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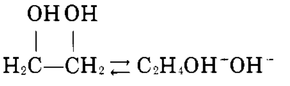
Autoprotolysis Constants of Ethylene Glycol and Propylene Glycol and Dissociation Constants of Some Acids and Bases in the Solvents at 30°C.

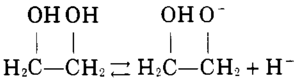
K. K. KUNDU and M. N. DAS
Jadavpur University, Calcutta, India

Autoprotolysis constants (K_s) of ethylene glycol and propylene glycol were determined at 30° C. electometrically by using a cell of the type H_2| MX, M-glycoxide, glycol | AgX-Ag without liquid junction. The pK_s values are found to be 15.60 and 16.76, respectively, for the two solvents. Thermodynamic dissociation constants of six uncharged carboxylic acids and 12 monopositively charged acids of the type BH^+ (conjugate to amine B) were determined in the two glycols at 30° C. by e.m.f. measurements on cells without liquid junction using hydrogen electrode and silver–silver halide electrode in suitable buffers. The corresponding dissociation constants of the conjugate bases have been calculated. The role of the solvent on acid-base equilibria has been discussed.

AUTOPROTOLYSIS. Like water and alcohols, glycols behave as amphiprotic solvents. Ethylene glycol is assumed to ionize in the following manner:

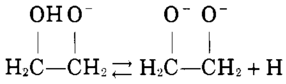


$$\overset{OH}{H_2C}—\overset{OH}{CH_2} \rightleftarrows C_2H_4OH^+OH^- \qquad (1)$$



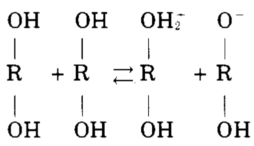
$$\overset{OH}{H_2C}—\overset{OH}{CH_2} \rightleftarrows \overset{OH}{H_2C}—\overset{O^-}{CH_2} + H^- \qquad (2)$$

The slow formation of chlorohydrin from glycol and hydrochloric acid as well as rapid formation of sodium-glycoxide from glycol and sodium metal is the chemical example for the above processes. The second stage of ionization of the glycol:



$$\overset{OH}{H_2C}—\overset{O^-}{CH_2} \rightleftarrows \overset{O^-}{H_2C}—\overset{O^-}{CH_2} + H^+ \qquad (3)$$

is a remote possibility. The ionization process represented by Equation 1 is presumably negligible and may occur in glycols (*1*) as:



$$\underset{OH}{\overset{OH}{R}} + \underset{OH}{\overset{OH}{R}} \rightleftarrows \underset{OH}{\overset{OH_2^+}{R}} + \underset{OH}{\overset{O^-}{R}} \qquad (4)$$

Representing the solvent molecule as SH and the ions as SH_2^+ and S^-, the autoprotolysis constant $K_S = a_{SH_2^+} \times a_{S^-}$, where "a" denotes activity.

The autoprotolysis constants of the two glycols were determined using a cell without transference of the type:

$$\text{Pt, H}_2\text{(gas, 1 atm.); Na-glycoxide, LiX, Glycol; AgX-Ag} \qquad (A)$$

where X stands for Cl or Br.

Dissociation of Carboxylic Acids. The dissociation of an acid, HA, in glycols, as in any other amphiprotic solvent, SH, is:

$$HA + SH \rightleftarrows SH_2^- + S^-$$

the dissociation constant is:

$$K_a = a_{SH_2^+} (a_{S^-}/a_{HA})$$

The dissociation constants of carboxylic acids were measured electrometrically using a cell, without liquid-junction, of Harned-Ehlers type:

$$\text{Pt, H}_2\text{(gas, 1 atm.); HA, NaA, LiX, Glycol; AgX-Ag} \qquad (B)$$

where HA represents an acid, NaA the sodium salt of the acid, and X the Cl or Br.

Dissociation of Bases. The equilibrium involved is represented as:

$$BH^- + SH \rightleftarrows B + SH_2^-$$

where B denotes an unchanged base (amine) and BH^+ the conjugate acid (aminium ion). The acid dissociation constant of the charged acid BH^+ is given by:

$$K_{BH^+} = a_B(a_{SH^+}/a_{BH^+})$$

For the dissociation constants of bases, a cell of the type:

$$\text{Pt, H}_2\text{(gas, 1 atm.); BH}^-\text{X}^-\text{, B, Glycol; AgX-Ag} \qquad (C)$$

was used where B denotes an amine base and BH^- the conjugate acid.

EXPERIMENTAL

The general experimental procedure has been described earlier (2). Temperature was maintained at 30° ± 0.1° C.

LiCl (G.R., Merck) was used after drying. LiBr solution in glycols was prepared by treating Li_2CO_3 (G.R., Merck) with HBr (pro-analysi, Merck), evaporating to dryness, and dissolving in a definite amount of glycol (avoiding contact with air as far as possible). The concentrations of LiX solutions were determined by the usual procedure.

To prepare sodium glycoxide solutions, freshly cut pieces of sodium (pro-analysi, Merck) were dipped into the distilled solvent, transferred hurriedly to the solvent in a Jena bottle, stoppered loosely, heated gently to accelerate the reaction and placed in a desiccator. The strength was found by titrating a weighed amount taken in water against a standard aqueous acid solution using phenolphthalein as indicator.

The cell solutions were prepared by weighing proper amounts of sodium glycoxide and lithium halide solutions in a stoppered Jena bottle and diluting with weighed amounts of solvents to give suitable ionic strengths.

Carboxylic acids. The acids were pro-analysi (Merck) samples which were purified by standard methods before use, if necessary. Acid solutions of proper strenghts were prepared by dissolving the acids in freshly distilled solvent in stoppered Jena bottles. Concentrations were found by titrating weighed amounts taken in water, with standard aqueous alkali, using phenolphthalein as indicator.

Fresh cell solutions were prepared by weighing in a Jena bottle proper amounts of standard acid solutions, lithium halide solutions, and sodium glycoxide solutions. The concentration of each species was calculated, assuming no volume change in the mixture. Buffer solutions of suitable ionic strengths were prepared by dilution with weighed amounts of solvents.

Bases. Ethylamine (B.D.H., Analar) sealed in an amber colored vial was used. Samples of monoethanolamine, pyridine, picoline, quinoline, aniline, piperidine of pure quality (Merck), and morpholine and triethylamine (B.D.H., Analar) were kept over KOH pellets (Merck) for one or two days and distilled. The purity of the samples was checked by boiling point determination. Pure di and triethanolamines (Merck) were distilled under reduced pressure after similar treatment with KOH pellets (Merck).

These bases and their hydrochlorides and hydrobromides are easily soluble in both the glycols with the exception of the hydrobromide of triethanolamine which is insoluble in propylene glycol.

Buffer solutions were prepared by weighing a suitable quantity of the base in a weighed quantity of solvent kept in a stoppered Jena bottle. To this solution, a quantity of standard acid solution in the same solvent was added and weighed. The resulting solution was a buffer of a definite ionic strength. Buffer solutions of lower ionic strengths were prepared by diluting with a weighed amount of solvent.

Because most of the amine bases studied are rather volatile, the buffer composition of the cell solutions during measurements could vary. This error was minimized by presaturating the hydrogen gas with the cell solution before introducing the gas into the cell.

Another source of error is possible dissolution of AgX in buffer solutions containing amines. No correction was applied since no data are available. Such correction factors, considered small in water, are expected to be small for glycols as well, especially when Ag-AgBr electrode is used.

If the base undergoes solvolysis, the composition of the buffer solution requires correction and when K_s for both solvents were known corrections were made.

RESULTS

Autoprotolysis Constants. The e.m.f. of the cell (*A*) is given by:

$$E = E^\circ_{(ag/AgX)} - \frac{RT}{nF} \ln(a_{SH_2^+}) \, (a_{X^-})$$

Assuming that the glycoxide and the halides are completely dissociated:

$$\frac{F(E - E^\circ_m)}{2.303\,RT} + \log \frac{m_{X^-}}{m_{S^-}} = -\log K_S - \log \left(\frac{\gamma_{X^-}}{\gamma_{S^-}}\right)$$

$$= pK_s - \log \left(\frac{\gamma_{X^-}}{\gamma_{S^-}}\right) \qquad (5)$$

where *m* denotes molality and γ the activity coefficient. The term $(\gamma_X / \gamma_{S^-})$, a ratio of activity coefficients of singly charged anions, would be nearly unity even at appreciable ionic strengths and becomes unity at infinite dilution.

The value of pK_s was obtained from extrapolation of the plot of the quantity represented on the left hand side (pK_s') *vs.* the corresponding ionic strength (μ). The E°_m values for Ag-AgCl and Ag-AgBr electrodes (2) were used. The e.m.f. data and the corresponding molalities of glycoxides and halides are presented in Tables I and II. The mean pK_s values for ethylene glycol and propylene glycol, using both types of halide electrodes, are 15.60 ± .02 and 16.76 ± .03, respectively, at 30° C.

Dissociation Constants of Acids. The relation between the observed e.m.f. (*E*) of the cell (*B*) and the dissociation constant (K_a) of the acid HA is:

Table I. pK_s of Ethylene Glycol at 30° C.

Cell: Pt, $H_2(g)$; LiX^a, Na-Glycoxide, Glycol; AgX-Ag

μ	m_{S^-}	m_X	E_{obs}	pK'_s
		Run I		
0.0216	0.0114	0.00812	0.8420	15.580
0.0481	0.0272	0.0163	0.8470	15.587
0.0732	0.0266	0.0396	0.8225	15.576
0.1123	0.0489	0.0526	0.8310	15.576
		Run II		
0.0370	0.0126	0.0208	0.8200	15.579
0.0574	0.0183	0.0336	0.8165	15.567
0.1451	0.0326	0.0986	0.8020	15.543
0.2328	0.0464	0.1640	0.7955	15.502
		Run III		
0.0164	0.00814	0.00664	0.9665	15.614
0.0465	0.0274	0.0146	0.9770	15.604
0.0905	0.0405	0.0413	0.9615	15.630
0.1216	0.0552	0.0547	0.9630	15.640
			Mean $pK_s = 15.60$	

[a] X = Br for runs I and II. X = Cl for run III.

Table II. pK_s of Propylene Glycol at 30° C.

Cell: Pt, $H_2(g)$; LiX, Na-glycoxide, Glycol; AgX-Ag

μ	m_{S^-}	m_{X^-}	E_{obs}	pK'_s
		Run I		
0.0162	0.00506	0.0107	0.8340	16.718
0.0353	0.0132	0.0211	0.8420	16.726
0.0656	0.0219	0.0419	0.8365	16.714
0.1191	0.0423	0.0735	0.8390	16.714
		Run II		
0.0331	0.0132	0.0190	0.8455	16.741
0.0598	0.0181	0.0400	0.8340	16.736
0.0889	0.0197	0.0667	0.8220	16.723
0.1142	0.0198	0.0912	0.8140	16.722
		Run III		
0.0156	0.00732	0.00784	0.9790	16.788
0.0384	0.0125	0.0253	0.9620	16.773
0.0783	0.0369	0.0392	0.9800	16.798
0.1061	0.0298	0.0733	0.9580	16.820
			Mean $pK_s = 16.76$	

[a] X = Br for runs I and II. X = Cl for run III.

$$\frac{F(E - E^{\circ}_{m})}{2.303\,RT} + \log m_{X^-} + \log (m_{HA}/m_{A^-}) = -\log K_a - \log \frac{\gamma_{HA}\gamma_{X^-}}{\gamma_{A^-}} \quad (6)$$

Using the term "acidity function," p_wH, after Bates (*3*), as defined by:

$$p_wH = \frac{F(E - E^{\circ}_{m})}{2.303\,RT} + \log m_{X^-} = -\log m_{SH_2^+}\gamma_{SH_2^+}\gamma_{X^-}$$

we can write

$$p_wH + \log (m_{HA}/m_{A^-}) = -\log K_a - \log \frac{\gamma_{HA}\gamma_{X^-}}{\gamma_{A^-}} \quad (7)$$

The right hand side of Equation 7 may be set equal to $-\log K'_a$, where K'_a becomes identical with K_a at infinite dilution when the activity coefficient factor $\log (\gamma_{HA}\gamma_{X^-}/\gamma_{A^-})$ becomes zero. For uncharged monobasic acid HA, the activity coefficient factor contains the ratio of the activity coefficients of two singly charged ions and the activity coefficient of the uncharged acid. According to Debye-Hückel equation, the total effect of the activity coefficient factor of a dilute solution is negligible.

From the standard potentials E°_{m} of Ag-AgX electrodes (*2*), the measured e.m.f. (E) of the cell (B) with buffer solutions of definite compositions containing acid HA (m_1), salt NaA (m_2) and halide LiX (m_3), the left hand side of Equation 7 was evaluated. These values ($-\log K'_a$) were plotted against ionic strengths (μ), and extrapolation of the curve to $\mu = 0$ gave the desired dissociation constant.

Because the dissociation of HA in the presence of NaA is negligible, $m_{HA} = m_1$ and $m_{A^-} = m_2$. Assuming that lithium halides dissociate completely, $m_{X^-} = m_{LiX} = m_3$. Buffer solutions of at least four different ionic strengths were used for each acid (HA). The ionic strength, $\mu = (m_{NaA} + m_{LiX})d_0$, ranged from 0.01 to 0.10 in most cases.

Table III presents typical data obtained for the evaluation of pK_a of acetic acid from the extrapolation of the plot of pK'_a against μ. Included are the data obtained by using both Ag-AgCl and Ag-AgBr electrodes in ethylene glycol. Table IV presents the corresponding data for propylene glycol. The pK_a values for acetic acid by both types of electrodes indicate the accuracy of the results. The reported pK_a values for acids have the average accuracy of ±0.03 unit. For the rest of the acids except phenyl acetic acid in ethylene glycol, relevant data were obtained with Ag-AgBr electrode only. For phenylacetic acid, Ag-AgCl electrode was used.

The pK_a values of the carboxylic acids studied are shown in Table V. The pK_b values of the corresponding conjugate bases (carboxylate ions) have been computed from the relation $pK_b = pK_s - pK_a$, using the values of pK_s for the glycols, 15.60 and 16.76, respectively. The pK values so calculated are shown in Table V.

Dissociation Constants of Bases. The e.m.f. (E) of the cell (C) is related to the dissociation constant (K_{BH^+}) of the acid BH^+ by:

$$-\log K_{BH^+} = \frac{F(E - E^{\circ}_{m})}{2.303\,RT} + \log m_{X^-} + \log \frac{m_{BH^+}}{m_B} + \log \frac{\gamma_{BH^+}\gamma_{X^-}}{\gamma_B}$$

$$= p_wH + \log \frac{m_{BH^+}}{m_B} + \log \frac{\gamma_{BH^+}\gamma_{X^-}}{\gamma_B} \quad (8)$$

The dissociation constants were obtained by linear extrapolation of the auxiliary function, $-\log K'_{BH^-}$ to zero ionic strength (μ):

$$-\log K'_{BH^+} = -\log K_{BH^+} - \beta\mu$$

$$= p_wH + \log \frac{m_{BH^+} + m_{S^-}}{m_B - m_{S^-}} - \frac{2S_f\mu^{1/2}}{1 + Ba_0\mu^{1/2}} \quad (9)$$

the activity coefficient term in Equation 8 being replaced by the Hückel equation:

$$\log \frac{\gamma_{BH^+}\gamma_{X^-}}{\gamma_B} = -\frac{2S_f\mu^{1/2}}{1 + Ba_0\mu^{1/2}} + \beta\mu \quad (10)$$

where S_f and B are Debye-Hückel constants, a_0 the ion size parameter and β an arbitrary adjustable parameter.

For the mono-positively charged acids in glycols the computation of the values of B and a_0, were unnecessary, since the substitution of $-2S_f\mu^{1/2}$ for the activity coefficient factor gave tolerably linear curves for extrapolation. The ionic strength (μ) was taken to be equal to $(m_{BH^+} + m_{S^-})d_0$, where d_0 represents the density of pure solvent at 30° C. The standard potentials of Ag-AgCl and Ag-AgBr electrodes in both the glycols used in calculations of pK'_{BH^-} were the values reported (*2*). Buffer solutions of at least

Table III. Dissociation Constant of Acetic Acid in Ethylene Glycol at 30° C.

Cell: Pt, $H_2(g)$; HA, NaA, LiX^a, Glycol; AgX-Ag

μ	m_{HA}	m_{NaA}	m_{X^-}	$E_{obs.}$	p_aH	pK'_a
			Run I			
0.0122	0.0248	0.00969	0.0138	0.4825	7.890	8.298
0.0415	0.0397	0.0155	0.0220	0.4690	7.862	8.277
0.0656	0.0629	0.0245	0.0348	0.4570	7.868	8.278
0.1041	0.0997	0.0389	0.0552	0.4440	7.852	8.261
						$pK_a = 8.30$
			Run II			
0.0204	0.00613	0.00727	0.01114	0.6460	8.423	8.349
0.0375	0.0114	0.0134	0.0205	0.6285	8.395	8.325
0.0689	0.0210	0.0246	0.0377	0.6120	8.385	8.317
0.1135	0.0345	0.0405	0.0621	0.5980	8.369	8.299
						$pK_a = 8.35$

[a] X = Br in run I, X = Cl in run II.

Mean $pK_a = 8.32 \pm 0.03$

Table IV. Dissociation Constant of Acetic Acid in Propylene Glycol at 30° C.

Cell: Pt, $H_2(g)$; HA, LiX^a, Glycol; AgX-Ag

μ	m_{HA}	m_{A^-}	m_{X^-}	$E_{obs.}$	p_aH	pK'_a
			Run I			
0.0184	0.0122	0.00868	0.00922	0.5065	8.913	9.062
0.0430	0.0285	0.0203	0.0215	0.4835	8.899	9.046
0.0707	0.0470	0.0333	0.0354	0.4695	8.882	9.032
0.1097	0.0729	0.0517	0.0549	0.4580	8.881	9.030
			Run II			
0.0165	0.0103	0.0073	0.0087	0.5080	8.912	9.062
0.0376	0.0137	0.0231	0.0134	0.5190	9.282	9.055
0.0730	0.0276	0.0366	0.0343	0.4865	9.150	9.027
0.0941	0.0421	0.0727	0.0187	0.5100	9.378	9.041
						$pK_a = 9.07$
			Run III			
0.0179	0.00635	0.00759	0.00977	0.6450	9.195	9.118
0.0500	0.0087	0.0138	0.0348	0.6190	9.315	9.115
0.0916	0.0298	0.0401	0.0489	0.6055	9.238	9.109
0.1442	0.0273	0.0368	0.1082	0.5825	9.200	9.070

Mean $pK_a = 9.10 \pm 0.03$

[a] X = Br in runs I and II. X = Cl in run III.

four different ionic strengths were used in each case. The ionic strengths ranged from 0.01 to 0.10 in most cases. The contributions due to m_{S^-} were negligibly small in the buffer regions for most of the amines studied. Table VI illustrates the typical data obtained for the evaluation of pK_{BH^+} of the anilinium ion from extrapolation of the plot pK'_{BH^+} against μ. Data obtained by using both Ag-AgCl and Ag-AgBr electrodes in ethylene glycol are included. Table VI presents the corresponding data for propylene glycol. The reported pK_{BH^-} values for several monopositively charged acids have the average accuracy of ± 0.03 unit. Data were obtained with Ag-AgBr electrode except for triethanol-ammonium ion in propylene glycol for which Ag-AgCl electrode was used.

The values of pK_{BH^-} for the cationic acids of the type BH^- studied in glycols at 30° C. are listed in Table VII which also shows the values of pK_b for the conjugate amine bases calculated from pK_{BH^-} by using the values of pK_s reported above.

DISCUSSION

The dissociation of an uncharged acid is accompanied by charge separation and so is affected by the dielectric constant in addition to the intrinsic and acid-base properties of the solvent. Thus, the pK_a values are, on the average, 3.7 and 4.4 units higher in ethylene glycol ($\epsilon = 36.73$) and propylene glycol ($\epsilon = 30.05$) than in water and indicate much larger dissociation in water. Between the two glycols, pK_a values in propylene glycol are appreciably higher than in ethylene glycol, and perhaps a reflection of the effect of the dielectric constant.

The electrostatic effect, depending on the dielectric constant, may be eliminated if we consider the equilibrium:

$$A^- + SH \overset{K_b}{\rightleftharpoons} HA + S^-,$$

which involves no charge separation. The equilibrium constant K_b represents the base strength of the anion A^- in the solvent SH, and, for the same anion, the values of K_b in different solvents may be expected to reflect the intrinsic acid strengths of the solvents. The values of pK_b in Table V indicate the base strengths of any anion in the two glycols lie in the order ethylene glycol > propylene glycol, and indicate that ethylene glycol is more acidic than propylene glycol. This might be expected from the inductive effect of the methyl group in propylene glycol. When the pK_b values for any anion in the glycols are compared with those in water (as reported in literature),

Table V. pK_a of Carboxylic Acids and pK_b of Conjugate Bases in Glycols at 30° C.

	Ethylene Glycol		Propylene Glycol	
Acids	pK_a	pK_b	pK_a	pK_b
Acetic	8.32	7.28	9.10	7.66
Phenylacetic	8.06	7.54	8.78	7.98
Benzoic	8.16	7.44	8.83	7.93
o-Bromobenzoic	6.87	8.73	7.59	9.17
Salicyclic	6.52	9.08	7.20	9.46
Phthalic	6.42	9.18	6.79	9.97

Table VI. Dissociation Constant (K_{BH^+}) of Anilinium in Glycols at 30° C.

Cell: Pt, $H_2(g)$; BH^-X^-, B, Glycol; AgX-Ag

μ	m_B	$m_{BH^+} = m_{X^-}$	$\log m_{X^-}$	$2S_f\mu^{1/2}$	$E_{obs.}$	p_wH	pK'_{BH^+}
			Ethylene Glycol ($X^- = Br^-$)				
0.0237	0.0249	0.0214	−1.670	0.478	0.3910	6.559	6.015
0.0544	0.0411	0.0492	−1.308	0.724	0.3665	6.513	5.867
0.0862	0.0648	0.0779	−1.108	0.911	0.3585	6.598	5.765
0.1226	0.1293	0.1108	−0.955	1.086	0.3620	6.792	5.639
						pK_{BH^+} =	6.09
			($X^- = Cl^-$)				
0.0304	0.0305	0.0275	−1.561	0.541	0.5150	6.635	6.049
0.0477	0.0704	0.0431	−1.365	0.678	0.5170	6.864	5.973
0.0766	0.1131	0.0692	−1.160	0.859	0.5090	6.953	5.881
0.1454	0.1454	0.1314	−0.881	1.184	0.4875	6.856	5.628
						pK_{BH^+} =	6.15
			Propylene Glycol ($X^- = Br^-$)				
0.0215	0.0296	0.0209	−1.680	0.615	0.3560	6.766	6.000
0.0456	0.0503	0.0443	−1.354	0.895	0.3400	6.826	5.876
0.0732	0.0806	0.0711	−1.148	1.135	0.3330	6.915	5.726
0.1142	0.1533	0.1110	−0.955	1.417	0.3335	7.116	5.559
						pK_{BH^+} =	6.10
			($X^- = Cl^-$)				
0.0278	0.0216	0.0270	−1.569	0.699	0.4640	6.627	6.095
0.0497	0.0673	0.0483	−1.316	0.935	0.4710	6.996	5.917
0.0756	0.1022	0.0735	−1.134	1.153	0.4650	7.078	5.782
0.1346	0.1047	0.1308	−0.883	1.539	0.4425	6.955	5.519
						pK_{BH^+} =	6.15

Table VII. pK_{BH^-} of Aminium Ions and pK_b of Conjugate Amine Bases in Glycols at 30° C.

	Ethylene Glycol		Propylene Glycol	
Amines	pK_{BH^-}	pK_b	pK_{BH^+}	pK_b
Monoethylamine	11.72	3.88	11.61	5.15
Diethylamine	11.86	3.74	11.65	5.11
Triethylamine	11.15	4.45	10.87	5.89
Monoethanolamine	11.21	4.39	11.10	5.66
Diethanolamine	10.53	5.07	10.37	6.39
Triethanolamine	9.30	6.30	9.19	7.57
Aniline	6.12	9.48	6.12	10.64
Pyridine	5.92	9.68	5.69	11.07
Quinoline	5.39	10.21	5.27	11.49
α-Picoline	6.38	9.22	6.09	10.67
Piperidine	11.92	3.68	11.71	5.05
Morpholine	10.14	5.46	10.05	6.71

the glycols are appreciably more acidic than water. The dissociation of charged acids of the type BH^- does not involve any charge separation and should not, be appreciably affected by the dielectric properties. K_{BH^-} values for any one acid in different solvents should provide a rough measure of the relative base strengths of the solvents. On the basis of the pK_{BH^-} values in the two glycols, propylene glycol is slightly more basic than ethylene glycol (Table VII). The comparison of these pK_{BH^-} values with the corresponding values in water (as reported in literature), indicates that water is appreciably more basic than the two glycols.

The glycols come out as more acidic and, at the same time, less basic than water. Comparing the two glycols, ethylene glycol is more acidic and less basic than propylene glycol. The former possesses a higher dielectric constant. The resultant effect of these three factors produces a higher autoprotolysis constant for ethylene glycol than for propylene glycol.

Table VII shows that pK_b for an uncharged base (an amine) is, on an average, 1.3 units higher in propylene glycol than in ethylene glycol, and indicates greater dissociation of the base in the latter. This process of dissociation, as for an uncharged acid, is accompanied by charge separation and is facilitated by greater dielectric properties. The higher acid strength and the greater dielectric properties of ethylene glycol enhance the dissociation of an uncharged base when compared with propylene glycol. With an uncharged acid, the average difference in pK_a values in the two glycols is smaller (0.7 unit), because the higher acidity of ethylene glycol exerts an adverse effect on the dissociation process. The net result is ultimately determined by the higher dielectric constant.

It may not, however, be logical to carry this analysis further, since factors other than acid-base interaction may be involved in acid-base equilibria in different solvents. Ethylamines are weaker in ethylene glycol than in water (as judged from the pK_b values), whereas the ethanolamines are slightly stronger in the glycol. In propylene glycol, the six amines were weaker than in water. The dissociation of a base (as also of an acid to some extent) is expected to be immensely affected by hydrogen bond formation, and hence K_b values may not necessarily reflect the intrinsic strengths of the bases even in the same solvent. Correlation of K_b values in different solvents is an intriguing problem, but before any serious attempt is made in this direction, it is essential to gather as much information as possible from changing the several parameters involved in proton transfer processes.

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