Polarographic Determination of Hydrogen Ion Activities. Part IV.[1] Basic Solutions Containing Alkali Metal Ions

By **Jiří Janata** *† and **James Taylor**, Imperial Chemical Industries Limited, Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire

Acidity functions of aqueous solutions of potassium and sodium hydroxide, of 0·01M-sodium methoxide in aqueous dimethyl sulphoxide, and of 0·011M-tetramethylammonium hydroxide in aqueous tetramethylene sulphone have been measured electrochemically. It has been shown that the acidity function of tetramethylammonium hydroxide solution measured with a hydrogen electrode is the same as that measured with a glass electrode.

APPLICATION of our method of measurement of hydrogen ion activities in strongly basic [1,2] and strongly acidic [3] media has so far been restricted to solutions not having a high concentration of alkali metal ions. The deviation of the glass electrode potential from the Nernstian response, caused by the presence of these ions in a high concentration, is called alkaline error.

We present here the results of measurements of hydrogen ion activities in solutions containing alkali metal ions, obtained by use of a hydrogen electrode instead of a glass electrode. We have also compared the acidity functions measured with these two electrodes in solutions containing tetramethylammonium cations and in solutions containing sodium cations. As before,[1,2] the acidity function is defined as the difference between the potential of the hydrogen electrode and the half-wave potential of the reduction of cobalticinium ion at a dropping mercury electrode.

EXPERIMENTAL

Apparatus.—The same three-electrode polarograph was used as before.[1-3] The hydrogen electrode was prepared according to the procedure recommended by Hills.[4] Hydrogen (white label) was further purified by passing it first through a column packed with copper catalyst and then through a column filled with 5A molecular sieves.

Because the presence of the cobalticinium–cobaltocene couple would affect the hydrogen electrode potential, solutions containing cobalticinium cation must be separated from this electrode. This was done by enclosing the electrode inside a Pyrex tube with medium porosity glass frit at the bottom. A low-alkaline error Corning Triple Purpose Electrode type 476022 was used. All experiments were carried out at 25·0 ± 0·05 °C.

Reagents.—Cobalticinium acetate (50% in ethylene glycol. Pfalz and Bauer Inc.) was used without purification as a 0·1M-solution. Sodium methoxide was prepared from vacuum-distilled sodium metal and methanol (B.D.H Aristar). Tetramethylene sulphone (B.D.H.) was purified by vacuum distillation from sodium hydroxide and calcium hydride. Dimethyl sulphoxide was purified as described previously.[1] All other chemicals were obtained from B.D.H. Ltd. and were used without purification. Distilled, deionised water was used for the preparation of all solutions.

Preparation of Solutions.—Stock saturated solutions of potassium and sodium hydroxide were estimated by titration with 0·2M-hydrochloric acid (Methyl Orange). Individual solutions were prepared by accurately weighing into the polarographic vessel *ca.* 20 ml of the stock solution and diluting it with a known volume of water.

A 2·175M-solution of sodium methoxide in methanol was used for preparation of 0·01M-solutions in methanol and in dimethyl sulphoxide. Appropriate volumes of these solutions were mixed to give the desired concentrations. The densities of these solutions were taken as equal to those of pure solvents.

0·011M-Solutions of tetramethylammonium hydroxide in tetramethylene sulphone and in water were prepared directly from concentrated aqueous tetramethylammonium hydroxide. In order to liquefy the sulphone, which in the pure state is solid at room temperature, a small amount of water was added. This was taken into account in calculating the mole fraction.

Procedure.—The hydrogen electrode was connected to the voltage-follower input of a three-electrode polarograph. The appropriate solution (25 ml) was added to the polarographic vessel and deoxygenated with nitrogen for at least 5 min. During this period the hydrogen electrode compartment remained closed. The solution was then admitted to this compartment, cobalticinium solution (0·01—0·03 ml) was added to the solution outside, and the reduction wave of cobalticinium was recorded. Between measurements the hydrogen electrode compartment was flushed with deoxygenated water and rinsed with the deoxygenated solution which was to be measured next. Because the measurements cannot be carried out by successive dilution of concentrated solutions as in the case of the glass electrode,[1-3] they are more laborious.

The foregoing procedure was carried out for a series of standard buffers (calibration) and then for solutions of unknown hydrogen ion activity. In accord with our previous work we will refer to the function obtained as H_{HC} (hydrogen–cobaltocene).

RESULTS

The values of H_{HC} for aqueous solutions of potassium and sodium hydroxide are compared in Table 1 with Hammett type functions H_-.[5] Because of the salting-out effect, the solubility of cobaltocene decreases as the concentration of alkali metal hydroxide increases. Above 8M concentration the solubility of cobaltocene is so low that, at the concentration of cobalticinium used, the polarographic wave is distorted by precipitation of cobaltocene on the mercury surface, and polarograms cannot be accurately evaluated.

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† *Present address:* Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, U.S.A.

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The solubility problem does not exist in aqueous mixtures of non-electrolytes and well developed waves are always obtained. The function H_{HC} for sodium methoxide in dimethyl sulphoxide–methanol is compared in Table 2 with the acidity function H_{GC}.

TABLE 1

Acidity functions H_{HC} and H_- (from ref. 5) at 25 °C

	KOH		NaOH	
Molarity	H_{HC}	H_-	H_{HC}	H_-
0·25	13·45		13·68	
0·50	13·70	13·75	13·87	13·71
0·75	13·85		14·07	
1·00	13·99	14·11	14·21	14·02
1·50	14·27	14·33	14·49	14·20
2·00	14·56	14·51	14·72	14·37
2·50	14·85	14·69	14·91	14·54
3·00	15·14	14·85	15·08	14·65
3·50	15·44	15·00	15·25	14·81
4·00	15·74	15·15	15·42	14·95
4·50	16·05	15·28	15·61	15·08
5·00	16·37	15·44	15·84	15·20
5·50	16·69		16·11	
6·00	17·03	15·72	16·45	15·40
6·50	17·37		16·85	
7·00	17·73	16·00		15·62
7·50	18·09			

TABLE 2

Acidity functions H_{HC} and H_{GC} at 25 °C

	Me_2SO–MeOH 0·01M–NaOMe		$[CH_2]_4SO_2$–H_2O 0·011M–Me_4NOH	
Mole fraction	H_{HC}	H_{GC}	H_{HC}	H_{GC}
0·000	16·80	16·89	12·68	12·74
0·025	17·06	16·94	13·19	13·19
0·050	17·29	17·14	13·57	13·59
0·075	17·56	17·34	14·01	14·01
0·100	17·73	17·54	14·38	14·38
0·150	18·18	17·94	15·12	15·11
0·200	18·59	18·32	15·81	15·79
0·250	19·01	18·67	16·44	16·43
0·300	19·41	19·03	17·02	17·02
0·350	19·81	19·37	17·57	17·58
0·400	20·20	19·70	18·09	18·12
0·450	20·61	20·01	18·58	18·63
0·500	20·99	20·31	19·07	19·13
0·550	21·39	20·58	19·54	19·63
0·600	21·80	20·88	20·02	20·12
0·650	22·20	21·15	20·51	20·62
0·700	22·65	21·41	21·01	21·13
0·750	23·08	21·66	21·54	21·66
0·800	23·55	21·91		
0·850	24·03	22·15		
0·900	24·54	22·38		
0·950	25·03	22·59		
1·000	25·63	22·82		

In order to test the relative effects of sodium and tetramethylammonium ions on the glass electrode, H_{HC} and H_{GC} values for 0·011M-tetramethylammonium hydroxide in tetramethylene sulphone–water were measured (Table 2).

The data in Tables 1 and 2 were obtained from experimental curves smoothed by a computer polynomial least-square program.

DISCUSSION

In agreement with our results for tetra-alkylammonium hydroxides [1,2] and for aqueous amine solutions,[2] the values of the electrochemically determined acidity functions of alkali metal hydroxides and of sodium methoxide are higher than the corresponding Hammett-type functions. We believe that this is due to the solvation of the Hammett indicator anions. The salting-out effect encountered in the measurement of aqueous solutions of potassium and sodium hydroxides renders the measurements less accurate. The accuracy for aqueous potassium and sodium hydroxide solutions is ±0·1 H_{HC}. The solubility problem could be circumvented by use of more sensitive pulse- or tast-polarography, which would allow a lower concentration of cobalticinium to be used.

Results of measurements of acidity functions of tetramethylammonium hydroxide in tetramethylene sulphone–water and of sodium methoxide in dimethyl sulphoxide–methanol with both hydrogen and glass electrodes are significant on two counts. First, the agreement between H_{HC} and H_{GC} for tetramethylammonium hydroxide (Table 2) shows that in non-aqueous and mixed aqueous solutions, a properly hydrated glass electrode gives results identical with those obtained with a hydrogen electrode. This is in agreement with conclusions reached by others.[6-12] Secondly, these results show that the deviation of H_{GC} from H_{HC} (alkaline error) is caused by the increased *activity* of sodium ions. The increase of basicity with increasing concentration of dimethyl sulphoxide is attributed to the progressive removal of water molecules from the solvation shells of the ions. This results in a decrease of the effective ionic radius of sodium ions and in their increased ability to penetrate the swollen layer of the glass electrode.

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