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CITATION:

ISE, Norio ...[et al]. Electrophoresis of Polyelectrolytes : II. Electrophoretic Study of Poly (vinyl alcohol) Partially Acetalized with Glyoxylic Acid. Memoirs of the Faculty of Engineering, Kyoto University 1958, 19(4): 417-425

ISSUE DATE:

1958-02-01

URL:

<http://hdl.handle.net/2433/280399>

RIGHT:

## Electrophoresis of Polyelectrolytes

### II. Electrophoretic Study of Poly(vinyl alcohol) Partially Acetalized with Glyoxylic Acid

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(Received August 23, 1957)

#### Abstract

Electrophoretic behaviors of a synthetic polyelectrolyte, poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG), were studied. The mobility was found to be almost independent of the degree of polymerization. The mobility-polymer concentration curve appears to have a minimum for materials of high charge density, whereas it is steadily decreasing for those of low charge density. Moreover the mobility variation with the ionic strength of buffer solution showed a tendency of decreasing under our experimental condition. The number of charges of this polyacid was estimated by means of Debye-Henry's relation from the observed (descending) mobility and found to be in a fairly good agreement with the value determined by conductometric titration with an exception at the very low ionic strength.

#### I. Introduction

Electrophoresis has been an invaluable method to attain a fuller knowledge of behaviors of protein in solutions. Unfortunately the vast progress has not been accompanied by a corresponding advancement in the fundamental interpretation, because of structural complexity of proteins. We therefore started the electrophoretic study of a synthetic polyelectrolyte with a hope that useful informations could be obtained to tide over such a gap.

In the present study, poly(vinyl alcohol) partially acetalized with glyoxylic acid (PVAG) is used. The carboxyl group content does not exceed about 10 mol % and the conclusions presented here might not be valid for the polyelectrolytes of a higher charge density. This limitation, however, would serve to lead us to an understanding of polyelectrolytes and low molecular ones from an unified stand-point. Attention is here focused on the estimation of the number of charges of PVAG by means of Debye-Henry's relation from the electrophoretic mobility and on other related problems.

## II. Results

1) Electrophoretic Pattern. Usually the Schlieren patterns of PVAG were symmetrical, as Fig. 1 shows, and as many moving boundaries were observed as the number of ionic species present would account for. In the buffer media of low ionic strengths, stationary  $\epsilon$ - and  $\delta$ -boundaries occurred: the lower the ionic strength, the more markedly the  $\delta$ -boundary becomes. (See Fig. 1). The displacement of  $\delta$ -boundary was not observed in the present experiments.<sup>1)</sup>

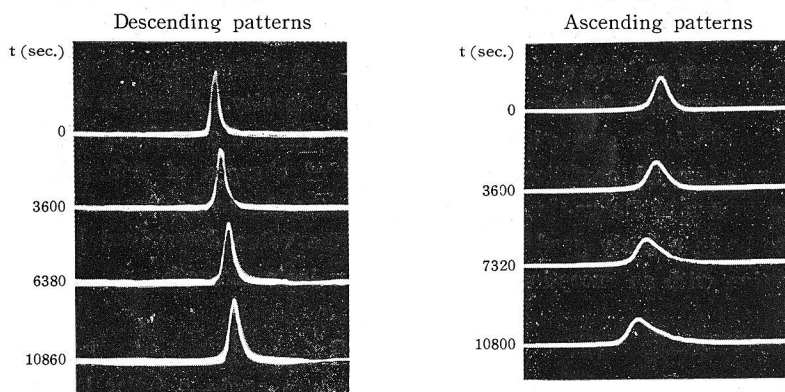
2) Electrophoretic Mobility. An electrophoretic mobility  $m$  is calculated by the relation

$$m = U/E, \quad (1)$$

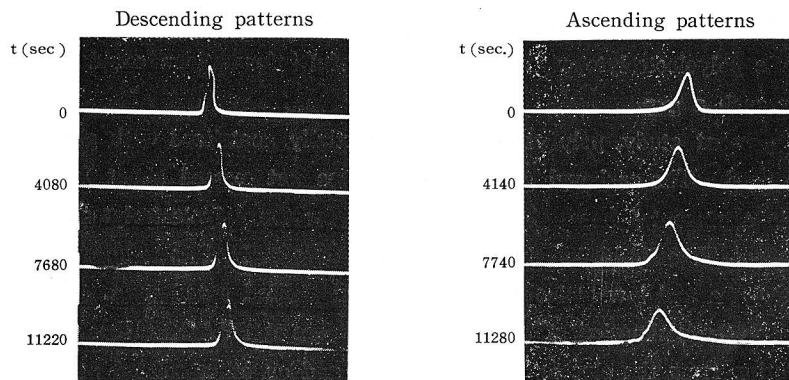
where  $U$  is the moving velocity of boundary determined from the displacement of the peak of pattern and  $E$  the intensity gradient of electric field evaluated from the con-

Fig. 1. Schlieren patterns of PVAG

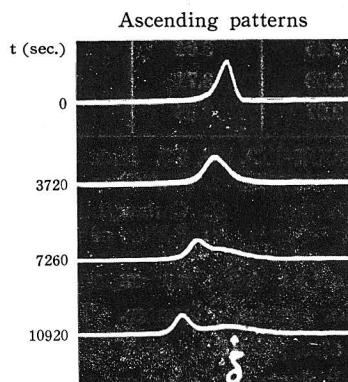
(A) Sample: S-7, Buffer:  $\text{CH}_3\text{COOK-HCl}$ ,  $\mu_s=0.050$ ,  $\text{pH}=5.3$ ,  
Polymer concn.=1.01 g./100 cc., Current=1.15 mA, Voltage gradient=0.34 v./cm..



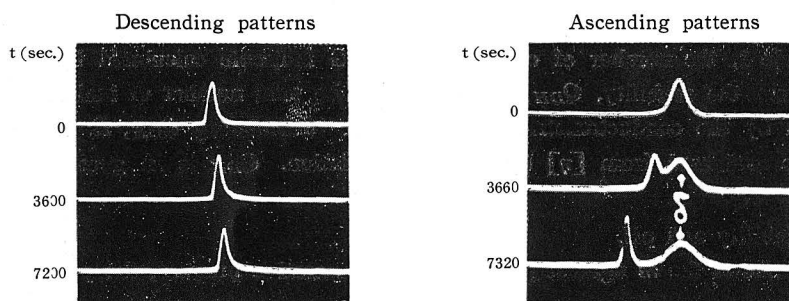
(B) Sample: S-8, Buffer:  $\text{CH}_3\text{COOK-HCl}$ ,  $\mu_s=0.096$ ,  $\text{pH}=5.3$ ,  
Polymer concn.=1.52 g./100 cc., Current=5.00 mA, Voltage gradient=0.86 v./cm..



- (C) Sample: S-8, Buffer:  $\text{CH}_3\text{COOK-HCl}$ ,  $\mu_s=0.028$ ,  $\text{pH}=5.3$ ,  
 Polymer concn.=0.98 g./100 cc., Current=1.65 mA, Voltage gradient=0.85 v./cm..



- (D) Sample: S-8, Buffer:  $\text{CH}_3\text{COOK-HCl}$ ,  $\mu_s=0.009$ ,  $\text{pH}=5.3$ ,  
 Polymer concn.=1.05 g./100 cc., Current=0.55 mA, Voltage gradient=0.88 v./cm..



ductivity of the dialyzed polymer-buffer solution. Two mobilities are obtained from the descending and ascending boundaries but the quantity in this paper refers only to the former.<sup>2)</sup> The boundaries travel toward the anode as expected: the mobility value is negative.

a) Mobility and Degree of Polymerization.

Table 1 shows the mobility values obtained with the materials of three different degrees of polymerization ( $P$ ) and of practically constant carboxyl group content.

This table indicates that the mobility hardly depends on the degree of polymerization. This is in accordance with the results with poly(vinyl alcohol) (PVA) by Hosono-Sakurada<sup>3)</sup> and with poly-4-vinyl-N-n-butyl pyridinium bromide by Fitzgerald et al.<sup>4)</sup> Assuming the proportionalities between  $P$  and the square of the radius of spherical macro-ion  $R^2$ , and between  $P$  and the number of charges on a macro-ion  $Q$ , this independency can be easily explained by Debye-Henry's relation,<sup>5)</sup> which holds for the virtually insulated rigid sphere,

$$m = f(\kappa R) Q / (6\pi\eta R [1 + \kappa R]), \quad (2)$$

where  $f(\kappa R)$  is the Henry function and  $\kappa$  the Debye reciprocal length, since  $f(\kappa R)$  is

Table 1. Effect of Degree of Polymerization on Mobility

Sample	$P$	$S$	$m \times 10^5$	$R$	$Q_{tit}$	$Q_{DH}$
S-8	1700	3.46	3.64	99	59	44
S-2	890	2.52	3.71	68	22	23
S-5	370	2.97	3.23	47	11	11

Buffer,  $\text{CH}_3\text{COOK-HCl}$ . pH, 5.3. Ionic strength, 0.099.

Polymer concentration, ca. 1 g./100 cc.

$P$ : Degree of polymerization       $S$ : Carboxyl group content (mol%)  
 $m$ : Mobility ( $\text{cm}^2 \cdot \text{volt}^{-1} \cdot \text{sec}^{-1}$ )       $R$ : Radius of macro-ion (spherical) ( $\text{\AA}$ )

not very sensitive to  $\kappa R$  and  $\kappa R \gg 1$  under our experimental conditions. The relation  $P \propto R^2$  was originally found for neutral polymers. The viscosity of PVAG used here in the buffer medium, ionic strength=0.1, does not display the dependence on concentration, characteristic of polyelectrolyte solutions; the linear variation characteristic of neutral polymers is obtained. Therefore, it does not seem unreasonable to introduce this relation in our case. The proportionality of  $Q$  to  $P$  can be easily admitted if PVA molecules were uniformly acetalized.

In Table 1, the number of charges on PVAG molecule calculated by means of Eq. (2) from the mobility,  $Q_{DH}$ , is given with the total number of ionizable groups determined by the conductometric titration,  $Q_{tit}$ . Calculating  $Q_{DH}$ ,  $R$ , tabulated in Table 1, is evaluated from  $[\eta]$  by Einstein's relation.  $Q_{DH}$  is in good agreements with  $Q_{tit}$ .

#### b) Mobility and pH.

Fig. 2 shows the  $m$  against pH plot; for comparative purpose, the potentiometric

Fig. 2. Effect of pH on mobility

Sample: S-8, Polymer concn., ca. 1 g./100 cc.

Buffer:  $\text{CH}_3\text{COOK-HCl}$ ,  $\mu_s=0.096$

Titration curves ( $\mu_s=0$ ): Polymer concn. I 0.69 g./100 cc.  
 II 0.07 g./100 cc.

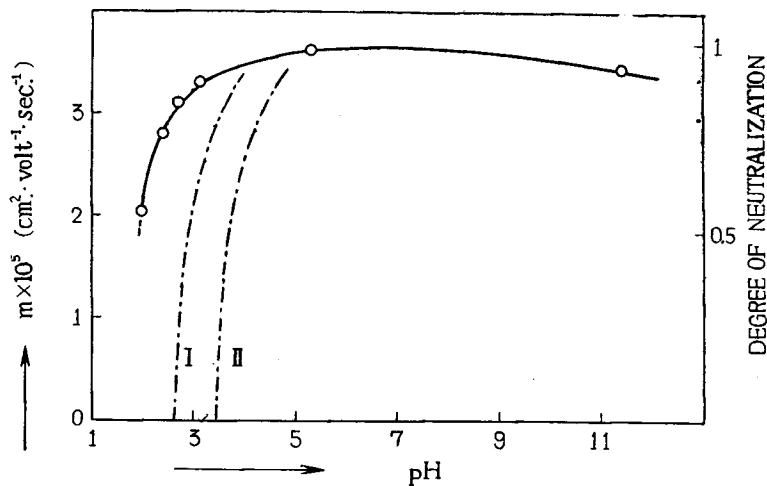


Table 2. Effect of Carboxyl Group Content on Mobility

Sample	S	P	$m \times 10^5$	R	$Q_{lit}$	$Q_{DH}$
S-C	10.80	970	9.09	102	110	117
S-1	5.73	890	6.80	72	51	47
S-2	2.52	890	3.71	68	22	23

Buffer,  $\text{CH}_3\text{COOK-HCl}$ . pH, 5.3. Ionic strength, 0.099.  
 Polymer concentration, ca. 1 g./100 cc.

titration curves are also given. This figure seems to suggest that almost all acidic groups are ionized at  $\text{pH} \geq 5$  and contribute to the electrophoretic motion.

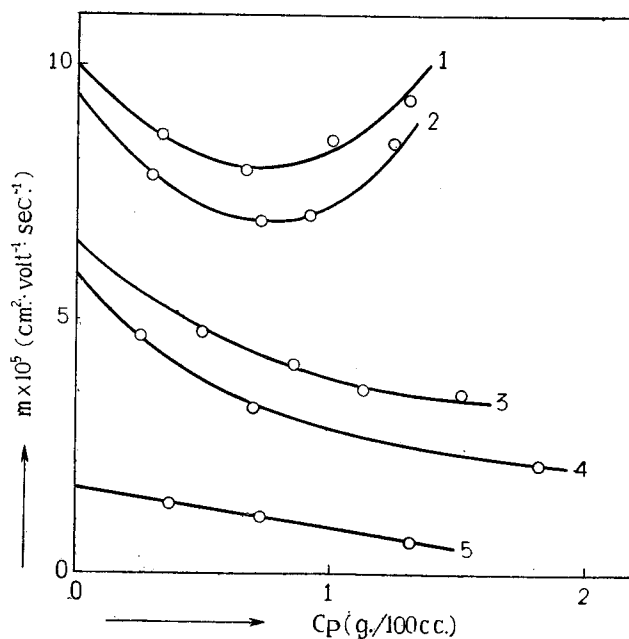
c) Mobility and Carboxyl Group Content.

The mobility values obtained with various carboxyl group contents S are illustrated in Table 2.  $Q_{DH}$  obtained from the observed mobility is given, which is also in good agreement with  $Q_{lit}$ . Interpolation of the mobility to that of PVA ( $10^{-5} \text{ cm}^2 \cdot \text{volt}^{-1} \cdot \text{sec}^{-1}$ ) gives the figure of about 0.7 mol % as the carboxyl group content, which is not so different from the number of charges of PVA previously determined in the buffer of this ionic strength.<sup>3)</sup>

d) Mobility and Polymer Concentration.

Fig. 3. Effect of polymer concn. on mobility

Curve	Sample	P	S	Buffer	pH	$\mu_s$
1	S-7	1700	5.82	$\text{CH}_3\text{COOK-HCl}$	5.30	0.050
2	S-1	890	5.73	$(\text{COOK})_2\text{-HCl}$	3.04	0.097
3	S-8	1700	3.46	$\text{CH}_3\text{COOK-HCl}$	5.30	0.096
4	S-2	890	2.52	$(\text{COOK})_2\text{-HCl}$	3.04	0.097
5	PVA	890	—	$(\text{COOK})_2\text{-HCl}$	3.04	0.097



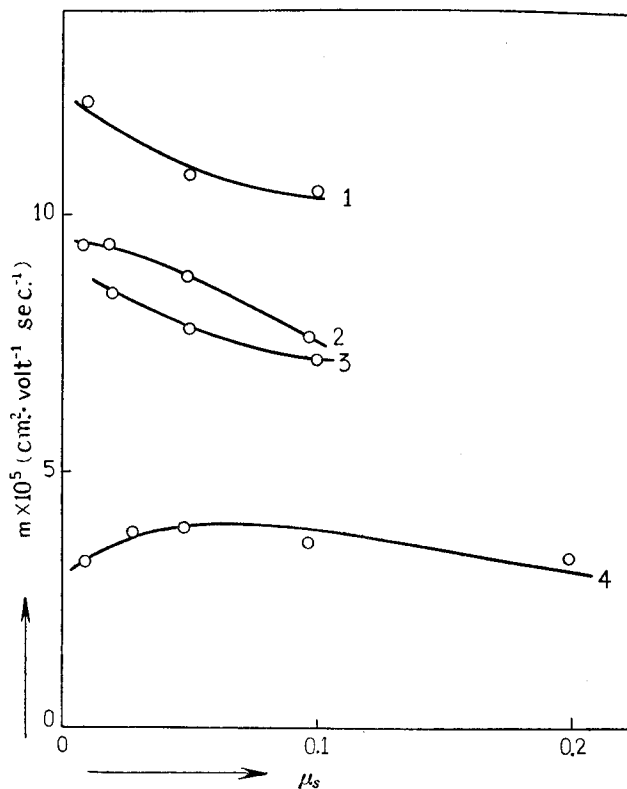
It has been already known that  $m$  varies with polymer concentration  $C_p^{3,6)}$ . Fig. 3 presents our results with PVAG's and PVA. The mobility of PVA was found to decrease steadily with increasing concentration, whereas a minimum appears for PVAG of higher carboxyl group content. This feature and the concentration-dependence of mobility in general, which can never be predicted by previous theories, has been successfully interpreted in terms of inter-macro-ion interactions elsewhere<sup>7)</sup>.

e) Mobility and Ionic Strength.

Finally the work was extended to a study on the mobility-ionic strength ( $\mu_s$ ) relation. Fig. 4 indicates that  $m$  has a tendency of increasing with decreasing  $\mu_s$ , which is well explained by Debye-Henry's relation, if  $m$  is determined predominantly by the charges due to ionizations of acidic groups, and if  $R$  is practically independent of  $\mu_s$ . In the very low ionic strength range, however,  $R$  would decrease together

Fig. 4. Effect of ionic strength on mobility

Curve	Sample	$P$	$S$	$C_p$	Buffer	pH
1	S-10	2150	12.08	0.9	CH <sub>3</sub> COONa-NaOH	12.0
2	S-4	370	6.37	0.4	CH <sub>3</sub> COONa-NaOH	6.2
3	S-4	370	6.37	0.7	CH <sub>3</sub> COONa-NaOH	6.2
4	S-8	1700	3.46	1.0	CH <sub>3</sub> COOK -HCl	5.3



with  $\mu_s$ . According to Debye-Henry's relation, then  $m$  could turn to the tendency of decreasing, which was evidently observed with materials of high charge density by Nagasawa<sup>8)</sup>.

### III. Discussion

In the foregoing section, some properties of electrophoretic mobility were shown to be described by Debye-Henry's relation and the quantitative examination was undertaken by comparison between  $Q_{DH}$  and  $Q_{tit}$ . However, the present theories of electrophoresis have dealt with only a single charged particle and Debye-Henry's theory is no exception. Strictly speaking, therefore, the validity is restricted to an extremely dilute solution or a solution which stands in an ideal state: in attempting to estimate the number of charges by Debye-Henry's relation, the mobility value should be preferably extrapolated to zero concentration.  $Q_{DH}$  so obtained, is shown in Table 3: it does not differ much from  $Q_{tit}$ . The discrepancy is too small to be attributed to such an adsorption of negatively charged small ions as considered in the case of PVA.

Table 3. Number of Charges Estimated from Extrapolated Mobility

Sample	$P$	$S$	pH	$\mu_s$	$[m] \times 10^5$	$R$	$Q_{tit}$	$O_{DH}$
S-7	1700	5.82	5.30	0.050	10.0	125	99	140
S-1	890	5.73	3.04	0.097	9.4	86	51	87
S-8	1700	3.46	5.30	0.096	6.5	99	59	78
S-2	890	2.52	3.04	0.097	5.8	73	22	40
PVA	890	—	3.04	0.097	1.7	71	—	41

$[m]$ : Extrapolated mobility to zero concentration.

It is always possible to estimate the number of charges from the mobility at any finite concentration if we admit its approximate nature. Such estimates are shown in Tables 1, 2, 4 and 5.  $R$ , found from  $[\eta]$  by means of Einstein's relation, is assumed to be constant in the concentration range in which the electrophoretic runs are observed. The agreement between  $Q_{DH}$  and  $Q_{tit}$  suggests, that the extrapolation is not always necessary under our experimental conditions; it must be borne in mind that this agreement can not necessarily be expected with materials of high charge density, or in the case the inter-macro-ion interaction remains prevailing.

This is clearly exemplified by comparison of  $Q_{tit}$  with  $Q_{DH}$  obtained at low ionic strength. Table 5 indicates that the discrepancy between  $Q_{DH}$  and  $Q_{tit}$  appears to grow while the ionic strength decreases. The shape factor might immediately come to mind. As already shown in previous papers<sup>7,9)</sup>, the shape and size of linear and ideally flexible polyelectrolytes in solutions are considered to be determined by not



Table 4. Number of Charges Estimated from Observed Mobility

Concentration (g./100 cc.)	$m \times 10^5$	$Q_{DH}$
1.31	9.35	130
1.01	8.54	120
0.67	7.96	110
0.34	8.66	120

Buffer,  $\text{CH}_3\text{COOK-HCl}$ , pH, 5.3.  
 Ionic strength, 0.050.  
 Sample, S-7 ( $P=1700$   $S=5.82$  mol %  
 $Q_{tit}=99$ ,  $R=125\text{\AA}$ )

Table 5. Number of Charges Estimated at Various Ionic Strengths

$\mu_s$	$m \times 10^5$	$R$	$Q_{DH}$
0.199	3.30	98	53
0.096	3.64	99	44
0.048	3.95	104	40
0.028	3.82	112	36
0.009	3.26	124	24

Buffer,  $\text{CH}_3\text{COOK-HCl}$  pH, 5.3.  
 Sample, S-8 ( $P=1700$ ,  $S=3.46$  mol %  
 $Q_{tit}=59$ )  
 Polymer concentration, ca. 1g./100 cc.

only the intra-macro-ion interaction, but also the inter-macro-ion one. In the dilute solutions, the polymer chain cannot be deemed to be shrunk or elongated only in a fixed direction: the chain in consideration is curled up to be spherical. By this guessing, it would seem rational to attribute the growing discrepancy mentioned above to the inter-macro-ion interaction, which has not been dealt with in Debye-Henry's theory but, in reality, would become prominent as the ionic strength decreases. (Taking no account of this interaction really results in an underestimation of  $\kappa$ , accordingly, of the number of charges.)

Two comments of general interest should be mentioned. Combining Debye-Henry's relation and Einstein's, some question might rise by lack of any rigorous proof on the equivalency of these two rigid sphere models. However, the use of other theories (i.e., Flory-Fox's and Debye-Bueche's) in preference to Einstein's for the present purpose seems no more consistent with Debye-Henry's theory in respect of the model. Secondly it is necessary to consider the possibility of gegen-ion fixation. As Wall has shown in an elegant manner,<sup>10)</sup> a number of gegen-ions travels with the polyions in a region of high degree of neutralization, but only a few are associated with the polymer coil at a low degree of neutralization. Therefore this kind of association could be presumably out of consideration with materials of a few ionized groups like ours. This could be said to confirm the agreements between  $Q_{DH}$  and  $Q_{tit}$ . (There might be another case, however, that a considerable number of gegen-ions is present in polymer coils in such a way, as they do not concern the mobility of polyions. This aspect of the problem should be under further investigation from other approaches.)

In conclusion, it is possible to say that the electrophoretic behaviors of linear polyelectrolytes with a few ionizable groups in solutions can be interpreted quantitatively by Debye-Henry's theory. (This would be considered to support the information electrophoretically obtained on the number of charges of PVA.) Fortunately only a single parameter,  $R$ , is involved in this theory, which serves as simplification of the

analysis, although the disregard of polymer concentration-effect should be made up for by another approach, if necessary.

#### IV. Experimental

**Material.** PVAG was prepared by acetalization of fractionated PVA, in the presence of sulphuric acid, with glyoxylic acid, which was obtained by the electrolytic reduction of oxalic acid. Details are given in another paper.<sup>11)</sup> The material in this paper is the same as that used for the potentiometric titration.<sup>9)</sup>

**Apparatus.** The Tiselius apparatus (Type HT-A manufactured by Hitachi Manufacturing Company) was used with the Schlieren diagonal method. All measurements were carried out at  $15 \pm 0.1^\circ\text{C}$ .

**Procedure.** The polymer solution was prepared by dissolving the material in buffer and was dialyzed against the buffer until equilibrium (indicated by the attainment of constant conductance) was reached. The concentration was determined by dry weight after dialysis. The electrophoretic current varied from 10 mA to 1 mA, depending on the electrical character of the material used and on the conductance of the solution.

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