

DERIVATION OF EQUATIONS TO ACCOUNT FOR THE VARIATION OF OSMOTIC PRESSURE, pH AND CONDUCTANCE OF SOLS OF POLYACIDS WITH DILUTION

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Equations have been derived to account for the variation, with dilution, of osmotic pressure, pH and specific conductance of polymeric acids which form colloidal solutions. It is assumed (as usual) that each colloidal particle of a polymeric acid is surrounded by an electrical double layer consisting of two parts—a fixed layer and a mobile diffuse layer, and the counter ions in the diffuse layer can record their activity on the osmometer membrane or the reversible electrode of the pH meter or an electrode of the conductivity cell, only when they are carried sufficiently close to it (i.e. membrane, etc.) by the particle. The number of counter ions per unit volume increases as the surface of the particle is approached from the outermost boundary of the diffuse layer according to the Boltzmann distribution law. It has been shown that if at a concentration C of the particles of the acid, a fraction θ per unit area of the surface of the membrane, etc., is in contact with the double layers of the particles, then the osmotic pressure P_o is proportional to θ , where θ has been proved to be equal to $C/(K+C)$, K being a constant. It has also been shown that, $(H_o - h_o)$ is proportional to θ , where H_o is the H^+ ion activity of the counter ions at a concentration C of the acid and h_o , the H^+ ion activity of the intermicellar liquid.

A similar equation has also been deduced for the variation of the specific conductance X_c with C .

These equations have been tested using the experimental data of Kern on polyacrylic acids of different degrees of polymerization and have been found to agree with them (i.e. the data) within the limits of experimental error.

INTRODUCTION

In analogy with the weak acids the degree of ionization of a weak polyacid is generally assumed (Pauli and Valko 1929; Maxwell and Partington 1935; Kern 1938; Wall and De Butts 1949) to increase with dilution. Kern has measured the pH, osmotic pressure and specific conductance of sols of polyacrylic acid (PAA) at various concentrations C and has proposed the following empirical equations

$$(H^+) = h_1 C^{2/3} \quad \dots \dots \dots (1)$$

$$P = p_1 C^{2/3} \quad \dots \dots \dots (2)$$

and hence

$$P = \frac{p_1}{h_1} (H^+) \quad \dots \dots \dots (3)$$

where C represents the concentration of PAA , (H^+) and P , the hydrogen ion activity and osmotic pressure respectively, and h_1 and p_1 are constants. He has also shown that the specific conductance of the sol depends mainly on its hydrogen ion activity as expected.

It may be pointed out that polymeric acids like PAA usually contain, as an impurity, some low molecular weight polymer which has got a small solubility, S and so long as this low molecular weight polymeric acid is present in the system in excess of S , dilution with water will not change the hydrogen ion activity, say h_0 , of the intermicellar liquid. Under this condition, therefore, change of degree of ionization of a sol of a polymeric acid with dilution should not occur. Consequently variation of osmotic pressure, pH , etc., of the sol with dilution is to be attributed to other causes.

EQUATION FOR OSMOTIC PRESSURE

It is assumed that in the case of polymeric acids like PAA , which form a colloidal solution, each particle of the acid in the sol is surrounded by an electrical double layer consisting of two parts; the fixed Stern-Mukherjee layer and the mobile Gouy-Chapman diffuse layer. The activity of the counter ions (*i.e.* the H^+ ions) in the diffuse layer will increase as the surface of the particle is approached from the outermost boundary of the double layer according to Boltzmann's distribution law.

When the colloidal solution of a polyacid is placed in the inner chamber of an osmometer the counter ions (*i.e.* the H^+ ions) in the diffuse part of the double layer can reach the membrane and thus record their osmotic activity only when the colloidal particles of the polyacid come in contact with (*i.e.* as close as possible to) the membrane.

For simplicity let us assume that in a sol of a polyacid, the particles are all of the same size and let θ be the fraction (per unit area) of the membrane surface with which the particles with their double layers are in contact at a concentration C . When a particle comes very close to the osmometer membrane its diffuse double layer is distorted and the hydrogen ions in this layer get the opportunity to register their activity. The concentration of the counter ions and consequently their osmotic pressure in the distorted portion of the double layer is greater than that in the intermicellar liquid and this tends to remove the particle from the surface of the membrane. Besides, the membranes are usually negatively charged and hence electrostatic force of repulsion also operates in expelling the particles of the polyacid from the surface of the membrane. Therefore, at equilibrium the following relation should hold good

$$K_1(1-\theta)C = K_2\theta \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

where the left-hand side represents the rate at which the particles strike the membrane and the right-hand side the rate at which they escape from the surface and K_2 and K_1 are the velocity constants.

It follows from equation (4) that

$$\theta = \frac{C}{K+C} \quad \dots \quad \dots \quad \dots \quad (5)$$

where $K = k_2/k_1$

The osmotic activity of the counter ions (i.e. the H^+ ions) will, therefore, be proportional to θ . If P_c represents the osmotic pressure of the counter ions at a concentration C of the sol, then

$$P_c = p_m \theta = p_m \frac{C}{K+C} \quad \dots \quad \dots \quad \dots \quad (6)$$

or

$$\frac{1}{P_c} = \frac{1}{p_m} \left(1 + \frac{K}{C} \right) \quad \dots \quad \dots \quad \dots \quad (6a)$$

where p_m is a proportionality constant.

It may be pointed out that in the aforesaid deduction the contribution of the colloidal particles to osmotic pressure has been assumed to be negligible. Furthermore, since the solubility, S , of the low molecular weight polymeric acid is very small and no other diffusible electrolyte is present in the system, the effect of Donnan membrane equilibrium due to S having (almost) the same value in the sol chamber and in the water chamber, can be neglected.

EQUATION FOR HYDROGEN ION ACTIVITY

If the sol of a polymeric acid like PAA contains some polymer of low molecular weight having a very small solubility, S , then so long as it is present in the system in excess of S (obviously the excess being in colloidal condition), the hydrogen ion activity, h_0 of the intermicellar liquid will not change on dilution with water. If a reversible hydrogen electrode is dipped into the colloidal solution of the polymeric acid, then the H^+ ions in the diffuse part of the double layer can record their activity on the electrode only when the particles of the acid come sufficiently close to the electrode surface. Therefore, if θ be the fraction (per unit area) of the electrode surface, covered by the double layers of the particles in contact with it at a concentration C , then the hydrogen ion activity H_c indicated by the reversible electrode should be given by the following expression

$$H_c = H_m \theta + h_0 (1 - \theta) \quad \dots \quad \dots \quad \dots \quad (7)$$

or

$$H_c - h_0 = (H_m - h_0) \theta = \frac{a_m C}{K+C} \quad \dots \quad \dots \quad \dots \quad (7a)$$

where H_m and a_m are constants and $a_m = (H_m - h_0)$.

Equation (7a) may also be written as follows

$$\frac{1}{H_c - h_0} = \frac{1}{a_m} \left(1 + \frac{K}{C} \right) \quad \dots \quad \dots \quad \dots \quad (7b)$$

It will be noticed from equation (7a) that when C approaches infinity, θ becomes unity and H_c attains the maximum value H_m . Since h_0 is very small compared to

H_m , it may be neglected and hence a_m will remain constant even when some polymeric acid of low molecular weight is absent and the sol is diluted with water.

EQUATION FOR SPECIFIC CONDUCTANCE

It may be pointed out that the main part of the current will be carried by the H^+ ions present in the electrical double layer surrounding each of the particles of the polyacid. Therefore, following the same line of argument as in the case of H^+ ion activity it can be shown that

$$X_c - X_0 = X_m \theta = X_m \frac{C}{K + C} \quad \dots \quad (8)$$

where X_c is the specific conductance of the sol of the polymeric acid at a concentration C , X_0 the specific conductance of the intermicellar liquid, and X_m and K are constants. Equation (8) may be written in the following form

$$\frac{1}{X_c - X_0} = \frac{1}{X_m} \left(1 + \frac{K}{C} \right) \quad \dots \quad (8a)$$

It may be mentioned, that as shown by Kern, the hydrogen ion activity H_c measured by the potentiometric method at the concentration C of the sol can also be found from the relation

$$H_c = \frac{X_c \cdot 1000}{324} \quad \dots \quad (9)$$

VERIFICATION OF THE EQUATIONS

The equations (6a), (7b) and (8a) have been subjected to test using the experimental data obtained by Kern (1938) and recorded in Tables I to V.

According to equation (6a) a plot of $\frac{1}{P_c}$ against $\frac{1}{C}$ should be linear and this has actually been found to be the case within the limits of experimental error. From the intercept of the straight line on $\frac{1}{P_c}$ axis and its slope the values of $\frac{1}{P_m}$ and K are found. Using these constants for different values of C , the values of $\frac{1}{P_c}$ are found and from these the corresponding values of P_c are calculated. They are recorded in the column 3 of Tables I and II.

According to equation (7b) a plot of $\frac{1}{H_c - h_0}$ against $\frac{1}{C}$ should be linear. Different probable values of h_0 are, therefore, tried in equation (7b) and that one is selected which makes the plot linear. From the intercept of the straight line on $\frac{1}{H_c - h_0}$ axis and its slope the constants $\frac{1}{a_m}$ and K are found. They are recorded in Tables III and IV. Using these constants, for different values of C , the corres-

TABLE I
Variation of osmotic pressure with dilution

D.P. 350	PAA	$\frac{1}{P_m}=12.3$	$K=0.16$ $h_0=6 \times 10^{-5}$
$C \text{ gm}^+$	$P \times 10^3$ atm % observed	$P_c \times 10^3$ atm % calculated from equation (6a)	$P_c = RT \times$ $(H_c - h_0) \times 10^3$ atm
0.2	46.0	45.2	46.8
0.1	29.8	31.3	31.0
0.05	18.3	19.4	18.5
0.025	11.3	11.0	10.2
0.0125	5.6	5.9	5.4
0.0063	4.0	3.1	2.9

TABLE II
Variation of osmotic pressure with dilution

D.P. 900	PAA	$\frac{1}{P_m}=9.4$	$K=0.24$ $h_0=7 \times 10^{-5}$
$C \text{ gm}$	$P \times 10^3$ atm	$P_c \times 10^3$ atm calculated from equation (6a)	$P_c = RT \times$ $(H_c - h_0)$ $\times 10^3$ atm
0.5	82.5	72.0	76.0
0.250	53.5	54.3	56.2
0.125	29.8	36.4	38.2
0.0625	20.9	22.0	23.3
0.0313	12.0	12.2	12.9
0.0156	6.5	6.5	6.9
0.0078	3.9	3.4	3.6

ponding values of $\frac{1}{H_c - h_0}$ are calculated and from the latter the values of H_c are found. They are recorded in Tables III and IV.

By adopting the same procedure as described above the values of X_0 , $\frac{1}{X_m}$ and K are found to be 2.3×10^{-5} , 7×10^2 and 21.2×10^{-2} respectively. They are recorded in Table V.

TABLE III
Variation of pH with dilution

D.P. 900	PAA	$\frac{1}{a_m} = 2.25 \times 10^3$	$K = 22.4 \times 10^{-2}$ $h_0 = 7 \times 10^{-5}$
C gm	pH found from		pH calculated from equation (7b)
	Potentiometric measurement	Conductance measurement	
0.5	2.40	2.48	2.49
0.25	2.62	2.61	2.62
0.125	2.81	2.80	2.78
0.0625	3.01	2.99	2.98
0.0313	3.21	3.20	3.21
0.0156	3.43	3.42	3.44

TABLE IV
Variation of pH with dilution

D.P. 350	PAA	$\frac{1}{a_m} = 2.5 \times 10^2$	$K = 0.21$ $h_0 = 6 \times 10^{-5}$
C gm	pH observed		pH calculated from equation (7b)
0.2	2.69		2.70
0.1	2.89		2.87
0.05	3.09		3.08
0.025	3.32		3.31
0.0125	3.62		3.55
0.0125	3.02		3.55
0.0063	3.74		3.75

+ gm stands for 'grundmolare', i.e. 72 grams in 1000 ml. of water

TABLE V
Variation of specific conductivity with dilution

D.P. 900	PAA	$\frac{1}{X_m} = 7 \times 10^2$	$K = 21.2 \times 10^{-5}$ $X_0 = 2.3 \times 10^{-5}$
C gm	X_c in recip. ohms observed for D.P. 900	X_c in recip. ohms calculated from equation (8a)	X_c in recip. ohms observed for D.P. 340
0.5	1.08×10^{-3}	1.03×10^{-3}	1.05×10^{-3}
0.25	0.794×10^{-3}	0.796×10^{-3}	0.731×10^{-3}
0.125	0.513×10^{-3}	0.533×10^{-3}	0.486×10^{-3}
0.0625	0.329×10^{-3}	0.348×10^{-3}	0.304×10^{-3}
0.0313	0.204×10^{-3}	0.206×10^{-3}	0.187×10^{-3}
0.0156	0.122×10^{-3}	0.121×10^{-3}	0.108×10^{-3}

DISCUSSION

The data of Kern on measurements of osmotic pressure, pH and conductance of polyacrylic acid of two different degrees of polymerisation denoted by D.P. 350 and D.P. 900 have been recorded in Tables I to V. It will be noticed from Table I that for PAA of D.P. 350, the agreement between the observed and calculated values of P_c is quite satisfactory for all the values of C . In column 4 of Table I are recorded the values of P_c^* , calculated from the expression $P_c = RT(H_c - h_0)$ where $(H_c - h_0)$ has been found for different values of C by using the equation (7b) and RT has been taken as 24 litre atmospheres at 20°C. It will be noticed that in this case also the agreement between the observed and calculated values of P_c is fairly satisfactory.

From the data recorded in Table II it would appear that for PAA of D.P. 900, the agreement between the observed and calculated values of P_c is satisfactory for all the values of C , except 0.5 gm and 0.125 gm. It may be pointed out that for PAA of D.P. 340 the value of P_c observed by Kern at $C = 0.125$ gm is 33.5×10^{-3} atm., and according to him the osmotic pressure of PAA at a given concentration is independent, within wide limits, of its D.P. Therefore, if 33.5×10^{-3} atm. is taken as the osmotic pressure of D.P. 900 also at $C = 0.125$ gm, then it would be fairly close to the calculated value, viz. 36.4×10^{-3} atm. The agreement between the observed values of P_c and those calculated from the expression $RT(H_c - h_0)$ may also be considered satisfactory for all the values of C , except 0.5 gm and 0.125 gm.

In Tables III and IV are recorded the observed and calculated values of pH of PAA of D.P. 900 and D.P. 350 respectively. In column 3 of Table III are also recorded the values of pH of PAA of D.P. 900 calculated from the conductance data using equation (9). It will be noticed that the agreement between the pH measured by the potentiometric method and that calculated from equation (7b) is quite satisfactory for all the values of C , except when $C = 0.5$ gm. For this value of C , however, the agreement between the pH found from conductance data and that calculated from equation (7b) is quite satisfactory.

It will also be noticed from the data recorded in Table IV that for PAA of D.P. 350 the agreement between the observed and calculated values of pH is quite satisfactory for all the values of C , except when $C = 0.0125$ gm. In this connection it may be pointed out that the limits of experimental error in the measurement of pH by Kern are sometimes quite large. For example for D.P. 340, he records at $C = 0.0625$ gm the H^+ ion activities 0.871×10^{-3} , 1.12×10^{-3} and 1.0×10^{-3} in Tables 6b, 9 and 11 of his paper. The values of pH corresponding to these H^+ ion activities are 3.06, 2.95 and 3.0 respectively. It is quite probable that in these experiments the device used for the elimination of the liquid junction potential failed to function properly.

In view of the aforesaid discussion, the agreement between the observed and calculated values of pH of D.P. 900 and D.P. 350 may be considered satisfactory.

A comparison of the data recorded in Table V shows that the agreement between the observed and calculated values of X_c is fairly satisfactory for all the values of C , except 0.125 and 0.0625 gm.

*It may be pointed out that, $P_c = P_m \theta = RT a_m \theta = RT(H_c - h_0)$ according to the equations (6) and (7a).

The value of specific conductance X_c of PAA of D.P. 340 are recorded in column 4 of Table V for comparison. According to Kern the specific conductance of PAA is independent of its D.P. (D.P. 200 to 2000). If his statement is accepted then such difference in the observed and calculated values of specific conductance X_c as has been discussed above falls within the limits of experimental error.

In conclusion it may be pointed out that since $(H_c - h_0) = a_m \theta$ and $P_c = P_m \theta = RT a_m \theta$ and $\theta \ll 1$, the observed activity of osmotic pressure of the counter ions is only a small fraction of what actually prevails within the diffuse double layer or the ion-atmosphere surrounding a colloidal particle. The activity and osmotic pressure within the diffuse double layer near the surface of the particle are a_m and P_m respectively.

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