European Online Journal of Natural and Social Sciences 2013; vol.2, No.1, pp.140-145 ISSN 1805-3602 www.european-science.com

Calculation of autoprotolysis constants and solvent effect using AB Initio method for water-ethanol mixture

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Received for publication: 20 February 2013.
Accepted for publication: 19 March 2013.

Abstract

The autoprotolysis constants (pK_{ap}) of water-ethanol mixtures containing 10-90 % v/v of ethanol have been measured at 298.15 K using ab initio and density functional theory (DFT) methods. Basis sets at the B3LYP/6-31+G(d) level of theory were used for calculations. These data show that water-ethanol mixtures are more basic media than pure water and the pK_{ap} value of this media increases with addition of ethanol. The effect of the dielectric constant of investigated mixture solvent on the autoprotolysis constant was described employing Yasuda-Shedlovsky procedure.

Keywords: Autoprotolysis constant, water-ethanol mixture, DFT method, solvent effect.

Introduction

Mixtures of water with alcohols are important in several engineering and industrial application. For example water-ethanol mixture is widely used in cosmetics, hairsprays, window cleaners, deicers and certain pharmaceutical preparations. Most people have experienced skin contact with alcoholic solutions (Koohyar *et al.*, 2012). The accessibility and diversity of these reaction media is strongly increased from the combination of pure water and alcohol solvents in binary mixtures. Among the thermodynamics properties of solvent, autoprotolysis constant (pK_{ap}) is one of the most important properties and knowledge of this parameter is considered as fundamental concept in application of the solvent. The pK_{ap} value of solvent indicates the range of pH of media and its importance for standardization of pH measurements have been described for both organic solvents and aqueous organic solvent mixtures (Serjeant, 1984; Mussini *et al.*, 1985). The autoprotolysis constant is an especially important criterion for the solvent selection, since determines the acidic or basic region available in the solvent used. The smaller the autoprotolysis constant, the greater the range of acid or base strengths that can exist in a solvent and the greater the likelihood that it will be a differentiating solvent. Hence, acid-base titrations are best carried out in solvents with small autoprotolysis constant values.

Different methods were employed for the determination of pK_{ap}. Among them, potentiometric titration is accurate method for measuring autoprotolysis constant (Serjeant. 1984; Izutsu, 1990; Rondinini *et al.*, 1987; Izutsu, 2002). On the other hand, during the last two decades there has been much interest in developing a methodology enabling theoretical prediction of pK values, employing various quantum theoretical techniques. As pK_a equals $\Delta G/2.303\ RT$, where ΔG is a free energy change of the reaction either in a gas or solution, autoprotolysis constant of a solvent can be determined by the ΔG value (Kiani *et al.*, 2010). Therefore, in this study pK_{ap} has been calculated using ab initio and density functional theory (DFT) method and compared with constants experimentally determined by potentiometric.

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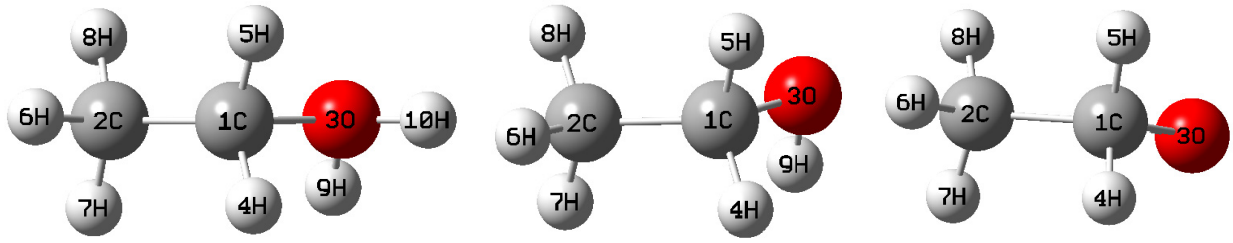
In mixtures of water and a miscible organic solvent such as ethanol, the dielectric constant of mixed solvent changes considerably with the proportion of ethanol (Akerlof, 1932). In respect to electrostatic interactions, the influence of dielectric constant of solvent can be used for elucidation of solvent composition effect on chemical equilibrium such as autoprotolysis constant.

The objective of this study is the determination of autoprotolysis constant of different water-ethanol mixtures involving 10-90 volume percent of ethanol using DFT method. Relationship between the calculated autoprotolysis constants with experimental autoprotolysis constants and dielectric constant of mixtures, over the whole experimental range studied, were examined and Yasuda-Shedlovsky plot (Yasuda, 1959; Shedlovsky, 1962) was used to correlate these parameters.

Materials and methods

Figure 1 shows the structures of ethanol cation, neutral molecule, anion and the practical numbering system adopted for performing the calculations. The initial geometries of the molecules by the semi empirical PM3 method are included in program CS Chem3D version 5.0 (Program CS Chem3D 5.0, (2000).



$C_2H_5OH_2^+$ C_2H_5OH $C_2H_5O^-$

Figure 1. Optimized Structures of $C_2H_5OH_2^+$, C_2H_5OH, $C_2H_5O^-$ for carrying out the calculations.

These geometries were optimized with the GAUSSIAN 98 program package using the B3LYP/6-31+G(d) method and the default convergence criteria (Frisch *et al.*, 1998). To analyze the solvent effects on all the specimens involved in the selected ionization reaction, the polarized continuum model (PCM) of Tomasi *et al.* was used (Miertus and Tomasi, 1982). Furthermore, to shed light on the experimental pK_{aq} values of ethanol in water, the different spicies molecular were tested by the program. All of the mentioned calculations were accomplished at different mixtures containing 10-90 % v/v of ethanol to calculate the autoprotolysis constants of ethanol in water (Table 1).

Table 1. Calculated total energy using the Tomasi's method at the B3LYP/6-31+G(d) level of theory for cationic, neutral and anionic specimen of ethanol, at 298.15 K.

Solvated Specimen	G°sol/molecule (kJ.mol^{-1})	Solvated Specimen	G°sol/molecule (kJ.mol^{-1})
$C_2H_5OH_2^+$	-4.07×10^5	H_3O^+	-2.01×10^5
C_2H_5OH	-4.06×10^5	H_2O	-2.00×10^5
$C_2H_5O^-$	-4.05×10^5	OH^-	-1.99×10^5

G°sol: total free energy in solution; G°sol/molecule: total energy of solvated specimen per water molecule.

Results and discussion

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

$$RH + RH \leftrightarrow RH_2^+ + R^- \quad (1)$$

In equation (1), RH_2^+ and R^- are solvated proton and produces ions of solvent respectively.

Therefore the conditional or stoichiometric autoprotolysis constant of water-ethanol mixture will be according to equation (2):

$$K_{ap} = [RH_2^+][R^-] \quad (2)$$

Kap, $[RH_2^+]$ and $[R^-]$ are the stoichiometric autoprotolysis constant, the concentration of solvated proton and the concentration of lyate ion, respectively. The autoprotolysis constant, can be divided into two acidic and basic regions. In acidic region, the porotonation constant at 298.15 K is given by following equation:

$$RH(aq) + H_3O^+(aq) \leftrightarrow RH_2^+(aq) + H_2O(L) \quad K_1 \quad (3)$$

In basic region of titration, by eliminating $[RH_2^+]$, and taking into account equation (2), the function for protonation constant takes the form of:

$$RH(aq) + OH^-(aq) \leftrightarrow R^-(aq) + H_2O(L) \quad K_2 \quad (4)$$

Besides the water also takes place:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad K_w \quad (5)$$

At 298.15 K, $K_w = 1.008 \times 10^{-14}$, shows that only a few of the water molecules are ionized (Atkins. 1998).

By combining Eqs. (3), (4) and (5) we obtain the reaction of Eq. (1), which defines autoprotolysis constant of ethanol (K_{ap}). It is evident that the constants K_1, K_2, K_w and K_{ap} are related by the Eq.

The calculated values using the Tomasi's method at the B3LYP/6-31+G(d) level of theory and experimental autoprotolysis constants values of water-ethanol mixtures involving 0 to 90 volume percent of ethanol, expressed in log unit, are summurized in Table 2 and plotted versus volume percentage of ethanol in Figure 2.

Relationships between pK_{ap} experimental of water-ethanol solutions and dielectric constant (ε_r) of the solvent were investigated using Yasuda-Shedlovsky approach (Akerlof, 1932; Yasuda, 1959). Yasuda-Shedlovsky approach is extrapolation method based on Born equation (Born, 1920) and Bjerrum's theory (Bjerrum and Larsson, 1927) of ion salvation. This extrapolation method was successfully used to determine the aqueous dissociation constant of low miscible compounds in water where the success of potentiometric method to direct determination of aqueous pK_a is sometimes dubitable by poor aqueous solubility (Avdeef *et al.*, 1999).

Considering this technique, the plot of pK + log $[H_2O]$ against A + B/ε_r leads to a straight line where empirical parameters A and B are the intercept and the slope of the plot respectively.

In present work, dielectric constant values for different aqueous mixtures of ethanol (Kiani *et al.*, 2010) are shown in Table 2.

Table 2. Autoprotolysis constants and the dielectric constants of different water-ethanol solution mixtures in 298.15 K.

ethanol %(v/v)	mole fraction of ethanol	pK_{ap} (exp) [18]	pK_{ap} (cal)	[a]ε_r	±γ	α	Ref.
0	0.00	13.78		78.56			This work
10	0.03	14.02	14.03	73.95	0.93	4.46E-08	
20	0.07	14.21	14.10	69.05	0.88	2.11E-08	
30	0.12	14.35	14.18	63.85	0.82	1.31E-08	
40	0.17	14.50	14.25	58.36	0.75	9.22E-09	
50	0.24	14.65	14.34	52.62	0.70	6.79E-09	
60	0.32	14.87	14.44	46.71	0.61	5.18E-09	
70	0.42	15.23	14.55	40.73	0.46	4.02E-09	
80	0.55	15.86	14.67	34.84	0.25	3.13E-09	
90	0.74	16.62	14.82	29.19	0.13	2.40E-09	
100	1.00		14.99	24.55			

[a] The values of ε_r were obtained from Akerlof, 1932.

The pK_{ap} + log $[H_2O]$ values were plotted against the reciprocal of the dielectric constant of solvent mixture in Figure 3. As the Figure 3 shows, a linear relationship with correlation coefficients of more than 0.98 is observed (Faraji *et al.*, 2009).

$$pK_{ap}(exp) + \log [H_2O] = (14.635 \pm 0.08) + (78.183 \pm \pm 3.78) \times (1/\varepsilon_r) \quad (6)$$

$$pK_{ap}(cal) = (13.645 \pm 0.05) + (34.516 \pm 1.91) \times (1/\varepsilon_r)$$

Analysis of the equation 6 shows that the pK_{ap} of mixture solvent decreases with increasing ethanol concentration. The linearity of the relationship indicates that the electrostatic interaction in dielectric constant form is an important parameter for elucidation of solvent effect over the whole range of this experimental solvent composition.

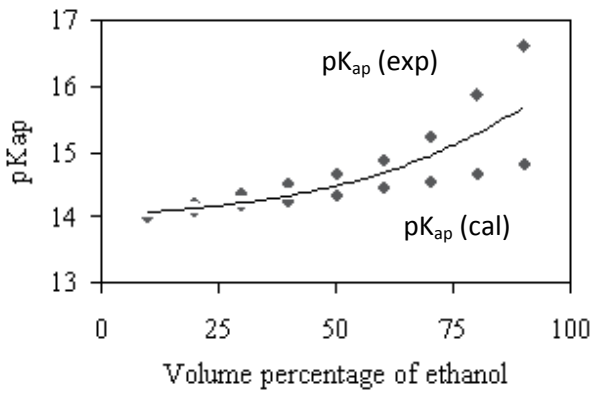


Figure 2. Illustration of the calculated and experimental values of pK_{ap} versus the volume percentage of ethanol in different mixed solvents.

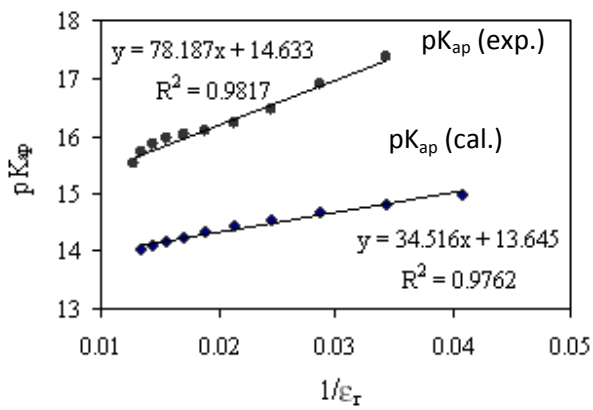


Figure 3. Illustration of pK_{ap} + log $[H_2O]$ values versus the reciprocal of the dielectric constant in different mixed solvents.

Conclusions

In this paper, the autoprotolysis constants of media in different water-ethanol mixture were measured using ab initio and density functional theory (DFT) methods. The calculations performed at the B3LYP/6-31+G(d) levels of theory using Tomasi's method. The autoprotolysis constants theoretically show a suitable agreement with the autoprotolysis constants experimentally determined by potentiometric (Figure 4).

The regression lines are also used for comparing of different methods. Each point on the graph represents a single sample analyzed by two separate methods. Obviously, if each sample yields an identical result with both methods, the regression line will have zero intercept and a slope and a correlation coefficient of one. In practice, of course, this never occurs even if systematic and maybe random errors are entirely absent. In practice, the analyst most commonly wishes to test for an intercept differing significantly from zero, and for a slope from one. Such tests are performed by determining the confidence limits for slope and intercept, generally at the 95% significant level (Miller and Miller, 1988). According to Figure (4a) for pK_{ap}, the regression calculated results are as follows:

$$y = 9.2341 + 0.3462x$$

Further calculations show that:

$$S_r = 0.05,\ S_\alpha = 0.54,\ S_\beta = 0.04$$

Where S_r, S_α and S_β are standard deviation regression, intercept and slope respectively.

The appropriate t-value for 6 degrees of freedom is 1.94. It gives 95% confidence limits for the intercept and slope as:

$$\alpha = 9.2341 \pm 1.94 \times 0.54 = 9.2341 \pm 1.0476$$
$$\beta = 0.3462 \pm 1.94 \times 0.04 = 0.3462 \pm 0.0776$$

Since these 95% confidence intervals clearly include one and zero respectively, thus we must conclude that the regression line indicates good agreement between the experimental and calculated methods. For pK_{ap} that is shown in Figure (4b) the regression calculations are as follows with the same results.

$$\alpha = (4.76 \times 10^{-15}) \pm (1.89 \times 7.92 \times 10^{-16}) = (4.76 \times \times 10^{-15}) \pm (14.97 \times 10^{-16})$$
$$\beta = 0.00 \pm 1.89 \times 0.00 = 0.00$$

However, the differences are mostly due to the different techniques, various ionic strengths with different background electrolytes. We conclude

that this fact constitutes a strong support for the reactions and equilibria of ionization in aqueous medium selected in this work.

These results indicate that pK_{ap} of media increase as the percentage of ethanol increased. When Yasuda-Shedlovsky plot was used, significant linear relationship between pK_{ap} and dielectric constant of solvents was reached. Therefore for each water-ethanol mixture in the experimental range of 0-90 volume percentage of ethanol, the derived equation 6 can be effectively used to calculate pK_{ap} values.

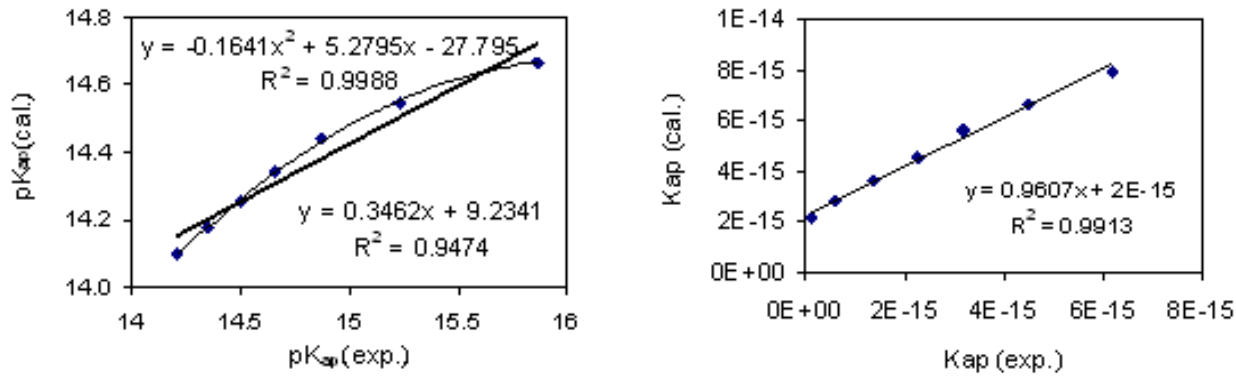


Figure 4. Comparison of calculated and experimental autoprotolysis constants in different mixed solvents.

Acknowledgements

The authors gratefully acknowledge the financial support form the Research Council of Islamic Azad University, Ayatollah Amoli Branch.

References

Akerlof G., 1932. Dielectric constants of some organic solvent-water mixtures at various temperatures. J. Am. Chem. Soc. 54:4125-4139.

Atkins P.W., 1998. Physical Chemistry, 6th ed., Oxford University Press, UK.

Avdeef A., Box K.J., Comer J.E.A., Gilges M., Hadley M., Hibbert C., Patterson W., Tom K.Y., 1999. PH-metric log P 11. pKa determination of water-insoluble drugs in organic solvent–water mixtures. J. Pharm. Biomed. Anal. 20:631-641.

Bjerrum N., Larsson E., 1927. Calculated the distribution coefficients of a number of ions. Z. Phys. 127:358-384.

Born M., 1920. Volumen und Hydratationswärme der Ionen., Z. Phys. 1:45-48.

Faraji M., Farajtabar A., Gharib F., 2009. Determination of water-ethanol mixtures autoprotolysis constants and solvent effect. J. Appl. Chem. Res. 9:7-12.

Frisch M. J. et al., 1998. Gaussian 98, Revision A.6, Gaussian, Inc.: Pittsburgh, PA.

Izutsu K., 1990. Acid-base dissociation constants in dipolar aprotic solvents, IUPAC chemical data series No. 35. Blackwell Scientific Publications, Oxford, UK.

Izutsu K., 2002. Electrochemistry in Nonaqueous Solutions, Wiley, New York.

Kiani F., Rostami A.A., Sharifi S., Bahadori A., Chaichi M.J., 2010. Determination of acidic dissociation constants of glycine, valine, phenylalanine, glycylvaline, and glycylphenylalanine in water using ab Initio Methods. J. Chem. Eng. Data. 55: 2732-2740.

Koohyar F., Kiani F., Sharifi S., Sharifirad M., Rahmanpour S.H., 2012. Study on change on refractive index on mixing, excess molar volume and viscosity deviation for aqueous solution of methanol, ethanol, ethylene glycol, 1-propanol and 1,2,3-propantriol at T = 292.15 K and atmospheric pressure. Res. J. Appl. Sci. Eng & Technol. 4(17): 3095-3601.

Miertus S., Tomasi E., 1982. Approximate evaluations of the electrostatic free energy and internal energy changes in solution processes. Chem. Phys. 65: 239-245.

Miller J.C., Miller J.N., 1988. Statistics for analytical chemistry. Ellis Horwood, New York, USA.

Mussini T., Covington A.K., Longhi P., Rondinini S., 198). Criteria for standardization of pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivities. Pure & Appl. Chem. 57: 865-876.

Program CS Chem3D 5.0, 2000. Program for Molecular Modeling and Analysis, Cambridge Soft Corporation: MA, USA.

Rondinini S., Longhi P., Mussini P.R., Mussini T., 1987. Autoprotolysis constants in nonaqueous solvents and aqueous organic solvent mixtures. Pure & Appl. Chem. 59: 1693-1702.

Serjeant E.P., 1984. Potentiometry and Potentiometric Titrations, Wiley, New York, USA.

Shedlovsky T., 1962. In: B. Pesce (Ed.), Electrolytes, Pergamon, New York, USA.

Yasuda M., 1959. Dissociation constants of some carboxylic acids in mixed aqueous solvents. Bull. Chem. Soc. Japan. 32: 429-432.