Studies in ' Isodielectric ' Media. Part II.[1] Autoprotolysis Constants of Methanol–Propylene Glycol at 25 °C

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The autoprotolysis constants (K_s) of a series of approximately ' isodielectric ' media comprising methanol and propylene glycol (PG) have been determined at 25° from the e.m.f. measurements of the cell: Pt, H_2(g, 1 atm)| NaS(m_1), NaCl(m_2), solvent|AgCl–Ag. Since the ' electrostatic effect ' arising from the little difference in dielectric constant values is negligibly small, the standard free-energy changes accompanying the transfer of solvent molecules acting as an acid as well as a base, from methanol to the solvent, have been shown to be dictated by the intrinsic acidity and basicity of the solvents. The results suggest that the acidity of the mixed solvents increases and the basicity decreases, as the proportion of PG is increased.

SINCE the autoprotolysis constant (K_s) is a unique parameter in understanding acid–base equilibria and as a quantitative measure of the extreme limits of acidity and basicity in any amphiprotic solvent, the evaluation of K_s values in this kind of solvent should be useful. Since this self protolysis is accompanied by charge separation, it should be dependent on the dielectric constant,[2] as well as on the ' intrinsic ' acidity and basicity of the solvents, as has been amply demonstrated in the cases of mixed solvents such as water–dioxan,[3] –methanol,[4] –ethanol,[5] and –glycol.[6] Consequently, it should be particularly interesting to see how, in a series of ' isodielectric ' media, the values of this quantity vary with composition of the mixed solvents, where the effect of dielectric constant is negligible. With this end in view, K_s values for a series of nearly isodielectric media obtained by mixing methanol and propylene glycol (PG) in different proportions have been determined.

As in glycol–water,[6] in a mixed medium comprising two amphiprotic solvents, methanol (MH) and propylene glycol (GH), autoprotolysis should involve the following ionization processes.

$$\mathrm{MH} + \mathrm{MH} \rightleftharpoons \mathrm{MH_2}^+ + \mathrm{M}^- \qquad (1)$$

$$\mathrm{MH} + \mathrm{GH} \rightleftharpoons \mathrm{MH_2}^+ + \mathrm{G}^- \qquad (2)$$

$$\mathrm{GH} + \mathrm{MH} \rightleftharpoons \mathrm{GH_2}^+ + \mathrm{M}^- \qquad (3)$$

$$\mathrm{GH} + \mathrm{GH} \rightleftharpoons \mathrm{GH_2}^+ + \mathrm{G}^- \qquad (4)$$

In the mixed medium, MH_2^+ and GH_2^+ are the lyonium ions, and M^- and G^- are the lyatic ions. Conveniently, all the processes [(1)—(4)] may be represented by the general equation (5), where SH denotes either methanol

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

or propylene glycol, and SH_2^+ and S^- the lyonium and lyate ions respectively. The autoprotolysis constant K_s of the mixed solvents is given by the equilibrium constant of the process (5), *i.e.* equation (6), where *a*

$$K_S = a_{\mathrm{SH_2}^+} a_{\mathrm{S}^-} / a_{\mathrm{SH_2}} = a_{\mathrm{SH_2}^+}\, m_{\mathrm{S}^-} \gamma_{\mathrm{S}^-} / a_{\mathrm{SH}}{}^2 \qquad (6)$$

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[1] Part I, K. K. Kundu, A. L. De, and M. N. Das, preceding paper.

[2] R. G. Bates, ' Hydrogen-Bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968.

[3] H. S. Harned and L. D. Fallon, *J. Amer. Chem. Soc.*, 1938, **61**, 2374.

[4] J. Koskikallio, *Soumen Kem.*, 1957, **30** *B*, 38, 43, 111.

[5] B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559, 665.

[6] S. K. Banerjee, K. K. Kundu, and M. N. Das, *J. Chem. Soc.* (*A*), 1967, 166.

denotes activity, m the molality, and γ the activity coefficient.

EXPERIMENTAL

The values of K_s for all these solvents have been determined at 25° using the cell A.

$$\mathrm{Pt,\ H_2(g,\ 1\ atm)|NaS}(m_1),\ \mathrm{NaCl}(m_2),\ \mathrm{solvent|AgCl\text{–}Ag} \qquad \mathrm{A}$$

The general experimental procedure has been described.[6-8] The Pt-foil electrode was sometimes found to be poisoned especially by methanol-rich solvents, as indicated by the rapidly decreasing e.m.f. values of the cell A. Stable and reproducible e.m.f. values were, however, obtained when a freshly platinized Pt-foil electrode was inserted. Such poisoning was also reported by other workers for methanol [9] and methanol-rich aqueous mixtures.[10] In the present study the Pt-foil electrode was usually inserted into the cell after hydrogen had been passed into the cell for at least 4 h. The e.m.f. values were checked by inserting freshly platinized Pt-foil electrodes.

RESULTS AND DISCUSSION

The p(K_s) values in these solvents were obtained from the plots of the p$(K_s)'$ values, defined by equation (7),[8] against the ionic strength (μ) by extrapolation to $\mu = 0$.

$$\mathrm{p}(K_s)' \equiv \frac{F[E - ({}_sE_m{}^\circ)_{\mathrm{AgCl\text{-}Ag}}]}{2{\cdot}303RT} + \log\frac{m_{\mathrm{Cl}^-}}{m_{\mathrm{S}^-}}$$

$$= \mathrm{p}(K_s) - \log\frac{\gamma_{\mathrm{Cl}^-}a_{\mathrm{SH}}}{\gamma_{\mathrm{S}^-}} = \mathrm{p}(K_s) + f(\mu) \qquad (7)$$

In Table 1 are the observed e.m.f. data (corrected to 1 atm H_2) at 25°, against the corresponding molalities of NaS and NaCl. Assuming that both NaCl and NaS are completely dissociated in these solvents, $m_{\mathrm{S}^-} = m_1$, $m_{\mathrm{Cl}^-} = m_2$, and $\mu = (m_1 + m_2)d_s$, where d_s is the density of the solvent. The required vapour pressure, density, and (${}_sE_m{}^\circ$) values for the AgCl–Ag electrode in these solvents are reported in Part I.[1] The extrapolations on the plots of p$(K_s)'$ *versus* μ for different solvents are illustrated in Figure 1. The average standard deviation of the p(K_s) values for all these solvents is of the order of ±0·01 unit.

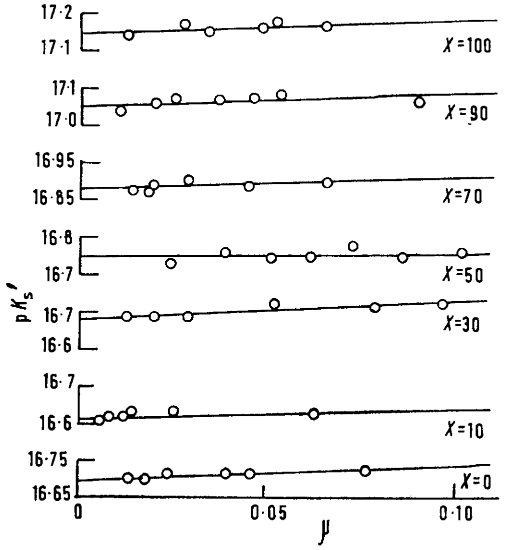

FIGURE 1 Evaluation of pK_s values of methanol–propylene glycol mixtures at 25°. X = Wt. % PG

The p(K_s) values at 25° for these solvents are presented in the second column of Table 2, and are referred to the conventional molal scale and henceforth will be denoted by p$(K_s)_m$. The values of p$(K_s)_m$ for both methanol and PG are in fair agreement with those determined earlier, 16·64 [11] and 17·21 [8] respectively.

TABLE 1

E.m.f. (E) of the cell A in methanol–propylene glycol at 25°

Methanol			10 Wt % PG			30 Wt. % PG		
m_{NaCl}	m_{NaS}	E/V	m_{NaCl}	m_{NaS}	E/V	m_{NaCl}	m_{NaS}	E/V
0·00826	0·00967	0·9827	0·00371	0·00392	0·9782	0·01098	0·00430	0·9559
0·0116	0·0116	0·9793	0·00499	0·00485	0·9787	0·0145	0·00955	0·9696
0·0150	0·0156	0·9804	0·00677	0·00735	0·9806	0·0201	0·0140	0·9707
0·0251	0·0255	0·9809	0·00666	0·00949	0·9882	0·0418	0·0189	0·9621
0·0292	0·0297	0·9810	0·0144	0·0174	0·9841	0·0465	0·0461	0·9821
0·0510	0·0473	0·9791	0·0304	0·0473	0·9904	0·0626	0·0507	0·9774

50 Wt. % PG			70 Wt. % PG			90 Wt. % PG			100 % PG		
m_{NaCl}	m_{NaS}	E/V	m_{NaCl}	m_{NaS}	E/V	m_{NaCl}	m_{NaS}	E/V	m_{NaCl}	m_{NaS}	E/V
0·0171	0·00960	0·9650	0·00678	0·00799	0·9862	0·00580	0·00480	0·9766	0·00591	0·00608	0·9827
0·0252	0·0142	0·9667	0·00969	0·00800	0·9796	0·01059	0·00915	0·9784	0·0132	0·0136	0·9841
0·0327	0·0183	0·9663	0·00106	0·00967	0·9797	0·0123	0·0128	0·9833	0·0164	0·0169	0·9835
0·0398	0·0223	0·9665	0·0166	0·0131	0·9771	0·0188	0·0177	0·9810	0·0235	0·0235	0·9836
0·0472	0·0264	0·9677	0·0233	0·0236	0·9825	0·0221	0·0236	0·9845	0·0251	0·0250	0·9840
0·0625	0·0344	0·9665	0·0333	0·0354	0·9847	0·0235	0·0291	0·9883	0·0367	0·0265	0·9754
0·0726	0·0406	0·9675				0·0407	0·0494	0·9880			

Since the concentration terms of the ions such as $SH_2{}^+$ and S^- are referred to the molal scale in the respective solvents, p$(K_s)_m$ values are liable to reflect a scale effect.[8,11] For the sake of comparison, p$(K_s)_m$

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[7] K. K. Kundu and M. N. Das, *J. Chem. and Eng. Data*, 1964, **9**, 82.

[8] K. K. Kundu, P. K. Chattopadhyay, Debabrata Jana, and M. N. Das, *J. Phys. Chem.*, 1970, **74**, 2633.

[9] E. W. Kanning and A. W. Campbell, *J. Amer. Chem. Soc.*, 1942, **64**, 517.

[10] D. Feakins and R. P. T. Tomkins, *J. Chem. Soc.* (*A*), 1967, 1458.

[11] W. L. Jolly, *J. Amer. Chem. Soc.*, 1952, **74**, 6199.

values in different solvents were, therefore, converted into the mole fraction scale, $p(K_s)_N$, by use of equation (8), where M_s is the average or actual molecular weight of the solvent. The values are recorded in Table 2.

TABLE 2

$p(K_s)_m$, $p(K_s)_N$, and $\Delta G_t°(SH - SH)_{sys}$ values for methanol–propylene glycol at 25°

Wt. % PG	$p(K_s)_m$	$p(K_s)_N$	$\Delta G_t°$ (SH − SH)$_{sys}$ (cal)
0	16·69	19·68	0
10	16·61	19·55	−177
30	16·68	19·50	−246
50	16·75	19·44	−327
70	16·88	19·42	−355
90	17·05	19·40	−382
100	17·15	19·39	−396

$$p(K_s)_N = p(K_s)_m + 2 \log (1000/M_s) \qquad (8)$$

The $p(K_s)$ value in any amphiprotic solvent is usually a composite function of the dielectric constant as well as the intrinsic acidity and basicity of the solvent. The term ' intrinsic ', however, refers to all the free-energy changes associated with the acidic or basic behaviour of the solvent molecules including those associated with the primary solvation of the resulting ions, the solvent molecules acting as the dielectrically saturated dipoles. The contribution associated with the secondary solvation of the ions is, however, largely dependent on the permittivity of the solvents.[12] Since the dielectric constants of these solvents do not vary considerably with the change in solvent composition, it is expected that the variation in $p(K_s)$ values with composition should necessarily reflect the change of intrinsic acidity and basicity of the solvents concerned.

The standard free-energy changes ($\Delta G°$) accompanying the autoprotolysis of a solvent with respect to that of methanol is given by equation (9), where the subscripts

$${}_s\Delta G° - {}_m\Delta G° = 2{\cdot}3026RT[p({}_sK_s)_N - p({}_mK_s)_N] \qquad (9)$$

s and m denote that the respective quantities are referred to solvent (SH) and methanol (MH) respectively. The quantity given by equation (9) yields a measure of the standard free-energy change for the transfer process of the solvent molecules acting as the acid–base system $(SH–SH)_{sys}$ from methanol to solvent, as represented by equation (10), where each of the reactants and products

$$MH_2^+(m) + SH(s) + SH(s) + M^-(m) \longrightarrow SH_2^+(s) + MH(m) + MH(m) + S^-(s) \qquad (10)$$

is in its standard state indicated by (s) or (m).

This is equivalent to the sum of the processes (11) and (12), the standard free-energy changes of which may be

$$MH_2^+(m) + SH(s) \longrightarrow SH_2^+(s) + MH(m) \qquad (11)$$

$$SH(s) + M^-(m) \longrightarrow MH(m) + S^-(s) \qquad (12)$$

denoted by $\Delta G_t°(H^+)$ and $\Delta G_t°(S^-)$ respectively. Thus giving (13).

$$\Delta G_t°(SH–SH)_{sys} = \Delta G_t°(H^+) + \Delta G_t°(S^-) \qquad (13)$$

Just as $\Delta G_t°(H^+)$, the standard free-energy change accompanying the transfer of H^+ from methanol to the other solvent, is a measure of the proton affinity of the solvent with respect to that of methanol,[1] the quantity $\Delta G_t°(S^-)$ gives a measure of the acidity of the solvent with respect to that of methanol. The free-energy change accompanying the process (12) should be equivalent to the difference of free-energy changes accompanying the processes (14) and (15). These represent the

$$SH(s) \longrightarrow S^-(s) + H^+(g) \qquad (14)$$

$$MH(m) \longrightarrow M^-(m) + H^+(g) \qquad (15)$$

acidic ionization of the solvent (SH) and methanol (MH) molecules acting as acids, where (g) indicates that H^+ is in the gaseous standard state.

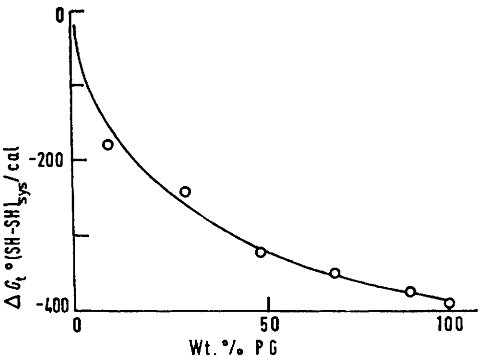

FIGURE 2 Variation of $\Delta G_t°$ $(SH–SH)_{sys}$ as a function of wt. % PG in methanol–propylene glycol mixtures at 25°

The values of $({}_s\Delta G° - {}_m\Delta G°)$ *i.e.* $\Delta G_t°(SH - SH)_{sys}$ for different solvents are in Table 2 and their variation with weight percent PG is illustrated in Figure 2. It can be seen that $\Delta G_t°(SH - SH)_{sys}$ values decrease sharply at first but less so afterwards, as the proportion of PG increases. This seems to indicate that at least two effects are presumably acting in opposite directions. As has been indicated in Part I,[1] with increasing proportion of PG, $\Delta G_t°(H^+)$ values tend to become increasingly positive, so it appears that $\Delta G_t°(S^-)$ values will have increasingly negative magnitudes. This implies that increasing the proportion of PG relative to methanol makes the resulting solutions less ' basic ' and at the same time more ' acidic '. The negative magnitudes of $\Delta G_t°(SH - SH)_{sys}$ further indicate that $\Delta G°_t(S^-)$ values at any composition exceed the $\Delta G_t°(H^+)$ values. This suggests that PG is a stronger acid, but at the same time a weaker base than methanol, the acidity of PG being, however, more pronounced than the basicity of methanol.

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[0/1548 *Received, September 2nd,* 1970]

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[12] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd rev. edn., Butterworths, London, 1965, p. 353—354.