Polarographic Determination of Hydrogen Ion Activities. Part III.[1] Basic Aqueous Mixtures of Nonelectrolytes

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Basicity functions of mixtures for aqueous tetra-alkylammonium hydroxides with dimethyl sulphoxide, pyridine, dioxan, and *NN*-dimethylacetamide have been measured electrochemically using glass and dropping mercury electrodes. In all cases the new basicity function, H_{GC}, has a higher value than the corresponding Hammett type functions H_- and H_{2-}. It follows from the measurement of H_{GC} in *NN*-dimethylacetamide–water that two types of complexes are formed: $DMA,3H_2O$ and $2DMA,3H_2O$.

APPLICATION of the polarographic method of measurement of hydrogen ion activity to aqueous basic solutions has been described in Part II.[1] In this paper we report the results of measurement of the basicities of aqueous solutions of nonelectrolytes.

Our basicity scale, H_{GC}, is derived from the liquid junction-free measurement of the potential of a glass electrode against the half-wave potential of reduction of cobalticinium ion at a dropping mercury electrode.[2] Its validity rests on the so called 'ferrocene assumption' which was introduced and thoroughly discussed by Strehlow.[3] As the polarographic reversibility of cobalticinium cation has been confirmed in both aqueous and nonaqueous media [4-9] the use of the half-wave potential of reduction of this cation as a reference potential is justified. Lithium based glass electrodes are known to function reversibly in basic nonaqueous and aqueous organic media.[10-16]

EXPERIMENTAL

Reagents.—Cobalticinium acetate, 50% in ethylene glycol (Pfalz and Bauer Inc.), was used without purification (Co, 13·1% by analysis) as a 0·1M aqueous solution. All other chemicals were purchased from B.D.H. Dimethyl sulphoxide (DMSO) was purified according to the method of Ritchie *et al.*[17] Dioxan was purified by refluxing and distillation from sodium metal.[18] *NN*-Dimethylacetamide (DMA) was dried over Linde 5A molecular sieves; the amount of water, determined by Karl Fischer titration, was <0·05%. AnalaR pyridine, tetramethylammonium hydroxide (TMAH), 25% aqueous solution, and tetraethylammonium hydroxide (TEAH), 25% aqueous solution, were used without purification. Distilled, deionised water was used for preparation of all solutions.

Preparation of Solutions.—*DMSO–water*, 0·011M-*TMAH*; 0·011M-*TEAH*. A *ca.* 0·1M solution of hydroxide (25 ml) was prepared by dissolving TMAH (1 g) [TEAH (1·5 g)] solution in DMSO or water (25 ml) respectively (solutions A). Each solution A (5·00 ml) was titrated with 0·1M-HCl using phenolphthalein as indicator. An appropriate amount of DMSO and aqueous solution A was then diluted to 50 ml to give 0·011M solutions (B) respectively. DMSO solution B (20·00 ml) was pipetted into the polarographic vessel, cobalticinium solution (0·02 ml) was added from an Agla syringe, and the concentration of water was increased in steps by addition of the aqueous solution B. The aqueous end of the scale was obtained by reversing this procedure.

DMSO–water, 0·047M-*TMAH*. TMAH solution (5 ml) was made up to 25 ml with DMSO and water respectively giving approximately 0·5M solutions. Each solution (5 ml) was titrated with 1M-HCl and the dilution factors were determined. An appropriate amount of each solution was diluted to 50 ml to give 0·047M solutions.

Pyridine–water 0·011M; *dioxan–water*, 0·011M-*TMAH*. The same procedure as for preparation of DMSO solutions was used but water (6·4 ml) had to be added to solution A to dissolve TMAH.

DMA–water, 0·011M-*TMAH*. Three different methods of preparation were adopted. (a) The first was as described for pyridine–water solutions with 5·0 ml of water added per 25 ml of solution A. (b) Solutions B were prepared directly by weighing out accurately the amount of 25% TMAH solution required to make a 0·011M solution. The composition of the mixture was then varied as before. (c) A series of separate solutions of various mole fraction of DMA was prepared and these solutions were left standing in the dark for 40 h before measurement.

The apparatus and measuring procedure were as described previously.[1,2] All experiments were carried out at 25·00 ± 0·05 °C.

RESULTS

A well developed, reversible reduction wave of cobalticinium cation was obtained in all solutions. Because the concentration of the base was relatively low the ratio of the charging to the faradayic current was 1 : 3 which is much lower than in the case of purely aqueous solutions. The maximum basicity which could be measured at a dropping

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[1] Part II, J. Janata and R. D. Holtby-Brown, *J. Electroanalyt. Interfac. Chem.*, in the press.

[2] J. Janata and G. Jansen, *J.C.S. Faraday I*, 1972, **68**, 1656.

[3] H. Strehlow in 'The Chemistry of Nonaqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1966, vol. 1, p. 1.

[4] J. A. Page and G. Wilkinson, *J. Amer. Chem. Soc.*, 1952, **74**, 6149.

[5] H. M. Koepp, H. Wendt, and H. Strehlow, *Z. Elektrochem.*, 1960, **64**, 483.

[6] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1965, **30**, 952.

[7] H. Schneider and H. Strehlow, *J. Electroanalyt. Interfac. Chem.*, 1966, **12**, 530.

[8] S. P. Gubin, S. A. Smirnova, and L. I. Denisovich, *J. Organometallic Chem.*, 1971, **30**, 257.

[9] G. H. Aylward, E. C. Watton, G. S. Buchanan, and R. W. Lee, *J. Electroanalyt. Interfac. Chem.*, 1972, **34**, 521.

[10] I. M. Kolthoff and M. K. Chantooni, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 4428.

[11] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 1721.

[12] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1968, **90**, 2821.

[13] G. Demange-Guerrin, *Talanta*, 1970, **17**, 1075.

[14] J. Juillard, *Bull. Soc. chim. France*, 1970, 2040.

[15] J. Juillard, *J. Chim. phys.*, 1970, 691.

[16] I. M. Kolthoff, M. K. Chantooni, jun., and H. Smagowski, *Analyt. Chem.*, 1970, **42**, 1622.

[17] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 1967, **89**, 2063.

[18] L. F. Fieser and M. Fieser, 'Reagents for Organic Syntheses,' Wiley, New York, 1967, p. 333.

mercury electrode was 27·5 (0·88 mole fraction DMSO, 0·011M-TMAH). Beyond this concentration the anodic dissolution of mercury overlapped the reduction of cobalticinium cation. In even more basic solutions cobalticinium cation slowly decomposed.

The basicity functions, H_{GC}, of aqueous DMSO, pyridine, and dioxan have been measured and compared in Figures 1—3 with available Hammett type basicity functions. The values of H_{GC} obtained from smoothed curves are given in the Table.

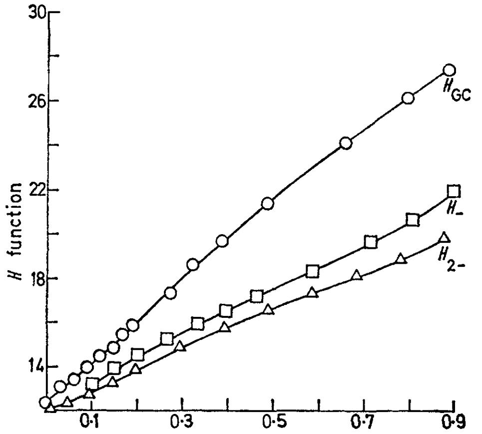

FIGURE 1 Basicity function for 0·011M-TMAH in DMSO–water. H_- Values taken from ref. 19, H_{2-} values taken from K. Bowden, A. Buckley, and R. Stewart, *J. Amer. Chem. Soc.*, 1966, **88**, 947

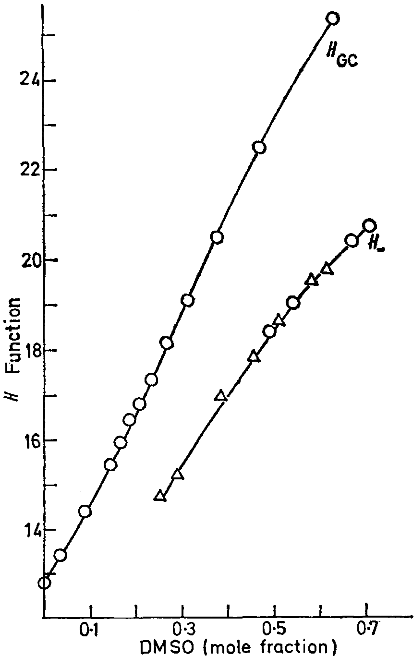

FIGURE 2 Basicity function for 0·047M-TMAH in DMSO–water. H_- Values taken from A. F. Cockerill and J. E. Lamper, *J. Chem. Soc.* (*B*), 1971, 503 (Δ) and K. Bowden and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1970, 173 (O)

We tried to establish the H_{GC} scale in aqueous DMA (0·011M-TMAH) solution. No fixed H_{GC} scale was obtained with this medium but an interesting pattern of behaviour emerged. In several repeated measurements (only three are shown in Figure 4B) a characteristic break on the H_{GC}–mole fraction plot always occurred. According to the way of preparation of the solutions the position of the break varied. Thus, usually when the measurement was done rapidly, with only 10 min purging with nitrogen after each addition of aqueous solution, the break appeared at higher mole fractions DMA (curve a, Figure 4B). When there were longer waiting intervals and when the DMA solution B was prepared several hours before the measurement the break appeared at the lower mole fraction DMA (curve b). There was, however, no clear relationship between the position of the break and the waiting period after the addition. The curve c (Figure 4B) was measured rapidly between points 1 and 2. After point 2 the solution was left under nitrogen for 16 h. The H_{GC} value dropped by 3·7 units (point 3) but after the next addition of the aqueous

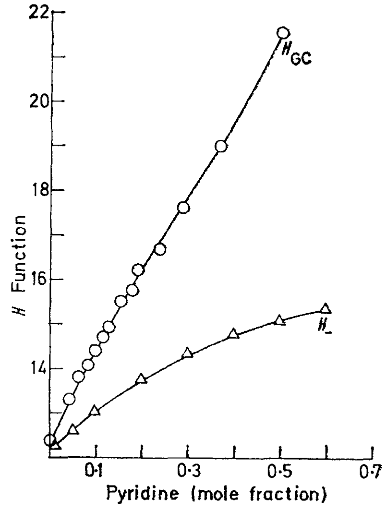

FIGURE 3 Basicity function for 0·011M-TMAH in pyridine–water. H_- Values taken from R. Stewart and J. P. O'Donell, *Canad. J. Chem.*, 1964, **42**, 1681

Basicity function H_{GC} at 25 °C

Mole fraction	DMSO, 0·001M-TMAH	DMSO, 0·047M-TMAH	DMSO, 0·011M-TEAH	Dioxan, 0·011M-TMAH	Pyridine, 0·011M-TMAH
0·000	12·30	12·80	12·30	12·30	12·30
0·025	12·75	13·25	12·55	12·65	12·95
0·050	13·25	13·75	12·90	13·25	13·45
0·075	13·65	14·20	13·30	13·80	13·95
0·100	14·07	14·65	13·75	14·40	14·45
0·150	15·00	15·65	14·75	15·45	15·30
0·200	15·98	16·70	15·70	16·55	16·15
0·250	16·98	17·80	16·70	17·55	16·95
0·300	17·96	18·95	17·60	18·45	17·80
0·350	18·90	20·05	18·65	19·40	18·65
0·400	19·84	21·15	19·50	20·20	19·50
0·450	20·75	22·25	20·35	20·70	20·40
0·500	21·60	23·20	21·15	21·15	21·25
0·550	22·42	24·10	21·90	21·65[c]	
0·600	23·22	24·95	22·55		
0·650	24·00	25·75[b]	23·15		
0·700	24·78		23·75		
0·750	25·52				
0·800	26·25				
0·850	26·95				
0·900	27·65[a]				

Extrapolated, highest measured value [a] 0·882, 27·40; [b] 0·628, 25·40; [c] 0·547, 21·63.

solution H_{GC} jumped up by 2·2 units (point 4) and after reaching the maximum decreased with decreasing concentration of DMA. In another experiment a set of 15 solutions containing 0·011M-TMAH and various amounts of DMA was measured 40 h after preparation. The minimum of the break appeared at 0·32 mole fraction DMA and maximum at 0·20 mole fraction DMA. The aqueous end of the curve was displaced towards lower values of H_{GC} apparently due to the alkaline hydrolysis of DMA.

Although the position of the break appeared to be largely random there were three common factors. The curve was displaced diagonally with slopes of individual portions similar, the minimum of the break never occured below 0·30 mole fraction DMA, and the maximum never occurred above 0·35 mole fraction DMA.

DISCUSSION

Dimethyl Sulphoxide, Pyridine, and Dioxan.—The increase of basicity with increasing concentration of nonelectrolyte is generally attributed to the decrease of activity of water.[19-21] The H_{GC} function has higher values than corresponding Hammett type functions (see Figures 1—3). There are two explanations for this difference. Either the hydrated layer of the glass electrode is excessively depleted of water as the concentration of the nonelectrolyte increases or the Hammett indicator anion is solvated to much greater extent than the cobalticinium cation and its activity is reduced. There are several reasons to believe that the difference between electrochemically and spectrophotometrically measured basicities is not due to the first cause. First, the H_{GC} function is considerably higher even at the aqueous end of the scale when there is plenty of free, unco-ordinated water in the solution. Secondly, the glass electrode was shown to behave reversibly in media containing little or no water. Thirdly, it has been suggested[22] that DMSO co-ordinates two molecules of water while pyridine co-ordinates only one. Therefore, for a given mole fraction of nonelectrolyte the difference between H_{GC} and H_- should be greater in DMSO than in pyridine; however, the reverse is true. We believe that the discrepancy is due to the solvation of the anion of the indicators and, consequently, to the variation of the ratio of the activity coefficients of the dissociated and undissociated form.

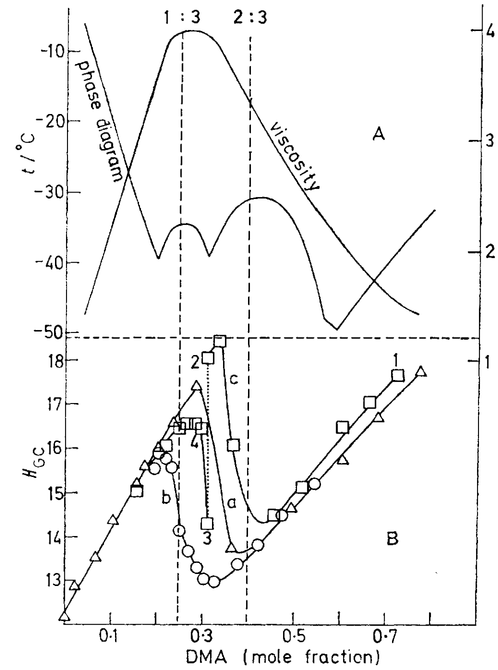

FIGURE 4 A, Phase diagram and viscosity of DMA–water; B, basicity function, H_{GC}, for DMA–water (see text for explanation)

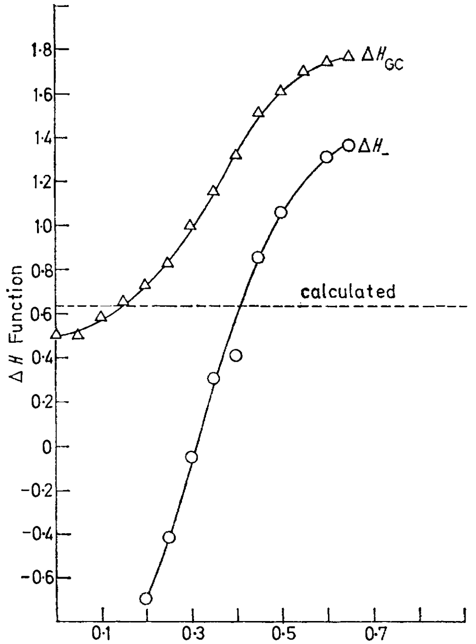

FIGURE 5 Comparison of ΔH_{GC} and ΔH_- values for 0·011M- and 0·047M-TMAH in DMSO–water

It has been suggested[20] that the difference ΔH between basicities for two concentrations of base $[OH]_a$ and $[OH]_b$ and the same concentration of nonelectrolyte can be expressed by equation (1). In order to test this

$$\Delta H = \log([OH]_a/[OH]_b) \qquad (1)$$

expression we have plotted the ΔH_{GC} and ΔH_- values for 0·011 and 0·047M solutions for the complete mole fraction scale in DMSO (Figure 5). It is evident that neither function obeys equation (1) although the ΔH_{GC} values up to 0·20 mole fraction DMSO are relatively close to the calculated value (+0·63). The negative values of ΔH_- (more concentrated base is less basic) are paradoxical. It is interesting to note that the inflection point on ΔH_{GC} curve occurs at 0·34 mole fraction DMSO which corresponds to a 2 : 1 complex as

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[19] D. Dolman and R. Stewart, *Canad. J. Chem.*, 1967, **45**, 911.

[20] K. Bowden, *Chem. Rev.*, 1966, **66**, 119.

[21] C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

[22] G. Yagil, *J. Phys. Chem.*, 1969, **73**, 1610.

suggested by Yagil.[22] However, his hydration equilibria treatment, based on the existence of trihydrated OH^- ion, applied to the H_{GO} function for DMSO and pyridine did not produce the same results as obtained from H_- function.

The basicity function of aqueous dioxan has not been determined previously. The attempt to measure such a function by conventional means using nitroaniline indicators failed. This has been attributed[23] to the lack of stabilisation of the anions of these indicators by solvation in dioxan. As no such stabilisation is required in the electrochemical method the H_{GO} function in this medium was established without difficulty.

NN-*Dimethylacetamide*.—Aqueous *NN*-dimethylformamide (DMF) is the only amide for which a basicity function has been determined.[13,14,24] Because of the alkaline hydrolysis of DMF the scale is of little practical value. There is no information about the alkaline hydrolysis of DMA under our conditions but it is expected to be slower than that of DMF. The lower values of basicity obtained after the basic aqueous DMA solutions were left for 40 h suggest that the hydrolysis does take place. However, we believe that the amount of hydrolysis during the determination of the basicity scale, which is approximately 4—5 h, is only small and cannot be responsible for the observed dramatic changes of the basicity.

It has been suggested[25] that DMA forms two complexes with water, $1\mathrm{DMA,3H_2O}$ and $2\mathrm{DMA,3H_2O}$. This is supported by the existence of two maxima at 0·25 and 0·40 mole fraction DMA on the phase diagram (Figure 4A) and by the presence of a very large maximum on the viscosity curve[25-27] (Figure 4A). There is also a very large maximum on the heat of mixing curve[25] between 0·20 and 0·40 mole fraction DMA. Alternatively, $2\mathrm{DMA,1H_2O}$ and $1\mathrm{DMA,1H_2O}$ complexes have been postulated on the basis of i.r. spectroscopic measurements.[28,29] Our results support the former hypothesis, *i.e.* formation of 2 : 3 and 1 : 3 complexes.

The abrupt changes in the basicity of the solution (referred to as 'break') between 0·20 and 0·40 mole fraction DMA can be tentatively explained by the changes in activity of free unco-ordinated water. When DMA is added to solutions containing over 0·20 mole fraction DMA it rapidly forms a 1 : 3 complex with free water thus increasing the basicity. If the subsequent

$$\mathrm{DMA} + 3\mathrm{H_2O} \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{DMA,3H_2O} \qquad (2)$$

formation of 2 : 3 complex is slow, as would be expected

$$\mathrm{DMA} + \mathrm{DMA,3H_2O} \xrightarrow{\text{slow}} 2\mathrm{DMA,3H_2O} \qquad (3)$$

more than an equilibrium concentration of 1 : 3 complex builds up and the solution becomes 'supersaturated' with 1 : 3 complex. At a certain point the conversion from 1 : 3 to 2 : 3 complex takes place and free water is released to the solution lowering its basicity. When

$$2(\mathrm{DMA,3H_2O}) \xrightarrow{\text{slow}} 2\mathrm{DMA,3H_2O} + 3\mathrm{H_2O} \qquad (4)$$

the scale is constructed from the DMA end of the scale at a certain point (always below 0·40 mole fraction DMA) the 1 : 3 complex is formed rapidly by breaking the existing 2 : 3 complex. This reaction will increase

$$2\mathrm{DMA,3H_2O} + \mathrm{H_2O} + 2\mathrm{H_2O} \longrightarrow 2(\mathrm{DMA,3H_2O}) \qquad (5)$$

the basicity as for each mole of water added another two moles of free water are complexed and the solution becomes again supersaturated with 1 : 3 complex. This scheme would account for the behaviour of curve c (Figure 4B) in which the H_{GO} value decreased by 3·7 units on standing for 16 h and increased by 2·2 units on addition of water.

A more detail study of this phenomenon is needed before any definitive interpretation of the basicity can be made. Our experiments demonstrate that the electrochemical method of measurement is ideally suited for such an approach.

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[23] K. Bowden, R. S. Cook, and M. J. Price, *J. Chem. Soc.* (*B*), 1971, 1778.

[24] E. Buncel, E. A. Symons, D. Dolman, and R. Stewart, *Canad. J. Chem.*, 1970, **48**, 3354.

[25] P. Assarsson and F. R. Eirich, *Adv. Chem. Ser.*, 1968, **84**, 1.

[26] P. Assarsson and F. R. Eirich, *J. Phys. Chem.*, 1968, **72**, 2710.

[27] R. C. Petersen, *J. Phys. Chem.*, 1960, **64**, 184.

[28] C. De Loze, P. Combelas, P. Bacelon, and C. Garrigou-Lagrange, *J. Chim. phys.*, 1972, **69**, 397.

[29] P. Bacelon and C. De Loze, *J. Chim. phys.*, 1972, **69**, 346.