Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 78 (10) 1561–1567 (2013)
JSCS–4518

UDC 541.138+543.554:54–145.2+
547.261+546.33'131
Original scientific paper

Autoprotolysis in water/methanol/NaCl ternary systems

ALI FARAJTABAR[1]*, FERESHTEH NADERI[2] and FARROKH GHARIB[3]

[1]*Young Researchers Club, Jouybar Branch, Islamic Azad University, Jouybar, Iran,*
[2]*Department of Chemistry, Shahr-e-Qods branch, Islamic Azad University, Tehran, Iran and*
[3]*Chemistry Department, Faculty of Sciences, Shahid Beheshti University, Tehran, Evin, Iran*

(Received 4 January, revised 10 March 2013)

Abstract: A potentiometric method was used to determine the autoprotolysis constant for aqueous solutions containing 0, 20 and 40 mass % of methanol over a wide range of NaCl concentrations at 25 °C. The ionic strength ranged between 0.25 and 2.00 mol L^{-1} at intervals of 0.25 units. The osmotic and activity coefficients of the mixed solvents were calculated as a function of ionic strength. The dependence on ionic strength was analyzed using the original specific ion interaction theory. The specific ion interaction parameters associated with the thermodynamic autoprotolysis constant were extracted. Results indicate that interaction between ions increases with increasing methanol content in the mixture.

Keywords: autoprotolysis; water–methanol; sodium chloride; specific ion interaction theory.

INTRODUCTION

Mixed solvent electrolyte systems, especially water/organic/salt mixtures, frequently occur in wide variety of chemical industries, such as supercritical technologies, environmental applications, production of energy sources and separation, electrochemical and hydrometallurgical processes.[1] A comprehensive knowledge of the physicochemical properties of mixed solvents is mandatory for the development of modeling a successful process in the chemical industry. The autoprotolysis constant is one of the most important properties of each medium that is essential for pH definition, chemical speciation and acid–base equilibrium calculation.[2] An autoprotolysis constant describes quantitatively the extent of self ionization of solvent molecules SH, when a solvated proton, SH_2^+, and lyate ion, S^-, are produced in a chemical reaction:

$$SH + SH \rightleftharpoons S^- + SH_2^+ \tag{1}$$

---

* Corresponding author. E-mail: a_farajtabar@yahoo.com
doi: 10.2298/JSC130104039F

Although autoprotolysis of various aqueous electrolytes and solvent mixtures has been extensively investigated in the literature,[2–5] to best of our knowledge, no effort has been made on the determination of the autoprotolysis constant of mixed solvent electrolyte systems. Therefore, in this work, the autoprotolysis constants of methanol–water mixtures (0, 20 and 40 mass % of methanol) were determined over a wide range of NaCl electrolyte concentrations. The autoprotolysis constant was modeled utilizing the specific ion interaction theory (SIT).

EXPERIMENTAL

All chemicals were purchased from Merck. Methanol was of highest available purity and used without further purification. Sodium chloride was dried under vacuum at room temperature for at least 72 h before use. NaOH and HCl solutions were prepared from a titrisol solution and their concentration was determined by several titrations. Water was double distilled with a conductivity equal to 1.3±0.1 $\mu\Omega^{-1}$ cm^{-1}. A Jenway research potentiometer, model 3520, with a combined glass pH electrode was used for electromotive force (e.m.f) measurement in the potentiometric titrations. The electrode was modified by replacing its aqueous KCl solution with NaCl solution (0.10 mol L^{-1}) saturated with AgCl in aqueous methanol mixture.[3] This method is useful to improve the response speed of the glass electrode and to keep the liquid junction potential constant at a small value.

The autoprotolysis constant of a mixed solvent was determined by the potentiometric titration method at 25 °C at different ionic strengths from 0.5 to 2.0 mol L^{-1}, supplied by sodium chloride as an inert electrolyte. 25 mL of acidic solution (0.01 mol L^{-1} HCl) in a double-walled thermostated reaction vessel was titrated with NaOH (0.10 mol L^{-1}) at each ionic strength. Potentiometric data were taken after every addition of titrant, after which the stabilization of e.m.f data was checked manually. The criterion for a stable e.m.f was ±0.1 mV deviation, which was achieved in a period of 1 min.

RESULTS AND DISCUSSION

Computation of the autoprotolysis constant

According to Eq. (1), the thermodynamic autoprotolysis constant, K°, can be defined by Eq. (2):

$$K^\circ = \frac{a_{SH_2^+} a_{S^-}}{a_{SH}^2} = \frac{\gamma_{SH_2^+}[SH_2^+]\gamma_{S^-}[S^-]}{a_{SH}^2} = K\frac{\gamma_{SH_2^+}\gamma_{S^-}}{a_{SH}^2} \tag{2}$$

where γ_i and a_i are the activity coefficient and the activity of the species, respectively. K is a conditional autoprotolysis constant and $[SH_2^+][S^-]$ the product at each constant ionic strength.

During a potentiometric titration, the potential of a potentiometric cell equipped with a glass electrode in the acidic region can be formulated as:[6]

$$E = E^\circ + k\log a_{SH_2^+} = E^\circ + k\log\gamma_{SH_2^+} + k\log[SH_2^+] \tag{3}$$

E° is value of the standard electromotive force; k is the Nernst slope equal to $2.303RT/F$ in which R, T and F have their usual meaning. At constant ionic strength, the activity coefficient of species should be constant; therefore, Eq. (3) can be rewritten as Eq. (4), with E_a being $E° + k \log\gamma$.

$$E = E_a + k\log[\mathrm{SH}_2^+] \tag{4}$$

The hydrogen ion concentration can be easily calculated by:

$$[\mathrm{H}^+] = \frac{M_\mathrm{H}V_0 - M_\mathrm{OH}V_1}{V_0 + V_1} \tag{5}$$

where M_H and M_OH are the molarities of the acid and base, and V_0 and V_1 are the initial volume of acid and the added volume of sodium hydroxide solution, respectively.

By introducing Eq. (2) into Eq. (4), the e.m.f value in the alkaline region can be represented as:

$$E = E_a + k\log K - k\log[\mathrm{S}^-] \tag{6}$$

The experimental e.m.f data were fitted simultaneously to Eqs. (4) and (6) using nonlinear least squares analysis to find the optimum values for the negative logarithm of K (pK). For each experiment at constant ionic strength, the slopes obtained from the least squares analysis were close to the theoretical Nernst value (59.167 mV at 25 °C) with correlation coefficients of nearly $r^2 = 0.99$. The pK values in both the molar and molal concentration scales are reported in Tables I–III. The average standard deviations of the calculated pK values were less than 0.01 units. Conversion from the molar to the molal scale was realized using literature data for the density of NaCl solution in water–methanol mixtures.[7]

TABLE I. Values of pK, activity coefficient of NaCl, osmotic coefficient and solvent activity in methanol–water mixture containing 0 % methanol in different ionic strengths at 25 °C

I / mol L^{-1}	I / mol kg^{-1}	pK / mol^2 L^{-2}	pK / mol^2 kg^{-2}	γ_NaCl	ϕ	a_SH
0.10	0.10	13.781	13.777	0.778	0.934	0.996
0.25	0.25	13.754	13.748	0.720	0.924	0.991
0.50	0.51	13.717	13.700	0.681	0.919	0.982
0.75	0.76	13.711	13.699	0.664	0.923	0.973
1.00	1.02	13.719	13.702	0.656	0.931	0.963
1.25	1.28	13.734	13.713	0.653	0.941	0.954
1.50	1.55	13.761	13.733	0.654	0.952	0.943
1.75	1.82	13.794	13.760	0.657	0.964	0.933
2.00	2.09	13.834	13.796	0.663	0.977	0.923

Computation of the activity and the osmotic coefficient of mixed solvent

The activity and osmotic coefficient of a mixed solvent were calculated according to Eqs. (7) and (8) from activity coefficients of NaCl and then tabulated in Tables I–III:

$$\ln a_{\mathrm{SH}} = \frac{-M_{\mathrm{S}} \nu m_j}{1000} \phi \tag{7}$$

$$\phi = 1 + \frac{1}{m_j} \int_0^{m_j} m_j \mathrm{d} \ln \gamma_{\mathrm{j}} \tag{8}$$

The symbol ν is the stoichiometric index, m_j stands for the molality of the salt. M_{S} and ϕ are the molecular weight and osmotic coefficient of the solvent, respectively. The activity coefficients of NaCl in water–methanol mixtures were taken from the literature.[8]

TABLE II. Values of pK, activity coefficient of NaCl, osmotic coefficient and solvent activity in methanol–water mixture containing 20 % methanol in different ionic strengths at 25 °C

I / mol L^{-1}	I / mol kg^{-1}	pK / mol^2 L^{-2}	pK / mol^2 kg^{-2}	γ_{NaCl}	ϕ	a_{SH}
0.10	0.10	13.720	13.689	0.720	0.910	0.996
0.25	0.26	13.684	13.651	0.643	0.892	0.991
0.50	0.52	13.598	13.564	0.592	0.883	0.982
0.75	0.79	13.591	13.546	0.571	0.890	0.973
1.00	1.06	13.631	13.580	0.563	0.905	0.963
1.25	1.33	13.697	13.643	0.563	0.923	0.953
1.50	1.60	13.769	13.713	0.567	0.944	0.942
1.75	1.88	13.826	13.764	0.576	0.966	0.931
2.00	2.16	13.846	13.779	0.588	0.988	0.919

TABLE III. Values of pK, activity coefficient of NaCl, osmotic coefficient and solvent activity in methanol–water mixture containing 40 % methanol in different ionic strengths at 25 °C

I / mol L^{-1}	I / mol kg^{-1}	pK / mol^2 L^{-2}	pK / mol^2 kg^{-2}	γ_{NaCl}	ϕ	a_{SH}
0.10	0.11	13.830	13.766	0.675	0.896	0.996
0.25	0.27	13.654	13.588	0.596	0.877	0.990
0.50	0.54	13.674	13.607	0.545	0.869	0.980
0.75	0.82	13.738	13.660	0.523	0.877	0.969
1.00	1.10	13.838	13.755	0.514	0.892	0.958
1.25	1.38	13.906	13.820	0.512	0.910	0.947
1.50	1.66	14.003	13.915	0.515	0.930	0.935
1.75	1.95	14.141	14.047	0.522	0.953	0.922
2.00	2.25	14.221	14.119	0.532	0.976	0.909

Ionic strength effect

To account for the ionic strength effect, the results were analyzed using the specific ion interaction theory (SIT) in which activity coefficient of ion i with charge z_i can be expressed by Eq. (9) in a solution of ionic strength I (in the molal scale) at 25 °C:[5,9–14]

$$\log \gamma_i = -z_i^2 \frac{A\sqrt{I}}{1 + B a_i \sqrt{I}} + \sum_j \varepsilon_{ij} m_j \tag{9}$$

where a_i is the effective diameter of the hydrated ion i. A and B are Debye–Hückel constants, the values of which can be calculated by:

$$A = 1.8247 \times 10^6 \frac{\rho^{0.5}}{(DT)^{1.5}} \tag{10}$$

$$B = 50.2901 \frac{\rho^{0.5}}{(DT)^{0.5}} \tag{11}$$

where ρ, D and T are the density, dielectric constant and temperature of the solvent, respectively. Dielectric constants were taken from the literature,[15] and are listed in Table IV. The ion interaction coefficient ε_{ij} interprets the specific short-range interactions of ion i with ion j in its molal concentration m_j.

TABLE IV. Values of pK° and $\Delta\varepsilon$ for every methanol–water mixture at 25 °C

Methanol content, mass %	D	pK°	$\Delta\varepsilon$ / kg mol^{-1}	r^2
0	78.38	13.992±0.006	0.090±0.005	0.981
20	70.00	13.899±0.023	0.158±0.018	0.915
40	60.94	13.945±0.021	0.317±0.022	0.966

Introducing the SIT model into the logarithmic form of Eq. (2), the effect of the NaCl concentration on the autoprotolysis constant can be modeled as:

$$\mathrm{p}K + 2\log a_{\mathrm{SH}} = \mathrm{p}K^\circ - \frac{2A\sqrt{I}}{1 + B\sqrt{I}} + \Delta\varepsilon I \tag{12}$$

where

$$\Delta\varepsilon = \varepsilon_{\mathrm{SH}_2^+,\mathrm{Cl}^-} + \varepsilon_{\mathrm{S}^-,\mathrm{Na}^+} \tag{13}$$

The pK° and $\Delta\varepsilon$ values were optimized by least squares analysis for all methanol–water mixture. The results are tabulated together with the correlation coefficient of the fitting procedure (r^2) in Table IV.

The value of ion interaction coefficient was positive and increased with increasing methanol content in the mixture. It is worthwhile to consider the effect of changing the dielectric constant on interaction parameter. As shown in Fig. 1, there is a linear dependence of the ion interaction coefficient on the reciprocal of dielectric constant.

The same behavior was found for β^1, an interaction parameter in the Pitzer Model, in the thermodynamic treatment of the activity coefficients of 1:1 electrolytes in mixed solvents.[15–22] Similar to β^1, the principal contribution to ε_{ij} in SIT model originated from the short-range interactions between ions of opposite charge. Based on the exponential form of the Debye–Hückel theory, Gupta showed that the radial distribution function for unlike charged ions, namely g_{+-} (which contributes to β^1 and ε_{ij}) is a function of the dielectric constant that increases greatly with decreasing dielectric constant.[18] This explanation is consistent with the presented results. The positive values of $\Delta\varepsilon$ indicate that there is an attractive force between unlike ions. Moreover, the linear dependency of $\Delta\varepsilon$ on the inverse of dielectric constant shows that this attractive force mainly originated from electrostatic interactions. This is reasonable because the electrostatic interaction between unlike charged ions increases with decreasing polarity of the media.

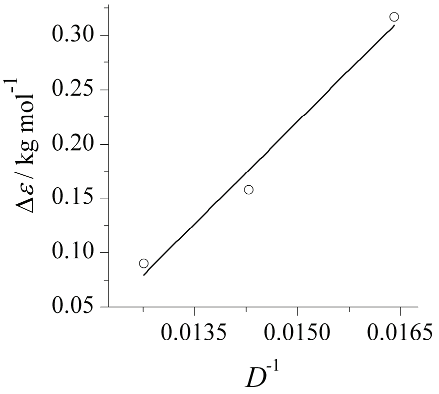

Fig. 1. Plot of $\Delta\varepsilon$ values as a function of the reciprocal of dielectric constant in water–methanol mixtures at 25 °C.

CONCLUSIONS

The autoprotolysis of some methanol–water mixture were successfully determined by an accurate potentiometric method over a wide range of ionic strength supplied by sodium chloride at 25 °C. The SIT theory was applied to describe the ionic strength dependency of the pK values. The thermodynamic autoprotolysis constant at infinite dilution was calculated together with the overall specific ion interaction coefficients.

Acknowledgement. The authors gratefully acknowledge the financial support from the Research Council of the Islamic Azad University, Jouybar Branch, Iran.

ИЗВОД

АУТОПРОТОЛИЗА У СИСТЕМУ ВОДА/МЕТАНОЛ/NaCl

ALI FARAJTABAR[1], FERESHTEH NADERI[2] и FARROKH GHARIB[3]

[1]Young Researchers Club, Jouybar Branch, Islamic Azad University, Jouybar, Iran, [2]Department of Chemistry, Shahr e Qods Branch, Islamic Azad University, Shahr e Qods, Tehran, Iran и [3]Chemistry Department, Faculty of Sciences, Shahid Beheshti University, Tehran, Evin, Iran

Потенциометријска метода је коришћена за одређивање константе аутопротолизе за водене растворе који садрже 0, 20 и 40 мас. % метанола у широком опсегу концентрација NaCl на 25 °C. Вредности јонске јачине биле су између 0,25 и 2,00 mol L^{-1}, са интервалима од 0,25 јединица. Осмотски коефицијенти и коефицијенти активности помешаних растварача израчунати су у зависности од јонске јачине. Зависност од јонске јачине анализирана је коришћењем теорије специфичних јонских интеракција. Параметри специфичне јонске интеракције добијени су заједно са термодинамичком константом аутопротолизе. Резултати указују да интеракција између јона расте са порастом садржаја метанола у смеши.

(Примљено 4. јануара, ревидирано 10 марта 2013)

REFERENCES

1. A. Anderko, P. Wang, M. Rafal, *Fluid. Phase Equilib*. **194–197** (2002) 123
2. T. Mussini, A. K. Covington, P. Longhi, S. Rondinini, *Pure. Appl. Chem*. **57** (1985) 865
3. E. Kiliç, N. Aslan, *Microchim. Acta* **151** (2005) 89
4. R. M. Dzudovic, L. N. Jaksic, *J. Serb. Chem. Soc*. **75** (2010) 1575
5. P. Sipos, *J. Mol. Liq*. **143** (2008) 13
6. F. Naderi, A. Farajtabar, F. Gharib, *J. Solution Chem*. **41** (2012) 1033
7. T. Guetachew, S. Ye, I. Mokbel, J. Jose, P. Xans, *J. Solution Chem*. **25** (1996) 895
8. A. Basili, P. R. Mussini, T. Mussini, S. Rondinini, *J. Chem. Thermodyn*. **28** (1996) 923
9. C. Bretti, C. De Stefano, C. Foti, S. Sammartano, G. Vianelli, *J. Chem. Thermodyn*. **44** (2012) 154
10. J. N. Brönsted, *J. Am. Chem. Soc*. **44** (1922) 877
11. F. Gharib, A. Farajtabar, *J. Mol. Liq*. **135** (2007) 27
12. F. Gharib, M. Jabbari, A. Farajtabar, *J. Mol. Liq*. **144** (2009) 5
13. E. A. Guggenheim, J. C. Turgeon, *Trans. Faraday Soc*. **51** (1955) 747
14. M. Faraji, A. Farajtabar, F. Gharib, *J. Serb. Chem. Soc*. **78** (2012) 681
15. F. Hernandez-Luis, M. V. Vazquez, M. A. Esteso, *J. Mol. Liq*. **108** (2003) 283
16. K. S. Pitzer, *Activity Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, FL, 1991
17. K. S. Pitzer, *Thermodynamics*, McGraw-Hill, New York, USA, 1995
18. R. A. Gupta, *J. Phys. Chem.* **83** (1979) 2986
19. D. S. P. Koh, K. H. Khoo, C.-Y. Chen, *J. Solution Chem.* **14** (1985) 635
20. F. Hernandez-Luis, H. R. Galleguillos, T. A. Graber, M. E. Taboada, *Ind. Eng. Chem. Res*. **47** (2008) 2056
21. F. Deyhimi, B. Ghalami-Choobar, *J. Mol. Liq*. **122** (2005) 116
22. F. Deyhimi, B. Ghalami-Choobar, *Fluid Phase Equilib*. **246** (2006) 185.