Indian Journal of Chemistry
Vol. 14A, April 1976, pp. 219-222

Dissociation Constant of Partly Neutralized Polyacrylic Acid from Measurement of Its *p*H at Different Salt Concentrations

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Received 25 *September* 1975; *accepted* 3 *December* 1975

An equation has been deduced which can account for the decrease in *p*H of solutions of polyacrylic acid (PAA) of a given degree of neutralization with an increase in concentration of an added neutral salt. Applying this equation to the experimental results of Samelson and Mandel, the *p*K of PAA has been found to be 4·75±0·03 and that it remains constant when the concentration of the acid, that of the added neutral salt and the degree of neutralization are varied.

A CONSIDERABLE amount of theoretical[1-4] and experimental work[5-12] has been done to find the dissociation constants of naturally occurring and synthetic polycarboxylic acids using potentiometric titration method. In the case of polyacrylic acids (PAA) of degree of polymerization greater than 100 so that they form colloidal solution it has been observed[9-12] that the dissociation constants, calculated from potentiometric data using Henderson equation, vary with the concentration, degree of neutralization (α) and with the concentration (C_s) of an added neutral salt.

The potentiometric titration curve being similar to that of a weak monobasic acid, it has been proposed that each of the COOH groups of a macromolecule of PAA has got the same intrinsic dissociation constant K_a, but it is modified by the electrostatic attraction which increases as the dissociation proceeds.

Calculations

According to Overbeek[1] the observed dissociation constant K is given by the expression

$$K = K_a \exp(-\Delta F/kT) \quad \ldots(1)$$

where ΔF represents the extra electrical energy required per COOH group to cause further dissociation when the macromolecule has already acquired a certain charge, Ze. Combining Eq. (1) with the Henderson equation we get

$$p\text{H} - pK_a - \log \alpha/(1-\alpha) = 0{\cdot}434\ \Delta F/kT \quad \ldots(2)$$

Assuming suitable molecular models and probable forms of charge distribution on these[1-4] expressions for electrical free energy have been deduced using Debye-Hückel linear approximation. These expressions can only qualitatively account for the variation of K with the degree of neutralization and ionic strength of the solution.

Katchalasky and Spitnik[9] have proposed Eq. (3) for the variation of pH with α and with the concentration C_s of a neutral salt during the neutralization of PAA.

$$p\text{H} = p\text{K} + n \log \alpha/(1-\alpha) \quad \ldots(3)$$

Samelson[11] has found that for a $0{\cdot}0179N$ solution of PAA (degree of polymerization 500), n varies from 1·95 to 2·00 when NaCl concentration is varied from $0{\cdot}414M$ to $0{\cdot}052M$.

Recently Mandel[12] has proposed Eq. (4) to account for the variation of K with α and salt concentration C_s;

$$pK = p\text{H} + \log(1-\alpha)/\alpha = pK_0 + \phi_1\alpha + \phi_2\alpha^2 \quad \ldots(4)$$

In Eq. (4) pK_0, ϕ_1 and ϕ_2 remain constant for different values of α, but vary with salt concentration. According to Mandel[12] Eq. (4) fits the experimental data within 0·03 units.

Equation connecting pH with pK and concentration of PAA — The aforesaid authors have not taken into consideration the effect of concentration of PAA on K. In a previous paper an equation has been deduced by the author[13] in which the dependence of K on concentration has been taken into account and which is briefly discussed here. In previous papers[14-16], the variation with dilution of H$^+$ ion activity, H_c of a colloidal acid like PAA has been accounted for by the following equation

$$\text{H}_c = \theta H_s + (1-\theta)\text{H}_i \quad \ldots(5)$$

where θ is the fraction per unit area of the surface of the electrode (used for measuring H$^+$ ion activity) covered by the diffuse double layers of the macromolecules of the acid and is equal to $C/(K_0+C)$, C being the concentration of the acid and K_0, a constant. H_s is a proportionality constant and may be interpreted to represent the H$^+$ ion activity associated with a unit area of the diffuse double layer at the plane of contact with the electrode and H$_i$ is the H$^+$ ion activity of the intermicellar solution.

For a well-dialysed acid sol H_i is very small and when θ is fairly large H_i $(1-\theta)$ can be neglected and Eq. (5) may be written as follows

$$\text{H}_c = \theta H_s \quad \ldots(6)$$

Now H_s may be different from H_a defined by the Henderson equation $H_a = K_a(1-\alpha)/\alpha$ in which the activity coefficients f_A and f_B of the COOH and COO$^-$ groups respectively have been assumed to be unity. Assuming $H_s = K'(H_a)^n$ the following expression (Eq. 6a) is obtained;

$$H_s = K'(K_a)^n[(1-\alpha)/\alpha]^n = K_s[(1-\alpha)/\alpha]^n \quad \ldots(6a)$$

where $K_s = K'(K_a)^n$, K' and n being constants.

Substituting this value of H_s in Eq. (6) and simplifying we get Eq. (7)

$$pH_c = p(\theta K_s) + n \log \alpha/(1-\alpha) \quad \ldots(7)$$

It is to be noted that θ in Eq. (7) depends on the concentration of the colloidal acid.

Derivation of equation connecting H_c *with the salt concentration* C_s — Neglecting θH_i in Eq. (5), since $\theta < 1$ and H_i is very small, it may be written as follows:

$$H_c = H_i(1+\theta H_s/H_i) \quad \ldots(8)$$

When at constant θ, a neutral salt like NaCl is added to a PAA sol the Na^+ ions enter the diffuse double layers of the PAA macromolecules and displace H^+ ions which enter the intermicellar solution. The removal of H^+ ions from the diffuse double layer decreases H_s and the equilibrium between H^+ and the COOH groups in the Stern[17]-Mukherjee[18] layer is disturbed. To restore equilibrium a few COOH groups dissociate. Therefore, the net effect of addition of NaCl is that H_s diminishes slightly and H_i increases appreciably. Since H_i increases and $(1+\theta H_s/H_i)$ diminishes as C_s increases, it is reasonable to assume that H_i varies directly as C_s and $(1+\theta H_s/H_i)$ varies inversely as $(1+BC_s)$ where B is a constant. Therefore, at constant θ Eq. (8) may be written as follows:

$$H_c = H_0 + A_1C_s/(1+BC_s) \quad \ldots(9)$$

where A_1 and B are constants and $H_0 = H_c$ when $C_c = 0$. Eq. (9) can also be written in the following form

$$H_e = H_0 + AC_s/(K_0+C_s) \quad \ldots(10)$$

where $A = A_1/B$ and $K_0 = 1/B$.

Eq. (9) can also be derived by applying virial expansion in the following way:

$$H_c = H_0 + A_1C_s + A_2C_s^2 + A_3C_s^3 + \text{etc.} \quad \ldots(11)$$

Neglecting terms higher than the second degree and noting that A_2 is generally negative in sign Eq. (11) may be written as

$$H_c = H_0 + A_1C_s\left(1 - \frac{A_2}{A_1}C_s\right)$$
$$= H_0 + A_1C_s(1+BC_s) \quad \ldots(11a)$$

where $B = A_2/A_1$.

Eq. (10) will be used in the remaining portion of this paper. The constants in Eq. (10) can be found by plotting $1/(H_c-H_0)$ against $1/C_s$, since H_0 is constant and its value is known. The intercept on the ordinate is equal to $1/A$ and the slope equal to K_0/A. Eq. (10) should hold good so long as $H_c \gg H_0$. At low values of C_s a serious source of experimental error creeps in, since the KCl solution in the calomel electrode is denser than the NaCl+PAA mixture it (KCl) may flow into the PAA mixture thereby increasing C_s and consequently H_c also. To avoid this error Marshall[19] has recommended the use of calomel electrode vessel with upturned tip.

Determination of the constant K_s — It follows from Eq. (10) that

$$(H_c-H_0)(K_0+C_s)/C_s = A \quad \ldots(12)$$

As C_s approaches infinity $(K_0+C_s)/C_s$ approaches unity and hence when $C_s = \infty$, the corresponding $H_c = H_0 + A$.

Furthermore, Eq. (5) may be written as

$$H_c - H_i = (H_s - H_i)\theta \quad \ldots(13)$$

As C_s is increased H_i increases and approaches H_c and H_s decreases and approaches H_i. In the case of a partially neutralized PAA, it is, therefore, reasonable to assume that when C_s is infinity $H_c = H_i$. Under this condition since θ is not zero so H_s H_i. Hence when $C_s = \infty$ we get the relation (14)

$$H_c = H_i = H_s = H_0 + A \quad \ldots(14)$$

Knowing H_s in this way pK_s can be found from Eq. (6a) written as follows

$$pH_s = pK_s + n \log \alpha/(1-\alpha) \quad \ldots(15)$$

Hence for given values of α and θ, H_0+A and so H_s can be found from measurements of H_c at different values of C_s including $C_s = 0$. Knowing H_s in this way equation (15) can be used to find K_s.

Results

Notes on the data recorded in Tables 1-3 — Under the head miscellaneous, conc, denotes concentration, α, the degree of neutralization, H_0, the H^+ ion activity when C_s is zero, A and K_0 are the constants in Eq. (10) and M, the molecular weight of PAA determined by the viscosity method. In Table 2 under the head Mandel's[12] data, pK_0 is the same as in Eq. (4) and it will be noticed that it varies with salt concentration. The values of pH, except the one marked with an asterisk, have been calculated for $\alpha = 0.5$ using Eq. (4). According to Mandel, Eq. (4) agrees with the observed data within 0·03 unit of pH. The one marked with an asterisk corresponds to observed data and has been taken from Fig. 2 of his paper[12].

In Table 3 are recorded the values of pH observed by Mandel and Samelson of PAA sols of comparable concentration corresponding to $\alpha = 0.5$. It appears from the data that the PAA sols of Mandel are slightly under-neutralized compared to those of Samelson.

Discussion

It will be noticed from the data recorded in Table 1 that the values of pH_c calculated from Eq. (10) agree well with those observed by Samelson when the concentration of NaCl used varies from 0·414 to 0·0518 equivalent per litre, the concentration of PAA being maintained constant at 0·0348 equivalent per litre. The data of Mandel recorded in Table 2 on the samples (A) and (B) of widely differing molecular weight also show that the values of pH_c calculated from Eq. (10) agree well with those observed when the concentration of the neutral salt used varies from 0·333 to 0·04 equivalent per litre.

TABLE 1 — DETERMINATION OF pK_S FROM SAMELSON'S TITRATION DATA ON PAA

Miscellaneous	C_S (equiv./litre)	Values of pH_c		(H_0+A)	pH_s	$1{\cdot}97 \log \frac{x}{1-\alpha}$	pK_s
		Obs.	Calc.				
Conc = 0·0348 equiv/litre	0·414	4·52	4·52	$5{\cdot}92\times10^{-5}$	4·23	−0·53	4·76
$\alpha = 0{\cdot}351$	0·207	4·70	4·69	$5{\cdot}73\times10^{-5}$	4·24	−0·53	4·77
$H_0 = 0{\cdot}16\times10^{-5}$	0·104	4·90	4·89	$5{\cdot}70\times10^{-5}$	4·24	−0·53	4·77
$A = 5{\cdot}7\times10^{-5}$	0·0518	5·08	5·10	$6{\cdot}28\times10^{-5}$	4·20	−0·53	4·73
$K_0 = 0{\cdot}42$	0·00	5·80	—	—	—	—	—
							Av. 4·76
Conc.= 0·0348 equiv./litre	0·414	5·57	5·58	$5{\cdot}28\times10^{-6}$	5·28	0·53	4·75
$\alpha = 0{\cdot}649$	0·207	5·77	5·75	$4{\cdot}89\times10^{-6}$	5·31	0·53	4·78
$H_0 = 0{\cdot}13\times10^{-6}$	0·104	5·97	5·99	$4{\cdot}87\times10^{-6}$	5·31	0·53	4·78
$A = 5{\cdot}56\times10^{-6}$	0·0518	6·20	6·18	$4{\cdot}69\times10^{-6}$	5·33	0·53	4·80
$K_0 = 0{\cdot}495$	0·00	6·89	—	—	—	—	—
							Av. 4·78

TABLE 2 — DETERMINATION OF pK_β FROM MANDEL'S TITRATION DATA ON PAA

Miscellaneous	C_s (equiv./litre)	Mandel's data		pH_c calculated from Eq. (10)	(H_0+A) i.e. H_s	pK_s
		pK_0	pH_c			
		SAMPLE (A)				
M = 790000	$3{\cdot}33\times10^{-1}$	4·33	4·99*	5·01	$1{\cdot}912\times10^{-5}$	4·72
Conc.= 0·0047 equiv./litre	$2{\cdot}00\times10^{-1}$	4·39	5·12	5·12	$1{\cdot}886\times10^{-5}$	4·72
$\alpha = 0{\cdot}5$	$1{\cdot}00\times10^{-1}$	4·50	5·35	5·32	$1{\cdot}737\times10^{-5}$	4·76
$H_0 = 0{\cdot}15\times10^{-6}$	$6{\cdot}0\times10^{-2}$	4·57	5·49	5·49	$1{\cdot}873\times10^{-5}$	4·73
$A = 1{\cdot}85\times10^{-6}$	$4{\cdot}0\times10^{-2}$	4·58	5·63	5·63	$1{\cdot}864\times10^{-5}$	4·73
$K_0 = 0{\cdot}298$	0·00	—	6·83	—	—	—
						Av. 4·73
		SAMPLE (B)				
M = 120000	$2{\cdot}0\times10^{-1}$	4.80	5·10	5·10	$1{\cdot}78\times10^{-5}$	4·75
	$1{\cdot}0\times10^{-1}$	4·68	5·28	5·28	$1{\cdot}78\times10^{-5}$	4·75
Conc.= 0·00604 equiv./litre	$5{\cdot}0\times10^{-2}$	4·72	5·44	5·48	$2{\cdot}02\times10^{-5}$	4·70
$\alpha = 0{\cdot}5$	—	—	—	—	—	—
$H_0 = 0{\cdot}48\times10^{-6}$	0·00	—	6·32	—	—	—
						Av. 4·73
$A = 1{\cdot}75\times10^{-5}$						
$K_0 = 0{\cdot}264$						

TABLE 3 — COMPARISON OF TITRATION DATA OF PAA FOR $\alpha = 0{\cdot}5$ (WITHOUT SALT)

	Mandel's data		Samelson'sd data	
	Sample (A)	Sample (B)	Sample (A)	Sample (B)
[PAA] equiv./litre	$4{\cdot}71\times10^{-3}$	$6{\cdot}04\times10^{-3}$	$4{\cdot}36\times10^{-3}$	$8{\cdot}71\times10^{-3}$
pH	6·83	6·32	7·12	6·88

From Samelson's data for $\alpha = 0{\cdot}351$ and $0{\cdot}649$, recorded in Table 1, the average values of pK_s found by using Eq. (15) are 4·76 and 4·78 respectively. It may be mentioned that the value of n in Eq. (15) has been found by plotting pH against $\log \alpha/(1-\alpha)$ using Samelson's data.

From Mandel's data for $\alpha = 0{\cdot}5$, recorded in Table 2, the average value of pK_s for each of the samples (A) and (B) is 4·73. The average of the values of pK_s found from the data of Samelson and Mandel is thus $4{\cdot}75 \pm 0{\cdot}03$.

It will be noticed from the data recorded in Table 3 that for $\alpha = 0{\cdot}5$, at comparable concentrations of PAA in the absence of a neutral salt, the values of pH of the sols investigated by Mandel is lower than that of the sols investigated by Samelson. Hence it may be concluded that Mandel's PAA sols are slightly under-neutralized. Assuming that the actual degree of neutralization is 0·49 instead of 0·5 the corrected value of pK_s calculated from Eq. (15) should be $4{\cdot}73-(-0{\cdot}03) = 4{\cdot}76$ which is almost the same as found from Samelson's data. It may, therefore, be concluded that pK_s calculated from the data of Mandel and Samelson has got a constant value $= 4{\cdot}75 \pm 0{\cdot}03$ which is independent of the degree of neutralization of the acid, its concentration and that of the neutral salt within the range investigated.

Lastly it may be mentioned that by modifying the assumptions discussed already, Eq. (7) can be deduced in the following way. Let us now assume that

$$H_s = H_a{\cdot}f_A/f_B = K_a[(1-\alpha)/\alpha]f_A/f_B$$
$$= K_a[(1-\alpha)/\alpha]\times[(1-\alpha)/\alpha]^x \qquad \ldots(16)$$

where the ratio of the activity coefficients f_A/f_B is not unity, but a function of $(1-\alpha)/\alpha$, the form of which as assumed above is $f_A/f_B=[(1-\alpha)/\alpha]^x$, α remaining unchanged over a certain range of α. In a macromolecule of PAA containing p groups of COOH as the degree of neutralization α increases, the electrical charge of the macromolecule increases and owing to increased electrostatic attraction the ability of each of the remaining $p(1-\alpha)$ groups of COOH to release a proton decreases while the ability of each of the $p\alpha$ COO$^-$ groups to bind a proton increases. Consequently the ratio f_A/f_B may vary in the way assumed above. Substitution of $K_a(1-\alpha/\alpha)^{1+x}$ for H_s in Eq. (6) and its conversion into the logarithmic form lead to Eq. (7) in which K_s is now identical with K_a and $(1+x)=n$.

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