Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3569-3578

Studies on the Protonation Constants of Some Triazoles in Ethanol-Water Mixtures

FATIH ISLAMOGLU*, BAHITTIN KAHVECI, MUSA ÖZIL and EMINE AKYÜZ
Department of Chemistry, Faculty of Sciences and Arts
Rize University, Rize 53100, Turkey
E-mail: fatihislamoglu53@hotmail.com

Several studies, involving the formation and investigation of biological activities of some triazoles derivatives. These derivatives have weak acidic properties. To gain more information about the effect of solvent on triazoles, the stoichiometric protonation constants of 17 triazoles (3 series) in ethanol-water mixtures were determined at an ionic strength of 0.10 M NaCl and at 25.0 ± 0.1 ºC under nitrogen atmosphere. A potentiometric method was used and the calculation was carried out using the PKAS computer program. The corresponding pK_a values of these triazoles were determined in ethanol-water mixtures mixtures. Thus, the effects of solvent and molecular structure upon acidity were investigated. The logarithm of the protonation constants of the triazoles decreased linearly with increasing ethanol content. The variation of these constants is discussed on the basis of specific solute-solvent interactions.

Key Words: Protonation constants, Triazoles, Solvent effect, Acidic properties, Potentiometry.

INTRODUCTION

Acidity measurements of organic compounds have a long history dating back to the end of the 19th century, when the first pKa was measured. Since then a vast data on acidities in various solvents has been collected[1-4]. The measurements have mostly been limited to polar solvents, however, with water being by far the most exploited medium, followed by alcohols and dipolar aprotic solvents.

Several articles on the acylation of some triazoles derivatives have been published[5-11]. In addition, these derivatives are reported to show a broad spectrum of biological activities such as antifungal, antimicrobial, hypoglycemic, antihypertensive, analgesic, antiparasitic, hypocholesteremic, antiviral, antiinflammatory, antioxidant, antitumor and anti-HIV properties[7,12-16]. On the other hand, it is known that triazoles rings have weak acidic properties, and thus some these derivatives were titrated potentiometrically in ethanol-water solvents and the pK_a values of the compounds were determined[8-11,15-22].

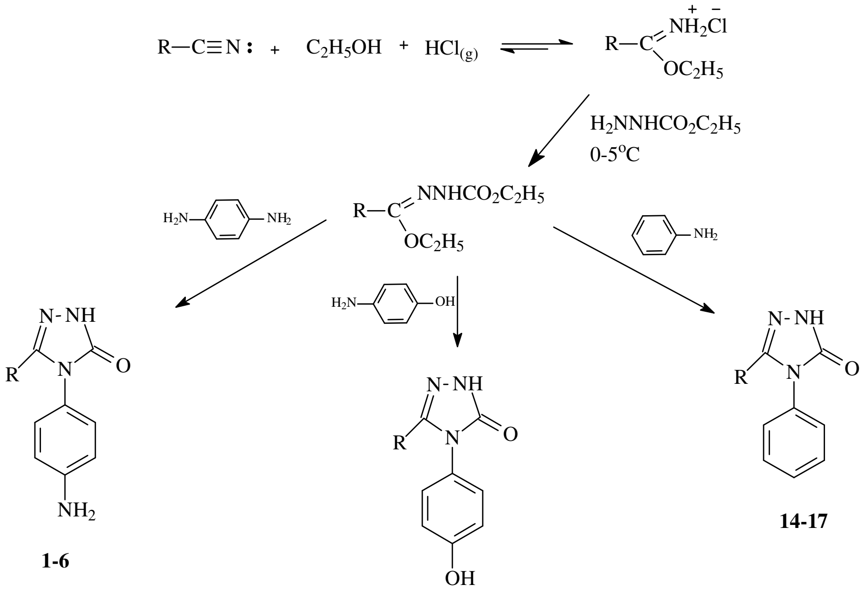
Furthermore, nowadays, antioxidants have become one of the major areas of scientific research. Antioxidants are extensively studied for their capacity to protect organism and cell from damage that is induced by oxidative stress. Scientists in many different disciplines become more interested in new compounds, either synthesized or obtained from natural sources that could provide active components to prevent or reduce the impact of oxidative stress on cell[23]. Exogenous chemicals and endogenous metabolic processes in human body or in food system might produce highly reactive free radicals, especially oxygen derived radicals, which are capable of oxidizing biomolecules, resulting in cell death and issue damage. Oxidative damages play a significantly pathological role in human diseases. For example, cancer, emphysema, cirrhosis, atherosclerosis and arthritis have all been correlated with oxidative damage. Also, excessive generation of reactive oxygen species induced by various stimuli and which exceeds the antioxidant capacity of the organism leads to a variety of pathophysiological processes such as inflammation, diabetes, genotoxicity and cancer[24].

EXPERIMENTAL

In this study, 17 triazoles [(**1 Series**), 3-methyl-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2, 4-triazol-5-one (**1**), 3-ethyl-4-(*p*-amino phenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**2**), 3-phenyl-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**3**), 3-benzyl-4-(*p*-amino phenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**4**), 3-(*p*-chlorobenzyl)-4-(*p*-amino phenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**5**), 3-(*p*-methylbenzyl)-4-(*p*-aminophenyl) -4,5-dihydro-1*H*-1,2,4-triazol-5-one (**6**), (**2 Series**), 3-methyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**7**), 3-ethyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**8**), 3-phenyl-4-(*p*-hydroxy phenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**9**), 3-benzyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**10**), 3-(*p*-chlorobenzly)-4-(*p*-hydroxyphenyl)-4,5 -dihydro-1*H*-1,2,4 -triazol-5-one (**11**), 3-(*p*-methylbenzyl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**12**), 3-(*p*-methoxybenzyl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**13**), (**3 Series**), 3-(3'-chloro)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**14**), 3-(2'-chloro)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**15**), 3-(2'-methyl)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**16**), 3-(3'-methyl)benzyl-4- phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**17**)] were synthesized. All product were synthesized according to the reported procedures[25,26]. The ethanol utilized was purified as described elsewhere[27]. Doubly distilled conductivity water was used as aqueous medium as well as for the preparation of ethanol-water mixtures. All other chemicals used in this investigation were reagent grade purity.

Hydrochloric acid solution 0.10 M was prepared in water and standardized against sodium carbonate. Same with the sodium hydroxide solutions 0.10 M were prepared as 20, 30, 40, 50, 60, 70 and 80 % (v/v) aqueous ethanol solutions and stored in a glass bottle protected against the atmosphere. The base solutions were standardized *via* a linear least-squares fit of Gran plots for end-point determination obtained from hydrochloric acid[28,29]. All potentiometric measurements were performed in an 80 mL jacketed titration cell thermostated at 25.0 ± 0.1 ºC and under nitrogen atmosphere. An Orion 720A Model pH-ionmeter, fitted with a combined pH electrode (Ingold) containing a filling solution of 0.10 M NaCl, was used for measuring the cell e.m.f. values.

The potentiometric cell was calibrated before each experiment[30,31]. For all the solvent mixtures examined, reproducible values of autoprotolysis constants (K_{ap}) were calculated from several series of (H^+) and (OH^-) measurements at 0.10 M NaCl[30-33].



1-6

7-13

14-17

R	Compounds	
-CH_3	1	7
-CH_2CH_3	2	8
-C_6H_5	3	9
-$CH_2C_6H_5$	4	10
-$CH_2C_6H_4$(-Cl,p)	5	11
-$CH_2C_6H_4$ (-CH_3, p)	6	12
-$CH_2C_6H_4$ (-OCH_3, p)		13

R	Compounds
-$CH_2C_6H_4$(-Cl,m)	14
-$CH_2C_6H_4$(-Cl,o)	15
-$CH_2C_6H_4$ (-CH_3, o)	16
-$CH_2C_6H_4$ (-CH_3, m)	17

Scheme-I

The following solutions prepared in water and each of the solvent mixtures studied (total volume 50.0 mL) were titrated potentiometrically with CO_2-free standard 0.1 M sodium hydroxide dissolved in the corresponding solvents: (i) 2.5×10^{-3} M HCl (for cell calibration); (ii) 2.0×10^{-3} M HCl + 2.5×10^{-3} M triazol compound. During each titration the ionic strength was maintained at 0.1 M NaCl and a potential reading was taken after a suitable time (normally 2-3 min) for equilibration.

The protonation constants of the these derivatives were calculated by analyzing the titration data using the computer programme developed by Motekaitis and Martell[30,33].

RESULTS AND DISCUSSION

The stoichiometric protonation constants (β) for these derivatives determined in ethanol-water mixtures 25.0 ± 0.1 ºC. All the values presented are the average of at least 5 measurements and the standard deviations of each are listed. These values are the equilibrium constants of the $A^- + H^+ \longleftrightarrow AH$, where AH show these derivatives and their protonated species, respectively. The protonation constants given in Table-1 are considered in more detail in order to gain more information about the effect of solvent composition and specific effects of substituents on the acidity of the these derivatives in solvent mixtures. The numerical log β values for these derivatives determined in ethanol-water mixtures decrease with increasing ethanol content in the solvent mixture (Figs. 1-3). They are observed that a nearly linear relationship exists between the aforementioned protonation constants and the mole fraction of ethanol from 0.0717 to 0.5527 for all these derivatives investigated. However, log β values at a mole fraction of ethanol of 0.5527 are slightly higher than those expected from the linear trend. The linear equations and the related correlation coefficients for all these derivatives are given Table-2.

Many studies have shown that the equilibrium constant is linearly related to the fraction of organic solvent[34-38]. The present results obtained for these derivatives are in good agreement with these observations. The dissociation constants of charged acids in ethanol-water mixtures vary with solvent composition in a manner that is not completely understood. Bates and co-workers[39,40] and Chattopadhyay and Lahiri[41] have examined the effect of a change in solvent composition on the dissociation of BH^+ and the related Gibbs energies of transfer in mixed solvents.

In present studies, it is suggested that electrostatic charging effects resulting from the change in dielectric constant with solvent effects and the solute-solvent interactions have greater significance in the interpretation of solvent effects. Thus, we can explain the present results obtained for these derivatives by specific solvation effects. The derivations of linearity

TABLE-1
STOICHIOMETRIC PROTONATION CONSTANTS OF SERIES **1-3** AT 25.0 ± 0.1 ºC FOR DIFFERENT ETHANOL-WATER MIXTURES (μ = 0.1 M NaCl, E = Ethanol, W = Water, x = the mole fraction of ethanol)

Compd. No.	%20E-%80W x = 0.0717 log β	%30E-%70W x = 0.1169 log β	%40E-%60W x = 0.1708 log β	%50E-%50W x = 0.2360 log β	%60E-%40W x = 0.3167 log β	%70E-%30W x = 0.4189 log β	%80E-%20W x=0.5527 log β
Series-1: 3-Alkyl(aryl)-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones							
1	7.16 ± 0.02	7.15 ± 0.03	7.14 ± 0.03	7.13 ± 0.02	7.11 ± 0.01	7.09 ± 0.03	7.08 ± 0.02
2	7.14 ± 0.02	7.13 ± 0.01	7.12 ± 0.02	7.09 ± 0.03	7.08 ± 0.04	7.06 ± 0.02	7.05 ± 0.03
3	6.95 ± 0.01	6.93 ± 0.02	6.92 ± 0.02	6.90 ± 0.03	6.89 ± 0.02	6.88 ± 0.01	6.85 ± 0.02
4	7.19 ± 0.01	7.17 ± 0.02	7.16 ± 0.03	7.15 ± 0.02	7.13 ± 0.02	7.12 ± 0.03	7.11 ± 0.02
5	6.40 ± 0.02	6.39 ± 0.02	6.38 ± 0.01	6.35 ± 0.02	6.34 ± 0.04	6.33 ± 0.01	6.31 ± 0.02
6	6.52 ± 0.02	6.51 ± 0.01	6.49 ± 0.02	6.47 ± 0.03	6.46 ± 0.02	6.44 ± 0.04	6.43 ± 0.01
Series-2: 3-Alkyl(aryl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones							
7	6.03 ± 0.01	6.02 ± 0.03	6.01 ± 0.02	5.98 ± 0.02	5.96 ± 0.03	5.95 ± 0.01	5.94 ± 0.01
8	5.54 ± 0.02	5.53 ± 0.02	5.52 ± 0.03	5.50 ± 0.03	5.47 ± 0.03	5.46 ± 0.02	5.44 ± 0.02
9	5.89 ± 0.02	5.88 ± 0.01	5.87 ± 0.03	5.85 ± 0.02	5.84 ± 0.02	5.82 ± 0.01	5.81 ± 0.02
10	5.63 ± 0.02	5.61 ± 0.01	5.60 ± 0.02	5.59 ± 0.02	5.57 ± 0.01	5.56 ± 0.02	5.54 ± 0.03
11	5.52 ± 0.02	5.51 ± 0.02	5.49 ± 0.01	5.47 ± 0.03	5.46 ± 0.02	5.45 ± 0.02	5.43 ± 0.01
12	5.69 ± 0.03	5.68 ± 0.02	5.66 ± 0.02	5.63 ± 0.01	5.62 ± 0.03	5.60 ± 0.02	5.58 ± 0.02
13	5.66 ± 0.02	5.64 ± 0.02	5.63 ± 0.01	5.61 ± 0.02	5.60 ± 0.02	5.59 ± 0.02	5.57 ± 0.02
Series-3: 3-(Aryl)-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ones							
14	5.26 ± 0.02	5.25 ± 0.02	5.24 ± 0.01	5.22 ± 0.02	5.21 ± 0.01	5.19 ± 0.03	5.18 ± 0.02
15	5.47 ± 0.01	5.46 ± 0.02	5.45 ± 0.02	5.44 ± 0.01	5.42 ± 0.02	5.40 ± 0.02	5.39 ± 0.01
16	5.54 ± 0.03	5.52 ± 0.02	5.51 ± 0.02	5.49 ± 0.03	5.47 ± 0.02	5.45 ± 0.02	5.42 ± 0.02
17	4.66 ± 0.02	4.65 ± 0.02	4.64 ± 0.02	4.62 ± 0.01	4.60 ± 0.02	4.59 ± 0.01	4.57 ± 0.02

TABLE-2
LINEAR RELATIONSHIP BETWEEN THE PROTONATION CONSTANTS OF SERIES **1-3** AND THE MOLE FRACTION OF ETHANOL (x) (FROM 0.0717 TO 0.5527)

	Compound	Equation	Correlation coefficient (r)
Series-1: 3-Alkyl(aryl)-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones			
(**1**)	3-Methyl-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.627 (x) + 6.736	- 0.997
(**2**)	3-Ethyl-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.821 (x) + 6.660	- 0.995
(**3**)	3-Phenyl-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.578 (x) + 6.528	- 0.993
(**4**)	3-Benzyl-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.862 (x) + 6.711	- 0.996
(**5**)	3-(*p*-Chlorobenzyl)-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.743 (x) + 5.948	- 0.994
(**6**)	3-(*p*-Methylbenzyl)-4-(*p*-aminophenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.796 (x) + 6.046	- 0.998
Series-2: 3-Alkyl(aryl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones			
(**7**)	3-Methyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.184 (x) + 5.464	- 0.998
(**8**)	3-Ethyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.217 (x) + 4.967	- 0.995
(**9**)	3-Phenyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.193 (x) + 5.332	- 0.994
(**10**)	3-Benzyl-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -1.997 (x) + 5.109	- 0.997
(**11**)	3-(*p*-Chlorobenzyl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.143 (x) + 4.974	- 0.995
(**12**)	3-(*p*-Methylbenzyl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.209 (x) + 5.119	- 0.994
(**13**)	3-(*p*-Methoxybenzyl)-4-(*p*-hydroxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.152 (x) + 5.102	- 0.996
Series-3: 3-(aryl)-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ones			
(**14**)	3-(3'-Chloro)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.326 (x) + 4.671	- 0.997
(**15**)	3-(2'-Chloro)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.421 (x) + 4.859	- 0.994
(**16**)	3-(2'-Methyl)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.433 (x) + 4.916	- 0.995
(**17**)	3-(3'-Methyl)benzyl-4-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one	log β = -2.487 (x) + 4.033	- 0.996

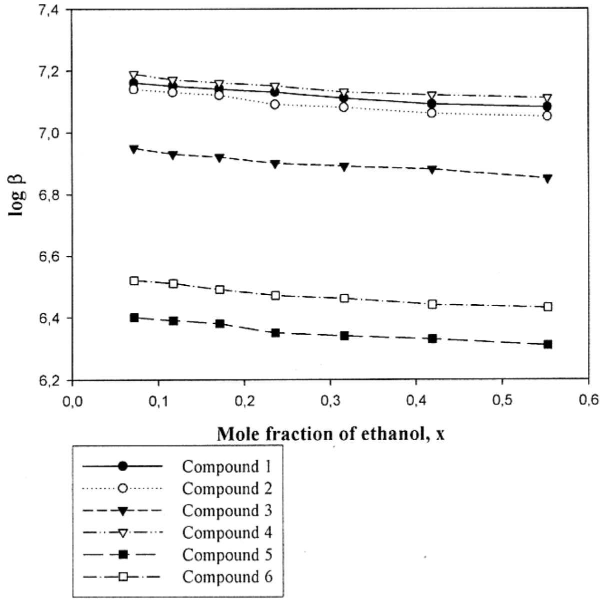


Fig. 1. Variation in the protonation constant of compound **1**, **2**, **3**, **4**, **5** and **6**

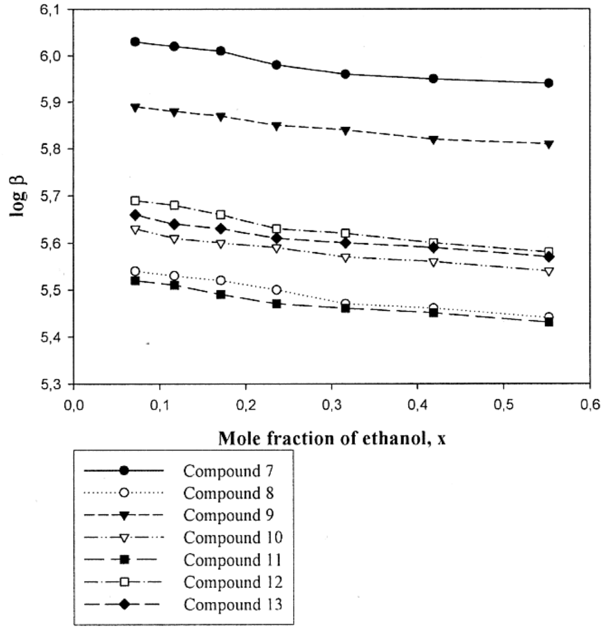


Fig. 2. Variation in the protonation constant of compound **7**, **8**, **9**, **10**, **11**, **12** and **13**

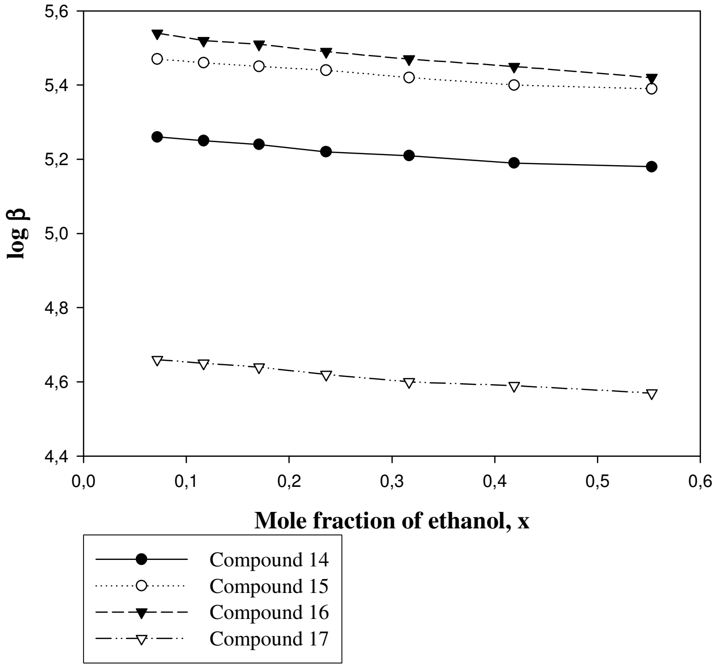


Fig. 3. Variation in the protonation constant of compound **14**, **15**, **16** and **17**

in 80 % ethanol may results from the preferential solvation of solute by one of the components of the solvent mixture that could change the effective dielectric constant value in the cibotactic region[42].

Furthermore, another factor why an increase in the log β values of all these derivatives are produced in ethanol-rich regions can be satisfactorily explained by differences in the solvent stabilization of the ionic species (H^+ and AH), brought about by changing the percentage of ethanol[40,43].

Using the protonation constants obtained in this work, the effects of the type substitute groups on the acidity of the these derivatives studied have been discussed. The most important factor that effects the acidity and therefore the protonation constant of a compound is the structural effect.

Conclusion

The acidity of a these derivatives is a result of various factors such as (i) the solvent effect; solvation power the tendency of forming hydrogen bonds, selective solvation, dielectric constant and the composition of the solution in the first solvation layer in the case of mixed solvents and (ii) structural effect, electronic effect, steric effect and the formation of hydrogen bonding.

REFERENCES

1. G. Kortüm, W. Vogel and K. Andrussow, Dissociation Constants of Organic Acidsin Aqueous Solution, Plenium Press, New York, p. 79 (1961).
2. V.A. Palm, Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions, Viniti, Moscow, p. 20 (1976).
3. K. Izutsu, Acid-base Dissociation Constants in Dipolar Aprotic Solvents, IUPAC Chemical Data Series No. 35, Blackwell Scientific, Oxford, p. 38 (1990).
4. F.G. Bordwell, *Acc. Chem. Res.*, **21**, 456 (1988).
5. A.A. Ikizler and H. Yüksek, *Org. Prep. Proced. Int.*, **25**, 99 (1993).
6. A. Ikizler, N. Dogan and A.A. Ikizler, *Rev. Roum. Chim.*, **43**, 741 (1998).
7. H. Yüksek, A. Demirbas, A. Ikizler, C.B. Johansson, C. Çelik and A.A. Ikizler, *Arzneim.-Forsch./Drug Res.*, **47**, 405 (1997).
8. H. Yüksek, M. Alkan, Z. Ocak, S. Bahçeci, M. Ocak and M. Özdemir, *Indian J. Chem.*, **43B**, 1527 (2004).
9. H. Yüksek, Z. Ocak, M. Alkan, S. Bahçeci and M. Özdemir, *Molecules*, **9**, 232 (2004).
10. S. Bahçeci, H. Yüksek, Z. Ocak, A. Azakli, M. Alkan and M. Özdemir, *Collect. Czech. Chem. Commun.*, **67**, 1215 (2002).
11. S. Bahçeci, H. Yüksek, Z. Ocak, C. Köksal and M. Özdemir, *Acta Chim. Slov.*, **49**, 783 (2002).
12. N. Demirbas and R. Ugurluoglu, *Turk. J. Chem.*, **28**, 679 (2004).
13. A.A. Ikizler, F. Uçar, H. Yüksek, A. Aytin, I. Yasa and T. Gezer, *Acta Pol. Pharm.-Drug Res.*, **54**, 135 (1997).
14. A.R. Bhat, G.V. Bhat and G.G. Shenoy, *J. Pharm. Pharmacol.*, **53**, 267 (2001).
15. H. Yüksek, M. Küçük, M. Alkan, S. Bahçeci, S. Kolayli, Z. Ocak, Ü. Ocak, E. Sahinbas and M. Ocak, *Asian J. Chem.*, **18**, 539 (2006).
16. H. Yüksek, S. Kolayli, M. Küçük, M.O. Yüksek, Ü. Ocak, E. Sahinbas, E. Sivrikaya and M. Ocak, *Indian J. Chem.*, **45B**, 715 (2006).
17. A.A. Ikizler, H.B. Sentürk and A. Ikizler, *Doga-Turk. J. Chem.*, **15**, 345 (1991).
18. A.A. Ikizler, A. Ikizler, H.B. Sentürk and M. Serdar, *Doga-Tr. Kimya D.*, **12**, 57 (1988).
19. H. Yüksek, Z. Ocak, M. Özdemir, M. Ocak, M. Bekar and M. Aksoy, *Indian J. Heterocycl. Chem.*, **13**, 49 (2003).
20. H. Yüksek, O. Üçüncü, M. Alkan, Z. Ocak, S. Bahçeci and M. Özdemir, *Molecules*, **10**, 961 (2005).
21. H. Yüksek, S. Bahçeci, Z. Ocak, M. Özdemir, M. Ocak, B. Ermis and T. Mutlu, *Asian J. Chem.*, **17**, 195 (2005).
22. H. Yüksek, S. Bahçeci, Z. Ocak, M. Alkan, B. Ermis, T. Mutlu, M. Ocak and M. Özdemir, *Indian J. Heterocycl. Chem.*, **13**, 369 (2004).
23. H.H. Hussain, G. Babic, T. Durst, J. Wright, M. Flueraru, A. Chichirau and L.L. Chepelev, *J. Org. Chem.*, **68**, 7023 (2003).
24. J. McClements and E.A. Decker, *J. Food Sci.*, **65**, 1270 (2000).
25. B. Kahveci, M. Özil and M. Serdar, *Heteroatom Chem.*, **19**, 38 (2008).
26. B. Kahveci, *Molecules*, **10**, 376 (2005).
27. D.D. Perrin and W.L.F. Armerega, Purification of Laboratory Chemicals, Pergamon, Oxford, edn. 2, p. 1112 (1966).
28. G. Gran, *Acta Chem. Scand.*, **4**, 559 (1950).
29. G. Gran, *Analyst*, **77**, 661 (1952).
30. A.E. Martell and R.J. Motekaitis, The Determination and Use of Stability Constants, VCH, Weinheim, p. 59 (1988).
31. M. Meloun, J. Havel and H. Högfelt, Computation of Solution Equilibria, Wiley, New York, p. 157 (1988).

32. E.M. Woolley, D.G. Hurkot and L.G. Hepler, *J. Phys. Chem.*, **74**, 3908 (1970).
33. R.J. Motekaitis and A.E. Martell, *Can. J. Chem.*, **60**, 168 (1982).
34. M.S.K. Niazi and J. Mollin, *Bull. Chem. Soc. (Japan)*, **60**, 2605 (1987).
35. C. Charanai, C.C. Panichajakul and E.M. Woolley, *Anal. Chem.*, **47**, 1860 (1975).
36. H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).
37. H. Irving and H. Rossotti, *Analyst*, **80**, 245 (1955).
38. P.S. Gentile, M. Cefole and A.V. Celiano, *J. Phys. Chem.*, **67**, 1447 (1963).
39. M. Paabo, R.G. Bates and R.A. Robinson, *J. Phys. Chem.*, **70**, 247 (1966).
40. R.G. Bates, *J. Electroanal. Chem.*, **29**, 1 (1971).
41. A.K. Chattopadhyay and S.C. Lahiri, *Electrochim. Acta*, **27**, 269 (1982).
42. N.S. Isaacs, Physical Org. Chem., Longman, New York, p. 158 (1987).
43. R.G. Bates, Determination of pH, Theory and Practice, Wiley, New York, edn. 2, p. 312 (1973).

(*Received*: 20 July 2007; *Accepted*: 4 February 2008) AJC-6289