

The Protonation Constants of Some Aliphatic Alkylamines in ethanol-water Mixtures

Esma KILIÇ*[†]; Gültekin GÖKÇE, Esin CANEL
*Department of Chemistry, Faculty of Science, Ankara University,
06100, Ankara-TURKEY*

Received 12.07.2001

Protonation constants of methyl-, ethyl-, propyl- and butylamines were determined potentiometrically using an electrode system calibrated in concentration units of hydrogen ion in ethanol-water mixtures (10% -80% ethanol, v/v) at an ionic strength of 0.1 and at 25 °C. The trend in the values of protonation constants of these aliphatic amines was explained in terms of the number of alkyl groups and solvent composition. The basicity orders were found to be $\text{NH}_3 < \text{R}_3\text{N} < \text{RNH}_2 < \text{R}_2\text{NH}$ (R:-CH₃, -C₂H₅, -n-C₃H₇ and -n-C₄H₉) in all the solvent mixtures studied.

Key Words: Aliphatic amines, potentiometry, protonation constant, ethanol-water mixtures.

Introduction

The aliphatic and aromatic amines and their salts are used in many sectors such as medicine, cosmetics, and the dye and soap industries as well as in many organic reactions. Therefore the investigation of their chemical behaviour in different media is of great importance for the determination of their general properties. The protonation constant is the equilibrium constant of the reaction of a base binding with a proton and most of the values given in the literature are those determined in aqueous media. However, it has been suggested that non-aqueous media and the media of an organic solvent mixed with water could provide a better model for in vivo reactions¹. There are numerous studies on the basicity aliphatic amines in various solvents²⁻¹⁵.

In the present study, the stoichiometric protonation constants (β) of ammonia and methyl-, ethyl-, propyl- and butylamines were determined in various ethanol-water mixtures. The changes in protonation constants with the type and number of alkyl groups attached and the correlation between the protonation constants and the mole fraction of ethanol was also investigated.

Experimental

Chemicals and Standard Solution

Ammonium chloride (98%, Merck), methylamine hydrochloride (97%, BDH), dimethylamine hydrochloride (99%, Merck), trimethylamine hydrochloride (98%, Merck), ethylamine hydrochloride (99%, Merck), di-

*Corresponding author

ethylamine hydrochloride (99%, Merck), triethylamine hydrochloride (98.5%, BDH), n-propylamine (99%, Merck) di-n-propylamine (99%, BDH), tri-n-propylamine (99%, BDH), n-butylamine (98%, BDH), di-n-butylamine (99%, BDH), and tri-n-butylamine (99%, BDH) were used and the purity of these compounds was checked by potentiometric titration.

Stock solutions (0.030 M) of ammonia, methyl-, dimethyl-, trimethyl-, ethyl-, diethyl- and triethylamines were prepared from the hydrochlorides of their amines in water. The preparation of the stock solutions of the other amines was carried out by dissolving amines in ethanol instead of water. The stock solutions were used by diluting in suitable concentrations.

Stock solutions of strong acid and strong base were prepared using analytical grade perchloric acid and sodium hydroxide respectively. Acid solutions were standardised by titrating against primary standard sodium carbonate. The standard base solutions employed were 10, 20, 30, 40, 50, 60, 70 and 80% (v/v) aqueous ethanolic solutions. These solutions were standardised with the use of linear least squares fit of Gran's plots used for the determination of the end point, obtained by the titration of these bases with perchloric acid^{16,17}.

The ionic strength was kept constant using a chemically pure sodium perchlorate and the ethanol used was purified as described in the literature¹⁸.

Potentiometric Apparatus and Procedure

All the potentiometric measurements were performed in a 80 mL jacketed titration cell thermostated at 25.0 ± 0.1 °C under nitrogen atmosphere. The cell potential was measured using an Orion 720 A model pH-ion meter equipped with a combined pH electrode (Ingold). The electrode was modified by replacing the aqueous solution with a solution of 0.01 M NaCl + 0.09 M NaClO₄ saturated with AgCl.

The potentiometric cell was calibrated for the use of the combined pH electrode as a hydrogen concentration probe rather than as an activity probe¹⁹⁻²¹. Reproducible autoprotolysis constants (K_{ap}) were calculated using several series of [H⁺] and [OH⁻] measurements at 0.1 M NaClO₄²²⁻²⁴.

All titrations were performed in a nitrogen atmosphere with carbonate free standard of 0.1 M NaOH and 50 mL solutions of 0.1 M NaClO₄ using (i) 2.5×10^{-3} M HClO₄ for cell calibration and (ii) 3.0×10^{-4} – 2.0×10^{-3} M HClO₄ + 1.5×10^{-3} M aliphatic amine.

The stoichiometric protonation constants of the aliphatic amines were calculated using software called PKAS developed by Motekaitis and Martell^{19,25}.

Results and Discussion

The stoichiometric protonation constants (β) of ammonia and methyl-, ethyl-, n-propyl- and n-butylamines were determined in ethanol-water media of varying solvent compositions (10-80 volume% ethanol) at 25.0 ± 0.1 °C and are tabulated in Table 1. All the values presented in this table are the average of at least five measurements. These values are the equilibrium constants of the reaction $B + H^+ \rightleftharpoons BH^+$, where B and BH⁺ show ammonia and aliphatic alkyl amines and ammonium or alkyl ammonium ions respectively.

Table 1. The stoichiometric protonation constants of the aliphatic alkylamines at $25.0 \pm 0.1^\circ\text{C}$, for different ethanol-water mixtures ($\mu = 0.1 \text{ M NaClO}_4$)

Aliphatic Amines	10% E + 90% W ($x = 0.03$)	20% E + 80% W ($x = 0.07$)	30% E + 70% W ($x = 0.117$)	40% E + 60% W ($x = 0.17$)	50% E + 50% W ($x = 0.24$)	60% E + 40% W ($x = 0.32$)	70% E + 30% W ($x = 0.42$)	80% E + 20% W ($x = 0.55$)
NH ₃	9.03 ± (0.02)	8.92 ± (0.02)	8.82 ± (0.02)	8.71 ± (0.02)	8.51 ± (0.03)	8.43 ± (0.02)	8.25 ± (0.04)	8.07 ± (0.07)
CH ₃ NH ₂	10.20 ± (0.01)	10.25 ± (0.01)	10.08 ± (0.01)	9.90 ± (0.01)	9.76 ± (0.01)	9.59 ± (0.01)	9.40 ± (0.03)	9.15 ± (0.03)
(CH ₃) ₂ NH	10.37 ± (0.05)	10.42 ± (0.01)	10.26 ± (0.01)	10.14 ± (0.01)	9.84 ± (0.01)	9.69 ± (0.01)	9.50 ± (0.05)	9.27 ± (0.02)
(CH ₃) ₃ N	9.50 ± (0.05)	9.48 ± (0.01)	9.31 ± (0.02)	9.18 ± (0.03)	8.84 ± (0.01)	8.55 ± (0.03)	8.26 ± (0.05)	7.97 ± (0.03)
(C ₂ H ₅) ₂ NH ₂	10.27 ± (0.01)	10.35 ± (0.05)	10.21 ± (0.01)	10.07 ± (0.01)	9.74 ± (0.01)	9.60 ± (0.02)	9.38 ± (0.02)	9.20 ± (0.02)
(C ₂ H ₅) ₂ NH	10.67 ± (0.05)	10.67 ± (0.01)	10.50 ± (0.01)	10.38 ± (0.01)	10.12 ± (0.02)	9.79 ± (0.04)	9.53 ± (0.03)	9.32 ± (0.02)
(C ₂ H ₅) ₃ N	10.34 ± (0.05)	10.22 ± (0.02)	10.06 ± (0.01)	9.85 ± (0.02)	9.69 ± (0.01)	9.40 ± (0.03)	9.02 ± (0.02)	8.83 ± (0.03)
n-C ₃ H ₇ NH ₂	10.25 ± (0.05)	10.27 ± (0.05)	10.33 ± (0.01)	9.86 ± (0.01)	9.76 ± (0.01)	9.57 ± (0.02)	9.26 ± (0.03)	8.94 ± (0.01)
(n-C ₃ H ₇) ₂ NH	10.53 ± (0.05)	10.50 ± (0.05)	10.38 ± (0.01)	10.22 ± (0.01)	9.89 ± (0.03)	9.70 ± (0.03)	9.33 ± (0.04)	9.11 ± (0.01)
(n-C ₃ H ₇) ₃ N	10.36 ± (0.05)	10.14 ± (0.05)	9.94 ± (0.05)	9.69 ± (0.01)	9.31 ± (0.01)	9.17 ± (0.03)	8.66 ± (0.04)	8.34 ± (0.01)
n-C ₄ H ₉ NH ₂	10.28 ± (0.05)	10.18 ± (0.05)	9.94 ± (0.05)	9.81 ± (0.01)	9.65 ± (0.02)	9.48 ± (0.01)	9.29 ± (0.03)	9.10 ± (0.01)
(n-C ₄ H ₉) ₂ NH	10.62 ± (0.05)	10.44 ± (0.05)	10.14 ± (0.05)	10.04 ± (0.01)	9.77 ± (0.01)	9.59 ± (0.02)	9.38 ± (0.02)	9.15 ± (0.01)
(n-C ₄ H ₉) ₃ N	10.69 ± (0.05)	9.71 ± (0.05)	9.54 ± (0.05)	9.36 ± (0.01)	9.09 ± (0.01)	8.95 ± (0.04)	8.52 ± (0.02)	8.43 ± (0.01)

x: the mole fraction of ethanol; E: ethanol; W: water

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 the specific effects of substituents on the basicities of aliphatic amines in ethanol-water mixtures.

Solvent effect

The numerical $\log \beta$ values for ammonia and 12 aliphatic amines determined in ethanol-water mixtures decrease with increasing ethanol content in the solvent mixture, an example of which is given in the Figure. It is observed that the relationships are linear over the range of ethanol mole fractions from 0.07 to 0.42 for ammonia and all the aliphatic amines investigated. However, $\log \beta$ values at a mole fraction of ethanol of 0.42 are slightly higher than those expected from the linear trend. The linear equations, the related regression coefficients and the standard deviations are listed in Table 2. This linear variation is very similar to that found for salicylideneanilines, 2-hydroxy-1-naphthalideneanilines and pyridine derivatives^{20,26–28}. Furthermore, similar results were found by De Ligny for primary aliphatic amines in methanol-water mixtures³. Paabo et al.²⁹, Bates^{30–31} and Chattopadhyay and Lahiri² 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 these publications it is suggested that electrostatic charging effects result from changes in the dielectric constant with solvent effects and that solute-solvent interactions have greater significance in the interpretation of solvent effects. Thus, we can explain our results obtained for aliphatic amines by specific solvation effects. Since ethanol would solvate aliphatic amines better than aliphatic ammonium ions, the $\log \beta$ values would decrease upon addition of ethanol. The deviations of linearity in 10% and 80% ethanol may result from the preferential solvation of solute by one of the components of the solvent mixture, which could change the effective dielectric constant value in the azeotropic region³². Furthermore, another factor causing an increase in the $\log \beta$ values of all amines in ethanol rich regions could be differences in solvent stabilisation of the ionic species (H^+ and aliphatic ammonium ions), brought about by changing the mole fraction of ethanol^{30,31}.

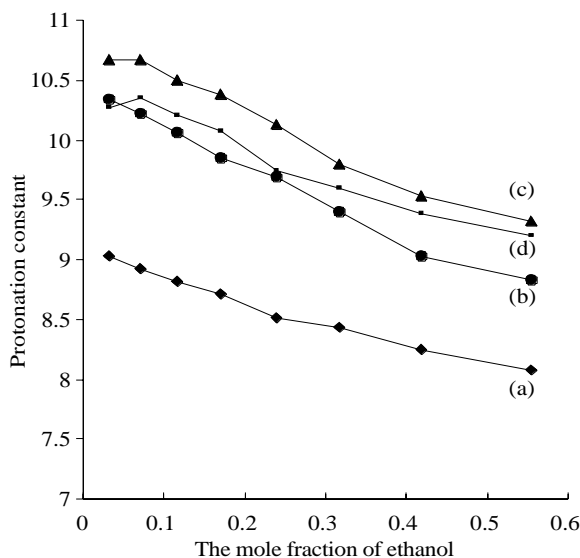


Figure. Plot of $\log \beta$ of ammonia(a), ethylamine (b), diethylamine (c) and triethylamine (d) against the mole fraction of ethanol in ethanol-water mixture.

Table 2. Linear relationships between the $\log \beta$ values of ammonia and aliphatic alkylamines and the mole fraction of ethanol (from 0.07 to 0.42).

Compounds	Equations	r^a	s^b
NH ₃	$\log \beta = 9.04 - 1.94x$	0.992	0.04
CH ₃ NH ₂	$\log \beta = 10.36 - 2.39x$	0.991	0.05
(CH ₃) ₂ NH	$\log \beta = 10.58 - 2.71x$	0.989	0.06
(CH ₃) ₃ N	$\log \beta = 9.74 - 3.62x$	0.996	0.04
C ₂ H ₅ NH ₂	$\log \beta = 10.53 - 2.87x$	0.989	0.06
(C ₂ H ₅) ₂ NH	$\log \beta = 10.91 - 3.36x$	0.997	0.04
(C ₂ H ₅) ₃ N	$\log \beta = 10.46 - 3.40x$	0.998	0.03
n-C ₃ H ₇ NH ₂	$\log \beta = 10.52 - 3.06x$	0.970	0.11
(n-C ₃ H ₇) ₂ NH	$\log \beta = 10.76 - 3.43x$	0.995	0.05
(n-C ₃ H ₇) ₃ N	$\log \beta = 10.41 - 4.18x$	0.994	0.07
n-C ₄ H ₉ NH ₂	$\log \beta = 10.27 - 2.44x$	0.986	0.06
(n-C ₄ H ₉) ₂ NH	$\log \beta = 10.55 - 2.94x$	0.983	0.08
(n-C ₄ H ₉) ₃ N	$\log \beta = 9.93 - 3.32x$	0.996	0.05

^a Regression coefficient^b Standard deviation of the regression line. x : the mole fraction of ethanol

Substituent Effect

Using the protonation constants obtained in this work, the effects of the type and number of alkyl groups on the basicity of the aliphatic amines have been discussed. The most important factor which affects the basicity and therefore the protonation constant of a compound is the structural effect. This effect can be explained by taking the electronic and sterical effects of the alkyl groups investigated into account. Since alkyl groups are electron donating, the replacement of hydrogen atoms in ammonia with alkyl groups is expected to increase the protonation constant. This is why the protonation constant of ammonia is the lowest in all the media investigated. For the very same reason one would have expected the basicity to increase with the increasing number of alkyl groups. However, except in 10% ethanol-80% water medium the basicity was found to change in the order NH₃ < R₃N < RNH₂ < R₂NH (R: -CH₃, -C₂H₅, -n-C₃H₇, -n-C₄H₉). Had there been only electronic effects active then the tertiary amines would have had the highest protonation constants. The steric effect, on the other hand, causes the protonation constants to decrease in contrast to the electronic effect. The above order shows that both of these contrasting effects are operative in alkyl amines. The order is identical with that found for these amines in water³³. In water, there are two main opposing effects influencing the basicities of amines, namely hydration and inductive effects. The hydration effect decreases the basicities of amines with an increase in the number of alkyl substitutions, whereas the inductive effect increases with an increase in the number of alkyl substitutions. The similarity of the orders of basicity in water and ethanol-water mixtures is probably due to the fact that ethanol and water are solvents with similar structures.

The changes in the protonation constants of the alkyl amines with the increasing number of carbon atoms was also investigated, but there was no order of change common to all media employed. This was attributed to the variety of the effects upon basicity and their relative contribution in various media.

In conclusion, the basicity of a compound is a result of various factors such as (i) the solvent effect: solvation power, the tendency to form 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) the structural effect: electronic effect, sterical effect and hydrogen bonding.

References

1. J. Crosby, R. Stone, and G.E. Lienhard, **J. Am. Chem. Soc.**, **92**, 2891, (1970).
2. A.K. Chattopadhyay, and C.S. Lahiri, **Electrochim. Acta**, **27**, 269, (1982).
3. C.L. De Ligny, **Recueil**, **79**, 731, (1960).
4. V. Frenna and N. Vivona, **J. Chem. Soc. Perkin Trans II.**, **12**, 1865, (1985).
5. J.J.P. Furiong, E.S. Lewkowicz and N.S. Nudelman, **J. Chem. Soc. Perkin Trans. II.**, **8**, 1461, (1990).
6. T. Gündüz, N. Gündüz, E. Kılıç, O. Atakol and A. Kenar, **Analyst**, **112**, 1735, (1987).
7. T. Gündüz, N. Gündüz, E. Kılıç, A. Kenar and G. Çetinel, **Analyst**, **111**, 1099, (1986).
8. T. Gündüz, N. Gündüz, E. Kılıç and A. Kenar, **Analyst**, **111**, 1345, (1986).
9. A.D. Headley, **J. Org. Chem.**, **53**, (1988) 312.
10. C.B. Herbert and C. Armo, **J. Am. Chem. Soc.**, **72**, 2939, (1950).
11. A. Kenar, T. Gündüz and E. Kılıç, **Anal. Chim. Acta**, **324**, 57, (1996).
12. R.G. Pearson and D.C. Vogelsong, **J. Am. Chem. Soc.**, **80**, 1038, (1957).
13. A. Reyes and R.M. Scott, **J. Phys. Chem**, **84**, 3600, (1980).
14. D.B. Robabacher, W.J. Mackellar, F.R. Shu and B.M Sister., **Anal. Chem.**, **43**, 561, (1971).
15. G. Velinov and M. Georgieva, **Anal. Chim. Acta.**, **140**, 339, (1982).
16. G. Gran, **Acta. Chem. Scand.**, **4**, 559, (1950).
17. G. Gran, **Analyst**, **77**, 661, (1958).
18. D.D. Perrin and W.L.F. Armerego, **Purification of Laboratory Chemicals**, Pergamon, Elmsford, NY, 1991.
19. A.E. Martell and R.J. Motekaitis, **The Determination and Use of Stability Constants**, VCH, 1988.
20. T. Gündüz, E. Kılıç, F. Köseoğlu and E. Canel, **Anal. Chim. Acta**, **282**, 489, (1993).
21. M. Melaun, J. Havel and E. Hogfeldt, **Computation of Solution Equilibria**, Ellis Harwood Limited, John Wiley and Sons, 1988.
22. E.P. Serjenat, **Potentiometry and Potentiometric Titrations**, John. Wiley and Sons, 1984.
23. E.M. Wolley, D.G. Hurkot and L.G. Hepler, **J. Phys. Chem.** **74**, 3908, (1970).
24. S. Rondinini, P. Longhi, P.R. Mussing and T. Mussini, **Pure Appl. Chem.**, **59**, 1963, (1987).
25. R.J. Motekaitis and A.E. Martell, **Can. J. Chem.**, **60**, 168, (1982).
26. E. Kılıç, F. Köseoğlu and Ö. Başgut, **Anal. Chim. Acta**, **294**, 215, (1994).
27. F. Köseoğlu, E. Kılıç, E. Canel and N. Yılmaz, **Anal. Chim. Acta**, **293**, 87, (1994).
28. F. Köseoğlu, E. Kılıç, and D. Uysal, **Talanta**, **42**, 1875, (1995).
29. M. Paabo, R.G. Bates and R.A. Robinson, **J. Phys. Chem.**, **70**, 247, (1965).

30. R.G. Bates, **J. Electroanal. Chem.**, **29**, 1, (1971).
31. R.G. Bates, **Determination of pH, Theory and Practice**, Wiley, New York, 2nd edn, 1973.
32. N.S. Isaacs, **Physical Organic Chemistry**, Longman, New York, 1986.
33. H.C. Brown, **J. Am. Chem. Soc.**, **67**, 374-378, (1945).