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Thermodynamics of Self-Ionization of Propylene Glycol–Water Mixtures at Different Temperatures

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The autoprotolysis constants (K_s) of propylene glycol (PH)–water mixtures with compositions of 20, 40, 75, and 90 wt % propylene glycol have been determined in the temperature range 15–45 °C by using the cell Pt, H_2 (g, 1 atm)|NaS, MBr, propylene glycol–water|AgBr–Ag where NaS is the sodium lyate of the solvent and M is Na or K. The experimental results have been expressed as a function of temperature in the form $pK_s = A/T - D + CT$ proposed by Harned and Robinson and the coefficients A, D, and C have been obtained by the method of least squares. The variation of pK_s with solvent composition has been discussed in terms of the properties of the mixed solvents. Thermodynamic quantities such as ΔG°, ΔH°, and ΔS° for the self-ionization process have been evaluated at 25 °C and discussed in terms of the structural aspects of the mixed solvents.

Introduction

The autoprotolysis constant (K_s) of a solvent is an important parameter in understanding acid–base equilibria in mixed solvents. It also determines (*1*, *2*) the extreme limits of acidity and basicity in a given solvent medium. The dielectric constant and the intrinsic acidic and basic strength of the solvent will influence the self-ionization process in these media. Since the components comprising the medium, i.e., H_2O and PH (propylene glycol), are amphiprotic in nature, the following equilibria must be considered:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (1)$$

$$H_2O + PH \rightleftharpoons H_3O^+ + P^- \qquad (2)$$

$$PH + PH \rightleftharpoons PH_2^+ + P^- \qquad (3)$$

$$PH + H_2O \rightleftharpoons PH_2^+ + OH^- \qquad (4)$$

In the mixed solvent, H_3O^+ and PH_2^+ are lyonium ions and OH^- and P^- are lyate ions. All the ionization processes 1–4 can be represented by the general equation

$$SH + SH \rightleftharpoons SH_2^+ + S^- \qquad (5)$$

where SH denotes either of the solvents and SH_2^+ and S^- represent lyonium and lyate ions, respectively. The autoprotolysis constant is given by

$$K_s = a_{SH_2^+}a_{S^-}/a_{SH}^2 \qquad (6)$$

where a denotes the activity of the various species involved in the process. Although the thermodynamics of self-ionization in some mixed amphiprotic media (aquoorganic) has been studied (*3–7*), to our knowledge, no results have yet been reported in propylene glycol–water mixtures.

The self-ionization behavior of propylene glycol–water mixtures in the composition range 20–90 wt % propylene glycol has, therefore, been investigated by employing the following cell:

Pt, H_2(g, 1 atm)|NaS (m_{S^-}), KBr (m_{Br^-}),
propylene glycol–water|AgBr–Ag (A)

Experimental Section

The experimental setup and the general procedure adopted in emf measurements are similar to that described in earlier measurements on hydrogen–silver, silver halide cells (*8*). Propylene glycol was purified as described previously (*9*). The sodium lyate of the solvent was prepared by dissolving the required amount of freshly cut pieces of dry sodium in the solvent at room temperature. The strength of the solution was determined by employing standard aqueous HCl. The solution of potassium bromide in the respective mixed solvents was prepared by weighing and dissolving the required quantity of the salt (AR, BDH). The hydrogen and silver, silver bromide electrodes were prepared as described earlier (*8*).

Results and Discussion

The emf of the cell A is given by

$$E = E^\circ - \frac{2.303RT}{F}\log\frac{a_{SH_2^+}a_{Br^-}}{a_{SH}} \qquad (7)$$

Substituting for $a_{SH_2^+}$ from eq 6 and rearranging the terms one gets

$$\frac{F(E - E^\circ)}{2.303RT} + \log\frac{m_{Br^-}}{m_{S^-}} = -\log K_s - \log\frac{\gamma_{Br^-}}{\gamma_{S^-}}a_{SH}$$

or

$$pK_s' = pK_s - \log\frac{\gamma_{Br^-}}{\gamma_{S^-}}a_{SH} = pK_s + f(\mu) \qquad (8)$$

A plot of the left-hand side of eq 8 (pK_s') against μ, the ionic strength, gives the pK_s value as the intercept on extrapolation to $\mu = 0$. Such a plot in 20 wt % propylene glycol, which is fairly linear and typical of the results in these mixtures, is shown in Figure 1. The E°_m values of the Ag–AgBr electrode in these solvent mixtures, required for this purpose, have been determined earlier (*9*). The emf data corrected for a partial pressure of 1 atm of H_2 gas at various molalities of lyate and halide in the different solvent mixtures are presented in Table I. The pK_s values of the solvent mixtures containing 20–90 wt % propylene glycol at various temperatures (15–45 °C) on the molal scale and at 25 °C on the mole fraction scale are given in Table II. The variation of pK_s with temperature may be expressed in the form

$$pK_s = A/T - D + CT \qquad (9)$$

and the values of the coefficients in the different solvent mixtures evaluated by a least-squares method are shown in Table III. The average standard deviation in pK_s values in different solvent mixtures calculated from eq 9 and those obtained experimentally were found to be about 0.005.

The thermodynamic quantities, ΔG°, ΔS°, and ΔH° on the molal scale for the self-ionization process at 25 °C were evaluated by using the coefficients of eq 9 in the following expressions (*10*, *11*):

$$\Delta G^\circ_m = A' - D'T + C'T^2 \qquad (10)$$

$$\Delta H^\circ_m = A' - C'T^2 \qquad (11)$$

$$\Delta S^\circ_m = D' - 2C'T \qquad (12)$$

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Table I. Emf Data[a] of Cell A (Volts)[b] from 15 to 45 °C in Propylene Glycol-Water Mixtures

m_{S^-}/(mol kg^{-1})	m_{Br^-}/(mol kg^{-1})	μ/(mol kg^{-1})	E/V 15 °C	E/V 25 °C	E/V 35 °C	E/V 45 °C
		20 wt % Propylene Glycol-Water Mixtures				
0.006 071	0.005 993	0.012 064	0.879 61	0.886 97	0.893 55	0.898 06
0.006 986	0.006 942	0.013 928	0.882 93	0.888 55	0.893 53	0.898 71
0.007 986	0.007 949	0.015 935	0.883 48	0.888 90	0.894 18	0.898 92
0.009 048	0.008 957	0.018 005	0.883 52	0.889 05	0.894 23	0.899 24
0.010 13	0.010 00	0.020 130	0.884 34	0.889 85	0.895 20	0.900 16
0.019 89	0.019 91	0.039 800	0.886 54	0.891 89	0.897 25	0.902 10
0.029 83	0.030 49	0.060 320	0.886 68	0.892 18	0.897 53	0.902 43
		40 wt % Propylene Glycol-Water Mixtures				
0.002 973	0.002 943	0.005 916	0.869 11	0.876 25	0.883 13	0.889 30
0.004 988	0.004 987	0.009 975	0.874 08	0.880 67	0.886 57	0.891 98
0.006 992	0.007 742	0.014 734	0.874 05	0.880 76	0.886 76	0.892 33
0.008 017	0.007 999	0.016 016	0.875 12	0.881 48	0.887 40	0.893 01
0.008 983	0.009 015	0.017 998	0.875 58	0.881 97	0.887 81	0.893 50
0.010 100	0.009 987	0.020 087	0.877 76	0.884 11	0.890 10	0.895 57
0.019 99	0.020 410	0.040 40	0.879 81	0.886 49	0.892 49	0.898 11
0.030 050	0.029 850	0.059 90	0.881 70	0.888 13	0.892 64	0.898 77
		75 wt % Propylene Glycol-Water Mixtures				
0.004 833	0.004 880	0.009 713	0.860 62	0.865 19	0.870 33	0.875 65
0.006 990	0.006 887	0.013 877	0.866 12	0.871 13	0.876 01	0.880 81
0.008 996	0.008 988	0.017 984	0.865 59	0.870 52	0.875 62	0.880 49
0.010 05	0.009 962	0.020 012	0.866 56	0.871 57	0.876 17	0.880 74
0.019 88	0.020 38	0.040 26	0.869 04	0.874 09	0.879 29	0.884 26
0.029 25	0.029 44	0.058 69	0.872 71	0.877 80	0.882 58	0.887 47
0.039 94	0.040 15	0.080 09	0.873 45	0.878 27	0.882 89	0.887 78
0.049 53	0.051 03	0.100 56	0.873 04	0.878 23	0.883 19	0.887 97
		90 wt % Propylene Glycol-Water Mixtures				
0.004 927	0.004 904	0.009 831	0.850 27	0.853 70	0.857 59	0.861 49
0.005 951	0.005 951	0.011 902	0.850 30	0.854 12	0.857 80	0.861 88
0.007 061	0.007 009	0.014 07	0.851 40	0.855 24	0.858 93	0.863 06
0.007 958	0.007 975	0.015 933	0.853 15	0.857 06	0.861 07	0.865 12
0.008 924	0.009 178	0.018 102	0.852 11	0.855 88	0.859 75	0.863 78
0.009 958	0.009 996	0.019 954	0.855 00	0.859 03	0.863 03	0.867 25
0.020 17	0.020 07	0.040 24	0.860 30	0.864 33	0.868 49	0.872 65
0.029 96	0.029 98	0.059 94	0.862 13	0.866 20	0.870 54	0.874 61

[a] Emf values are accurate to within ±0.05 mV. [b] Corrected for 1-atm pressure of hydrogen.

Table II. $pK_{s(m)}$[a] Values of Propylene Glycol-Water Mixtures at Different Temperatures and $pK_{s(N)}$ Values at 25 °C

[propylene glycol]/ wt %	$pK_{s(m)}$ 15 °C	$pK_{s(m)}$ 25 °C	$pK_{s(m)}$ 35 °C	$pK_{s(m)}$ 45 °C	$pK_{s(N)}$ at 25 °C
20	14.31	13.98	13.71	13.45	17.33
40	14.30	13.88	13.61	13.36	17.05
75	14.75	14.52	14.30	14.10	17.27
90	15.21	15.00	14.80	14.63	17.48
100[b]	17.50	17.21	16.96	16.73	19.45

[a] Values are accurate to ±0.01 unit. [b] Data from ref 6.

Table III. Coefficients of the Empirical Equation 9

$$pK_s = A/T - D + CT$$

[propylene glycol]/ wt %	A	D	C
20	4791.22	9.313	0.024 26
40	12340.35	58.502	0.104 00
75	2092.35	-7.171	0.001 11
90	2793.68	-2.328	0.011 06
100[a]	3372.00	-2.571	0.011 20

[a] Taken from the ref 6.

wherein $A' = 2.303RA$, $C' = 2.303RC$, and $D' = 2.303RD$. These results are recorded in Table IV. The standard free energy and entropy changes on the mole fraction scale ($\Delta G°_N$ and $\Delta S°_N$) were calculated by using the equations

$$\Delta G°_N = \Delta G°_{s(m)} + 4.606RT \log (1000/M_{xy}) \quad (13)$$

$$\Delta S°_N = \Delta S°_{s(m)} - 4.606RT \log (1000/M_{xy}) \quad (14)$$

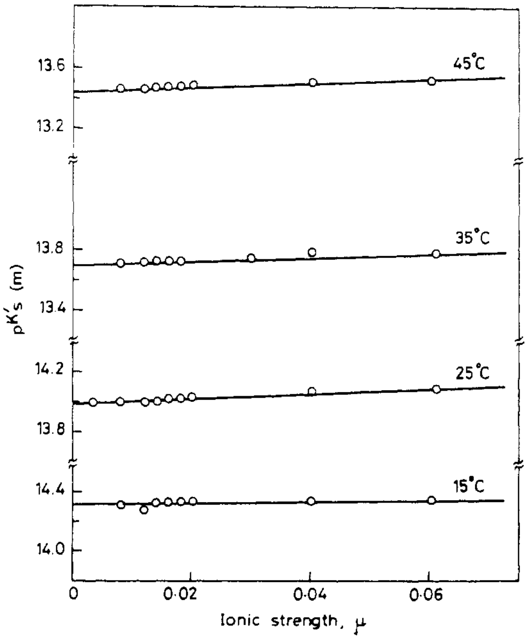

Figure 1. Extrapolation of $pK'_{s(m)}$ against μ (eq 8) in 20 wt % propylene glycol-water mixtures at different temperatures.

and are recorded in Table IV. M_{xy} in eq 13 and 14 represents the mean molecular weight of the solvent mixture.

The estimated error in $\Delta G°$ is about ±60 J mol^{-1} whereas the average standard deviations in $\Delta S°$ and $\Delta H°$ in the various solvent compositions are about ±0.2 J deg^{-1} mol^{-1} and ±120

Table IV. Thermodynamic Quantities Accompanying the Self-Ionization of Propylene Glycol–Water Mixtures at 25 °C on Molal (m) and Mole Fraction (N) Scales

[propylene glycol]/ wt %	$\Delta G°_m$/ (kJ mol^{-1})	$\Delta G°_N$/ (kJ mol^{-1})	$\Delta H°_m$ = $\Delta H°_N$/ (kJ mol^{-1})	$\Delta S°_m$/ (J mol^{-1} K^{-1})	$\Delta S°_N$/ (J mol^{-1} K^{-1})
0[a]	79.90	99.81	56.59	−78.18	−144.98
20	79.86	98.96	50.45	−98.66	−162.72
40	79.32	97.43	59.26	−67.26	−128.02
75	82.89	98.59	40.06	−149.98	−202.65
90	85.84	99.77	34.66	−170.87	−218.36
100[b]	98.30	111.08	45.50	−177.14	−220.00

[a] Calculated by using data from ref *10*. [b] Calculated by using data from the ref *6*.

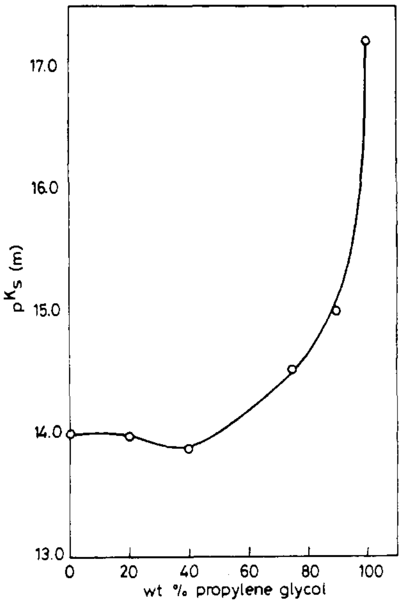

Figure 2. Variation of p$K_{s(m)}$ with solvent composition in propylene glycol–water mixtures at 25 °C.

J mol^{-1}, respectively. $\Delta H°$ values, however, remain unchanged and are independent of the concentration unit chosen. Figure 2 gives the variation of p$K_{s(m)}$ of propylene glycol–water mixtures as a function of solvent composition at 25 °C.

It is seen (Figure 2, Table II) that the pK_s of propylene glycol–water mixtures decreases slightly when propylene glycol is added to water, passes through a minimum at about 40 wt % propylene glycol, and then increases, the increase being sharp for mixtures containing higher proportions of (90–100 wt %) propylene glycol. A similar variation in pK_s was observed by Kundu et al. (*7*) in ethylene glycol–water mixtures and by Kalidas et al. (*12*) in diethylene glycol–water mixtures. As mentioned earlier, the autoprotolysis constant of a solvent is a composite function of the intrinsic acidic and basic strengths of the solvent and its dielectric constant. Qualitatively, the addition of propylene glycol to water would result in a lowering of dielectric constant of the solvent mixtures, resulting in an increase of pK_s values, if propylene glycol were not participating in the self-ionization process. But propylene glycol and water both being amphiprotic, the above trend is not observed in these media. Our earlier studies in propylene glycol–water mixtures (*9*, *14*) reveal that all propylene glycol–water mixtures including pure propylene glycol are more basic than water. On this basis, equilibrium 2, where propylene glycol acts as an acid, should be relatively unimportant and a decrease in dielectric constant must result in a lowering of the equilibrium constants of equilibria 1, 3, and 4. The observed variation of pK_s values suggests that their variation with solvent composition is a net result of competition between the dielectric constant and the relatively greater basicity of the medium as compared to water. The minimum around 40 wt % propylene glycol most probably indicates a balancing of the two opposite effects. The large rise in pK_s in the region 90–100% propylene glycol suggests the predominance of equilibrium 4. A comparison of pK_s values of ethylene glycol–water mixtures (*7*) with those of propylene glycol–water mixtures shows that the values are slightly lower in the former media than in the latter at comparable compositions, which may presumably be due to the higher dielectric constants of ethylene glycol–water mixtures than propylene glycol–water mixtures.

Table V. Changes in Thermodynamic Quantities $\Delta(\Delta Y°)$ on Mole Fraction Scale for the Self-Ionization of Propylene Glycol–Water Mixtures at 25 °C

[propylene glycol]/ wt %	($\Delta G°_s$ − $\Delta G°_{H_2O}$)/ (J mol^{-1})	($\Delta H°_s$ − $\Delta H°_{H_2O}$)/ (J mol^{-1})	T($\Delta S°_s$ − $\Delta S°_{H_2O}$)/ (J K^{-1} mol^{-1})
0	0	0	0
20	−847	−6142	−5289
40	−2380	+2693	+5057
75	−1216	−16533	−17194
90	−47	−21926	−21878
100[a]	+11264	−11093	−22367

[a] Obtained by using data from ref *6*.

Table IV gives the various thermodynamic quantities accompanying the autoprotolysis of the solvent mixtures. It is seen that the $\Delta G°_s$ values for self-ionization decrease slightly with the addition of propylene glycol to water up to about 40 wt % propylene glycol and subsequently increase. According to Feakins et al. (*16*) and Franks and Ives (*15*), the changes in $\Delta S°_s$ and $\Delta H°_s$ with solvent composition throw light on the structural changes associated with the self-ionization processes. Actually, the changes in the thermodynamic quantities $\Delta(\Delta Y°)$ = $\Delta Y°_s - \Delta Y°_w$ where $Y = G$, H, or S and $\Delta Y°_s$ and $\Delta Y°_w$ represent changes in the quantity Y for self-ionization in the solvent (s) and water (w) with solvent composition are given in Table V. It is seen (Table V) that the standard free energy difference of self-ionization [$\Delta(\Delta G°_s)$] decreases with the addition of propylene glycol to water up to about 40 wt % propylene glycol and then increases gradually, the increase being large in the region of pure glycol. A similar behavior was noted by Srinivas Rao (*12*) in the self-ionization of diethylene glycol–water mixtures.

The entropy and enthalpy differences of self-ionization show parallel changes in these solvent mixtures. The values are initially negative, then increase to a positive value at 40 wt % propylene glycol, and then gradually decrease beyond this composition. Although these variations are complex, the negative values of $\Delta(\Delta S°_s)$ and $\Delta(\Delta H°_s)$ beyond 40 wt % propylene glycol are indicative of the strong influence of structure-making ion–solvent interactions which are aided by the decreased dielectric constant of the mixtures and the breakdown of water structure by the addition of propylene glycol at higher compositions.

Registry No. Propylene glycol, 57-55-6.

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Vapor Pressure of 1-Nitropropene

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The vapor pressure of 1-nitropropene is reported over the temperature range 28–100 °C. The measurements are for an experimentally obtained equilibrium mixture of cis–trans isomers. The vapor pressure equation was determined to be ln $P = -(4.458 \times 10^3)(1/T) + 17.27$. The molar enthalpy of vaporization is 8.854 kcal/mol.

Introduction

In the course of the study of the thermal decomposition of nitroalkenes, it became necessary to measure the vapor pressure of 1-nitropropene over the temperature range of 28–100 °C. At the higher temperature limit 1-nitropropene begins to undergo thermal decomposition. The vapor pressure of 1-nitropropene has been previously reported by Redemann, Chaikin, and Fearing (*1*). Since the previous study did not report the method of synthesis employed, it is not clear whether the study dealt with a pure material or an equilibrium mixture of cis and trans isomers.

Experimental Section

A mixture of the cis and trans forms of 1-nitropropene was synthesized by dehydration of 1-nitro-2-propanol by using phthalic anhydride according to the procedure of Buckley and Scaife (*2*). The middle fraction boiling at 80 °C at 78 torr was collected. NMR spectra (Figure 1) showed the isomeric composition to be 32% cis form and 68% trans form. 1-Nitro-2-propanol was prepared by the aldol condensation of acetaldehyde and nitromethane in 2-propanol by using a potassium fluoride catalyst (*3*). The middle fraction boiling at 77 °C at 7 torr was collected.

The vapor pressure was measured with an isoteniscope. The procedure is similar to that described by Weissberger (*4*) except that in our experiments we used the original method of Smith and Menzies (*5*) in which the U-tube was charged with the material whose vapor pressure was to be measured. Measurements were made on water to check the validity of the method. Measurements made over a temperature range of 25–35 °C when averaged reproduced literature values (*6*) to within 1%.

Table I. Vapor Pressure Data for 1-Nitropropene

T, °C	P, torr	T, °C	P, torr	T, °C	P, torr
28.0	11.7	62.7	54.7	88.7	143.4
34.3	16.4	70.6	74.4	90.2	149.9
40.1	20.4	75.1	88.7	95.8	177.5
46.1	27.5	78.0	97.3	98.3	195.1
51.8	34.9	80.9	107.2	100.0	203.7
57.2	43.9	84.2	120.6		

A sample was degassed in the isoteniscope by alternate freezing, pumping, and thawing 3 times in a liquid-nitrogen bath. The sample was then allowed to thermally equilibrate for 20 min in a heated, circulating silicone oil bath. The temperature of both the bath and the vapor in the isoteniscope were measured with thermocouples connected to a digital thermometer; bath and vapor pressures were within 0.3 °C during any set of measurements. Vapor pressure readings were made by different readings from an open-end mercury manometer.

Results and Discussion

The measured vapor pressures are shown in Table I. A least-squares fit to a Clapeyron equation yields (pressure in torr and T in kelvin)

$$\ln P = [(-4.458 \pm 0.02) \times 10^3](1/T) + (17.27 \pm 0.13)$$

The resulting molar enthalpy of vaporization is 8.854 ± 0.040 kcal/mol.

Since the isomeric sample composition in the previously reported study of the vapor pressure of 1-nitropropene is not known, comparison of our data with previously measured data is difficult. Using the values obtained in the vapor pressure equation, we predict the normal boiling point of the mixture to be 147 °C while Redemann and co-workers predict it to be 140 °C. Our experimental error is largest at the lower end of the vapor pressure scale. For example, our least-squares fit showed the largest residuals to be associated with the data points at the lower end of the vapor pressure scale. Since our method reproduces results for known materials, we have no