

Autoprotolysis constants determination of water-methanol mixtures and solvent effect

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Abstract

The autoprotolysis constants (pK_{ap}) of water-methanol mixtures were determined at 25°C over the composition range of 0 to 90 vol. % methanol using potentiometric method with a glass electrode. The electromotive forces (emf) values and titration data of both acidic and basic range for all mixtures were obtained by combined pH electrode that its aqueous KCl solution was replaced with 1M KCl in appropriate mixed solvent saturated with AgCl. In all titrations the ionic strength of each mixture was maintained at 0.1M by appropriate concentration of NaClO₄ solution. The pK_{ap} values were calculated by titration data for each medium studied at 25°C and under nitrogen atmosphere. The solvent effect and variation of solvent composition on pK_{ap} values was perused by different methods.

Keywords: *water-methanol mixture solvent; autoprotolysis constant; solvent effect.*

1. Introduction

The mixed aqueous organic solvents such as water-methanol mixtures are widely used in different area of chemistry such as evaluation of acidity constants of poor solubility and drug substances [1,2]. Some of non-aqueous and mixed aqueous organic solvents have a larger pH scale and a better ability to dissolve more compounds than water. Therefore, they are utilized as reaction media for a variety of organic and analytical processes such as synthesis, titrations or liquid chromatographic separations [3]. The application of mixed aqueous organic solvents in physicochemical investigations needs an understanding of the autoprotolysis constants that indicate the conditions for acids-base titrations to a great extent so that these constants determine the length of the pH scale of mixed solvent [3]. So the importance of the autoprotolysis constant has been previously described on the criteria for standardization of pH measurements in organic solvents and aqueous organic solvent mixtures [4].

Potentiometry is a useful and reliable method to determine autoprotolysis constant of different solvents. The International Union of Pure and Applied Chemistry (IUPAC) have proposed a method to determine autoprotolysis constant in organic solvents of high permittivity and in water-organic solvent mixtures [5]. This method can give reliable pK_{ap} values in amphiprotic organic solvents and water-organic solvent mixtures. One of the methods is to prepare the solution of a strong acid and that of a strong base and measure the potentials of the pH sensor in the two solutions. Then, pK_{ap} can be obtained approximately from the potential difference between the two solutions. This method has been used to determine pK_{ap} in some aprotic solvents [6]. Another method of

obtaining autoprotolysis constant is an indirect method that uses the relation $K_{ap} = K_a \times K_b$, where K_a is the dissociation constant of a monoprotic acid and K_b is that of its conjugate base. The dissociation constant of an acid and conjugate base is determined independently by such methods as spectrophotometry, conductimetry and potentiometry [7]. In this study, determination of autoprotolysis constant water-methanol mixtures is performed using combined glass electrode. Present potentiometric technique is convenient and reliable method for determination of pK_{ap} in extensive range of aqueous organic mixture solvents.

The influence of solvent on physicochemical properties has been intensively studied but the problem is yet far from being completely understood. There are two more important approaches to the quantitative description of this effect. The theoretical approach describes the solvent as an isotropic environment of dissolved particles and characterizes it by its bulk properties. Unfortunately, this approach involves only the influence of the nonspecific interactions. The other approach is based on the description of the solvent effect by suitably chosen empirical parameters measuring specific and nonspecific interactions [8-11]. Macroscopic parameters of media such as dielectric constant (ϵ_r) and microscopic solvatochromic parameters α , β and π^* have extensively used for explanation of solvent effects. The solvent dielectric constant is often predicted to serve as a quantitative measure of solvent polarity that imposed solvents as a continuum media with non-structure isotropic system. Since solvents do not compose of individual solvent molecule with their own solvent-solvent interaction therefore, dielectric constant of media is inadequate for describing solvent effect. However any methods to

analyze solvent effect have to take into account specific solute-solvent interactions such as hydrogen-bonding interactions which often play dominant role in solute-solvent interactions. Usually, the functional relationships between solvent parameters and various solvent-dependent processes take the form of a linear Gibbs energy relationship that take into account empirical parameters of solvents such as α , β and π^* [12]. Therefore three parameters are measured from spectroscopy analyzing of the maximum absorption of an prob. α , β and π^* are the Kamlet-Taft solvatochromic parameters that indicate hydrogen bond donor acidity, hydrogen bond acceptor basicity and dipolarity-polarizability property of solvents respectively [12,13].

The aim of this study is determination of autoprotolysis constant in different water-methanol mixture solvents by potentiometric method and explanation the influence of macroscopic and microscopic solvent properties on it.

2. Materials & Methods

Methanol was purchased from Merck and was purified as described in literature [14]. Stock solutions of NaOH and HCl were prepared from titrisol solution (Merck) and its concentration was determined by several titrations. The water used was double-distilled water with conductivity equal to $1.3 \pm 0.1 \mu\Omega^{-1} \text{ cm}^{-1}$. Sodium perchlorate was supplied from Merck Company as analytical reagent grade materials and was used without further purification. Working solutions of HCl and NaOH were prepared in water-methanol mixtures. All mixtures were prepared by volume and concentrations of HCl and NaOH in these were 0.01 M and 0.1 M respectively. Potentiometric measurements carried out in a double-walled thermostated reaction vessel at 25 °C and ionic

strength of mixtures was maintained to 0.1 M with sodium perchlorate. A Jenway research potentiometer, model 3520, with a combined pH electrode was used for e.m.f measurement in potentiometric titrations of acidic solution mixtures.

For each experiment, into double-walled reaction vessel, 2 ml of stock solution of hydrochloric acid, required amount of methanol and sodium perchlorate was diluted with double-distilled water to 20 ml. The vessel solution was titrated with small addition of the sodium hydroxide solution with same proportion of methanol and the same ionic strength. E.m.f readings of solution were taken after every addition of titrant when stabilization of solution potential was achieved. This stabilization criterion was 0.2 mV within at least 2 min. E.m.f data versus added volume of titrant in both acidic and basic region of titration were used for the determination of autoprotolysis constant of water-methanol mixtures.

3. Results & Discussion

The ionization process in mixed solvent such as water-methanol mixture can be presented by



In equation (1), RH_2^+ and R^- are solvated proton and lyate ion in mixed solvent respectively. Therefore the conditional or stoichiometric autoprotolysis constant of water-methanol mixture obtained from potentiometric titration will be as equation (2)

$$K_{\text{ap}} = [\text{RH}_2^+][\text{R}^-] \quad (2)$$

Here K_{ap} , $[RH_2^+]$ and $[R^-]$ are the stoichiometric autoprotolysis constant, the concentration of solvated proton and the concentration of lyate ion, respectively. In potentiometric determination of the stoichiometric autoprotolysis constant, the titration curve can be divided into two acidic and basic regions. At acidic region, the solution potential is given by following equation at 25°C.

$$E = E^{\circ}_{acidic} - 59.16 \log \gamma_{RH_2^+} - 59.16 \log [RH_2^+] \quad (3)$$

Where E°_{acidic} is the specific constant of the potentiometric cell in the acidic range that involving the standard potential of the glass and reference electrodes and liquid junction potential. γ_{H^+} is activity coefficient of solvated proton in solution. Under constant ionic strength of solution throughout titration process, activity coefficient of solvated proton will be invariable. So equation (3) can be expressed by

$$E = E^{\circ}_{acidic} - 59.16 \log [RH_2^+] \quad (4)$$

In every titration point, value of $[RH_2^+]$ can be calculated from known total analytical concentration of hydrochloric acid in vessel solution and known total analytical concentration of added sodium hydroxide solution. Therefore in acidic region of titration curve, concentration of solvated proton can be expressed by

$$[RH_2^+] = (A \cdot V_0 - B \cdot V) / (V_0 + V) \quad (5)$$

Where A and B are initial concentration of hydrochloric acid and sodium hydroxide in reaction vessel and titrant solutions respectively. So V_0 and V are initial vessel solution and volume of the titrant added in every titration point

respectively. Inserting equation (5) into equation (4), it follows that

$$E = E^{\circ}_{acidic} - 59.16 \log [(A \cdot V_0 - B \cdot V) / (V_0 + V)] \quad (6)$$

Therefore E°_{acidic} can be easily calculated from measured e.m.f and concentration of solvated proton in every titration point of acidic region by using linear regression.

In basic region of titration, eliminating $[RH_2^+]$, taking into account equation (2), the function for e.m.f takes the form

$$E = E^{\circ}_{basic} + 59.16 \log [R^-] \quad (7)$$

Where E°_{basic} is the specific constant of the potentiometric cell in the basic range that including standard potential of the glass electrode, standard potential of the reference electrode, liquid junction potential and the activity coefficients. Similar to acidic region, value of $[R^-]$ can be calculated from known total analytical concentration of hydrochloric acid in vessel solution and known total analytical concentration of added sodium hydroxide solution. So concentration of lyate ion can be expressed in every titration point by

$$[R^-] = (B \cdot V - A \cdot V_0) / (V_0 + V) \quad (8)$$

Therefore in basic region, potential of the cell follows that

$$E = E^{\circ}_{basic} + 59.16 \log [(B \cdot V - A \cdot V_0) / (V_0 + V)] \quad (9)$$

Considering equation (9), E°_{basic} can be simply calculated from measured e.m.f and concentration of lyate ion in every titration point of basic region by using linear regression. At the end, the stoichiometric auto-protolysis constant of water-methanol mixtures can be obtained at 25 °C by means of the known relation [15].

$$pK_{ap} = (E'_{\text{basic}} - E'_{\text{acidic}})/59.16 \quad (10)$$

The autoprotolysis constant values of water-methanol mixtures involving 0 to 90 vol. % methanols, expressed in log unit, are collected in table 1. Relationships between pK_{ap} of water-methanol solution mixtures and different physicochemical properties of the solvent (Kamlet-Taft's solvatochromic parameters and $1/\epsilon_r$) were investigated. Therefore the Kamlet-Taft α , β and π^* for methanol-water mixtures over the entire range of methanol concentration were calculated with procedure used in previous work by equation 11 [11].

$$P_{\text{mixture}} = P_{\text{MeOH}}\Phi_{\text{MeOH}} + P_{\text{H}_2\text{O}}\Phi_{\text{H}_2\text{O}} \quad (11)$$

Where P is the property of interest and Φ is the volume fraction of the component in the solution. The calculated values of solvatochromic parameters used for different aqueous mixtures of methanol are listed in Table 1. The pK_{ap} values were plotted versus the reciprocal of the dielectric constant of solvent mixture in Fig. 1. As the Fig. 1 shows, a linear relationship with correlation

coefficients more than 0.97 is observed

$$pK_{ap} = 12.74 + 82.77(1/\epsilon_r) \quad (12)$$

But plot of pK_{ap} against Kamlet-Taft parameters show linearity only for α and π^* (figs. 2 and 3) in the range from 0-60 % (V/V) of methanol and no linearity obtained for β parameter. These linearity plot for α and π^* parameters with correlation coefficients 0.95 and 0.96 respectively can be expressed by

$$pK_{ap} = 18.13 - 3.69(\alpha) \quad (13)$$

$$pK_{ap} = 15.37 - 1.43(\pi^*) \quad (14)$$

Analysis of the fig. 1 or equation 12 shows pK_{ap} of mixture solvent decreases with increasing methanol concentration. The linearity of plot indicates that electrostatic interaction in dielectric constant form is more important than Kamlet-Taft parameters for elucidation of solvent effect over the whole range of this experimental solvent composition. Therefore equation 12 can be effectively used to calculate pK_{ap} value of any water-methanol mixture in the experimental range of 0-90 % (V/V) methanol.

Table 1. pK_{ap} , Kamlet-Taft's solvatochromic parameters and the dielectric constants of different water-methanol solution mixtures in 25°C.

methanol % (V/V)	mole fraction of methanol	pK_{ap}	ϵ_r^a	α	β	π^*
0.00	0.00	13.76	78.60	1.17 ^b	0.47 ^b	1.09 ^b
10.00	0.05	13.92	74.83	1.15	0.49	1.04
20.00	0.10	13.99	70.86	1.13	0.51	0.99
30.00	0.16	14.03	66.67	1.11	0.53	0.94
40.00	0.23	14.07	62.26	1.09	0.55	0.89
50.00	0.31	14.13	57.60	1.08	0.57	0.85
60.00	0.40	14.24	52.70	1.06	0.58	0.80
70.00	0.51	14.42	47.54	1.04	0.60	0.75
80.00	0.64	14.68	42.15	1.02	0.62	0.70
90.00	0.80	15.11	36.66	1.00	0.64	0.65
100.00	1.00		32.66	0.98 ^b	0.66 ^b	0.6 ^b

^{a, b} The values α , β , π^* and ϵ_r have been obtained from ref [16] and [17] respectively.

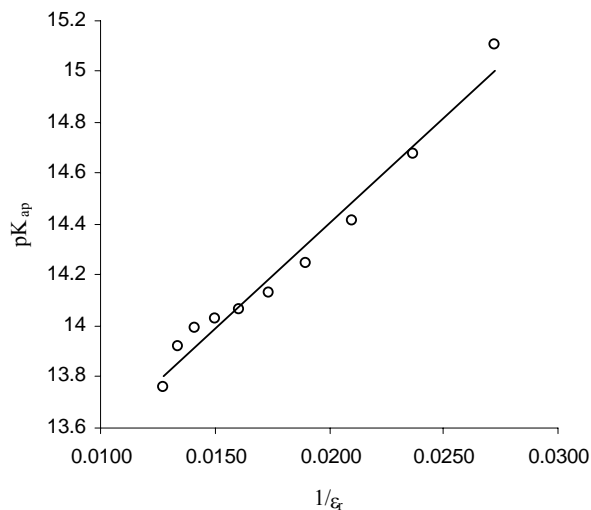


Fig. 1. Plots of the experimental values of pK_{ap} versus the reciprocal of dielectric constant of different mixed solvents.

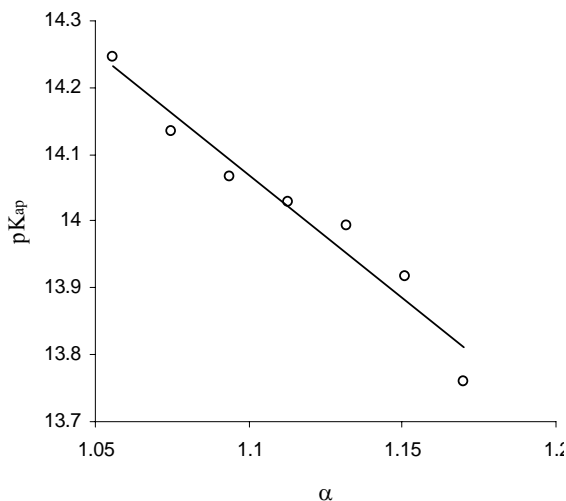


Fig. 2. Plots of the experimental values of pK_a versus the Kamlet-Taft α parameter of different mixed solvents.

with addition of methanol content. The autoprotolysis constant of water-methanol mixture solution is linearity dependent to the reverse of the dielectric constant of solution media. Therefore macroscopic property of a solvent such as dielectric constant is sufficient to describe the solvent effect on autoprotolysis constant in water-methanol mixtures.

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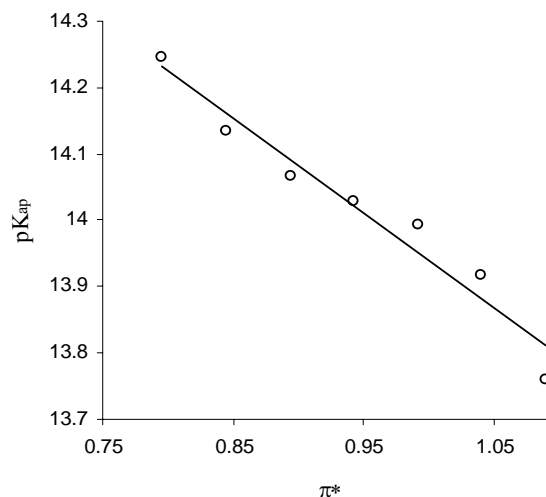


Fig. 3. Plots of the experimental values of pK_{ap} versus the Kamlet-Taft π^* parameter of different mixed solvents.

4. Conclusions

The use of the combined glass electrode is appropriate instrument for potentiometric determination of autoprotolysis constant in water-methanol co-solvents. Increase of pK_{ap} value of media indicates pH scale range of media increases

References

- [1] Benet, L.Z., Goyan, J.E. (1967). *J. Pharm. Soc.* **56**: 665-680.
- [2] Albert, A. and Serjeant, E.P. (1984). *The Determination of Ionization Constants*. Chapman and Hall, London.
- [3] Serjeant, E.P. (1984). *Potentiometry and Potentiometric Titrations*. Wiley, New York.
- [4] Mussini, T., Covington, A.K., Longhi, P. and Rondinini, S. (1985). *Pure Appl. Chem.* **57**: 865-876.
- [5] Rondinini, S., Longhi, P., Mussini, P.R. and Mussini, T. (1987). *Pure Appl. Chem.* **59**: 1693-1702.
- [6] Izutsu, K. (1990). *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*. IUPAC Chemical Data Series No. 35. Blackwell Scientific Publications, Oxford.
- [7] Izutsu, K. (2002). *Electrochemistry in Nonaqueous Solutions*. Wiley, New York.
- [8] Gharib, F., Zare, K. and Mohammadi, B. (2006). *J. Mol. Liq.* **124**: 63-67.
- [9] Gharib, F. (2005). *J. Chem. Eng. Data.* **50**: 196-200.
- [10] Gharib, F., Sadeghi, F. (2007). *Appl. Organomet. Chem.* **21**: 218-225.
- [11] Gharib, F., Jabbari, M., Farajtabar, A. and Shamel A. (2008) *J. Chem. Eng. Data.*, in Press. doi: 10.1021/je800106j.
- [12] Reichardt, C. (2003). *Solvents and Solvent Effects in Organic Chemistry*. 3rd edn. Wiley, Weinheim.
- [13] Kamlet, M.J., Abboud, J.L.M., Abraham, M.H. and Taft, R.W. (1983). *J. Org. Chem.* **48**: 2877-2887.
- [14] Perrin, D.D., Armarego, W.L.F. and Perrin, D.R. (1991). *Purification of Laboratory Chemicals*. Pergamon Press, Oxford.
- [15] Tencheva, J., Velinov, G. and Budevsky, O. (1976). *J. Electroanal. Chem.* **68**: 65-74.
- [16] Akerlof, G. (1932). *J. Am. Chem. Soc.* **54**: 4125-4139.
- [17] Moyano, F., Biasutti, M.A., Silber, J.J. and Correa N.M. (2006). *J. Phys. Chem. B.* **110**: 11838-11846.