m. p. 155 °C), *m*-iodobenzoic (m. p. 192 °C), and *p*-iodobenzoic (m. p. 283 °C), were dehydrated and purified by crystallizing twice from an appropriate solvent or solvent mixture and dried at 50 °C in a vaccum oven.

Phenols. — *m*-nitrophenol (m. p. 96 °C), *p*-bromophenol (m. p. 55 °C), 2,4-dinitrophenol (m. p. 114 °C), and picric acid (m. p. 122 °C), were purified by several crystallizations from the proper solvents and dried over P_2O_5 in a vacuum desiccator.

Bases. — Piperidine, was dried with BaO and fractionally distilled from P_2O_5 (b. p. 106 °C). Bu_4NOH was prepared in AN by a method similar to that Cundiff and Markunas[8]. The resulting solution was further purified by passing through the amberlite IRA-400 resin. Freshly prepared stock solution should be always used since the solution turns yellow after few days.

Salts. — Tetra-*n*-butylammonium iodide (purity 99%) was used without further purification. Tetra-*n*-butylammonium picrate (m. p. 89.5 °C) was prepared by neutralizing aqueous solutions of picric acid with Bu_4NOH. The salt was double crystallized from water-ethanol mixture and dried at 50 °C in vacuo. Tetra-*n*-butylammonium trifluoroacetate, was prepared by the neutralization of methanolic solutions of trifluoroacetic acid and Bu_4NOH. Excess methanol was evaporated under reduced pressure and the water of neutralization was evaporated by azeotropic distillation from benzene. The salt was crystallized twice from benzene-*n*-hexane mixture and dried at 50 °C in vacuo. The tetra-*n*-butylammonium salts of the following acids: acetate, chloroacetate, dichloroacetate (m. p. 78 °C), trichloroacetate (m. p. 74 °C), *p*-toluenesulfonate (m. p. 77 °C), 3,5-dinitrobenzoate (m. p. 106 °C), *p*-nitrobenzoate (m. p. 117 °C), and 2,4-dinitrophenolate (m. p. 108 °C), were prepared by allowing the silver salt of the corresponding acid to react with a methanolic solution of tetra-*n*-butylammonium iodide. Methanol was evaporated and the salt was crystallized from a proper solvent mixture.

Instruments. — In order to obtain reliable results from emf measurements, a Beckman glass electrode is calibrated in solutions of known pa_{H^+}. As recommended by Kolthoff[2] and Coetzee and Padmanabhan[9], the glass electrode (type 3903) is calibrated in buffer solutions of picric acid (HPi) and tetra-*n*-butyl ammonium picrate (Pi) in AN. pa_{H^+} values are calculated from equation (1)

$$pa_{H^+} = pK_{HPi} - \log \frac{c_{HPi}}{c_{Pi}} + \log f \tag{1}$$

where, $pk_{HPi} = 11$ as reported by Kolthoff[2], and $f = f_{H^+} = f_{Pi}$ is the activity coefficient as calculated from the limiting law:

$$-\log f = 1.5 \sqrt{\mu}$$

A plot of the electrode potential against $\log c_{HPi}/c_{Pi}$ gives a straight line with a slope of 59.1 which indicates that the electrode is behaving properly.

The dependence of the glass electrode potential upon activity of the solute is given by the Nernst equation,

$$E_G = E_G{}^0 - 0.0591\ pa_{H^+} \tag{2}$$

where, $E_G{}^0$ amounts to 1020 mV at 25 °C. From equation (2), pa_{H^+} values can be readily estimated from electrode potential values. Just before measurement, the glass electrode was rinsed with absolute alcohol, dried in a stream of nitrogen, then inserted into the titration cell.

A Beckman 39400 calomel electrode with quartz junction was used. An inner filling of aqueous saturated KCl solution was used. It has been proved that acetonitrile — KCl solutions affect the mercurous chloride, leading to destabilisation of the electrode potential[10].

A one piece jacketed cell was used for all emf measurements. The cell was thermostated at 25° ± 0.01 using a Haake model NB_{22} thermostat unit.

A Beckman 76008 Digital pH meter, accurate to ± 0.5 mv was used.

Procedure

Titration of acids with bases. — 5 ml Of the acid solution in AN were taken (1×10^{-2} mol/dm^3 — 5×10^{-3} mol/dm^3) and diluted to 25 ml with AN-methanol solvent mixtures. The titrant which is prepared in the same solvent (AN) was added from a semimicroburette. Purified nitrogen was passed over the solution throughout the whole run. A stable potential within ± 2 mV was reached in 5—10 minutes.

Measurement of homo- and heteroconjugation constants. — Increments of the free acid solution in AN (1×10^{-2} mol/dm^3 — 6×10^{-2} mol/dm^3) were added to 25 ml of a solution of the tetra-*n*-butylammonium salts of the acid under study (5×10^{-3} — — 9×10^{-3} mol/dm^3) in AN, and the corresponding potentials were recorded after each increment.

RESULTS AND DISCUSSION

Simple Acid Dissociation Constants, K_{HA}

Table I presents K_{HA} values as calculated from the measured potentials at equal concentrations of the acid and its tetra-*n*-butylammonium salt,$E_{1/2}$. A plot of $pK_{HA(H_2O)}$ vs. $pK_{HA(AN)}$ for these acids is given in Figure 1. It is seen that the plot shows a great deal of irregularity, which is not an unusual behaviour in inert aprotic solvents[11].

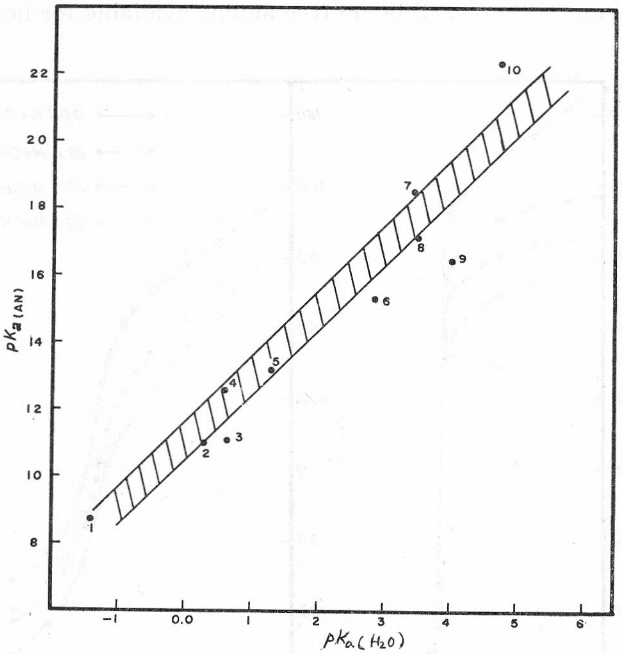

Figure 1. Relationship between $pK_{a(AN)}$ and $pK_{a(H_2O)}$ for the acids: p-toluenesulfonic(1), picric(2), trifluoroacetic(3), trichloroacetic(4), dichloroacetic(5), chloroacetic(6), *p*-nitrobenzoic(7), 3,5-dinitrobenzoic(8), 2,4-dinitrophenol(9), and acetic acid(10).

However, the general trend as shown by the area enclosed by the dotted lines indicates a rather positive effect.

TABLE I

Acid Dissociation and Homoconjugation Constants

SYSTEM	$\log K_{HA_2^-}$	$pK_{a(AN)}$
Chloroacetate	2.94	15.34
Dichloroacetate	2.81	13.20
Trichloroacetate	2.48	10.57
Trifluoroacetate	3.88	12.65
p-toluensulfonate	2.95	8.73
p-nitrobenzoate	3.69 (3.85) (3)	18.50 (18.70) (3)
3,5-dinitrobenzoate	3.97 (4.00) (3)	17.00 (16.90) (3)
2,4-dinitrophenolate	— (2.00) (14)	18.40 (16.45) (14)

Titration curves using piperidine as titrant

Potentiometric titration curves of the acids: chloroacetic, dichloroacetic, trifluoroacetic, *p*-toluensulfonic, picric, *o*-nitrobenzoic, and *p*-nitrobenzoic with piperidine in AN-methanol solvent mixtures were performed. Figure 2. shows examples of the titration curves of *o*-nitrobenzoic and *p*-toluenesulfonic acids. It can be noticed that these curves resemble those obtained in water in having only one inflection at the equivalence point. This behaviour can be explained in the light of Kolthoff's view[12] that piperidinium salts are weakly dissociated in AN and therefore, there will be no free anions available for homoconjugation reactions.

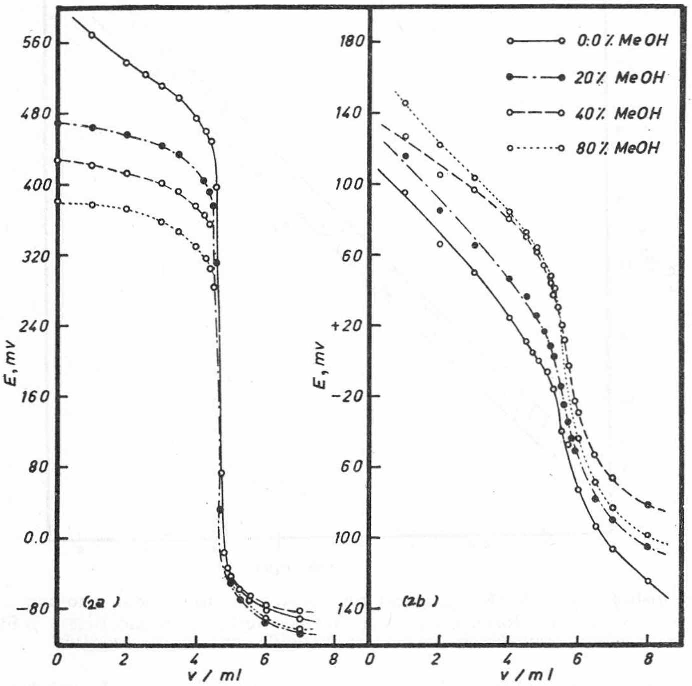

Figure 2. Potentiometric titration curves of *o*-nitrobenzoic and *p*-toluenesulfonic acids with piperidine in AN-MeOH solvent mixtures.

The effect om methanol addition (from 0.0 to 80 v/v %) to AN on the shape of the potentiometric curves is also presented in Figure 2. It has been noticed that methanol addition in some cases decreases the magnitude of the potential change at the end point, (Figure 2a), while in other cases it makes the end point more accurate (Figure 2b). Moreover, the increase in the potential change by the addition of methanol (Figure 2b) (specially for weak acids) can be attributed to the much higher tendency of methanol to accept protons from acids as compared to AN[13].

Titration curves using Bu_4NOH

Figure 3 represents the titration curves for dichloroacetic and *p*-toluenesulfonic acids using Bu_4NOH in AN-methanol mixtures. In this case, the curves show two distinct inflections. The presence of the first in inflection — nearly at the mid point, where equal concentrations of the acid and salt exist can be attributed to completion of the homoconjugation reaction of the acid and the formed anion: $(CHCl_2 . COO . . H . . OOC . CHCl_2)^-$. At this point, the amount of free acid is small, and H^+ ion concentration becomes very low. On further addition of Bu_4NOH, titration of the complex acid anion starts. Similar curves were also obtained for HCl, chloroacetic, trifluoroacetic, and *p*-nitrobenzoic acids. These findings are in agreement with those of Jasinski and Pawlak[15-20], who studied homoconjugation reactions in acetone, nitromethane and nitrobenzene as well as for other acid-base systems. It might be worthy to point

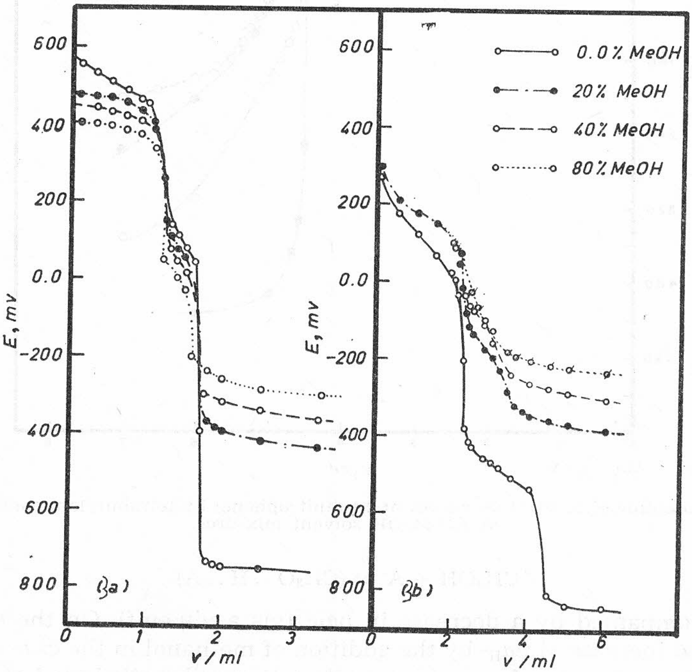

Figure 3. Potentiometric titration curves of dichloroacetic and *p*-toluenesulfonic acids using Bu_4NOH in AN-MeOH solvent mixtures.

out that when there is no homoconjugation reaction, the titration curve becomes similar to that in water as shown for 2,4-dinitrophenol and picric acid (Figure 4.).

Addition of methanol in the case of Bu_4NOH show more effects than those in the case of piperidine, as the effect of methanol on the solvation of anions may be considered. Methanol competes with the excess of acid for the anion in the beginning of the titration, but, however, the effect near the end point (where a higher salt concentration is present) is much larger, methanol decreases the equilibrium anion concentration by solvation, thus the equilibrium:

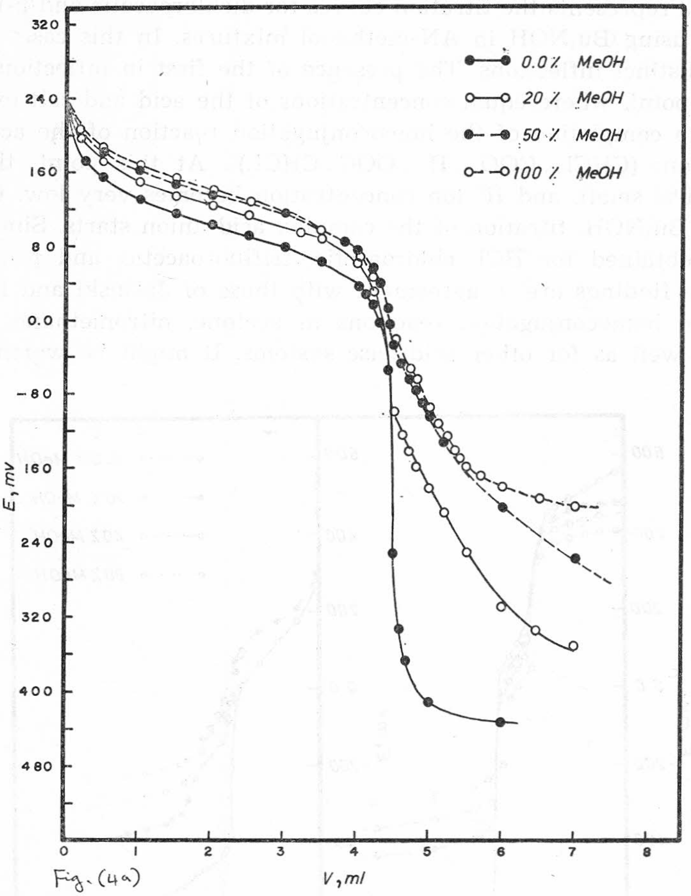

Fig. (4a)

Figure 4. a- Potentiometric titration curves of 2,4-dinitrophenol by tetrabutylammonium hydroxide in AN-MeOH solvent mixtures.

$$CH_3OH + A^- \rightleftharpoons (CH_3O\,..\,H\,..\,A)^-$$

will be accompanied by a decrease in pa_{H^+} (vis a vis emf). On the other hand, the observed increase of pa_{H^+} by the addition of methanol in the case of mixtures containing large excess of an acid over its salt may be attributed to the ability of methanol to act as a proton acceptor.

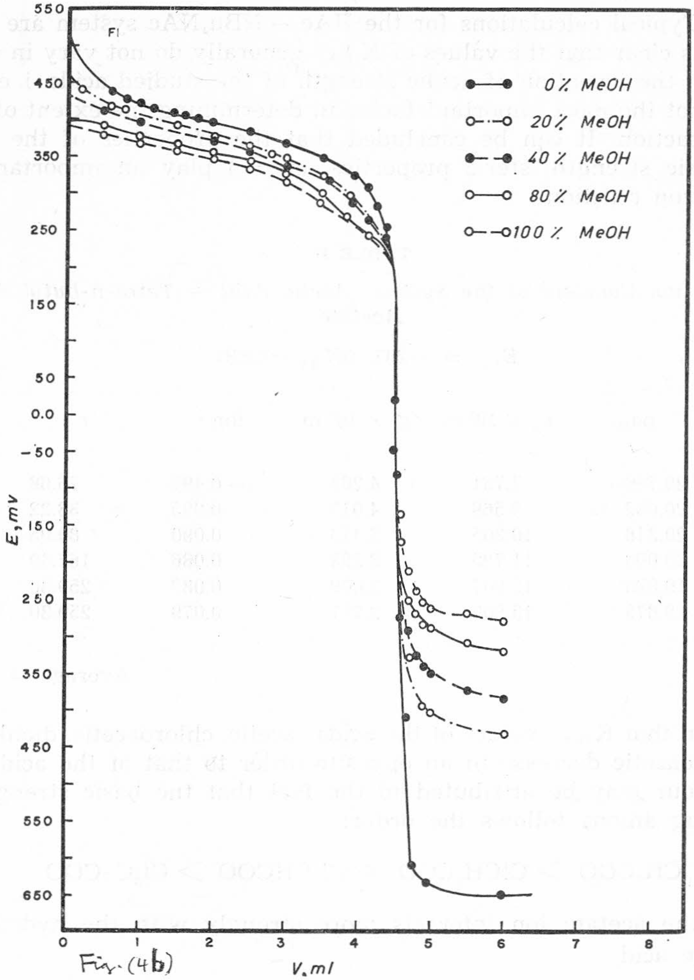

Fig. (4b)

Figure 4. b- Potentiometric titration curves of picric acid by tetrabutylammonium hydroxide in AN-MeOH solvent mixtures.

Homoconjugation constants

$K_{HA_2^-}$ and $K_{AHA_1^-}$ values were determined using the potentiometric data obtained from measurements in buffer mixtures consisting of an acid and the corresponding tetra-n-butylammonium salt in AN. These constants were evaluated by applying the equation derived by Kolthoff and Chantooni[2].

$$K_{HA_2^-} = \frac{c_s\, r^2 - r\,(c_a + c_s) - c_a}{r\,(c_s - c_a)^2} \tag{3}$$

where, $r = (a_{H^+} \cdot f)/(a_{H1/2^+} \cdot f_{1/2})$,

and c_a and c_s are the analytical concentrations of the acid and salt, respectively. The subscript 1/2 denotes values at $c_a = c_s$. The values of $K_{HA_2^-}$ are presented in Table I. Typical calculations for the HAc — NBu_4NAc system are shown in Table II. It is clear that the values of $K_{HA_2^-}$ generally do not vary in a parallel manner with the variation of acidic strength of the studied acids, i. e. the acid strength is not the most important factor in determining the extent of homoconjugation reaction. It can be concluded that the properties of the anion, A, (namely, basic strength, steric properties, etc...) play an important role in the conjugation reaction.

TABLE II

Homoconjugation Constant of the System : Acetic Acid — Tetra-n-butyl Ammonium Acetate

$E_{1/2} = -297$, $pK_{HA} = 22.31$

emf	pa_{H^+}	$c_a \times 10^3$ m	$c_s \times 10^3$ m	log f	r	$K_{HA_2^-}$
— 196	20.786	7.761	4.203	— 0.497	26.68	7900
— 187	20.632	8.569	4.015	0.095	38.22	6800
— 168.5	20.316	10.305	3.413	0.090	80.05	6900
— 150	20.000	11.725	3.283	0.086	167.40	7500
— 140	19.829	12.907	3.009	0.082	250.30	7500
— 131	19.675	13.907	2.777	0.079	259.30	7900

Average = 7400 ± 500

It is seen that $K_{HA_2^-}$ values of the acids : acetic, chloroacetic, dichloroacetic, and trichloroacetic decrease in an opposite order to that of the acid strength. This behaviour may be attributed to the fact that the basic strength of the corresponding anions follows the order:

$$CH_3COO^- > ClCH_2COO^- > Cl_2CHCOO^- > Cl_3C \cdot COO^-$$

Therefore, the acetate ion interacts more strongly with the hydrogen bond donor, acetic acid.

The effect of substitutents on the benzene ring observed on comparing the stability of the homoconjugation anions: 3,5-dinitrobenzoate and *p*-nitrobenzoate, the former cannot delocalize its charge through resonance while the other is still able to delocalize its charge.

Heteroconjugation constants

Table III presents the heteroconjugation constants, $K_{AHA_1^-}$ of the anions: acetate, dichloroacetate, trichloroacetate, *p*-nitrobenzoate, 3,5-dinitrobenzoate, and *p*-toluenesulfonate with several acids.

It is obvious that for a series of acids of the same type e. g. RCOOH with a given anion as reference, and in the absence of steric interference, the value of $K_{AHA_1^-}$ increases with the increase in the acid strength. The observed high values of the highly basic anions: Acetate, 3,5-dinitrobenzoate and *p*-nitrobenzoate with strong acids may be attributed to the strong interaction of the strong acid and strong base in the absence of solvation in acetonitrile. On the

TABLE III

Heteroconjugation Constants

Anion	Acid	$K_{AHA_1^-}$
Tetra-*n*-butylammonium Acetate	$ClCH_2COOH$	29000
	$Cl_2CHCOOH$	714000
	CF_3COOH	1040000
	m-nitrobenzoic	67700
	p-nitrobenzoic	94700
	p-clorobenzoic	31400
	m-chlorobenzoic	40700
	m-iodobenzoic	35500
	p-iodobenzoic	28200
	m-bromobenzoic	53100
	m-nitrophenol	4640
	p-bromophenol	1600
	p-methoxyphenol	160
Tetra-*n*-butylammonium *p*-nitrobenzoate	$ClCH_2COOH$	11700
	p-toluenesulfonic	1000000
	2,4-dinitrophenol	330000
Tetra *n*-butylammonium 3,5-dinitrobenzoate	$Cl_2CHCOOH$	30000
	CF_3COOH	576000
	p-toluenesulfonic	1000000
Tetra-*n*-butylammonium dichloroacetate	*p*-toluenesulfonic	2400
	CF_3COOH	14600
	CCl_3COOH	740
	2,4-dinitrophenol	75
Tetra-*n*-butylammonium trichloroacetate	$ClCH_2COOH$	24
	$Cl_2CHCOOH$	710
	p-nitrobenzoic	0.00

other hand, $K_{AHA_1^-}$ values for weakly basic anions, e. g. Cl_3COO^- with weak acids is close to zero, e. g. for the system: $CCl_3COONBu_4$-*p*-nitrobenzoic acids.

An attempt was made to correlate the hydrogen bonding donating ability of substituted benzoic acids, as measured by heteroconjugation constants with

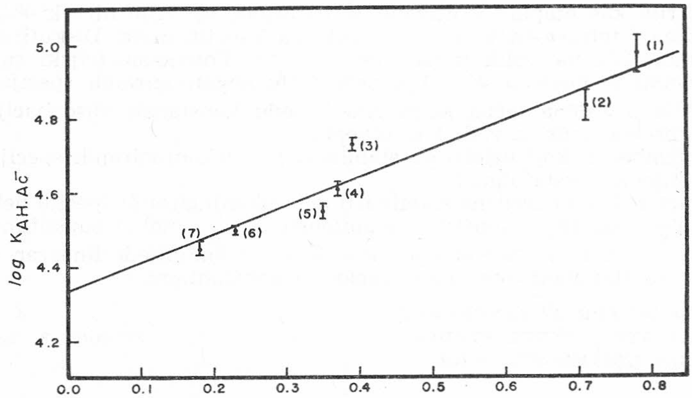

Figure 5. Plot of log K_{AHAC^-} vs δ of the substituted benzoic acids: *p*-nitro-(1), *m*-nitro(2), *m*-bromo(3), *m*-chloro(4), *m*-iodo(5), *p*-chloro(6), and *p*-iodo(7).

acetate ion, log K_{AHAc^-}, with the corresponding Hammett substituent constant, σ, as shown in Figure 5. A straight line was obtained having a least squre slope and intercept of 0.75 and 4.33, respectively. This figure, shows that such hydrogen bonding properties with respect to a reference ion follow a linear free energy relationship with substituents on the aromatic nucleus[3], in the form:

$$\log K_{AHAc^-} = \log K^{0}_{AHAc^-} + \varrho_{AHAc^-} \qquad (4)$$

where, ϱ is the reaction constant.

REFERENCES

1. S. Bruckenstein and A. Saito, *J. Amer. Chem. Soc.* **87** (1965) 689.
2. I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.* **87** (1965) 4428.
3. M. K. Chantooni and I. M. Kolthoff, *ibid.* **92** (1970) 7025.
4. M. K. Chantooni' and I. M. Kolthoff, *J. Phys. Chem.*, **77** (1973) 527.
5. T. Jasinski and Z. Pawlak, *Rocziniki chem.* **44** (1970) 1577.
6. I. M. Kolthoff and M. K. Chantooni Jr., *J. Amer. Chem. Soc.*, **85** (1963) 2195.
7. J. F. Coetzee and D. K. McGuire, *J. Phys. Chem.*, **67** (1963) 1810.
8. R. Cundiff and P. Markunas, *Anal. Chem.* **30** (1958) 1447, 1450.
9. J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.* **68** (1962) 1708.
10. G. J. Jans and H. Taniguchi, *Chem. Rev.* **53** (1953) 397.
11. E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86** (1964) 4517.
12. I. M. Kolthoff and M. K. Chantooni Jr., *ibid.* **85** (1963) 426; **87** (1965) 1004.
13. I. M. Kolthoff and M. K. Chantooni Jr., *J. Anal. Chem.* **39** (1967) 1080.
14. I. M. Kolthoff and M. K. Chantooni Jr., *J. Amer. Chem. Soc.* **91** (1969) 4621.
15. T. Jasinski and Z. Pawlak, *Roczniki Chem.* **41** (1967) 1943.
16. T. Jasinski and Z. Pawlak, *ibid.* **44** (1970) 1577.
17. T. Jasinski and Z. Pawlak, *Zesz. Nauk. WSP Gdansk, Mat. Fiz. Chem.* **8** (1968) 115.
18. T. Jasinski and Z. Pawlak, *ibid.* **6** (1966) 59.
19. T. Jasinski and Z. Pawlak, *ibid.* **8** (1968) 141.
20. T. Jasinski and Z. Pawlak, *ibid.* **9** (1969) 51.

SAŽETAK

Potenciometrijsko ispitivanje interakcija kiselina i baza u acetonitrilu

T. Jasinski, A. A. El-Harakany, F. G. Halaka i H. Sadek

U acetonitrilu kao otapalu ispitivane su titracione krivulje niza kiselina uz primjenu piperidina i tetra-*n*-butilamonij hidroksida kao titranata. Diskutiran je utjecaj dodatka metanola na oblik titracionih krivulja. Potenciometrijski su određene konstante disocijacije kiselina, K_{HA} i konstante homokonjugiranih specija, $K_{HA_2^-}$, u acetonitrilu. Nije utvrđena točna korelacija između konstanata disocijacije kiselina u acetonitrilu prema istim u vodi kao otapalu.

Temeljni čimbenici koji utječu na stabilnost heterokonjugiranih specija su svojstva kiseline, aniona i vrsta otapala.

Potenciometrijski su određene stabilnosti heterokonjugiranih specija nekih aniona sa nizom različitih kiselina. Konstante stabilnosti, $K_{AHA_1^-}$, nekih supstituiranih benzoevih kiselina u odnosu na acetat ion kao referentni ion slijede linearan odnos slobodne energije sa Hammett-ovim supstitucionim konstantama.

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

Prispjelo 8. listopada 1976.