A METHOD FOR THE DETERMINATION OF THE DISSOCIATION CONSTANTS OF ACIDS WITH AN UNCALIBRATED GLASS ELECTRODE

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In the development of acid–base titrations in non-aqueous media, the determination of acid–base dissociation constants and the establishment of the pH scale in the solvent of interest is very important. By potentiometry with either the hydrogen or glass electrode in cells with or without a liquid junction, these dissociation constants can be determined over a wide range[1–3]. It is generally assumed[1] that the hydrogen or glass electrode should first be calibrated in solutions of known pH, prepared from either strong acids or from weak acids with known dissociation constant.

To establish a pH scale in some solvents, it is thus necessary to determine at least one acid dissociation constant by means of another technique. For this purpose differential vapor pressure measurements, conductivity measurements or spectrophotometry are often used. In this paper it is shown that dissociation constants of weak acids can also be determined directly with an uncalibrated glass electrode.

THEORY

The dissociation constant of a weak acid in a solvent in which no ion pairs are formed, can be expressed by:

$$K_{HX} = a_H \cdot a_X / a_{HX} \tag{1}$$

If the activity coefficient of the uncharged species is assumed to be unity and the degree of dissociation is low, then the activity of the solvated proton is given by:

$$a_H \cdot = (K_{HX} C_{HX})^{\frac{1}{2}} \tag{2}$$

For a solution of a mixture of the acid and its salt (which is assumed to be completely dissociated), the activity of the solvated proton can be calculated from:

$$a_H \cdot = K_{HX} \frac{a_{HX}}{a_X} = K_{HX} \frac{C_{HX}}{C_X} \frac{1}{f_X} \tag{3}$$

With the use of equimolar amounts of acid and its salt this reduces to:

$$a_H \cdot = K_{HX}/f_X \tag{4}$$

The response at 20 °C of a glass electrode–reference electrode set following Nernst's law can be written as:

$$E_{mv} = E'_0 + 58 \log a_H \cdot \tag{5}$$

E'_0 contains the standard potential of the glass electrode, the potential of the reference electrode and the liquid junction potential, which is assumed to be constant. Combination of eqns. (2) and (5) gives for the potential of the glass electrode in a solution of pure acid, HX:

$$E_{acid} = E'_0 - 29 \, pK_{HX} + 29 \log c_{HX} \tag{6}$$

Combination of eqns. (4) and (5) gives

$$E_{buffer} = E'_0 - 58 \, pK_{HX} - 58 \log f_X \tag{7}$$

Subtraction of eqns. (6) and (7) finally gives:

$$E_{acid} - 29 \log c_{HX} - E_{buffer} - 58 \log f_X \cdot = 29 \, pK_{HX} \tag{8}$$

If f_X is estimated by the limiting Debye–Hückel law, then all quantities on the left-hand side of eqn. (8) are known and pK_{HX} can be calculated. Now also E'_0 can be calculated, which calibrates the glass electrode set.

EXPERIMENTAL

Solvents

Acetonitrile containing less than 0.01% water was obtained from Eastman. Dimethylsulfoxide (Merck, reagent grade) was heated to 60 °C with barium oxide and potassium permanganate for 1 h; the mixture was then filtered and the DMSO was kept for 24 h over activated molecular sieve (3A, Union Carbide). Further purification of the DMSO was performed by vacuum distillation (3 mm, 42 °C), during which the middle 80% fraction was kept. Finally the DMSO was kept over molecular sieve for 24 h and vacuum-distilled again. The water content of the end-product was less than 0.01% (Karl Fischer titration). N,N-dimethyl-formamide (Merck, reagent grade) was kept for 24 h over molecular sieve (3A, Union Carbide) and then vacuum-distilled (18 mm, 52 °C); the middle 80% fraction was used in the experiments.

Acids, bases and salts

Picric acid (Merck, reagent grade), tetraethylammonium perchlorate, TEAP (Eastman), 2,6-dinitrophenol (Merck, indicator grade), 2,4-dinitrophenol (Merck, indicator grade), 2-nitrophenol (Fluka, puriss.) and 3-nitrophenol (Fluka, puriss) were recrystallized from ethanol and dried *in vacuo* at 30 °C. 1,1,3,3-Tetramethyl-guanidine (Eastman), benzoic acid (UCB, reagent grade), salicylic acid (ACF, reagent grade), sodium hydroxide (Merck, titrisol), tetraethylammonium iodide (Merck, für die polarographie), and tetramethylammonium bromide (Merck, für die Polarographie) were used as received.

Apparatus

A Radiometer pH-meter type PHM 26 was used in the expanded-scale mode for the determination of the e.m.f. values of the glass electrode to ± 0.2 mV. As reference electrode in the organic solvents a silver chloride-coated silver wire

immersed in 0.01 M tetramethylammonium chloride in the solvent of interest was used. This electrode was connected to the solution via a 0.1 M tetraethylammonium perchlorate salt bridge. Separation between reference electrode, salt bridge and solution was by glass frits.

In aqueous solution, a Radiometer 3 M KCl calomel electrode, type K 411, was used.

In all cases the cell was thermostatted to (20.0±0.05) °C.

Procedure

A sample of a standardized solution of the acid was placed in the cell and mV readings of the glass electrode set were taken at 5-min intervals until a stable reading (within ±0.5 mV) was obtained. This usually occurred within 10–20 min in the solvents used, except for DMF, for which 60–80 min were necessary. Then a calculated amount of base was added to give an equimolar amount of acid and its salt and mV measurements were continued.

In some instances buffer solutions were prepared separately from the acid and its salt. It was noticed, however, that reproducibility was then less good, probably because the electrode set has to be transferred from one solution to another, which can change its E'_0 value[3]. When not in use, the glass electrode was stored in aqueous buffer of pH 7.

RESULTS AND CONCLUSIONS

The results of the e.m.f. measurements with the glass electrode in water are given in Table I. Tables II, III and IV show the data obtained with the glass electrode in DMSO, DMF and acetonitrile. From a comparison of the

TABLE I

POTENTIOMETRY WITH THE GLASS ELECTRODE IN WATER

Compound	e.m.f. (mV)	$f_\pm{}^a$ ·	pK_a	E'_0 (mV)
Benzoic acid, 10^{-2} M	182.0			
Benzoic acid–Na benzoate, 10^{-3} M	120.8	0.95	4.15	360.5
Benzoic acid, 10^{-3} M	153.0			
Benzoic acid–Na benzoate, 10^{-3} M	120.8	0.95	4.15	360.5
Acetic acid, 0.1224 M	195.8			
Acetic acid–Na acetate, 0.0490 M	95.0	0.77	4.62	356.2
Acetic acid, 0.01224 M	168.0			
Acetic acid–Na acetate, 0.00490 M	92.8	0.92	4.58	356.3
2,5-Dinitrophenol, $5.82 \cdot 10^{-4}$ M	122.8			
2,5-Dinitrophenol–Na salt, $1.16 \cdot 10^{-3}$ M	67.0	0.95	5.17	366.5
2-Nitrophenol, 5.10^{-3} M	88.0			
2-Nitrophenol–Na salt, 10^{-3} M	−49.0	0.95	7.04	357.7
3-Nitrophenol, 0.100 M	68.0			
3-Nitrophenol–Na-salt, $2.67 \cdot 10^{-3}$ M	−110.5	0.94	8.20	364.0

^{a} Calculated with Debye–Hückel limiting law: $-\log f = 0.5010 \, (\mu)^{\frac{1}{2}}$.

TABLE II

POTENTIOMETRY WITH THE GLASS ELECTRODE IN DMSO

Compound	e.m.f. (mV)	$f_{\pm}{}^a$	pK_a	E_0' (mV)
2,6-Dinitrophenol, 0.100 M	248.0			
2,6-Dinitrophenol–TMG salt, 0.0342 M	160.0	0.62	4.45	405.9
2,4-Dinitrophenol, 0.100 M	243.0			
2,4-Dinitrophenol–TMG salt, 0.0339 M	149.5	0.62	4.64	406.4
Salicylic acid, 0.100 M	198.0			
Salicylic acid–TMG salt, 0.0339 M	65.0	0.62	6.00	400.9
Benzoic acid, 0.100 M	30.0			
Benzoic acid–TMG salt, 0.0342 M	−192.5	0.62	9.08[h]	322.4

[a] Calculated with Debye–Hückel limiting law: $-\log f = 1.11\ (\mu)^{\frac{1}{2}}$.
[b] pK_a (benzoic acid) = 10.3 calculated from buffer potential with $E_0' = 403$ mV.

TABLE III

POTENTIOMETRY WITH THE GLASS ELECTRODE IN DMF

Compound	e.m.f. (mV)	$f_{\pm}{}^a$	pK_a	E_0' (mV)
2,4-Dinitrophenol, 0.100 M	375.0			
2,4-Dinitrophenol–TMG salt, 0.0333 M	235.8	0.53	6.36	588.4
2,6-Dinitrophenol, 0.100 M	372.0			
2,6-Dinitrophenol–TMG salt, 0.0333 M	239.3	0.53	6.13	578.9

[a] Calculated with Debye–Hückel limiting law: $-\log f = 1.53\ (\mu)^{\frac{1}{2}}$.

TABLE IV

POTENTIOMETRY WITH THE GLASS ELECTRODE IN ACETONITRILE

Compound	e.m.f. (mV)	$f_{\pm}$	pK_a	E_0' (mV)
Hydriodic acid, 0.0834 M	981.0			
Hydriodic acid–TEA iodide, 0.0668 M	935.0	0.59[a]	3.12	1102.9
Hydrobromic acid 0.1997 M	907.3			
Hydrobromic acid–TMA bromide, 0.0100 M	784.0	0.70[b]	5.26	1080.1
Bromophenol blue, 0.0100 M	651.5			
Bromophenol blue TMG salt, 4.73·10⁻³ M	399.7	0.79[b]	10.90[c]	1025.4

[a] Calculated with extended Debye–Hückel expression: $-\log f = \dfrac{1.53\ (\mu)^{\frac{1}{2}}}{1 + 2.82\ (\mu)^{\frac{1}{2}}}$.

[b] Calculated with Debye–Hückel limiting law: $-\log f = 1.53\ (\mu)^{\frac{1}{2}}$.
[c] $pK_a = 12.0$ calculated with buffer potential and $E_0' = 1092$.

obtained pK_a values and the literature values (Table V), it can be seen that the direct potentiometric method gives results which are generally accurate to ±0.2 pK units. Exceptions are the experiments for the determination of pK_a values above 10; probably this is due to impurities in either the solvent or acid used. Basic impurities in the solvent, even in low concentrations, cause deviations from

TABLE V

COMPARISON OF pK_a VALUES FROM THE POTENTIOMETRIC METHOD AND LITERATURE VALUES

System	pK_a found	pK_a lit.	Ref.
Benzoic acid–water	4.15	4.19	4
Acetic acid–water	4.60	4.75	4
2,5-Dinitrophenol–water	5.17	5.15	4
2-Nitrophenol–water	7.04	7.17	4
3-Nitrophenol–water	8.20	8.28	4
2,6-Dinitrophenol–DMSO	4.45	4.9	5
2,4-Dinitrophenol–DMSO	4.64	5.2	6
Salicylic acid–DMSO	6.00	6.9	5
Benzoic acid–DMSO	9.08/10.3[a]	11.0	5
2,4-Dinitrophenol–DMF	6.36	6.3	7
2,6-Dinitrophenol–DMF	6.13	5.7/6.18	7
Hydriodic acid–acetonitrile	3.12	—	
Hydrobromic acid–acetonitrile	5.26	5.5	8
Bromophenol blue–acetonitrile	10.90/12.0[a]	12.0	9

[a] Determined from buffer potential with E_0' from the other experiments.

the expression $a_{H^+} = (KC_{HX})^{\frac{1}{2}}$ for solutions of the acid. This problem has also been encountered in connection with the conductance method[1], but the potentiometric method compares favourably with this method as much higher concentrations of the acid can be used.

SUMMARY

A method is presented for the determination of absolute pK_a values of acids in solvents with a high dielectric constant by potentiometry with an uncalibrated glass electrode; in the determination, the glass electrode becomes calibrated. The method has the advantage that it is rapid and simple. Moreover, the range of pK_a values that can be determined by this method is about 3 pK units greater than for the direct conductivity method.

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