Studies on the Application of the Quinhydrone Electrode in Formamide. V*
The Ionization Constants of Chloro- and Phenyl-Substituted Acetic Acids from E.M.F. Measurements at Different Temperatures and the Effect of Substituents on the Strength of Acetic Acid in Formamide
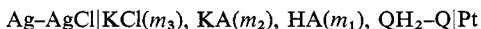
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Abstract

From the study of the cell
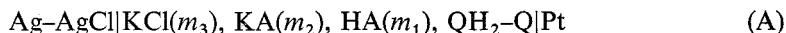
$$Ag-AgCl|KCl(m_3), KA(m_2), HA(m_1), QH_2-Q|Pt$$

(where HA stands for acid) the ionization constants of chloroacetic acid in formamide have been determined at 25, 30 and 35°, and those of phenylacetic acid at nine different temperatures in the range 5–45°. The cell

$$Pt, H_2|HA(m_1), KA(m_2), KCl(m_3)|AgCl-Ag$$
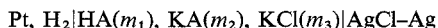
has also been used to redetermine the ionization constants of chloroacetic acid in formamide in the range 5–45°; the ionization constants of chloroacetic are in good agreement with those of an independent study. The effect of substituents on the strength of acetic acid has been examined in formamide.

Introduction

In previous communications,[1-4] the cell

$$Ag-AgCl|KCl(m_3), KA(m_2), HA(m_1), QH_2-Q|Pt \qquad (A)$$

has been successfully employed in the determination of the ionization constants of acids in formamide. In the present investigation, with this cell, the ionization constants of chloroacetic acid in formamide have been determined at 25, 30 and 35° and those of phenylacetic acid at temperatures ranging from 5° to 45°.

The ionization constants of chloroacetic acid in formamide over the range 15–40° were reported earlier by Mandel and Decroly[5] from the study of the cell

$$Pt, H_2|HA(m_1), NaA(m_2), NaCl(m_3)|AgCl-Ag$$
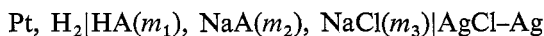
Subsequently, Agarwal and Nayak[6] recalculated the values on the basis of their more accurate E^0 values for the Ag–AgCl electrode.[6,7]

* Part IV, *Aust. J. Chem.*, 1975, **28**, 797.

[1] Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, **26**, 111.
[2] Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, **26**, 115.
[3] Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, **28**, 793.
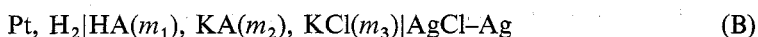[4] Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, **28**, 797.
[5] Mandel, M., and Decroly, P., *Trans. Faraday Soc.*, 1960, **56**, 29.
[6] Agarwal, R. K., Ph.D. Thesis, Indian Institute of Technology, Kharagpur, India, 1968.
[7] Agarwal, R. K., and Nayak, B., *J. Phys. Chem.*, 1967, **71**, 2062.

In the present work, the cell

$$\text{Pt, } H_2|HA(m_1), \text{ KA}(m_2), \text{ KCl}(m_3)|AgCl\text{–Ag} \qquad \text{(B)}$$

has been used and the ionization constants of chloroacetic acid have been determined at temperatures ranging from 5° to 45°. In order to avoid all uncertainties regarding the true values of the ionization constants for chloroacetic acid, the cell (B) has been investigated using the same range of molalities in formamide as used in cell (A). The ionization constants at 25, 30, and 35° obtained from both cells are in close agreement with each other.

From the values of the ionization constants of acetic, chloroacetic, and phenylacetic acids at 25°, the effect of substituents on the strength of acetic acid has been examined in formamide.

Experimental

Chloroacetic acid (BDH, AnalaR) was dried in a vacuum desiccator before use. Phenylacetic acid (Laboratory Reagent) was recrystallized thrice from benzene–light petroleum (b.p. 100–120°). Potassium salts of the acids were prepared and dried by a method similar to that described elsewhere.[8] Purification of potassium chloride and formamide was described earlier.[8,9]

Solutions for e.m.f. measurements were prepared by dissolving the appropriate weighed amounts of salts and acids in known weights of formamide.

The cell measurements were carried out with electrodes prepared and set up as described earlier.[1]

Results and Discussion

The method of calculation of K_a, the ionization constant of chloroacetic acid, was based on the evaluation of the apparent hydrogen ion molality of the solution as recommended by Harned and Owen[10] for acids of moderately weak strength. As in previous papers[2,4,8] the apparent ionization constant K_a' was calculated with the help of equation (1)

$$\log K_a' = -2A(\mu d_0)^{1/2} + \log\frac{m'(H^+)[m_2 + m'(H^+)]}{m_1 - m'(H^+)} \qquad (1)$$

and K_a was found by the method[1,2,8] of extrapolating the auxiliary function K_a' given by refs[4,8] to ionic strength $\mu = 0$.

For the molalities used in the case of phenylacetic acid, $m(H^+)$ could be neglected with respect to m_1 and m_2. As usual, values of K_a' were calculated with the help of equation (2)

$$-\log K_a' = \frac{(E - E^0)F}{2\cdot303RT} + \log\frac{m_1 m_3}{m_2}$$

$$= -\log K_a - \log\frac{\gamma(Cl^-) \cdot \gamma(HA)}{\gamma(A^-)} \qquad (2)$$

and the ionization constant of phenylacetic acid, K_a was found by the method[1,8] of extrapolating the auxiliary function $-\log K_a'$ to zero ionic strength, as

[8] Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1972, **25**, 941.

[9] Dash, U. N., and Nayak, B., *Indian J. Chem.*, 1970, **8**(7), 659.

[10] Harned, H. S., and Owen, B. B., 'The Physical Chemistry of Electrolytic Solutions' p. 498 (Reinhold: New York 1950).

$\log[\gamma(Cl^-) \cdot \gamma(HA)/\gamma(A^-)]$ tends to zero. The symbols in equations (1) and (2) have their usual significance.

The values of $E^0(Ag-AgCl)$, $E^0(QH_2-Q)$, d^0 and A at different temperatures needed for the calculations were obtained as described earlier.[3]

Table 1. pK_a values in formamide

Acid	5°	10°	15°	20°	25°	30°	35°	40°	45°
Chloroacetic[A]	4·35	4·31	4·09	4·09	4·10	3·86	3·64	3·36	3·23
	±0·13	±0·14	±0·02	±0·02	±0·08	±0·05	±0·09	±0·05	±0·06
Chloroacetic[B]					4·13	3·95	3·62		
					±0·09	±0·05	±0·07		
Chloroacetic[C]			4·71	4·59	4·57	4·57	4·61	4·64	
Chloroacetic[D]			4·68	4·66	4·65	4·64	4·62	4·58	
Phenylacetic[B]	6·62	6·56	6·51	6·45	6·57	6·30	6·34	6·21	6·24
	±0·02	±0·02	±0·02	±0·02	±0·05	±0·03	±0·02	±0·04	±0·04

[A] Present work, cell (B).   [B] Present work, cell (A).   [C] Ref. 5.   [D] Ref. 6.

The pK_a values of chloroacetic and phenylacetic acids at different temperatures in formamide are presented in Table 1 together with previously reported values[5,6] for chloroacetic acid. It was found that there is rather poor agreement between the present data and those reported by Mandel and Decroly[5] or their revised values as calculated by Agarwal and Nayak.[6] This necessitated the redetermination of the ionization constant of this acid over the temperature range covered by the earlier workers while extending it to the temperatures 5, 10 and 45°. It was found that the redetermined values of pK_a show poor agreement at all temperatures with the previously reported values. But since there is good corroboration between the two sets of pK_a values obtained in the present study at 25, 30 and 35° with independent cells (A) and (B), the present set of data on pK_a values appears to be more reliable.

Comparison of the pK_a values of the acids at 25° in formamide with those in water,[11a] methanol,[11a] ethanol[11a] and butan-1-ol[11b] at 25° shows that they are higher in formamide than in water but lower than in methanol, ethanol or butan-1-ol—a behaviour similar to that shown by weak acids in solvents of this class.[1-4,8,12]

It is of interest to examine the effect of substituents on the strength of acetic acid in formamide medium. Considering the pK_a values for acetic acid[1] (6·96), chloroacetic acid (4·13) and phenylacetic acid (6·57) at 25°, in formamide, their strengths appear in the order

$$ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH$$

which is the same as that found in water. The similarity in order of the strength of these acids in both formamide and water points to the validity of the qualitative theory of substituent effects[13] in formamide medium.

[11] Charlot, G., and Trémillon, B., 'Chemical Reactions in Solvents and Melts' (Transl. P. J. J. Harvey) (a) p. 278; (b) p. 301 (Pergamon: New York 1969).
[12] Dawson, L. R., Vaughn, J. W., Pruitt, M. E., and Eckstrom, H. C., *J. Phys. Chem.*, 1962, 66, 2684.
[13] Hammett, L. P., 'Physical Organic Chemistry' pp. 349–75 (McGraw–Hill: New York 1970).