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F. Gubenšek[a][b][c]; S. Lapanje[d]
[a] Nuclear Institute Jožef Stefan, Ljubljana, Yugoslavia [b] Ph.D. thesis of F. Gubenšsek, University of Ljubljana, [c] Department of Chemistry, University of Arizona, Tucson, Arizona [d] Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

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Potentiometric Titration Studies of Diethylaminoethyl Dextran Base

F. GUBENŠEK*,†

Nuclear Institute Jožef Stefan
Ljubljana, Yugoslavia

and S. LAPANJE

Department of Chemistry
University of Ljubljana
Ljubljana
Yugoslavia

SUMMARY

The potentiometric behavior of DEAE-dextran base in aqueous solutions of varying ionic strengths was investigated. Owing to the presence of three different basic groups in the compound, the analysis of the titration curves obtained is quite complicated. Therefore, only the titration range of one of the basic groups present was analyzed in detail and the values of the electrostatic potential at the surface of the polyion were obtained. These values were compared with those calculated from a cylindrical model for the polyion assuming a uniform distribution of charges on the surface. Agreement between the two sets of values is rather poor, which indicates that the model is inappropriate.

INTRODUCTION

Potentiometric titration studies of polyacids, polybases, and polyampholytes have supplied valuable information regarding the properties of these compounds in the solution. For detailed reviews,

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*Present address: Department of Chemistry, University of Arizona, Tucson, Arizona.

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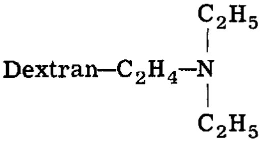
the reader is referred to the books of Rice and Nagasawa [1], Tanford [2], and Morawetz [3].

The subject of the present study is DEAE-dextran base, which is one of the few commercially available electropositive polyelectrolytes. This compound is especially interesting, since, having a composition similar to cellulose, it would be expected to produce relatively stiff polyions which, in turn, should be reflected in the potentiometric behavior of the polybase. The titrations were carried out in aqueous solutions with added salt whose concentration ranged from low to medium. The evaluation of the titration curves is complicated by the presence of the single and double diethylaminoethyl groups in DEAE-dextran, but fortunately they are titrated one after another. From the titration curves the values of the electrostatic potential at the surface of the polyions may be obtained and compared with those calculated from an appropriate model.

EXPERIMENTAL

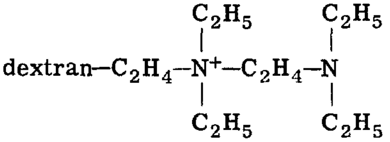
Materials

DEAE-dextran hydroxide (DDOH) was prepared from the DEAE-dextran hydrochloride (DDHCl), which was obtained from Pharmacia, Uppsala. An approximately 20% aqueous solution of DDHCl was passed through columns containing cation- and anion-exchange resins in the hydrogen and hydroxide forms, respectively. The pure solution of DDOH prepared in this way was analyzed for nitrogen by the Kjeldahl method to determine the concentration. The molecular weight of the sample obtained by the sedimentation-diffusion method was 135, 000, which would correspond to an average degree of polymerization of 520. From the nitrogen content the degree of etherification was estimated at 0. 43. It is to be noted, however, that there are single and double diethylaminoethyl groups in each molecule of DEAE-dextran:



$$\text{Dextran—}C_2H_4\text{—}N(C_2H_5)_2$$

and



$$\text{dextran—}C_2H_4\text{—}N^{+}(C_2H_5)_2\text{—}C_2H_4\text{—}N(C_2H_5)_2$$

i.e., three different groups which are reflected in the form of the titration curves, the pK's of the quaternary group (a strong base) being around 14, and those of the first tertiary (single) 9. 5 and of the second (double) 5. 7, respectively [4]. In the present sample, as can be inferred from the titration curves, the ratio of the groups is (approximately) 1 : 1 : 1 (cf. Figs. 1 to 4).

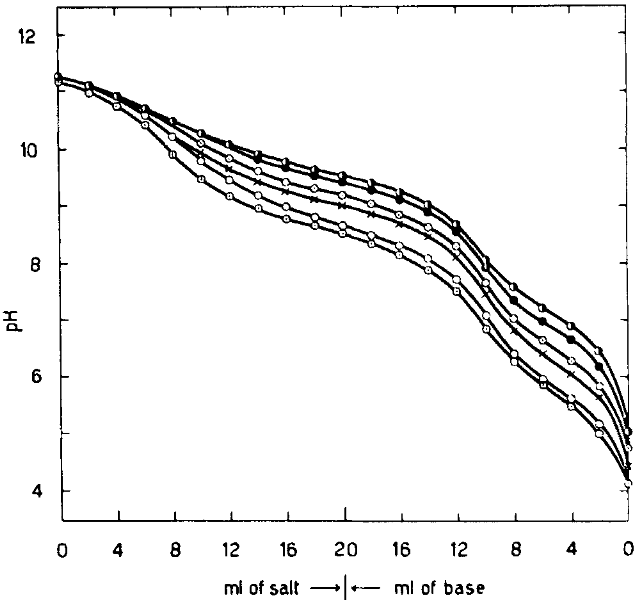


Fig. 1. Potentiometric titration curves of DEAE-dextran. $c_p =$ 0.005 N. KCl concentrations: ◑, 1.0 M; ●, 0.5 M; ⊗, 0.1 M; ×, 0.05 M; ○, 0.01 M; ⊕, 0 M.

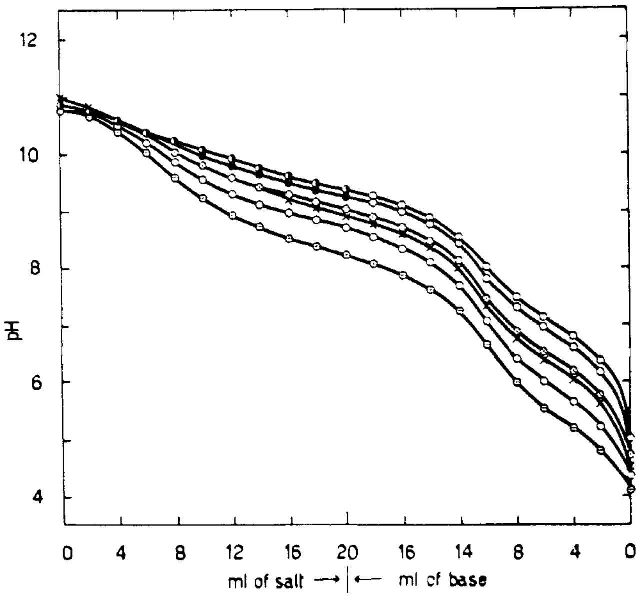


Fig. 2. Potentiometric titration curves of DEAE-dextran. $c_p =$ 0.01 N. KCl concentrations the same as in Fig. 1.

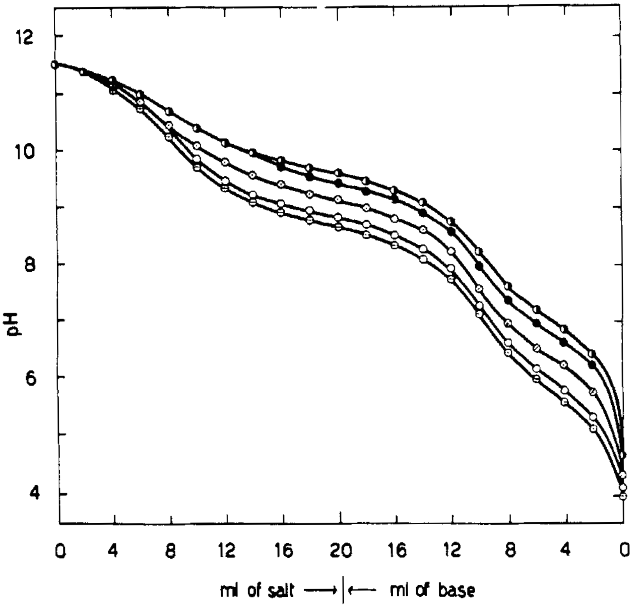


Fig. 3. Potentiometric titration curves of DEAE-dextran. c_p = 0.02 N. KCl concentrations the same as in Fig. 1.

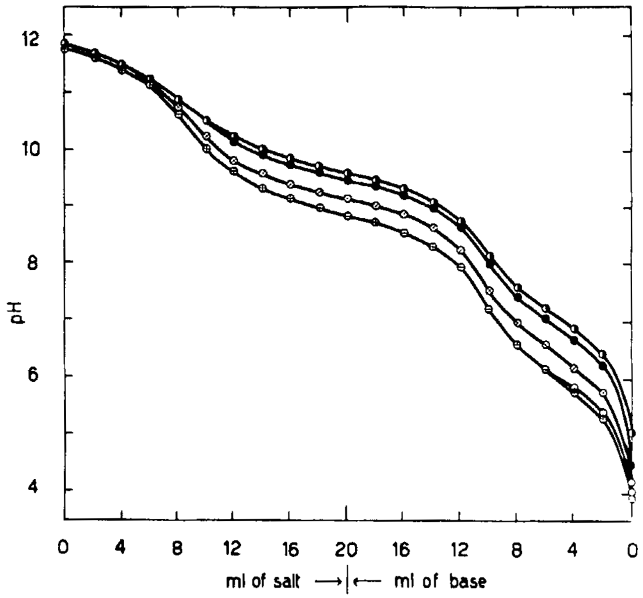


Fig. 4. Potentiometric titration curves of DEAE-dextran. c_p = 0.04 N. KCl concentration the same as in Fig. 1.

Apparatus and Procedure

Potentiometric titrations were carried out at 25.0 ±0.1°C using a Radiometer Model 4c pH meter. A glass electrode and a saturated potassium chloride calomel electrode with a porous tip were used. The leak of potassium chloride from the electrode was found to be negligible. The pH meter was calibrated with the phosphate buffers of pH 6.86 and 9.18, at 25°C. For each concentration of the polyelectrolyte and added salt, two solutions were prepared, one of the free polybase and added salt (a), and the other of the polysalt, which was obtained by neutralizing the polybase, and added salt (b): 20 ml of solutions (a) was then titrated by solution (b) and vice versa. In this way the ionic strength originating from added salt and polyelectrolyte was kept constant. In all cases studied the added salt was potassium chloride [5].

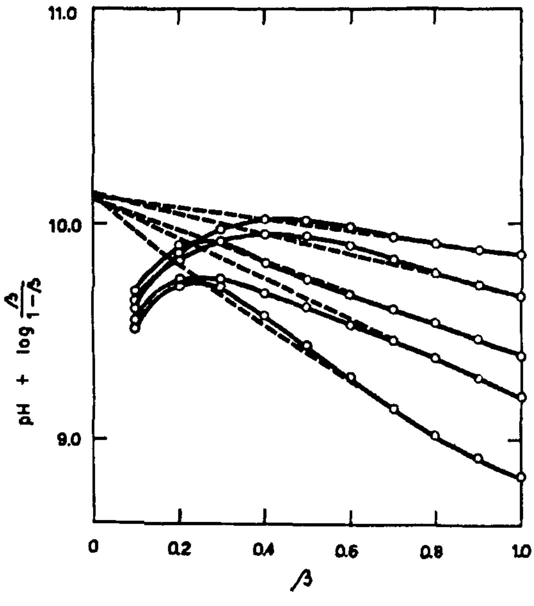


Fig. 5. Intrinsic titration curves of DEAE-dextran. KCl concentrations from up to down: $c_{KCl} = 1.0, 0.5, 0.1, 0.05$, and 0.01 M.

RESULTS

The titration curves obtained in our experiments are presented in Figs. 1 to 4. In Fig. 4 the curves for 0.05 M and 0.01 M KCl have been omitted since they practically coincide with those for 0.1 M KCl and pure water, respectively.

Inspection of our titration curves shows, as has been mentioned above, that they have three inflection points which correspond to the three basic groups. The presence of the three basic groups naturally complicates the existing situation. Considering, however that their K's differ by nearly four orders of magnitude, we can safely assume that up to the first inflection point only the quaternary ammonium base is titrated. This range is not particularly interesting since we are titrating a strong base. In the range between the first and second inflection point the (single) tertiary ammonium base is titrated. This is a relatively weak base. In the range between the second and third inflection point the other (double) tertiary ammonium base, which is even weaker than the former, is titrated. We will restrict our treatment of experimental data to the part of the titration curves between the first and second inflection points. It is relatively simple to estimate the distance between the charged groups on the polymer from the normal contour length by constructing the model of a monomer unit of the DEAE-dextran molecule from proportionally dimensioned elements. This distance is an important parameter determining the electrostatic potential at the surface of the polyion. It is to be noted that in this range the overall degree of neutralization changes from 0.33 to 0.67.

The change of pH in solutions of polybases can be represented by [5]

$$\mathrm{pH} + \log\left(\frac{\beta}{1-\beta}\right) - \mathrm{pK}_0 = -\,(0.434/kT)(\partial G_e/\partial \nu)_\kappa \qquad (1)$$

where β is the degree of ionization of the single basic group, pK_0 the ionization constant of the cationic acid conjugate to the single basic group of the polybase, G_e the electrostatic Gibbs free energy of a polyion carrying ν positively charged groups, and κ the Debye-Hückel reciprocal radius. The left side of Eq. (1) is readily obtained from experimental data and the values found can then be plotted vs. the degree of ionization. Owing to the fact that the ratio of the three basic groups is 1 : 1 : 1 and we consider the titration curves only to the second inflection point, the degree of ionization, β, during the titration of the single tertiary group has been taken to change from 0.5 to 1.0.

For each concentration of added salt as well as for the pure polybase, different curves have been obtained for different concentrations of the polyelectrolyte. From these the intrinsic titration curves have been obtained by extrapolation, at the same concentration of added salt, to zero concentration of the polyelectrolyte. The extrapolation was performed using plots of pH + log $[\beta/(1-\beta)]$ vs. the square root of the polymer concentration. Such an extrapolation has been successfully used by Nagasawa et al. [6] for some polyacids. Although in our case it has not proved quite satisfactory, we were unable to find a better one. In Fig. 5 all intrinsic titration curves are assembled. If we now draw tangents at the stretched part of the curves, they all intercept the ordinate axis in the same point which gives us the value of pK_0. The extrapolated value is 10.1. By subtracting at single β's pK_0 from $pH + \log[\beta/(1-\beta)]$, the values of $(\partial G_e/\partial \nu)_\kappa$ can be obtained which can subsequently be compared with those given by an appropriate model and theory.

DISCUSSION

Inspection of the titration curves (cf. Figs. 1 to 4) shows that they are similar to those obtained for some other polybases, e.g., polyethyleneimine [7] and polyvinylamine [8], and, in addition, reflect the presence of three basic groups. We will limit our discussion to the part of the titration curves lying between the first and second inflection points.

We first transform Eq. (1) to the following form:

$$pH + \log\left(\frac{\beta}{1-\beta}\right) - pK_0 = -0.434 e_0 \psi / kT \qquad (2)$$

where e_0 is the elementary charge and ψ the electrostatic potential at the surface of the polyion and can thus be obtained from experiment. The values of ψ, however, can also be computed using an appropriate model. We feel that in the present case a cylindrical model should better reflect the experimental situation than a spherical one, since our polyelectrolyte is a dextran derivative and the amount of added salt was very low to medium. Numerical solutions of the Poisson-Boltzmann equation for the cylindrical model have been obtained by Kotin and Nagasawa [9] and, recently, by Gross and Strauss [10]. We have used the plots given by the latter authors since they cover a wider range of the cylinder radii, distances between charges, and ionic strengths.

The cylinder radius and the distance between charges have been obtained from a model constructed from proportionally dimensioned elements. The charges have been assumed to be uniformly distributed along the cylinder. The length of the monomer unit has been found to be 5.6 Å. However, there is less than one charge per unit since the degree of etherification is only 0.43. This gives a value of 13.0 Å for the average distance between charges at the second equivalent point. The radius of the cylinder, on the other hand, was estimated to be 9.0 Å. To this value the radius of the counterion has to be added since counterions cannot approach the cylindrical polyions to distances smaller than their radius, which is for the chloride ion 1.8 Å. Using these values we can now calculate the quantity Q, which is defined in the following way [10]:

$$Q = 2e_0^2/DkTb \tag{3}$$

where b is the distance between charges. An error of 0.5 Å in the estimation of cylinder radius would correspond to approximately 5% of the value of 0.434ϕ.

From the known value of the Q it is possible to obtain the values of ψ at different ionic strengths; in Fig. 6 the plots are given of ϕ as a function of $Y = \alpha Q$. ϕ is the usual abbreviation for $e_0\psi/kT$. The value of Q for our model is 1.09. Comparison of theoretical and experimental plots (cf. Figs. 6 and 7) shows that the latter are much higher. Now it is possible to make use of Fig. 6 to obtain the value of Y which brings into accord the theoretical and experimental plots. This value of Y is 2.70, and from Eq. (3) the distance b at $\beta = 1$ can be calculated. In this way the value 5.30 Å is found for b and the ratio b_{mod}/b_{exp} is 2.47. On the basis of this it can be concluded that under our experimental conditions the polyions are far from being fully extended. The same conclusion has been

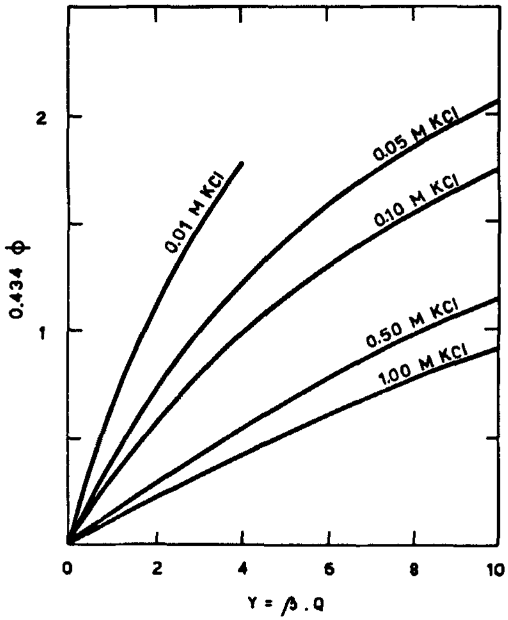


Fig. 6. Theoretic titration curves obtained by interpolation of data of Gross and Strauss [10].

arrived at from the studies of single ion activity coefficient in aqueous solutions of DDHCl [11]. The new theoretical curves obtained by using the value of b = 5.30 Å are presented in Fig. 7. As expected, agreement is observed only at values of β higher than 0.5. This can easily be explained. In the range of β from 0 to 0.5 the quaternary base is titrated. During this titration the charge on polyions practically does not change, so that the electrostatic potential should have a more or less constant value. However, starting from the first inflection point the single tertiary groups are titrated, and the charge as well as the electrostatic potential are gradually increasing. Also, the charges originating from quaternary groups may by assumed to contribute to the electrostatic potential, owing to small structural difference, in the same way as those from tertiary ones. Therefore, the extrapolation of pH + log $[\beta/(1-\beta)]$ vs. β (cf. Fig. 5) yields straight lines with a common intercept and a reasonable value for pK_0 and justifies in our opinion the procedure. It is to be noted, furthermore, that the new value of b refers to what we might call the equivalent cylinder, whereas the real polyions are more or less coiled, the extent of coiling being dependent on ionic strength.

The nearest-neighbor charge effect, which is increasingly important at a higher degree of ionization of polyvinilamine [8], can be neglected in our case, owing to a relatively large distance between charges, which is even augmented by low degree of ionization.

Concluding, we can say that the cylindrical model does not satisfactorily reflect the conformation of DDOH in aqueous solutions with added salt and that DDOH is rather flexible regardless of its polysaccharide backbone and the charge it is carrying.

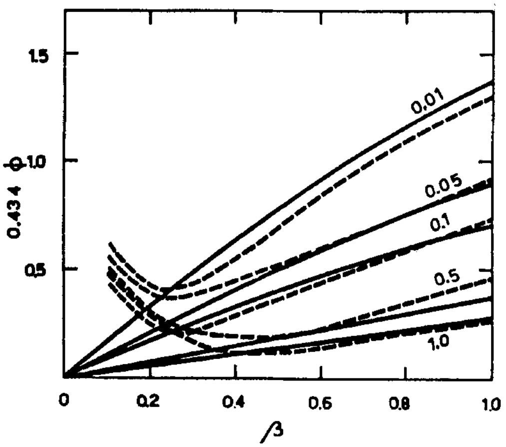


Fig. 7. Comparison of theoretical (—) and experimental curves. $\beta = 1.0$ corresponds to $Y \doteq 2.70$ in Fig. 6.

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