Asian Journal of Chemistry Vol. 5, No. 1 (1993), 164–172

Thermodynamics of the Ionization of Hydroxylamine In Methanol-Water and 1,4-Dioxane-Water

F. H. JUMEAN
Department of Chemistry
University of Jordan, Amman, Jordan.

The ionisation of hydroxylamine was studied in aqueous methanol and aqueous 1,4-dioxane solutions at 5° intervals in the range 5—35°C. The composition of the organic cosolvent was varied up to 60% (w/w) for each system. Anomalous behaviour was observed in the regions of maximum structure enchancement of water by methanol and 1,4-dioxane. The results are discussed in terms of changes in the structural and dielectric properties brought about by cosolvent addition.

INTRODUCTION

The dissociation behaviour of weak acids in mixed aqueous solvents has been the subject of a number of investigations, particularly with methanol and ethanol as cosolvents. The type of dependence of pK on solvent composition has proved useful in assessing the relative importance of electrostatic and nonelectrostatic factors in the dissociation process as well as assignment of charge types to the acidic and basic species. In some cases, insight is obtained into the role played by the solvent and the mode of interaction between the solvent and the dissociating species. Only a relatively small number of these investigations dealt with the effect of temperature[1–4]. This is unfortunate in view of the potentially important information that can be derived from a knowledge of the values of the enthalpy, entropy and heat capacity of dissociation and their dependence on solvent composition. This paper deals with the thermodynamics of dissociation of hydroxylamine in methanol-water and dioxane-water. Hydroxylamine was selected because it is a useful buffer in the 5-7 pH range and a knowledge of its dissociation behaviour in mixed aqueous solvents may be of value to investigators concerned with such media. Of the two cosolvents, methanol is a polar protic molecule with a substantial dielectric constant ($\epsilon^{25}=32.6$) whereas dioxane is aprotic and nonpolar ($\epsilon^{25}=2.21$). The dissociation equilibrium is :

$$NH_3OH^+ = NH_2OH + H^+ \qquad (1)$$

EXPERIMENTAL

Hydroxylammonium chloride was a Merck reagent of analaR grade and was used as such. Methanol and 1,4-dioxane were of spectro quality. pH measurements were conducted on a Beckman 4500 digital pH meter using a combination glass electrode. Due to the possibility of slow oxidation of hydroxylamine by air[5], titrations were performed on fresh solutions under nitrogen atmosphere, 0.1 dm^3 mol^{-1} carbonate-free NaOH was used as titrant. The calibration of the pH meter was checked by two standard aqueous buffers at each of the seven temperatures investigated. The glass electrode has been shown to be adequately responsive in methanol-water[6] and dioxane-water[7] media. Its sensitivity was improved by frequent immersions in dilute HCl. Measurements were conducted on solutions containing 0, 10, 20, 30, 40, 50 and 60% (w/w) of the cosolvent. Each solution was titrated at 5, 10, 15, 20, 25, 30 and 35±0.02°C. At least three independent measurements were carried out for each composition. Reproducibility in the pK values was generally within 0.01 units but tended to be somewhat less for the cosolvent rich solutions.

RESULTS AND DISCUSSION

When the pH meter is calibrated with an aqueous buffer, its readings for nonaqueous solvents are referred to the standard state in water. Since the activity coefficient of the proton in the mixed solvent may be substantially different from that in pure water, not much meaning may be attached to the derived thermodynamic values unless these readings are corrected to the standard state in the same solvent medium. This situation is further complicated by the presence of a residual liquid junction potential (E_j), in the mixed solvent. In order to take into account these two factors, a correction term (δ) is introduced[8] and is given by

$$\delta = E_j - \log {}_m\gamma_H = pH - pH^* \qquad (2)$$

where ${}_m\gamma_H$ is the activity ratio of the proton in water to that in the solvent, pH is the operational meter reading and pH* is the meter reading had been standardized by a buffer of the same solvent composition as as that of the solution investigated. Values of δ at 25°C for methanol-water[6,9–11] and dioxane-water[7,10,11] have been measured and tabulated. As interpolated from measurements[10] at 25°C, these are −0.015, −0.030, −0.046, −0.094, −0.155 and 0.218 for solutions containing 10, 20, 30, 40, 50 and 60% methanol, respectively. For dioxane-water, the corresponding values are +0.025, +0.030, +0.050, +0.070, +0.130 and +0.280. The temperature coefficient of δ in methanol-water was estimated to be *ca.* 0.3% per degree. This estimate was derived from data[2] collected for 50% aqueous methanol over the temperature range 10–40°C. The temperature corrections were made on the assumption that $d\delta/dT$ is insensitive to composition changes. Since this is a second order correction, possible errors arising from this assumption should be very small. Furthermore, it has been shown[11] that for solutions of ionic strength below 0.08 mol dm^{-3}, δ remains essentially invariant.

Once the operational pH values are corrected using the appropriate δ's, the pK values obtained, although properly referenced to the solvent medium, are only 'apparent' and need to be corrected to zero ionic strength in order to convert them to thermodynamic (pK^0) ones. Since the ionic strength of 0.05 mol dm^{-3} is fairly low, the Debye-Hückel theory may be used to evaluate the needed activity coefficients. If γ for NH_2OH, a neutral species, is taken as unity, one needs to evaluate only $\gamma(NH_3OH^+)$ since $\gamma(H^+)$ is included in the pH term ($pH = -\log a_H$). The following equation[12] may be readily shown to apply to the dissociation of the hydroxylammonium ion :

$$pK' = pK^0 \log \sigma(NH_3OH^+) = pK^0 + AI^{1/2} / (1 + aBI^{1/2}) \qquad (3)$$

where, $A = (1.8246 \times 10^6)\, d_0^{1/2} / \epsilon T)^{1/2}$, and

$$B = (50.29 \times 10^6)\, d_0^{1/2} / (\epsilon T)^{1/2}$$

Here d_0 and ϵ are the solvent density and dielectric constant, I is the ionic strength and the constant (a) is an 'ion size parameter'. Based on the estimates of Kielland[13] on ions of comparable size and charge, this parameter for NH_3OH^+ was taken as 3.5 A. In order to carry out the needed calculations, it was assumed that this value is retained upon changing the temperature and solvent composition. This assumption may not be entirely sound but it may seem more justifiable when it is recognized that the term $aBI^{1/2}$ of equation (3) is often ignored. Values of d_0, A and B for methanol-water were either taken or interpolated from data listed by Bates and Robinson[8] whereas those for 1,4-dioxane were collected from several sources[14-16].

The pK^0 values obtained from equation (3) were fitted to the following expression[17]

$$pK^0 = a/T + b + cT \qquad (4)$$

The constants *a*, *b*, and *c* were evaluated for each solvent composition by means of a linear regression computer program. Table 1 lists the 'best fit' pK^0 values at the various temperatures and solvent compositions investigated and Fig. 1 shows plots of these results. The values in pure water agree within 0.02 units with those reported[18,19] at 15, 20, 25 and 35°C. The pK^0 behaviour in methanol-water is seen to be markedly different from that in dioxane-water. For whereas in the former system the pK^0 values exhibit a decreasing tendency with higher methanol content, the reverse is observed with the latter. This observation may be explained on the basis of electrostatic and nonelectrostatic components[8] of pK. For the case of the dissociation of the hydroxylammonium ion, the former component ought to be fairly small when compared with the second since no net charge is created. Here it should be noted that, as

TABLE 1

DEPENDENCE OF pK^0 FOR THE HYDROXYLAMMONIUM ION ON TEMPERATURE AND SOLVENT COMPOSITION : (A) METHANOL-WATER, (B) DIOXANE-WATER.

pK^0

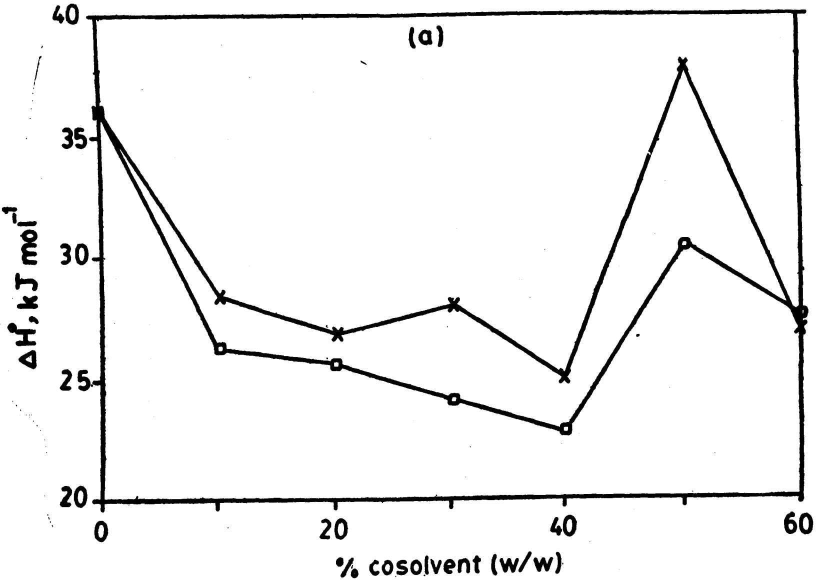
(a) % methanol (w/w)

T, °C	0	10	20	30	40	50	60
5	6.389	6.337	6.281	6.287	6.231	6.195	6.100
10	6.290	6.208	6.148	6.141	6.110	6.058	5.979
15	6.189	6.095	6.033	6.017	6.006	5.935	5.871
20	6.086	5.997	5.934	5.915	5.917	5.827	5.773
25	5.976	5.913	5.851	5.834	5.843	5.731	5.687
30	5.874	5.843	5.783	5.773	5.783	5.647	5.545
35	5.765	5.785	5.729	5.730	5.736	5.575	5.545

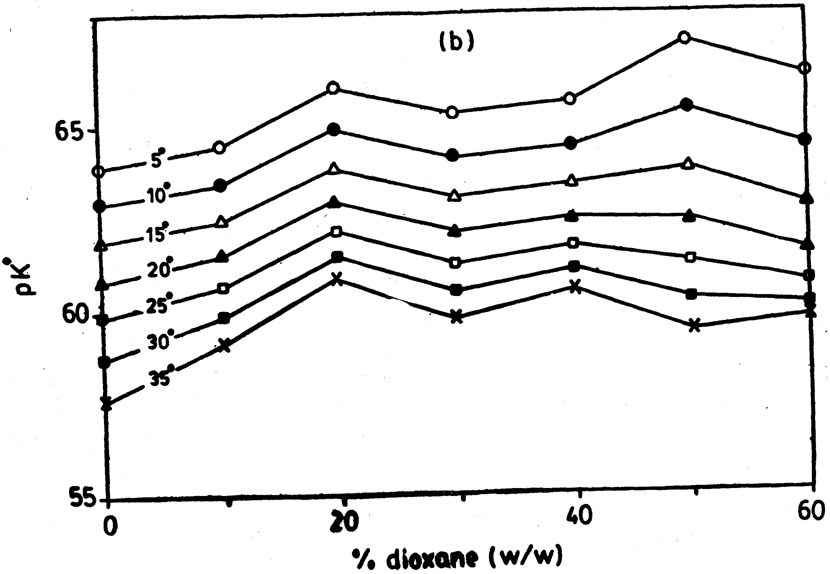
(b) % dioxane (w/w)

T, °C	0	10	20	30	40	50	60
5	6.389	6.447	6.604	6.527	6.554	6.715	6.624
10	6.290	6.343	6.491	6.411	6.436	6.535	6.433
15	6.189	6.245	6.390	6.305	6.333	6.377	6.277
20	6.086	6.153	6.299	6.209	6.244	6.240	6.154
25	5.976	6.067	6.219	6.123	6.168	6.122	6.063
30	5.874	5.986	6.149	6.045	6.104	6.023	6.002
35	5.765	5.910	6.088	5.976	6.052	5.942	5.970

predicted by the Born[20] equation, the creation of charge in media of low dielectric constants is an unfavourable process and hence results in higher pK values. The decrease in pK^0 with increasing methanol content may be attributed to increased basicity of the solvent[8] with methanol addition. In the case of dioxane-water, however, although no net charge is created, the formation of a proton with its high charge to mass ratio probably becomes increasingly unfavourable with further addition of cosolvent. This is because dioxane has a much lower dielectric constant than methanol.



(a)



(b)

Fig. 1. pK° of the hydroxylammonium ion in (a) methanol-water and (b) dioxane-water temperatures are indicated.

Table 2 lists the standard values the dissociation parameters ΔH°, ΔS°, ΔG° and ΔC°_p at 25°C. The regression constants *a*, *b* and *c* as well as the value of log $\gamma_{(\mathrm{NH_3OH^+})}$ at 25°C are tabulated for each solvent composition. The following equations, which follow from equation (4), were employed :

TABLE 2

THERMODYNAMIC PARAMETERS AT 25°C FOR THE DISSOCIATION OF THE HYDROXYLAMMONIUM ION IN (A) METHANOL-WATER AND (B)DIOXANE-WATER. THE CONSTANTS OF EQUATION (4) ARE ALSO TABULATED.

(a) % methanol (w/w)

	0	10	20	30	40	50	60
a	−994.9	7132	7935	10500	7421	6562	5510
b	18.98	−37.33	−42.89	−60.35	−39.95	−32.95	−26·45
c	−0.032	0.065	0.074	0.104	0.070	0.056	0.046
ΔG^0 / kJ mol^{-1}	34.1	33.8	33.4	33.3	33.4	32.7	32.5
ΔH^0 / kJ mol^{-1}	36.1	26.3	25.6	24.1	22.8	30.5	27·5
ΔS^0 J K^{-1} mol^{-1}	+6.55	−25.1	−26	−30.7	−35.5	−7.43	−16.5
ΔC^0_p / J K^{-1}mol^{-1}	+370	−740	−847	−1190	−800	−638	−523
−log $\gamma_{(\mathrm{NH_3OH^+})}$	0.094	0.100	0.108	0.118	0.130	0.143	0.161

(b) % dioxane (w/w)

	0	10	20	30	40	50	60
a	−994.9	2790	5280	4376	6298	9951	15920
b	18.98	−7.74	−24.76	−18.5	−32.00	−54.32	−96·33
c	−0.032	0.015	0.044	0.033	0.056	0.09	0.163
ΔG^0 / kJ mol^{-1}	34.1	34.3	34	33.9	33.6	33.1	32.9
ΔH^0 / kJ mol^{-1}	36.1	28.4	26.9	28.1	24.9	37.9	27.0
ΔS^0 / JK^{-1} mol^{-1}	6.55	−19.7	−23.8	−19.2	−29.0	15.9	−19.9
ΔC^0_p / JK^{-1} mol^{-1}	370	−168	−498	−373	−642	−1020	−1860
−log $\gamma_{(\mathrm{NH_3OH^+})}$	0.094	0.109	0.131	0.160	0.208	0.281	0.408

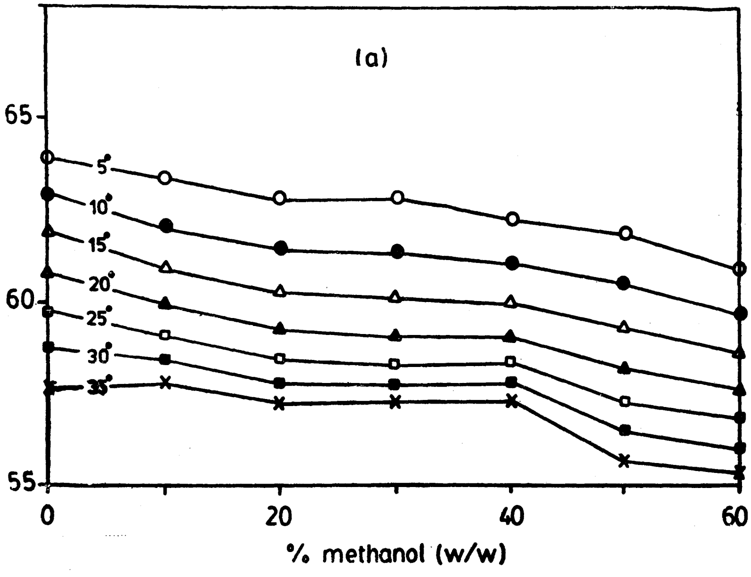
$$\Delta H^0 = 2.303\ R(a - cT^2) \tag{5}$$

$$\Delta S^0 = -\ 2.303\ (b + 2cT) \tag{6}$$

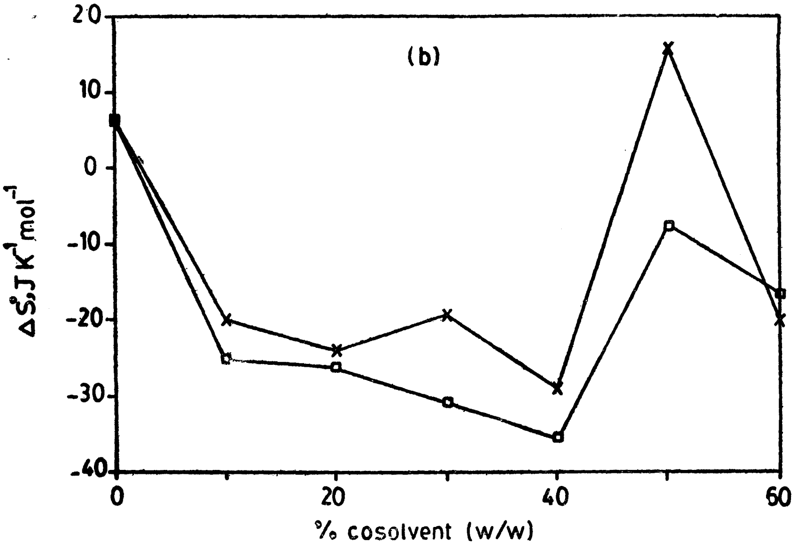
$$\Delta G^0 = 2.303\ R(a + bT + cT^2) \tag{7}$$

$$\Delta C^0_p = -\ 4.606\ RcT \tag{8}$$

Fig. 2 shows the dependence of ΔH^0 and ΔS^0 on solvent composition. The marked similarity in the behaviour of each of these two parameters in methanol-water and dioxane-water suggests that similar processes take place in both solvent systems. This seems somewhat surprising in view of the pronounced difference between the nature of two cosolvents, as reflected in the marked contrast between the pK^0 profiles (Fig. 1). The sharp decline in ΔH^0 with the addition of either cosolvent occurs within a composition interval in which the structure of water is enhanced by either methanol[21,22] or dioxane[23] addition. This enhancement may lead to the incorporation of the dissociated proton within a tight water-cosolvent cage structure with the possibility of formation of shorter and stronger H-bonds. Such a conjecture is lent credence by the ΔS^0 behaviour. Here, the large drop in ΔS^0 within the same composition interval is consistent with a higher degree of restriction of the proton, as would be expected when it enters a solvent cage. Inspection of Table 2 reveals that ΔC^0_p is highly sensitive to solvent composition. In methanol-water, it drops from 370 JK^{-1} mol^{-1} in pure water to a minimum of -1170 JK^{-1} mol^{-1} in



(a)



(b)

Fig. 2. Standard values of (a) ΔH^0 and (b) ΔS^0 at 25°C for the dissociation of the hydroxylammonium ion in methanol-water (x) and dioxane-water (o).

30% methanol then rises again to 523 JK^{-1} mol^{-1} in the 60% cosolvent. In dioxane-water, by contrast, a generally decreasing trend is observed, with ΔC_p^0 reaching -1860 JK^{-1} mol^{-1} in 60% dioxane. These sharp changes indicate that the enthalpic contribution to the Gibbs free energy should make the dissociation process significantly more favourable at the higher temperatures. If it is assumed that the first step in the dissociation involves "stripping"[24] of the solvation shell around the hydroxylammonium ion, increasing the temperature would be expected to facilitate such a process. The higher ΔC_p^0 values would then be consistent with more compact, less temperature sensitive shells.

ACKNOWLEDGEMENTS

The author is grateful to the University of Jordan for supporting this work.

REFERENCES

1. R. N. Roy, J. J. Gibbons and R. Snelling, *J. Solution Chem.*, **6**, 475 (1977).
2. M. Paabo, R. A. Robinson and R. G. Bates, *J. Am. Chem. Soc.*, **87**, 415 (1965).
3. R. C. Das, U. N. Dash and K. N. Panda, *J. Chem. Soc., Faraday I*, **76** 2152 (1980).

4. R. G. Bates, R. N. Roy and R. A. Robinson, *J. Solution Chem.*, **3**, 905 (1974).
5. J. H. Anderson, *Analyst*, **89**, 357 (1964).
6. R. G. Bates, M. Paabo and R. A. Robinson, *J. Phys. Chem.*, **67**, 1833 (1963).
7. L. G. Van Uitert and C. G. Hass, *J. Am. Chem. Soc.*, **75**, 451 (1981).
8. R. G. Bates and R. A. Robinson, in B. E. Conway and R. G. Barradas (eds.) Chemical Physics of Ionic Solutions, Wiley, New York, pp. 211—235 (1966).
9. C. L. deLigny and M. Rehbach, *Rec. Trav. Chim.*, **79**, 727 (1960).
10. S. C. Lahiri and S. Aditya, *J. Indian Chem. Soc.*, **51**, 319 (1974).
11. S. Grace and D. Dunaway Mariano *Biochemistry*, **22**, 4238 (1983).
12. E. J. King, in The International Encyclopedia of Physical Chemistry and Chemical Physics, Pergamon Press, New York, topic 15, Vol. 4, pp. 78—9 (1965).
13. J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).
14. F. E. Critchfield, J. A. Gibson and J.L. Hall, *J. Am. Chem. Soc.*, **75**, 1991 (1953).
15. G. J. Janz and R. P. Tomkins, Nonaqueous Electrolytes Handbook, Academic Press, New York, vol. 1 (1972).
16. P. K. Das and U. C. Mishra, *Electrochim. Acta*, **22**, 59 (1977).
17. H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).
18. P. Lumme, P. Lahermo and J. Tummavuori, *Acta Chem. Scand.*, **19**, 2175 (1965).
19. R. A. Robinson and V. E. Bower, *J. Phys. Chem.*, 65, 1279 (1961).
20. M. Born, *Z. Physik*, **1**, 45 (1920).
21. D. Feakins, in F. Franks (ed.), Physicochemical Processes in Mixed Aqueous Solvents, Elsevier, New York, pp. 71-90 (1967).
22. F. Franks, ibid., pp. 50-70.
23. J. S. Sandhu, P. Kaur and U. Kashyap, *J. Indian Chem. Soc.*, **58**, 729 (1986).
24. K. Bose and K.K. Kundu, *Can. J. Chem.*, **55**, 1977 (1961).

[*Received*: 14 October 1991; *Accepted*: 1 March 1992] AJC-408