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Titration Curves of Polyacids

KATE BAK

Institute for Physical Chemistry, University of Copenhagen, Denmark

The present investigation deals with titration curves of polyacids and the information which can be obtained from them.

The polymer molecule is considered as a one-dimensional lattice, and an expression for the relation between the apparent pK, the degree of neutralization and the energy of interaction is derived.

The analogy of this approach to previous work by Linderstrøm—Lang and J. Bjerrum is demonstrated.

Finally the theory is compared with experimental results for a polyacrylic acid, containing 25—30 monomer units per molecule. The titration curves were corrected for changes in ionic strength during the titration.

It is concluded that the shape of polyacrylic acid in solution is such that each carboxyl group is surrounded by eight other carboxyl groups within a sphere, the approximate radius of which is the distance between two adjacent carboxyl groups.

INTRODUCTION

1. It was early discovered that the titration curves for polyacids, such as gum arabic and pectic acid, differed significantly from those of monobasic acids in that the apparent pK for the polyacid increased during the titration. Originally this was attributed to the existence of different acidic groups, but as the theory of high molecular substances progressed it became clear that in polyacrylic acid, for instance, there is only one type of carboxyl group. The explanation for the increasing pK must therefore rather be sought in the fact that the negative charge of the molecule increases during a titration, thus making it more and more difficult for the protons to be removed.

One way of treating this problem would be a Debye-Hückel approach in which it is assumed that the polymer molecule is a more or less free drained sphere with fixed charges on it. The Poisson-Boltzmann equation for this case has been solved approximately by Hermans and Overbeek [1], and this leads then to an expression for pK as a function of the charge and the ionic strength, as put forward by Overbeek [2]. The agreement between theory and experiment is, however, somewhat unsatisfactory.

An essentially much simpler approach is to elaborate the model for calculation of dissociation constants of acids due to N. Bjerrum[3] in which it is assumed for instance that pK_1-pK_2 for a dibasic acid is determined only by the electrostatic forces and the symmetry of the three molecular species involved in the equilibria. If one assumes that the (linear) polyacid can be treated as a one-dimensional lattice, and that only nearest neighbour interaction need be considered, the problem is an example of a solvable case of the Ising model[4]. Since comparison with experiments shows that in this application of the Ising model the difference between the exact solution and the solution using the Bragg—Williams approximation is negligible, it is possible to drop the assumption of a one-dimensional lattice and also to estimate the influence of next nearest neighbours. In this way, we believe the titration curve can be used as a means of determining the degree of coiling in a polyacid.

Since the Bjerrum approach to dissociation constants also has been used extensively in the theory of the formation of metal complexes, we further compare the results obtained here with formulae given by J. Bjerrum[6] and with analogous expressions derived earlier by Linderstrøm—Lang in a paper on protein solutions[7].

It should be quite clear that the present theory is only a crude one. A large number of factors, such as the effects of binding of counter-ions, and the entropy of distribution of un-ionized groups, ions and bound ion pairs among the possible configurations on the polymer molecule, which are considered for instance in the papers by Harris and Rice[8], have been neglected. In this way it has been possible to obtain simple formulae which can be compared with experiments. In the more involved theories, which only rarely lead to results which can be checked experimentally, it is not always clear which of the many factors considered are the important ones.

EXPERIMENTAL

2. The polyacrylic acid used was presented to us by Dr. V. Shashona, E. I. Du Pont de Nemours and Co. (Inc.), Wilmington, Delaware, U.S.A., as a concentrated aqueous solution. The number-average molecular weight was determined osmometrically by a Christiansen osmometer[9] to be 1.9×10^3, corresponding to about 27 monomer units. This value is the extrapolation of measurements at three different concentrations, performed by Dr. K. Marcker.

The concentration of polyacrylic acid in the solutions titrated was 5.6×10^{-4} g/ml of solution. The base used was 1.2 N NaOH.

The titration curves were determined using a Radiometer pH-meter 3 with glass-electrode and a calomel electrode as a reference. The apparatus was standardized on a 0.05 M solution of potassium hydrogen phthalate, following National Bureau of Standards' standardizing procedure. The titration vessel was stirred with a magnetic stirrer which was switched off during each measurement. In the earlier experiments, CO_2-free air was bubbled through the solution, but since experiments showed that this did not affect the results, this extra precaution was abandoned in later experiments.

The microburette used *, and which was calibrated with mercury, was a syringe, the body of which was made of hard polyethylene, the piston of teflon. The syringe was held in a brass tube and the piston was moved by a micrometer screw. The syringe contains 0.708 ml and can be read with a precision of 0.708/2500 ml.

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* Constructed by Dr. Jørgen Koefoed.

The temperature of the solution was kept constant at 25 ± 1°C by surrounding the titration vessel with a small water bath. Titration vessel, water bath and magnetic stirrer were encased in a grounded metal box.

The titrations were carried out two to three times each and were reproducible to within 0.05 pH-unit.

Titration curves for glutaric acid were also determined using solutions which contained the same equivalents of acid as the above solutions of polyacid.

Both for glutaric acid and polyacrylic acid the titrations were performed on solutions containing from 0 to 0.5 mole/l NaCl.

From the titration curves of polyacrylic acid and glutaric acid, the apparent pK was calculated as a function of the degree of neutralization,

$$\mathrm{p}K = \mathrm{pH} - \log\vartheta/(1-\vartheta)$$

The direct calculation of pK in different salt solutions gave, especially for low salt concentration, curves of a shape as in Fig. 1.

The ionic strength changed considerably during a titration, especially at low salt concentrations. To compensate for this, titration curves were made at eight different concentrations of added NaCl, such that the ionic strength at the start of each run varied from 0 to 0.5. (At higher ionic strength than 0.5 the acid was salted out). For each titration curve the apparent pK was calculated at $\vartheta = 0.1 - 0.9$ (0.05) and the ionic strength was likewise calculated at each point. From the curves of pK *versus* $\sqrt{\mu}$ for each value of ϑ, values of pK at $\sqrt{\mu} = 0.2 - 0.7$ (0.1) were read. In this way one obtains pK as a function of ϑ for various fixed values of μ.

The results are given in Table 1, and it will be seen that d$\mathrm{p}K/\mathrm{d}\vartheta$ is independent of ϑ, within the error of measurement, such that the curve of pK as a function of ϑ becomes a straight line, which differs markedly from the directly calculated curve given in Fig. 1.

This way of obtaining curves of pK *versus* ϑ is fairly time-consuming, but it is absolutely necessary if one wants significant values, since for instance a titration curve determined at an average ionic strength of 0.025 is almost useless, if for instance μ changes from *ca.* 0.07 to *ca.* 0.045 during the run.

The titration curves of glutaric acid were determined in exactly the same way as those for polyacrylic acid, and were corrected for ionic strength in the same way.

THEORY

3. For a polyacid it is not very profitable to use the dissociation constants for each step in the neutralisation, since they do not differ much from each other. Moreover, the acid would have to be completely homomolecular if we should have any chance of measuring each pK.

To specify the equilibrium between partly neutralized polyacid and hydrogen ions we shall therefore use the apparent pK, defined above.

The apparent pK is a function of ϑ, and is a convenient quantity to work with, in that it measures how much the actual dissociation constant depends on the charge of the acid. However, it can even be advantageous to work with this quantity for a dibasic acid, as we shall see below.

The first to give a theory of the calculation of the ratio of the two dissociation constants for a dibasic acid H_2B was Niels Bjerrum [3] who showed that to a first approximation

$$K_2/K_1 = \tfrac{1}{4}\exp(-e^2/DrkT)$$

In this expression r is the distance between the two carboxyl groups, D is the dielectric constant of the medium, and e is the elementary charge.

This expression is most easily derived in the following way. In the expression

$$K_2/K_1 = [H_2B]\,[B^{2-}]/[HB^-]^2$$

the partition functions are substituted for the concentrations. All the partition functions are identical with respect to translation, vibration, rotation, and electronic state, if we assume the H_2B molecule to be so large that its mass and moment of inertia only undergo negligible changes when one or two protons are taken off. That is, we can set

$$Q_{H_2B} = Q$$

$$Q_{HB^-} = 2Q$$

$$Q_{B^{2-}} = Q \exp(-e^2/DrkT)$$

the molecules B^{2-} and H_2B both being more symmetric than HB^-, such that one obtains their Q's by dividing that of HB^- with a symmetry number $\sigma = 2$. Moreover, the lowest state of energy of B^{2-} contains an electrostatic contribution of e^2/Dr, while the two other species do not contain this contribution, and as we wish to use the partition functions to calculate an equilibrium constant, their energies must be calculated on the same energy scale. By substitution we get Bjerrum's result.

Comparison of Bjerrum's theoretical expression with experiment gives reasonably good agreement for acids with large distances between the carboxyl groups, but for acids like oxalic acid where the carboxyl groups are very near to each other, or for alkyl substituted malonic acids where the material between the carboxyl groups is a hydrocarbon rather than water, there is a considerable discrepancy between theory and experiment.

The work of Bjerrum has been extended in various ways, taking the paraffin part of the molecule into account by assuming it to act as a cavity with a low dielectric constant (Kirkwood—Westheimer theory [10]). It is now well known that this is a highly artificial representation of an organic ion, which only gives reasonable results when one limits oneself to considering solutions of ions in one solvent and at one temperature. Since we are not directly interested in measuring molecular distances, we shall only use that the term appearing in the exponential is the interaction energy between two negative charges located on the carboxyl groups divided by kT. In the following we shall use measured values of K_2/K_1 to calculate the interaction energy $w(\sim e^2/rD)$ and compare w for different acids with each other.

We shall now use N. Bjerrum's method to calculate the titration curve for a polyacid. This method differs considerably from those of Overbeek [2] and of Katchalsky and Spitnik [11], but is in many ways analogous to the treatment given by Marcus [12].

4. As a model for a polyacid we shall use a one dimensional lattice. We shall let the carboxyl groups be the lattice points on which we distribute minus-signs, *i.e.*, from which we take away protons.

If we have M lattice sites ($M \rightarrow \infty$) on which we distribute N particles we have for the partition function, if we only take nearest neighbour interaction into account

$$Q(N,M,T) = [q\,\mathrm{e}^{-w/kT}]^N \sum_{N_{01}} g(N,M,N_{01})\,(e^{w/2kT})^{N_{01}}$$

where q is the partition function for the individual particle and

$$g = \frac{2N!(M-N)!}{\left(\frac{N_{01}}{2}\right)!\left(N-\frac{N_{01}}{2}\right)!\left(M-N-\frac{N_{01}}{2}\right)!\left(\frac{N_{01}}{2}\right)!}$$

where N_{01} is the number of 01 pairs, *etc.*, see Hill[13], p. 238.

Maximising Q we find that the corresponding number of pairs N_{01}^*, N_{00}^* and N_{11}^* satisfy the equation

$$N_{11}^*\,N_{00}^*/(N_{01}^*)^2 = \tfrac{1}{4}\exp(-w/kT)$$

that is, for systems where $w/kT \ll 1$ we have $4N_{11}^*\,N_{00}^* \sim (N_{01}^*)^2$, *i.e.*, we have a random distribution between 01, 00 and 11 pairs. Under these conditions we are therefore justified in using the Bragg—Williams approximation and write the partition function for the molecule with M carboxyl groups, N of which are ionized, as

$$Q(N,M,T) = \frac{M!}{N!(M-N)!}\,q^N\,\mathrm{e}^{-N^2w/MkT}$$

The most serious approximations so far have been the assumption of a linear molecule and the fact that we only take nearest neighbour interaction into account. The assumption of a random distribution is, as we have seen, fairly well justified.

In the Bragg—Williams approximation the difference between a linear lattice and a three-dimensional lattice disappears, and in the following calculations therefore the approximation of primary importance seems to be the assumption of nearest neighbour interaction only.

From this partition function we get the chemical potential of the protons absorbed on the lattice (*i.e.*, which have neutralized the carboxyl groups) by differentiating the logarithm with respect to ($M - N$), the number of protons on the polymer molecule,

$$\begin{aligned}\mu_{\mathrm{H}^+}(\mathrm{poly}) &= -kT[\partial \ln Q/\partial(M-N)]_{M,T}\\ &= -kT\ln[\vartheta \exp(2w\vartheta/kT)]/q(1-\vartheta)\end{aligned}$$

using Stirling's formula. $\vartheta = N/M$ is the degree of neutralization used previously.

The chemical potential of the hydrogen ions present in the solution is

$$\mu_{\mathrm{H}^+}(\mathrm{soln}) = \mu_0 + kT\ln c_{\mathrm{H}^+}$$

and as we define the apparent acid dissociation constant by

$$\ln K = \ln c_{\mathrm{H}^+} + \ln[\vartheta/(1-\vartheta)]$$

we have by substitution

$$\mu_{H+}(\text{soln}) = \mu_0 + kT \ln K - kT \ln[\vartheta/(1-\vartheta)]$$

The dependence of the apparent dissociation constant on ϑ is now determined by the condition of equilibrium $\mu_{H+}(\text{soln}) = \mu_{H+}$ (poly) and we get

$$-kT\ln[\vartheta\exp(2\vartheta w/kT)]/q(1-\vartheta) = \mu_o + kT \ln K - kT\ln[\vartheta/(1-\vartheta)]$$

or

$$\ln K = (\ln q - \mu_o/kT) - 2w\vartheta/kT$$

The term in parenthesis is $\ln K_0$, *i.e.* the logarithm to the dissociation constant for the first carboxyl group, so that we have

$$\text{p}K = \text{p}K_o + 2\chi\vartheta\log \text{e}$$

where χ is the interaction energy divided by kT.

In the Bragg—Williams approximation therefore $\text{d}\text{p}K/\text{d}\vartheta$ is a constant $=$ 2 log e and one can determine the energy of interaction directly from the slope of the experimental curve. This relation between equilibrium constants and the over-all degree of reaction for molecules with several sites is analogous to equations obtained by J. Bjerrum and by Linderstrøm—Lang.

5. J. Bjerrum considered metal complex formation by the reactions

$$\begin{aligned}&\text{Me} + \text{A} \rightleftharpoons \text{MeA}\\&\text{MeA} + \text{A} \rightleftharpoons \text{MeA}_2\\&\quad\cdot\ \cdot\ \cdot\\&\quad\cdot\ \cdot\ \cdot\\&\text{MeA}_{M-1} + \text{A} \rightleftharpoons \text{MeA}_M\end{aligned}$$

M being the maximum number of ligands A that can be attached to the metal atom Me. He further defined $\bar{n}$, the average number of ligand atoms bonded to a metal atom as

$$\bar{n} = \frac{[\text{MeA}] + 2[\text{MeA}_2] + \ldots + M[\text{MeA}_M]}{[\text{Me}] + [\text{MeA}] + [\text{MeA}_2] + \ldots + [\text{MeA}_M]}$$

If the kinetics were only determined by statistical factors, we should have very simple ratios of the constants. At equilibrium there will be formed as much of the compound MeA_N as will be broken down. Moreover, the probability of dissociation of an A-unit will be proportional to N, the number of A's already there, whereas the probability for addition of an A-unit will be proportional to $M - N$, the number of free sites. We therefore have for the reactions

$$\begin{aligned}&\text{MeA}_{N-1} + \text{A} \rightleftharpoons \text{MeA}_N\\&\text{MeA}_N + \text{A} \rightleftharpoons \text{MeA}_{N+1}\\&(M-N+1)\,[\text{MeA}_{N-1}]\,[\text{A}]k_{\text{on}} = N\,[\text{MeA}_N]\,k_{\text{off}}\\&(M-N)\,[\text{MeA}_N]\,[\text{A}]k_{\text{on}} = (N+1)\,[\text{MeA}_{N+1}]k_{\text{off}}\end{aligned}$$

from which we get

$$\frac{k_{\text{on}}}{k_{\text{off}}} = \frac{(N)}{(M-N+1)} \frac{[\text{MeA}_N]}{[\text{MeA}_{N-1}]\,[\text{A}]} = \frac{N}{(M-N+1)} k_N$$
$$= \frac{(N+1)}{(M-N)} \frac{[\text{MeA}_{N+1}]}{[\text{MeA}_N]\,[\text{A}]} = \frac{N+1}{M-N} k_{N+1}$$

or

$$\frac{k_N}{k_{N+1}} = \frac{(N+1)(M-N+1)}{(M-N)N}$$

(Bjerrum[4], eqn. (1) p. 24, also Pauli and Valkó[14], p. 114).

To allow for an interaction energy Bjerrum multiplies the right hand side of the equation by x^2, where x is a spreading factor which is a constant characteristic of the whole system, so the equation reads

$$\frac{k_N}{k_{N+1}} = \frac{(M-N+1)(N+1)}{(M-N)N} x^2$$

If we calculate the same ratio on the basis of the partition functions we obtain

$$\frac{k_N}{k_{N+1}} = \frac{(Q_{\text{MeA}^{N-}})^2}{Q_{\text{MeA}^{(N+1)-}} Q_{\text{MeA}^{(N-1)-}}} = \frac{(Q(N,M,T))^2}{Q(N+1,M,T)\,Q(N-1,M,T)}$$
$$= \frac{(N+1)(M-N+1)}{N(M-N)} \exp(2w/MkT)$$

we see that the two results are identical if $x^2 = \exp(2w/MkT)$ or, calling $\chi = w/kT$, $\chi = M\ln x$.

Bjerrum further defines a quantity Δ by $\Delta = (\partial\bar{n}/\partial\ln\text{A})_{\bar{n}=M/2}$ which in our nomenclature corresponds to

$$\Delta = (\partial(M-N)/\partial\ln\text{H}^+)_{N=M/2}$$
$$= M \log \text{e}\, (\partial\vartheta/\partial\text{pH})_{\vartheta=\frac{1}{2}}$$
$$= \frac{M \log \text{e}}{\left\{\frac{\partial}{\partial\vartheta}\left[\text{p}K + \log(\vartheta/(1-\vartheta))\right]\right\}_{\vartheta=\frac{1}{2}}}$$
$$= \frac{M}{2\chi+4}$$

when we insert $\chi = M\ln x$ we get

$$\Delta = M/(2M\ln x+4) = 1/(2\ln x + 4/M)$$

This expression is identical with an expression given by Bjerrum[6] (eqn. 24, p. 34), a formula originally derived by Linderstrøm—Lang[7] in 1924 to describe the average charge on a polyelectrolyte. In his derivation the polyelectrolyte is described as a ball with sites which can adsorb either positive or negative charges, dependent on the pH of the medium. The average number of charges on each ball is calculated, using the Debye—Hückel theory, the Helmholtz double layer theory, and the law of mass action.

The interaction energy χ stems from the interaction between a pair of nearest neighbours. If next nearest neighbour interaction plays a considerable role, the χ we get from experiments will contain a contribution from this effect also, contributing for a linear lattice at most half of the measured value. However, this contribution should fall off rapidly with increasing ionic strength, as the screening by the medium will make next nearest neighbour interaction negligible, if the molecule remains streched. On the other hand, if the molecule is not stretched, but coiled up in such a way that more than two sites are within the nearest neighbour distance from a single site, this contribution will also be included in the measured χ. This contribution should be expected to increase as the polymer molecule coils up, *i.e.* with increasing ionic strength, although it should not be expected to hide completely the first effect.

Instead of trying to calculate the interaction energy between two sites by considering charges and distances, we have measured it directly by titrating solutions of glutaric acid under conditions identical to those for polyacrylic acid, glutaric acid having the same number of carbon atoms between the two carboxyl groups as has polyacrylic acid.

6. As an illustration of the usefulness of the apparent pK, even for a dibasic acid, we shall derive a connection between K_2/K_1 and d$pK/d\vartheta$.

For a dibasic acid H_2B being titrated with NaOH one has

$$x_0 = [H_2B] + [HB^-] + [B^{2-}]$$
$$[Na^+] = 2\vartheta x_0 = 2[B^{2-}] + [HB^-]$$

denoting by x_0 the total concentration of acid. Here again we use ϑ to denote the total degree of neutralization, and we neglect the concentrations of H^+ and OH^- as compared to the other concentrations. Expressing both equations in terms of B^{2-} and dividing the second by the first equation we obtain:

$$[H^+]^2 + [H^+]\,K_1\left(1 - \frac{1}{2\vartheta}\right) + K_1K_2\left(1 - \frac{1}{\vartheta}\right) = 0$$

From this we see that at $\vartheta = \frac{1}{2}$, $[H^+]^2 = K_1K_2$

Differentiating with respect to ϑ and putting $\vartheta = \frac{1}{2}$ we get

$$K_1 = -\left(\frac{d[H^+]}{d\vartheta}\right)_{\vartheta=\frac{1}{2}} -2[H^+]$$

and so we get for K_2/K_1

$$\begin{aligned} K_2/K_1 &= [H^+]^2/K_1{}^2 \\ &= [H^+]^2/\{2[H^+] + (d[H^+]/d\vartheta)_{\vartheta=\frac{1}{2}}\}^2 \\ &= \{2 + (d\ln[H^+]/d\vartheta)_{\vartheta=\frac{1}{2}}\}^{-2} \end{aligned}$$

Another way of calculating this quantity is by using the slope of the apparent pK *versus* ϑ-curve at $\vartheta=\frac{1}{2}$. We differentiate the expression defining pK

$$pK = pH + \log[(1-\vartheta)/\vartheta]$$

with respect to ϑ, and using the previously obtained value of K_1, we get

$$K_1/[\mathrm{H}^+] = 2 + \ln 10(\mathrm{d}pK/\mathrm{d}\vartheta)_{\vartheta=\frac{1}{2}}$$

or

$$K_2/K_1 = [2 + \ln 10(\mathrm{dpK}/\mathrm{d}\vartheta)_{\vartheta=\frac{1}{2}}]^{-2}$$

Thus we can calculate χ directly from the experimental curves by $K_2/K_1 = \frac{1}{4}\exp(-\chi)$

COMPARISON WITH EXPERIMENT

7. Table 1 gives values for pK for polyacrylic acid at varying values of ϑ and μ. As will be seen from this, pK *versus* ϑ is a straight line within the experimental error. In Fig. 2 the values of pK are plotted as functions of ϑ. The lowest line in Table 1 shows dpK/dϑ, calculated from the pK-values.

Table 2 shows $\chi_P = \frac{1}{2}\ln 10(\mathrm{d}pK/\mathrm{d}\vartheta)$ calculated from the values in Table 1, together with χ_G calculated from K_2/K_1 for glutaric acid from titration curves. As will be seen, both χ_P and χ_G decrease with increasing ionic strength as it was to be expected. The last column in Table 2 shows the interaction energy for polyacrylic acid divided by that for glutaric acid. It will be seen that χ_P is roughly $4\chi_G$, the ratio increasing only very slightly with the ionic strength.

Table 1. pK for polyacrylic acid at different values of ϑ and μ.

	$\mu = 0.040$ $\sqrt{\mu} = 0.20$	$\mu = 0.090$ $\sqrt{\mu} = 0.30$	$\mu = 0.160$ $\sqrt{\mu} = 0.40$	$\mu = 0.250$ $\sqrt{\mu} = 0.50$	$\mu = 0.360$ $\sqrt{\mu} = 0.60$	$\mu = 0.490$ $\sqrt{\mu} = 0.70$
$\vartheta = 0.20$	4.88	4.75	4.64	4.545	4.48	4.43
0.25	5.04	4.86	4.75	4.65	4.57	4.49
0.30	5.18	4.98	4.845	4.725	4.63	4.55
0.35	5.305	5.06	4.92	4.805	4.70	4.61
0.40	5.41	5.16	5.015	4.89	4.78	4.68
0.45	5.54	5.265	5.11	4.97	4.85	4.735
0.50	5.68	5.38	5.20	5.05	4.92	4.80
0.55	5.82	5.49	5.30	5.145	5.00	4.87
0.60	5.965	5.61	5.395	5.23	5.08	4.94
0.65	6.095	5.73	5.51	5.34	5.17	5.02
0.70	6.23	5.85	5.61	5.41	5.24	5.09
0.75	6.38	5.97	5.705	5.49	5.31	5.16
0.80	6.54	6.105	5.81	5.595	5.40	5.235
dpK/dϑ	2.70±0.03	2.23±0.05	1.93±0.03	1.72±0.02	1.52±0.02	1.34±0.02

The fact that χ_P/χ_G is almost independent of the ionic strength shows that the neglect of more than nearest neighbour interaction is reasonable, or alternatively that the coiling of the polymer with increasing ionic strength compensates for the screening effect of the medium. Experimentally one cannot decide between these possibilities, but we believe the latter effect to be of minor importance.

On the other hand, the fact that the measured χ_P is four times what we expected can only be explained by the hypothesis that instead of 2 nearest

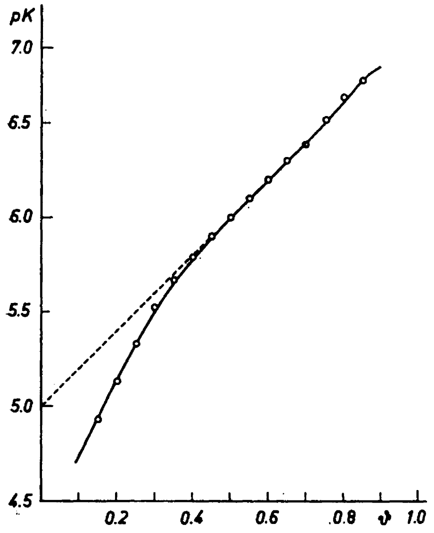

Fig. 1. p*K* *versus* ϑ not corrected for ionic strength.

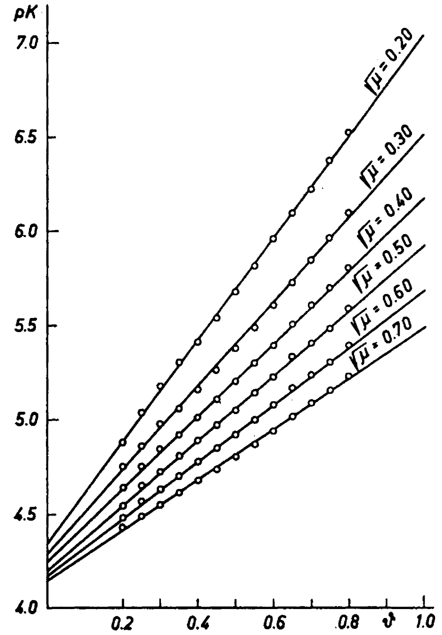

Fig. 2. p*K* *versus* ϑ at different values of the ionic strength.

neighbours each site must have approximately 8 nearest neighbours, *i.e.*, the polymer must be coiled up in such a way that each carboxyl group on the average is surrounded by 8 other carboxyl groups within a sphere, the radius of which is the distance between the carboxyl groups in glutaric acid.

If one tries to build a polyacrylic acid molecule from Catalin models, one finds that it is indeed possible to have a conformation in which every carboxyl group has 8 neighbours within a distance which is only slightly larger than the distance between two carboxyl groups in glutaric acid. This fact renders the hypothesis of eight nearest neighbours in the actual polyacrylic acid molecule somewhat more plausible.

Table 2. Energies of interaction divided by kT for glutaric acid and for polyacrylic acid at various values of the ionic strength.

μ	$\sqrt{\mu}$	χ_G	χ_P	χ_P/χ_G
0.04	0.2	0.812	3.356	3.83
0.09	0.3	0.679	2.568	3.78
0.16	0.4	0.557	2.222	3.99
0.25	0.5	0.475	1.980	4.19
0.36	0.6	0.413	1.750	4.24
0.49	0.7	0.363	1.543	4.25

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