

DISSOCIATION CONSTANT OF ACETIC ACID IN WATER-ACETONE MIXTURES

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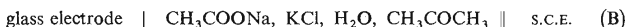
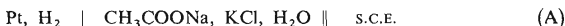
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Dissociation constants of acetic acid in mixed solvents, containing besides water 20, 40, 60 and 70% (w) of acetone, were calculated from the slopes of potentiometric titration curves, obtained using glass or quinhydrone electrode and saturated calomel electrode. Parallel courses of the potentials of glass and quinhydrone electrodes justify their application in the above-mentioned mixtures in which the hydrogen electrode fails.

Recently a number of workers were concerned with the measurement of dissociation constants of acids in non-aqueous or partially non-aqueous solvents. Up to now, however, no exact data have been reported on the dissociation constant of acetic acid in water-acetone mixtures with a higher content of acetone and therefore an attempt has been made to measure their values.

Dissociation constant of acetic acid was measured at 25°C in the mixtures of water with 20, 40, 60 and 70% (w) of acetone by means of the following cells:



The value of the dissociation constant was measured from the rate of the potential change of the indication electrode in the vicinity of the equivalence point in retitration of sodium acetate with hydrochloric acid¹.

The method used was first verified by determining the dissociation constant of acetic acid in pure water by means of cell A. In solvents with higher acetone content potentials of hydrogen electrode did not attain a constant value and consequently this electrode was not applicable for the intended purpose. Evidently acetone underwent gradual hydrogenation under the catalytic effect of platinum black, as mentioned by some authors². Therefore we made an attempt to replace the hydrogen electrode by a glass one³. Simultaneously the problem arose, whether the calibration

* The work was carried out at the Department of Analytical Chemistry, Institute of Chemical Technology, Prague 6.

curve of the glass electrode in the given acidity region and with the used mixed solvents has the theoretical value, since the comparison with the potential course of the hydrogen electrode was not feasible for the above mentioned reasons. It was however found that titration curves of identical solutions of sodium acetate when measured by means of glass and quinhydrone electrodes have perfectly parallel courses, their slopes in the region of equivalence point being absolutely identical. There is only very little probability that two, physically so essentially different electrodes like the glass and the quinhydrone, might show in the given solvent entirely identical deviations, and therefore the assumption that the change in their potential with changing acidity in the given media is theoretical, seems to be plausible. For this reason the cell B was employed in further experiments.

EXPERIMENTAL

Chemicals and Apparatus

The chemicals used (Lachema, Brno) were of reagent grade purity. Redistilled, boiled and under nitrogen atmosphere cooled water and freshly distilled acetone were used as solvents. Mixed solvents were prepared by weighing the components and the content of acetone was expressed in weight per cent. Solutions of acetic acid in mixed solvents were prepared by weighing the appropriate amounts. If necessary, pure acetone was added both to the solution to be titrated and to the titration agent to make the correction to the amount of water brought into the solution with the reagents.

The solution of sodium hydroxide, which was used prior to titration for total neutralisation of acetic acid, was prepared according to Sørensen so as to contain minimum amount of carbonate. It was kept in flasks, protected from atmospheric carbon dioxide by a stopper filled with soda lime. Its concentration was determined by titration with oxalic acid against methyl orange. 0.1—0.01M-HCl standardized by sodium hydroxide of known titer was used for retitrations of sodium hydroxide solution. Ionic strength of the titrated solutions was adjusted by potassium chloride.

Electromotive forces were measured on a compensation pH-meter (Metra, Prague) with the sensitivity of ± 0.2 mV. Glass electrodes were made of Corning 015 glass. Prior to measurement they were immersed for 24 h at minimum in appropriate water-acetone mixtures. Hydrogen electrodes were platinized from solutions of chloroplatinic acid with a mixture of lead acetate and were saturated with hydrogen from an electrolytic generator. Prior to each measurement the electrodes were freed from the former deposit of platinum black and then coated with platinum anew. The traces of adhering electrolyte were removed by alternating cathodic and anodic polarization. All values of electromotoric forces were read off after the potentials had attained a reproducibly constant value, even in measurements repeated in 3 min intervals. Titration reagents were added in the vicinity of the equivalence point in amounts of 0.02 ml.

RESULTS

In the titration of a weak base (CH_3COONa) with a strong acid (HCl) according to the scheme $\text{A}^- + \text{H}^+ = \text{HA}$, the concentration of the lyonium ion, expressed as a function of the titration degree, is given by equation:

$$c_{\text{H}} \cdot \frac{c_{\text{H}} - (\varepsilon - 1)c}{c - c_{\text{H}} + (\varepsilon - 1)c} = K_{\text{A}} \frac{y_{\text{HA}}}{y_{\text{H}} \cdot y_{\text{A}}} = K'_{\text{A}}, \quad (1)$$

where c denotes the molar concentration of the titrated solution, K_{A} is the thermodynamic and K'_{A} the concentration dissociation constant and y the molar activity coefficient.

The change of proton activity in dependence on the titration degree in the vicinity of the equivalence point $(\text{dpH}/d\varepsilon)_{\varepsilon=1}$ is in this case only a function of the titration variable, τ , defined by equations (2) and (3)

$$\tau = \sqrt{(K'_{\text{A}}/c_0)}, \quad (2)$$

$$\tau^{-1} = -4.605 (\text{dpH}/d\varepsilon)_{\varepsilon=1} \pm \frac{c_0}{c_{\text{HCl}}} - 1, \quad (3)$$

TABLE I

Dissociation Constant of Acetic Acid in Water-Acetone Mixtures at 25°C

Acetone weight %	$c_0 \cdot 10^3$ mol l ⁻¹	$I \cdot 10^3$	dpH/dε	$K'_{\text{A}} \cdot 10^5$	pK'_{A}	$K_{\text{A}} \cdot 10^5$
0	7.51	5.99	3.38	3.51	4.45	1.76 ^a
	4.19	3.41	2.78	2.97	4.52	
	2.13	1.79	2.18	2.54	4.59	
20	15.03	11.08	8.45	1.037	4.98	0.794
	8.07	6.16	6.48	0.976	5.01	
	4.19	3.67	4.86	0.912	5.03	
	2.13	1.69	3.58	0.886	5.05	
40	13.79	10.50	19.16	0.180	5.74	0.145
	7.40	5.68	14.44	0.172	5.76	
	3.84	2.96	10.74	0.163	5.78	
	1.96	1.52	7.92	0.155	5.80	
60	13.79	10.42	35.79	0.0509	6.29	0.010
	7.39	5.60	31.20	0.0363	6.44	
	3.84	2.91	26.41	0.0264	6.57	
70	1.01	3.04	32.22	0.00465	7.33	0.002
	0.74	2.22	29.23	0.00415	7.38	
	0.38	1.15	23.05	0.00348	7.45	
	0.19	0.59	17.29	0.00328	7.51	

^aCf. the value $1.753 \cdot 10^{-5}$ reported in the literature⁴.

where c_0 is the molar concentration of the titrated electrolyte in the equivalence point and c_{HCl} is the molar concentration of hydrochloric acid. According to Grunwald¹, the calculation of dpH/ϵ_A is based on the assumption that the change of proton activity in dependence on ϵ has in the vicinity of the equivalence point a practically linear course, so that the experimental course of the titration curve may be approximated by a straight line the empirical slope of which, s , lies close to the value of $\text{dpH}/d\epsilon$. Therefore the values of s were calculated from separate titration curves, using the method of least squares. The values of dpH were obtained from the equation

$$\text{dpH} \approx \Delta \text{pH} = \frac{\Delta E}{0.05916}, \quad (4)$$

where E is the electromotive force, and the values of concentration dissociation constants K'_A were calculated using equation (2) and (3). No detectable dependence of K'_A on concentration was found in the concentration interval $c_0 < 0.0001$; 0.01 .

Thermodynamic dissociation constant K_A was obtained by usual extrapolation to ionic strength $I = 0$, neglecting the ionic strength referring to the ionization of free acetic acid and assuming that $y_{\text{HA}} = 1$.

Results of the measurement of thermodynamic dissociation constant of acetic acid in the system water–acetone are summarized in Table I. These values are an arithmetic mean of three parallel independent measurements. The values of thermodynamic dissociation constants were obtained by extrapolation to $I = 0$. Fig. 1 gives the dependence of $\text{p}K_A$ on the content of acetone, showing the monotonous increase in pH with increasing acetone content.

In solvents containing more than 70% (w) of acetone the slope s of the titration curves in the vicinity of the equivalence point is so steep that its reproducibility is insufficient. At the same time the permittivity of the solvents at higher acetone

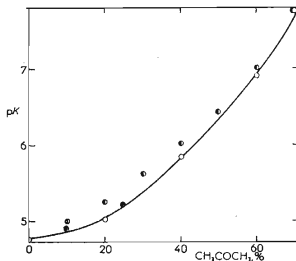


FIG. 1

Dependence of $\text{p}K_A$ of Acetic Acid on the Concentration (in weight %) of Acetone

○ This paper, ● ref.⁵, ⊙ ref.⁶.

content approaches a limit, when the simple equilibrium $HA \rightleftharpoons H^+ + A^-$ cannot be presumed any more.

The chosen procedure gave results which are in very good accordance with the values of the dissociation constant of acetic acid reported by Mac Innes and Shedlovsky⁴ and Dippy, Hughes and Rozanski⁵. Our data are also in good agreement with the data of Morel⁶ for concentrations of 50–70%(w) of acetone; considerable deviations from his values were found in the range of lower acetone concentrations (Fig. 1).

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