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AUTHOR(S):

SAKURADA, Ichiro; HOSONO, Masao; ISE, Norio

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Potentiometric Titrations of a Polyelectrolyte

By

Ichiro SAKURADA, Masao HOSONO and Norio ISE

Department of Textile Chemistry

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Abstract

A study was carried out on the potentiometric titrations of poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG). The titration curves were known to fulfil the relation proposed already by Pals and Hermans and the dissociation exponents were determined thereby. The radius of this polyacid was estimated from the electrostatic free energy change by means of our theoretical treatment of polyelectrolyte solutions: it was found that the size decreased with the concentration, consistently with the well-known variation of the viscosity. Moreover, a potential potentiometrically obtained was shown not to be in agreement with the surface potential electrophoretically determined. This could be understood by referring the former to an average potential inside the spherical macro-ion.

Introduction

A great deal of research has been accumulated on the potentiometric study of typical and weak polyelectrolytes. An empirical relation was established by Katchalsky^{1,2}) to describe the titration curve. However, so much effort has not been devoted to the polyelectrolytes of larger dissociation constant as to those of small one. In an attempt to improve this situation, we have carried out the potentiometric study of poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG). In this paper, confirming the validity of Pals-Hermann's relation on the titration, the size of macro-ion in non-extremely dilute solution and the radical discrepancy between electrophoretic and potentiometric potentials will be discussed from an unified theoretical stand-point.

Titration Curve

As is shown in Fig. 1, the titration curve of this polyacid differs clearly from that of weak polyacids in its shape, which is very close to that of strong normal acids. In order to obtain an empirical relation fitting this experimental result, it seems

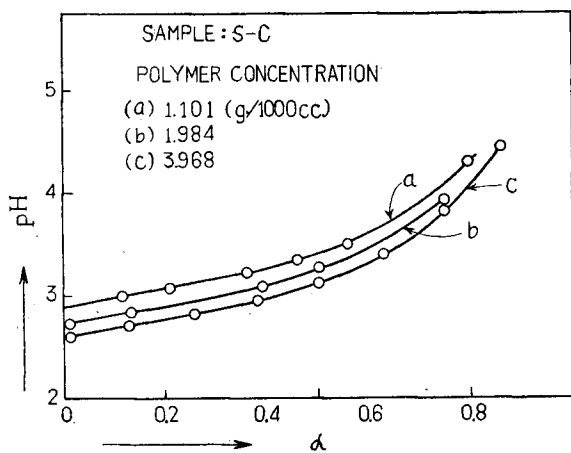


Fig. 1. Titration Curves of PVAG (I)

concentration of hydrogen-ions, $[C]$ the total concentration of ionizable groups. $\alpha + [H^+]/[C]$ corresponds to the ratio of the number of ionized groups to the total number of ionizable groups and it can be considered the extended degree of neutralization. Eq. (1) has been already used by Pals and Hermann³⁾ and, as is shown in Fig. 2, is found to fit our experimental data very closely. The values of pK evaluated are tabulated in Table 1.

pK is practically constant over the concentration range covered by our experiment and shows a tendency to increase with the carboxyl group content, which can be interpreted reasonably in terms of the electrostatic interaction. Katchalsky observed

reasonable to introduce a correction term due to self-dissociations of ionizable groups into Katchalsky's relation. Calculation leads to the final expression

$$pH = pK + n \log \frac{\alpha + [H^+]/[C]}{1 - \alpha - [H^+]/[C]}$$

$$= pK + n \log \frac{\alpha'}{1 - \alpha'}, \quad (1)$$

where α is the degree of neutralization in its usual sense of word, pK the apparent dissociation exponent, n a constant, $[H^+]$ the

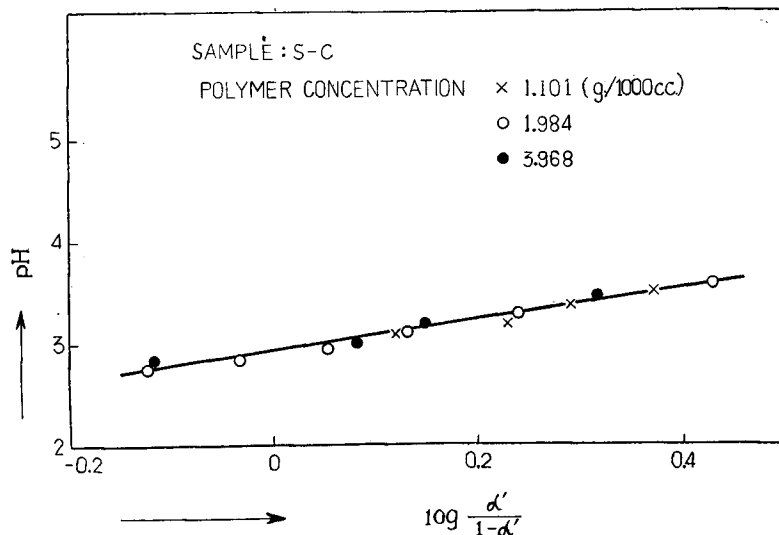


Fig. 2. Titration Curves of PVAG (II)

Table 1. Dissociation Exponents of PVAG

Sample	DP	COOH-Content (mol %)	Concentration (g./1000 cc.)	pK
S-A	2150	12.08	4.030	3.33
			2.015	3.33
			0.918	3.33
S-7	1700	5.82	2.916	2.60
			0.972	2.60
S-8	1700	3.46	6.940	2.55
			3.470	2.55
			2.082	2.45
S-C	970	10.80	3.968	2.90
			1.984	2.90
			1.101	2.90
S-1	890	5.73	4.058	2.90
			2.960	2.93
			1.976	2.95
			0.998	2.85
S-2	890	2.55	7.364	2.50
			3.682	2.53
			2.210	2.65

the concentration dependence of pK of polymethacrylic acid and showed that it disappeared when account was taken of the activity coefficient¹⁾. It seems most likely that such correction becomes necessary also for our case, upon going to higher carboxyl group contents and concentrations.

Estimation of Molecular Size

The ionized groups of polyelectrolytes are bound together on the polymer chain and are subjected to the interaction, much more stronger than that in the normal electrolyte solutions. The anomaly observed in its titration curve can be also attributed to this effect and measured by the electrostatic free energy F_e . Generally,

$$pH = pK_0 + \log \frac{\alpha'}{1-\alpha'} + \frac{0.434}{kT} \frac{\partial F_e}{\partial Z} \quad (2)$$

holds, where pK_0 denotes the dissociation exponent of the ionizable group in ideal state, k the Boltzmann constant, T the absolute temperature, Z the number of ionized groups of a macro-ion. On the other hand, the inter-macro-ion interaction has been brought to bear on the macroscopic behaviors of polyelectrolyte solutions by us,⁴⁾ on the bases of the model used by Hermans and Overbeek⁵⁾ and the interionic theory of Wicke and Eigen,⁶⁾ and the thermodynamic quantities have been derived. In the case where the solution is salt-free and the number of gegen-ions fixed in the macro-ion is negligibly small compared to Z , and if $m_p' \ll Z m_p$, it gives

$$\begin{aligned} \partial F_e / \partial Z = & \frac{-e_0^2 Z \kappa}{\epsilon} \frac{1}{3} [2\tau(\kappa R) + \sigma(\kappa R)] - \left[\frac{6}{5} \frac{Z}{R} - \frac{1}{2\delta_1} \right] \\ & + \frac{\kappa}{3} [\tau(\kappa\delta_1) + \sigma(\kappa\delta_1)], \end{aligned} \quad (3)$$

where R is the radius of macro-ion, δ_1 the radii of ionized group and gegen-ion (assumed to be rigid spheres), e_0 the electronic charge, κ the extended Debye reciprocal radius $\kappa^2 = \frac{4\pi e_0^2}{kT} \{Zn_p(Zm_p + m_p')\}$, $m_p = 1 - n_p \left(\frac{4}{3}\pi R^3\right)$, $m_p' = 1 - Zn_p \left(\frac{4}{3}\pi \delta_1^3\right)$, n_p the average number of macro-ions per unit volume of solution, $\sigma(y) = \frac{3}{y^3} \left\{ 1 + y - \frac{1}{1+y} - 2 \ln(1+y) \right\}$ and $\tau(y) = \frac{3}{y^3} \left\{ \ln(1+y) - y + \frac{1}{2}y^2 \right\}$.

Combining Eq. (3) with the value of $\frac{\partial F_e}{\partial Z}$ obtained by Eq. (2) taking $pK_0 = 2.50$, which is found by the graphical extrapolation of pK to zero carboxyl group content, the size of the macro-ion can be estimated. These values of R so obtained are tabulated in Table 2, with R' , the extension of macro-ion viscometrically determined. The concentration dependence of R invites some interesting discussion.

Table 2. Radii of PVAG from the Titration Data at $\alpha' = 0.5$

Sample	DP	COOH-Content (mol %)	Concentration (g./1000 cc.)	R (Å)	R' (Å)
S-C	970	10.80	4	57	300
			2	66	
			1	72	
			0	240	
S-1	890	5.73	4	52	290
			2	60	
			1	67	
			0	170	
S-2	260	2.52	8	39	260
			4	46	
			2	51	
			0	90	

$2R'$: The root mean square end-to-end distance of macro-ion determined by the intrinsic viscosity number by means of Flory-Fox Eq.

The well-known variation of η_{sp}/c with concentration has been interpreted in terms of "intramolecular" interaction⁷. However it seems to us unrealistic to take no account of the "intermolecular" interaction even in the dilute solutions of polyelectrolytes and the anomaly of viscosity can be attributed to this interaction, which becomes greater with concentration. We could say this alternative interpretation is supported by Table 2, judged from the very nature of our treatment.

We are not in a position to quantitatively examine the magnitudes of R 's in the non-extremely dilute solution: convincing information has not been obtained from other approaches. It can, however, be said that the decreasing tendency of R with concentration would be close to reality.

Potentiometric and Electrophoretic Potentials

The electrophoretic mobility m of a charged particle is related to the electrophoretic potential ζ_{ele} (surface potential) by

$$m = K \frac{\zeta_{ele} \cdot \epsilon}{\eta} \quad (4)$$

where η is the viscosity coefficient of the solvent, K a constant dependent on the size, shape and conductivity of the particle and so on. The potentiometric potential, which is defined by the relation

$$\frac{\partial F_e}{\partial Z} = e_0 \zeta_{pot}, \quad (5)$$

is described as the potential of field inside the macro-ion, from which H^+ -ion is brought to infinity. ζ_{pot} may be equal to ζ_{ele} only when the potential inside the macro-ion is independent of the distance from the centre. As illustrated in Table 3, however, the observed potentiometric potential, $\zeta_{pot\ obs}$, considerably differs from $\zeta_{ele\ obs}$.⁸⁾

The discrepancy can be clearly understood if ζ_{pot} is to be referred to an average potential inside the spherical macro-ion. According to our calculation,⁴⁾ the potential inside the macro-ion ψ_2 as a function of the distance r from the centre is given by

$$\psi_2 = \frac{-Ze_0^2}{2\epsilon R^3} \left(\frac{\kappa R + 3}{\kappa R + 1} R^2 - r^2 \right). \quad (6)$$

Assuming $\zeta_{pot} = \bar{\psi}_2 = \frac{1}{R} \int_0^R \psi_2 dr$, we obtain

$$\zeta_{pot}/\zeta_{ele} = (\kappa R + 4)/3, \quad (7)$$

since $\zeta_{ele} = (\psi_2)_{r=R}$.

In Table 3, the observed electrophoretic potentials are compared with the observed potentiometric ones, and the validity of Eq. (7) undergoes an examination.

Table 3. Comparison between Potentiometric and Electrophoretic Potentials

Sample	$\zeta_{ele\ obs} \times 10^5$ (e.s.u.)	$\zeta_{pot\ cal} \times 10^5$ (e.s.u.)	$\zeta_{pot\ obs} \times 10^5$ (e.s.u.)
S-C	3.6	12	9.9
S-1	2.7	6.2	4.9
S-2	1.5	2.6	3.0
S-8	1.8	4.3	3.9

All values of $\zeta_{ele\ obs}$ are obtained, from the extrapolated value of observed descending mobilities (at the concentration 4 g./1000 cc.) to zero ionic strength, by means of Eq. (4) with $K = \frac{1}{6\pi}$. Using the values of κ at the concentration 4 g./1000 cc. and those of R at this concentration shown in Table 2, $\zeta_{pot\ cal}$ is calculated from $\zeta_{ele\ obs}$ according

to Eq. (4). $\zeta_{pot\ obs}$, which is evaluated by Eq. (5) from the observed values of $\frac{\partial F_e}{\partial Z}$, is in a good agreement with $\zeta_{pot\ cal}$.

Experimental

Preparation of PVAG. PVAG was prepared by acetalization of poly(vinyl alcohol) with glyoxylic acid. The details are found elsewhere⁹⁾. The degree of polymerization was determined by the viscosity measurement of parent PVA and the carboxyl group content was evaluated by the conductometric titration.

Potentiometric titrations. The titrations were performed with a glass electrode at room temperature (about 25°C). The sensitivity of the potentiometer was 0.01 pH unit and the reproducibility of the data was 0.03 pH unit.

Electrophoretic measurements. The electrophoresis was carried out by the moving-boundary method using the Tiselius apparatus. The details are given in another paper⁸⁾.

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