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**AUTOPROTOLYSIS CONSTANTS  
IN NONAQUEOUS SOLVENTS AND  
AQUEOUS ORGANIC SOLVENT  
MIXTURES**

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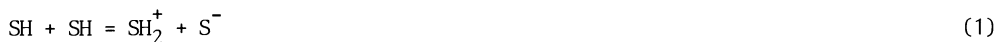
# Autoprotolysis constants in nonaqueous solvents and aqueous organic solvent mixtures

The recent IUPAC document on standardization of pH measurements in nonaqueous solvents and aqueous-organic solvent mixtures (P.A.C. 57, 865 (1985)) underlines the importance of the autoprotolysis constant,  $K_{ap}$ , which defines the normal range of pH in the relevant solvent. The recommended e.m.f. method of determination and the standard states implied by different  $K_{ap}$  definitions are duly focused. This compilation is articulated in two Tables the first of which reports  $K_{ap}$  data for 100% pure solvents mostly at 298.15 K and the other concerns binary aqueous-organic mixtures of different compositions and at various temperatures.

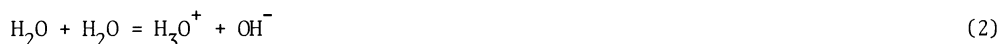
## 1. INTRODUCTION

The recent IUPAC document on the criteria for standardisation of pH measurements in organic solvents and aqueous organic solvent mixtures (ref. 1) underlines the importance of the autoprotolysis constant,  $K_{ap}$ , of each solvent in determining the so-called "normal range of pH" (as given by  $pK_{ap} = -\log K_{ap}$ ) in such a solvent (refs. 1,2). (This subject also has important bearings on acidimetric titrations in nonaqueous or mixed media, where the "pH jump" at the equivalence point is larger, the greater the  $pK_{ap}$  value).

A solvent SH (a pure solvent or *e.g.* a binary aqueous-organic solvent mixture  $SH = H_2O + ZH$ , cf. equations (5) to (8)) capable of being both a proton donor and a proton acceptor can undergo autoprotolysis according to the general process:



The auto-ionisation of water:



is the best known example of such behaviour.

The general equilibrium constant for (1) is called the *autoprotolysis constant*,  $K_{ap}$ , and is defined by:

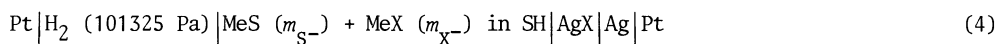
$$K_{ap} = \alpha_{SH_2^+} \alpha_{S^-} / \alpha_{SH}^2 = m_{SH_2^+} m_{S^-} \gamma_{SH_2^+} \gamma_{S^-} / \{ (m^\circ)^2 x_{SH}^2 f_{SH}^2 \} \quad (3)$$

where  $\alpha_{SH_2^+}$  and  $\alpha_{S^-}$ , and  $\gamma_{SH_2^+}$  and  $\gamma_{S^-}$  are ionic activities and activity coefficients at the molalities  $m_{SH_2^+}$  and  $m_{S^-}$ , respectively,  $m^\circ = 1$  mol/kg,  $\alpha_{SH}$  and  $f_{SH}$  are the activity and rational activity coefficient of the undissociated species SH at the mole fraction  $x_{SH}$ .

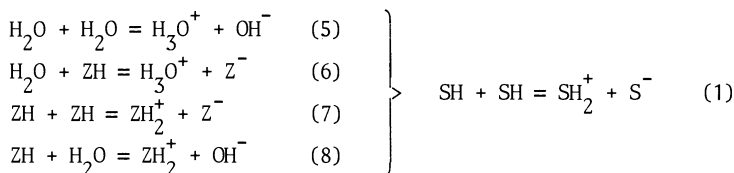
The standard state for the ionic species is the *hyp.*  $m = 1$  (implying reference to  $\gamma = 1$  at infinite dilution in the solvent SH) and  $x = 1$  for the undissociated solvent SH (to be understood in terms of  $x = x_{H_2O} + x_{ZH} = 1$  for a binary aqueous-organic solvent mixture  $SH = H_2O + ZH$ , cf. equations (5) to (8), and Table 2). Thus  $K_{ap}$  is a dimensionless thermodynamic quantity, whose magnitude reflects the combined acidic and basic character of the solvent SH (pure or mixed).

The theme of autoprotolysis constants in relation to pH ranges was introduced by Bates (refs. 2-4), and the methods of determination were also touched by King (refs. 5,6). These methods vary from that of electromotive force (e.m.f.) of reversible cells (both in the direct role

and in the titrimetric role) to conductance, density, calorimetry, cryoscopy, *etc.*, but the most convenient (and recommended) one is that of reversible e.m.f. of the cell:



where  $X = \text{Cl}, \text{Br}, \dots$ ,  $\text{Me} = \text{Li}, \text{Na}, \text{K}, \dots$ ,  $\text{S}^-$  is the lyate ion and  $\text{SH}_2^+$  is the lyonium ion (cf. equation (1)) in the case of the pure nonaqueous solvent SH. In the more general case of a binary aqueous-organic solvent mixture ( $\text{H}_2\text{O} + \text{ZH}$ ), the following equilibria must be considered simultaneously:



and the process (1) can be, and shall here be, taken to symbolize them altogether (refs. 7-9). Evidently, if ZH were a completely aprotic, nonpolar, inert solvent, the processes (6) to (8) would be practically not existent, and (5) would be the actual significant process, *i.e.* the autoprotolysis of water in an aqueous organic mixture. In the general case of the equations (5) to (8),  $\text{H}_3\text{O}^+$  and  $\text{ZH}_2^+$  are the lyonium ions and  $\text{OH}^-$  and  $\text{Z}^-$  are the lyate ions. The e.m.f. of the cell (4) is expressed by:

$$E = E^\circ - k \log(\alpha_{\text{SH}_2^+} \alpha_{\text{X}^-} / \alpha_{\text{SH}}) \quad (9)$$

where  $k = (\ln 10) RT / F$  and  $E^\circ$  is the standard e.m.f. of that cell. Eliminating  $\alpha_{\text{SH}_2^+}$  from eqs. (3) and (9) gives:

$$(E - E^\circ) / k + \log(m_{\text{X}^-} / m_{\text{S}^-}) = -\log K_{\text{ap}} - \log(\alpha_{\text{SH}} \gamma_{\text{X}^-} / \gamma_{\text{S}^-}) \quad (10)$$

Expressing the single-ion activity coefficients through an extended Debye-Hückel equation of the type:

$$\log \gamma_i = -Az_i^2 I^{1/2} / (1 + a_0 b_i I^{1/2}) + b_i I \quad (11)$$

where  $I$  is the ionic strength of solution and the other symbols keep their usual meanings, from eq. (10) one can define the extrapolation function  $\text{p}K'_{\text{ap}}$ :

$$\text{p}K'_{\text{ap}} = (E - E^\circ) / k + \log(m_{\text{X}^-} / m_{\text{S}^-}) = \text{p}K_{\text{ap}} + \text{p}\alpha_{\text{SH}} + (b_{\text{S}^-} - b_{\text{X}^-}) I \quad (12)$$

Plotting  $\text{p}K'_{\text{ap}}$  vs.  $I$  and extrapolating to  $I = 0$  (where  $\alpha_{\text{SH}} = 1$  and  $\text{p}\alpha_{\text{SH}} = 0$ ) the intercept gives  $\text{p}K_{\text{ap}}$ .

This method gives particularly precise and reliable results and lends itself best for systematic determinations over wide ranges of temperatures and solvent compositions, and its only occasional limitations of applicability could come from possible chemical incompatibility of cell electrodes with certain solvents ZH. It was by this method of reversible e.m.f. that were obtained the greater part of  $\text{p}K_{\text{ap}}$  values hitherto available (see Tables 1 and 2), particularly those of the aqueous organic solvent mixtures (Table 2).

An indirect way of obtaining  $\text{p}K_{\text{ap}}$  is provided by the fact that the product of the acidity constant  $K_A$  and the basicity constant  $K_B$  of an acid-base conjugate pair gives the autoprotolysis constant of the solvent:

$$K_{\text{ap}} = K_A K_B \quad (13)$$

For instance, the acidity constant  $K_A$  for an acid HA may be determined by spectrophotometry or potentiometry and combined with the basicity constant  $K_B$  of its conjugate base  $A^-$  determined independently by conductance or by other methods, to give  $K_{ap}$  through (13).

TABLE 1 - Values of autoprotolysis constants  $K_{ap}$  on logarithmic scale ( $pK_{ap} = -\log K_{ap}$ ) for some nonaqueous solvents at various temperatures: data for water are quoted for comparison. The standard state is chosen so that the activity of the undissociated solvent is unity in the pure solvent ( $x = 1$ ), and the (molal scale) activities of the involved ionic species are referred to unit activity coefficient at infinite dilution in that solvent.

T/K	SOLVENT			
	WATER	DEUTERIUM OXIDE	ETHYLENE GLYCOL	PROPYLENE GLYCOL
273.15	14.944			
278.15	14.734	15.740	16.47	17.81
283.15	14.535	15.526	16.30	17.64
288.15	14.346	15.326	16.14	17.50
293.15	14.167	15.136	15.99	17.35
298.15	13.997	14.955	15.84	17.21
303.15	13.833	14.784	15.71	17.08
308.15	13.680	14.622	15.57	16.96
313.15	13.535	14.468	15.44	16.83
318.15	13.396	14.322	15.33	16.73
323.15	13.262	14.103		
Constants of $pK_{ap} = A/T + B + CT$				
A/K	4471.33	4913.14	3487.25	3372.00
B	-6.0846	-7.5117	0.927	2.571
C/K <sup>-1</sup>	0.017053	0.0200854	0.01079	0.01120
Method of determination : reversible e.m.f. of cell (4)				
Refs.	10-12	16	8	8

SOLVENT	$pK_{ap}$	T/K	Refs.	SOLVENT	$pK_{ap}$	T/K	Refs.
HYDROGEN PEROXIDE	12.7	$\alpha$ 298.15	17	1-BUTANOL	21.56	$\alpha$ 298.15	31
METHANOL	16.708	$\alpha$ 298.15	18-20	2-METHYL- -2-PROPANOL	28.5	$\alpha\sigma$ 298.15	32,33
	16.45	$\alpha$ 298.15	21				
	16.45	$e$ 298.15	22	1-PENTANOL	20.65	$\alpha$ 298.15	31
	16.72	$\alpha$ 298.15	23	1-HEXANOL	19.74	$\alpha$ 298.15	31
	16.47	$\alpha$ 298.15	24	1-OCTANOL	19.44	$\alpha$ 298.15	31
ETHANOL	19.5	$\alpha$ 298.15	15	DIETHYLENE GLYCOL	17.4	$\alpha$ 298.15	24
	18.9	$\alpha$ 298.15	25		17.49	$\alpha$ 298.15	24a
	18.72	$\alpha$ 298.15	26	ETHYL CELLOSOLVE	19.3	$\alpha$ 298.15	24
	18.95	$\alpha$ 293.15	27,28	AMMONIA	32.	$\alpha$ 213.15	34
1-PROPANOL	18.67	$\alpha$ 298.15	27,28		29.	$\alpha$ 223.15	35
	18.91	$e$ 298.15	22		32.7	$\alpha$ 223.15	29
	19.33	$\alpha$ 293.15	27,28		32.5	$b$ 240.15	36
	19.24	$\alpha$ 298.15	27,29		27.7	$b$ 298.15	36
2-PROPANOL	20.84	$\alpha$ 293.15	27,29		29.8	$b$ 298.15	37-39
	20.58	$\alpha$ 298.15	27,28				
	20.8	$e$ 298.15	2,30				

(CONTINUES)

TABLE 1 (CONTINUED)

SOLVENT	$pK_{ap}$	$T/K$	Refs.	SOLVENT	$pK_{ap}$	$K/K$	Refs.
ETHYLENE DIAMINE	15.2 <i>f</i>	298.15	40	FORMIC ACID	6.5 <i>e</i>	298.15	62
	15.3 <i>a</i>	298.15	40,41		6.65 <i>a</i>	298.15	62a
					6.2	298.15	63
ETHANOLAMINE	5.1 <i>a</i>	293.15	2,43		6.17 <i>e</i>	298.15	64
	5.15 <i>e</i>	293.15	44		$\geq 6.83$ <i>e</i>	298.15	65
	5.2 <i>a</i>	293.15	45	ACETIC ACID	10.7	273.15	2
	5.7 <i>e</i>	298.15	46		12.55 <i>a</i>	292-293	66
HYDRAZINE	13. <i>e</i>	298.15	47		14.45 <i>af</i>	298.15	67
FORMAMIDE	17.0 <i>a</i>	293.15	48		14.5	298.15	63
	16.8 <i>a</i>	293.15	2		12.6 <i>cb</i>	298.15	38,68
					13.0 <i>e</i>	378.8	69
DIMETHYL FORMAMIDE	27-29 <i>ae</i>	298.15	14,49	SULPHURIC ACID	3.8	283.15	70
ACETAMIDE	10.5 <i>a</i>	367.15	49a		3.46 <i>b</i>	298.15	71
	14.6 <i>a</i>	371.15	50		3.57 <i>b</i>	298.15	72,73
					3.64 <i>e</i>	298.15	74
ACETONITRILE	28.6 <i>a</i>	298.15	51		3.33 <i>g</i>	298.15	75
	26.5 <i>f</i>	298.15	52	DEUTERIUM SULPHATE	4.34 <i>e</i>	298.15	76
	26.0 <i>a</i>	298.15	53	FLUOSULPHONIC ACID	7.4 <i>e</i>	298.15	77
	$>32.2$ <i>f</i>	298.15	54	SELENIC ACID	$\sim 2.$ <i>e</i>	298.15	78
ACETONE	$>32.5$ <i>a</i>	298.15	55	PHOSPHORIC ACID	0.8 <i>e</i>	298.15	78
ETHYL-METHYLKETONE	31.0	298.15	49	HYDROFLUORIC ACID	10.5 <i>e</i>	298.15	79
NITROMETHANE	$\geq 24.$ <i>a</i>	298.2	56				
DIMETHYL SULPHOXIDE	$\sim 32.$ <i>e</i>	298.15	57	<i>Methods:</i> <i>a</i> , e.m.f.; <i>b</i> , calorimetry; <i>c</i> , conductance; <i>d</i> , density; <i>e</i> , acidity functions; <i>f</i> , $K_A \times K_B$ ; <i>g</i> , cryoscopy; <i>h</i> , kinetics; <i>i</i> , indicators.			
	33.4 <i>a</i>	298.15	58				
	32-33 <i>h</i>	298.15	59				
	32.9 <i>ei</i>	298.15	59-61				

## 2. PRESENTATION OF DATA AND DISCUSSION

The available  $pK_{ap}$  data have been grouped in two Tables of which Table 1 reports  $pK_{ap}$  values for 100% pure solvents (generally at only one temperature, mostly 298.15 K), whereas Table 2 reports  $pK_{ap}$  values for aqueous organic mixtures of diverse compositions and at various temperatures.

The temperature dependence of  $pK_{ap}$  can be expressed by such a typical equation (refs. 10-12) as:

$$pK_{ap} = A/T + B + CT \quad (14)$$

Whenever available, the constants for eq. (14) have been inserted in the Tables, for interpolation purposes.

The standard state chosen here for  $pK_{ap}$  is that currently in use and is stated in each Table heading for convenience: these  $pK_{ap}$  's can be called "molal". If one wishes to switch to a

TABLE 2 - Values of autoprotolysis constants  $pK_{ap}$  on logarithmic scale ( $pK_{ap} = -\log K_{ap}$ ) for some organic solvents ZH in various binary mixtures with water, at various temperatures. The standard state is chosen so that the activity of the undissociated (single or mixed) solvent is unity in the pure (single or mixed) solvent ( $\alpha = 1$ , or  $\alpha = \alpha_{H_2O} + \alpha_{ZH} = 1$ , respectively), and the (molar scale) activities of the involved ionic species are referred to unit activity coefficient at infinite dilution in that (single or mixed) solvent.

T / K		298.15 K															Refs.			
ZH	wt %	0	5	10	20	28.5	30	35	40	50	60	65	70	80	90	95	98	99	100	Refs.
METHANOL	$\alpha$	0.0000		0.0588	0.1232	0.1831				0.3599	0.4575		0.5675	0.6922	0.8350		0.9650	0.9824	1.0000	18-20
	$pK_{ap}$	13.997		14.037	14.055	14.067				14.097	14.127		14.218	14.423	14.845		16.029	16.310	16.708	
ETHANOL	$\alpha$	0.0000			0.0891			0.1739		0.2811		0.4207		0.6100					1.0000	15
	$pK_{ap}$	13.997			14.33			14.57		14.88		15.29		15.91					19.5	
FORMIC ACID	$\alpha$	0.0000	0.0202	0.0417	0.0891		0.1436		0.2069	0.2813	0.3699		0.4773	0.6102	0.7789	0.8814			1.0000	81
	$pK_{ap}$	13.997	3.66	3.29	3.07		2.97		2.91	2.79	2.95		3.09	3.40	3.91	4.44			6.65	
T / K		298.15 K															Refs.			
ZH	wt %	$\alpha$	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	Constants of $pK_{ap} = A/T + B + C/T$								Refs.
ETHYLENE GLYCOL	0	0.00000	14.734	14.535	14.346	14.167	13.997	13.833	13.680	13.535	13.396	4471.33	-6.0846	0.017053	10-12					
	10	0.03124	14.51	14.16	14.00	13.85	13.68	13.55	13.29	13.22	3009.97	2.77	0.00329	7						
	30	0.1106	14.31	14.00	13.92	13.72	13.58	13.45	13.22	13.22	3017.70	1.49	0.00708	7						
	50	0.2249	14.21	13.92	14.05	13.66	13.54	13.43	13.22	13.22	4172.07	-7.11	0.02271	7						
	70	0.4038	14.32	14.05	14.62	13.82	13.71	13.61	13.40	13.40	2429.05	4.38	0.00433	7						
	90	0.7232	14.89	14.62	16.14	14.37	14.26	14.17	13.97	13.97	3560.93	-2.67	0.01711	7						
	100	1.00000	16.47	16.30	16.14	15.99	15.84	15.71	15.57	15.44	3487.25	0.927	0.01079	8						
	PROPYLENE GLYCOL	0	0.00000	14.734	14.535	14.346	14.167	13.997	13.833	13.680	13.535	13.396	4471.33	-6.0846	0.017053	10-12				
		20	0.05587			14.31	13.98	13.71	13.45	13.45	13.45	4791.22	-9.313	0.02426	9					
		40	0.1363			14.30	13.88	13.61	13.36	13.36	12340.35	-58.502	0.10400	9						
75		0.4152			14.75	14.52	14.30	14.10	14.10	2092.35	7.171	0.00111	9							
GLYCOL	90	0.6805			15.21	15.00	14.80	14.63	14.63	2793.68	2.328	0.01106	9							
	100	1.00000	17.81	17.64	17.50	17.35	17.21	17.08	16.83	3372.00	2.571	0.01120	8							

"molar" standard state of *hyp.*  $c = 1$  (with the relevant molar activity coefficient  $\gamma = 1$  in the infinitely dilute solution) for the ions involved in (1), or to a "mole-fractional" standard state of *hyp.*  $x = 1$  (with the relevant *rational* activity coefficient  $f = 1$  for the ions in the infinitely dilute solution), the conversion formulae are:

$$pK_{ap} \text{ (molar)} = pK_{ap} \text{ (molal)} - 2 \log (\rho/\rho^\circ) \quad (15)$$

and

$$pK_{ap} \text{ (mole-fractional)} = K_{ap} \text{ (molal)} - 2 \log (M_{SH}/M^\circ) \quad (16)$$

where  $\rho$  is the density of solvent SH in  $\text{kg}/\text{dm}^3$ ,  $\rho^\circ = 1 \text{ kg}/\text{dm}^3$ ,  $M_{SH} = x_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}} + x_{\text{ZH}}M_{\text{ZH}}$  is its molar mass in  $\text{kg}/\text{mol}$ , and  $M^\circ = 1 \text{ kg}/\text{mol}$ .

Looking over the  $pK_{ap}$  results in aqueous organic mixtures, it is seen that in both ethylene glycol/water and propylene glycol/water mixtures,  $pK_{ap}$  decreases slightly upon addition of the glycol to water, passes through a minimum at about 40 wt percent of glycol, and then increases. This peculiar behaviour was attributed by Sastry and Kalidas (ref. 9) to  $pK_{ap}$  being a composite function of the intrinsic acidic and basic strength of the solvent and its relative permittivity. It is interesting to note that both for the ethylene glycol/water (refs. 7,8) and the propylene glycol/water mixtures (ref. 8,9) the silver-bromide electrode was used in cell (4) instead of the more usual silver-chloride electrode currently used for determinations of pH standards in nonaqueous solvents and aqueous organic solvent mixtures. This is not due to any demerit or misbehaviour of the silver-chloride electrode in these solvents but undoubtedly to the authors' related programme of systematic determinations of the standard potentials of the silver-bromide electrodes in various solvents. The  $pK_{ap}$  results for ethylene glycol and ethylene glycol/water mixtures at 298.15 K obtained by Aleksandrov and associates (ref. 8a) are in good agreement with, and superseded by, those obtained by Kundu and associates (refs. 7,8) which were thus quoted in these Tables.

$pK_{ap}$  values of exploratory nature, such as  $pK_{ap} = 17.4$  for dimethylsulphoxide (ref. 13) and  $pK_{ap} = 18$  for dimethylformamide (ref. 42) have been discarded. The problem of solvent impurities is important. For instance, even after careful purification, dimethylformamide always contains some diethylamine (B) and formic acid (HA), and a value of  $pK_{ap} = 18$  may have been determined largely by the reaction  $B + HA = BH^+ + A^-$ . The  $pK$  values found by Harned and Fallon (ref. 11) for water/1,4-dioxane mixtures can be considered as only first approximations to  $pK_{ap}$  due to their definition in terms of ionisation constants of water in these solvent mixtures, where the equilibrium (8) takes place to some extent: therefore they have not been included in the present compilation. It is also noted that the  $pK_{ap}$  values for ethanol/water mixtures, obtained by Gutbezahl and Grunwald (ref. 15), are averages of results from three completely different cells with liquid junctions, involving different non-thermodynamic assumptions but leading to  $pK_{ap}$  values in fairly close agreement.

### 3. CONCLUSIONS

It is disappointing that the present availability of  $pK_{ap}$  data is highly unsatisfactory, especially for binary aqueous-organic solvent mixtures, where the lack of  $pK_{ap}$  values pertaining to the mixtures of water with many popular solvents is huge.

Systematising the matter is long overdue, and one does hope that the present growing interest in this field, and the availability of established, sound methods of determination, may lead to the necessary rapid acquisition and analysis of the relevant  $pK_{ap}$  data.

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