474. *The Ionization of Ethyleneimine and Polyethyleneimine.*

By E. J. SHEPHERD and J. A. KITCHENER.

The titration curves of ethyleneimine and polyethyleneimine have been determined in the presence and absence of potassium chloride. The former behaves as a normal base of strength $pK_a = 7{\cdot}88$; the latter gives an unusual, highly extended, titration curve. The early part of the curve corresponds to titration of a few primary NH_2 end-groups of $pK = 9{\cdot}0$; the middle section is the titration of $\cdot[CH_2]_2\cdot NH\cdot[CH_2]_2\cdot$ groups of $pK_0 = 10{\cdot}0$ and is influenced by the chain polyelectrolyte interaction effect according to the theory of Katchalsky *et al.*; at high degrees of ionization intense interaction from two neighbouring $\cdot NH_2^+\cdot$ groups at 3·7 Å distance greatly depresses the pH curve. In order of magnitude this effect is accounted for by the Kirkwood–Westheimer theory.

THE titration curves of weak poly-acids or poly-bases are well known to differ markedly from those of the corresponding monomers. The curves extend over a much wider range of pH than indicated by the Henderson–Hasselbach formula for the titration of an ordinary monobasic acid, namely,

$$pH = pK + \log \alpha/(1 - \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where α is the degree of neutralization); as α increases, the growing charge on the poly-ion has the effect of progressively weakening the remaining acid (or base) groups.

Several theoretical treatments of this effect have been put forward. Those assuming a spherical poly-ion are appropriate only to proteins and hyper-coiled chain molecules at low values of α, while other treatments based on a rod model are applicable only to highly extended chain molecules, *e.g.*, intrinsically stiff polyelectrolytes, or flexible chain polyelectrolytes at high values of α in media of low ionic strength. A more versatile theory for flexible chain polyelectrolytes is that of Kuhn, Künzle, and Katchalsky,[1] further developed by Katchalsky and his co-workers.[2,3,4]

This theory allows for the expansion of the statistical coil which occurs, on account of mutual repulsion of segments of the chain, when a polymer becomes ionized. The individual acid or base groups are considered to retain their normal *chemical* affinity, but the total free energy of the polymer molecule is dependent also on (*a*) the energy required for the stretching of the molecules from their normal end-to-end distance, h_0, to a greater average length, h, (*b*) the energy required for the building of the ionic atmospheres (of reciprocal Debye "thickness," κ), and (*c*) the repulsive energy due to interaction of the ν fixed charges, which are considered to be uniformly distributed over the N statistical chain elements (each of length A). It seems reasonable to suppose that as the chain becomes ionized, it may also become inherently less flexible, for steric and solvation reasons. Katchalsky and Lifson[3] therefore modified Kuhn, Künzle, and Katchalsky's statistical chain theory by assuming that the number of monomer units, S, comprising one "statistical element" increases linearly with the degree of ionization, α, from that for the un-ionized polymer, s_0, to that for the fully ionized polymer, s_i. On this basis, and with introduction of certain reasonable approximations, Katchalsky and Lifson gave the following equation for potentiometric titration:

$$pH = pK_0 + \log\frac{\alpha}{1-\alpha} + \frac{2\nu e}{DhkT}\left[\log\left(1 + \frac{6h}{\kappa h_0^2}\right) - \frac{0{\cdot}4343\alpha(s_i - s_0)\dfrac{6h}{\kappa h_0^2}}{2s\left(1 + \dfrac{6h}{\kappa h_0^2}\right)}\right] \quad . \quad (2)$$

(Here D = dielectric constant, e = electronic charge, and pK_0 is the intrinsic dissociation constant.) Methods of estimating h_0, h, and s have been given by Katchalsky *et al.*,[2,4]

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[1] Kuhn, Künzle, and Katchalsky, *Helv. Chim. Acta*, 1948, **31**, 1944; *J. Polymer Sci.*, 1950, **5**, 283.

[2] Katchalsky and Gillis, *Rec. Trav. chim.*, 1949, **68**, 879.

[3] Katchalsky and Lifson, *J. Polymer. Sci.*, 1953, **11**, 409.

[4] Katchalsky, Shavit, and Eisenberg, *ibid.*, 1954, **13**, 69.

and it has been demonstrated that the theory represents fairly well the middle part of the titration curves of substances such as poly(methacrylic acid).*

In view of the success of Katchalky's theory in a number of cases, it was of interest to see whether it could account for the remarkable titration curve exhibited by polyethyleneimine, $(\cdot CH_2\cdot CH_2\cdot NH\cdot)_n$.

EXPERIMENTAL

Materials.—Ethyleneimine was prepared, *via* 2-aminoethyl hydrogen sulphate, by Wenker's method.[5] It was stored in a refrigerator over solid potassium hydroxide.

Polyethyleneimine was prepared from the monomer as follows. The polymerization is catalysed by acids, but is liable to be dangerously explosive if strong acids are added to neat monomer. A mixture containing 25 g. of ethyleneimine, 25 ml. of methanol, and 1 g. of acetic acid was kept at room temperature for 10 days and then heated in a sealed ampoule at 100° for 12 hr. to complete the reaction. The highly viscous product was diluted with water, and the solution passed down a column of strong-base ion-exchange resin (Deacidite FF) in the hydroxyl form to remove acetic acid and carbon dioxide (absorbed from the air).

FIG. 1. *Titration curves of ethyleneimine, alone and in* 1·0N-KCl.

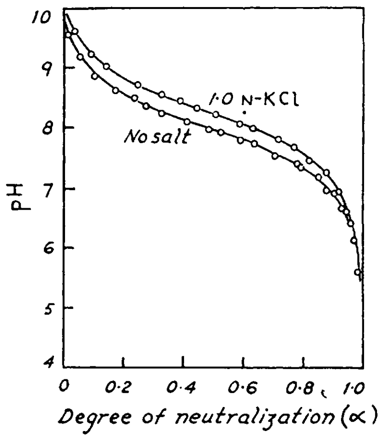
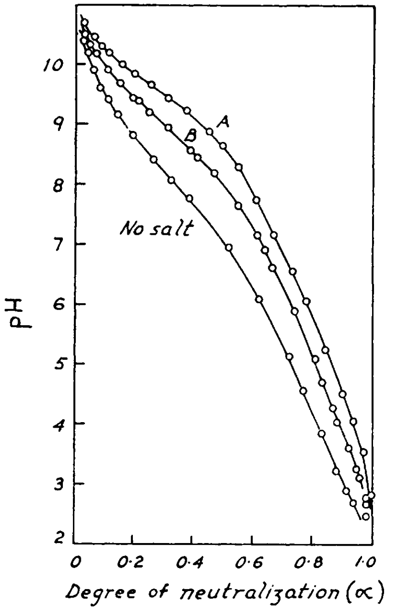


FIG. 2. *Titration curves of polyethyleneimine, alone and in (A)* 1·0N- *and (B)* 0·1N-KCl.



Titrations.—Solutions of free-base ethyleneimine and polyethyleneimine were titrated under nitrogen by means of the glass electrode with hydrochloric acid, alone, and in the presence of 0·1 and 1·0N-potassium chloride. At low values of pH the correction for the free acid present was determined from a blank titration. The results obtained are shown in Figs. 1 and 2.

Molecular Weights of Polyethyleneimine.—Only very approximate values for molecular weight and dimensions, etc., of polyethyleneimine are needed for the purpose of testing the applicability of the Katchalsky theory. The molecular weight is relatively low. Kern and Brenneisen[6] have provided data on the viscosity and osmotic pressure of solutions of the free base; by use of their results, the degree of polymerization of the sample used in the present

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* The theory cannot be expected to apply to polymethacrylic acid at very low values of α, as this substance is then hyper-coiled by hydrogen bonding; also, at high values of α, and low salt concentration, the molecule is practically fully extended, and the rod model is then a more appropriate approximation.

[5] Wenker, *J. Amer. Chem. Soc.*, 1935, **57**, 2328; cf. *Org. Synth.*, **30**, p. 38.

[6] Kern and Brenneisen, *J. prakt. Chem.*, 1941, **159**, 219.

work was estimated from viscosity measurements to be about 40 monomer units. An independent estimate made by determining the minimum amount of cross-linking agent (ethylene dibromide) required to produce an insoluble gel, assuming an average of 1 cross-link needed per chain, indicated 35 units. These figures are of the same order as those found by previous workers for polyethyleneimine prepared under different conditions.

DISCUSSION

Ethyleneimine.—If pK_a is the negative logarithm of the thermodynamic dissociation constant of the conjugate acid of ethyleneimine, $(CH_2)_2NH_2^+$, the usual treatment gives

$$\mathrm{pH} = \mathrm{p}K_a - \log\,[(\mathrm{CH_2})_2\mathrm{NH_2}^+]/[(\mathrm{CH_2})_2\mathrm{NH}] - \log f_\pm$$

where $f_\pm$ is mean ion activity coefficient, and the activity coefficient of the uncharged species is assumed to be unity. For the titration in absence of salt, $f_\pm$ was assumed to be the same as for ammonium chloride (0·85); this titration gave a value of pK_a of 7·88. Similarly, the titration in presence of N-potassium chloride, $f_\pm$ being taken as 0·58, gave $pK_a = 7{\cdot}93$. The former value is likely to be the more reliable, as activity coefficients are subject to less uncertainty in more dilute solutions.

Polyethyleneimine.—Although the theory of Katchalksy *et al.* is applicable strictly only to a polyelectrolyte of high molecular weight and at moderate degrees of extension, the effect proves not to be very sensitive to variation of the parameters which must be assumed in the calculation, and its application to the titration curve of polyethyleneimine gives a useful indication of the magnitude of the polyelectrolyte interaction effect.

The following values were assumed: degree of polymerization, $z = 43$; hydrodynamic length of monomer, $b = 3{\cdot}74$ Å; the number of monomers per statistical chain element, s, was taken to be the same as in polyethylene glycol,[8] namely, 2·5, and assumed independent of degree of ionization; the reciprocal of the Debye atmosphere radius, κ, was calculated to be $1{\cdot}08 \times 10^7$ cm.$^{-1}$; the root-mean-square end-to-end distance, h_0, for the un-ionized molecule $(zsb^2)^{\frac{1}{2}} = 3{\cdot}88 \times 10^{-7}$ cm. The equilibrium mean length at a degree of ionization, α, was determined by solving the equation:[3]

$$kT\left(\frac{3h}{h_0{}^2} - \frac{2}{h}\right)\left[1 + \frac{0{\cdot}6\left(\dfrac{h}{zb}\right)^2}{1 - \left(\dfrac{h}{zb}\right)^2}\right] = \frac{z^2e^2\alpha^2}{Dh^2}\left[\ln\left(1 + \frac{6h}{\kappa h_0{}^2}\right) - \frac{6h/\kappa h_0{}^2}{1 + \dfrac{6h}{\kappa h_0{}^2}}\right]$$

As s_i was assumed the same as s_0, the last term in equation (2) disappears; the simplified equation (3), applicable to poly-bases, was used to calculate the value of pK_0. The results of these calculations are summarized in Table 1.

$$\mathrm{pH} = \mathrm{p}K_0 - \log\frac{\alpha}{1-\alpha} - \frac{2ze^2\alpha}{DkTh}\left[\log\left(1 + \frac{6h}{\kappa h_0{}^2}\right)\right] \quad . \quad . \quad . \quad . \quad (3)$$

TABLE 1. *Titration of polyethyleneimine with* HCl *in presence of* 0·1N-KCl.

pH	α	h/h_0' *	pK_0	pH	α	h/h_0' *	pK_0	pH	α	h/h_0' *	pK_0
10·62	0·023	1·01	9·12	8·97	0·306	2·24	10·07	6·90	0·632	3·60	9·54
10·48	0·032	1·03	9·20	8·45	0·408	2·78	10·09	5·90	0·735	3·89	9·04
10·42	0·040	1·04	9·31	8·06	0·488	3·10	10·06	4·72	0·828	4·08	8·38
10·24	0·061	1·09	9·42	7·93	0·510	3·12	10·04	4·04	0·881	4·17	8·02
9·68	0·150	1·45	9·75	7·61	0·556	3·38	9·92	3·26	0·942	4·27	7·77
9·40	0·204	1·74	9·85	7·18	0·606	3·51	9·72	2·68	0·983	4·31	7·85

* h_0' is the *most probable* end-to-end distance of the molecule in its un-ionized form; $h_0' = h_0\sqrt{(2/3)}$; h is the equilibrium length in the partially ionized state.

The progressive expansion of the chain molecule on ionization is reflected in the values of h/h_0' in the third column; the completely stretched molecule would have $h/h_0' \approx 5$.

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[7] Scatchard and Prentiss, *J. Amer. Chem. Soc.*, 1933, **55**, 4355.

[8] Kuhn, W., and Kuhn, H., *Helv. Chim. Acta*, 1943, **26**, 1451.

Assumptions in the theory, and the fact that it has been applied to a low-molecular-weight polymer, indicate that it should be valid only in the central region of the titration curve, *i.e.*, where the chain is appreciably, but not highly, extended. In fact, the theory is seen to fit very well over the range $0{\cdot}3 < \alpha < 0{\cdot}5$, the value obtained for pK_0 being constant within the experimental error at 10·0(6).

For comparison, the Henderson–Hasselbach titration curve for a monomeric acid of pK = 10·0 is also shown in Fig. 3. The effect of electrostatic interaction between the chain segments amounts to a depression of the titration curve by 2·0 pH units at $\alpha = 0{\cdot}5$.

It is evident, however, that the polyelectrolyte theory does *not* account for the titration curve at high degrees of ionization; around $\alpha = 0{\cdot}9$, the groups appear to be about 2 pH units weaker than predicted. There is no reason to think that these groups are *chemically* different from the rest. It is probably significant that the deviations set in immediately above $\alpha = 0{\cdot}5$, for then every new NH group ionized must be situated between two which are already ionized, thus $-N^+H_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}N^+H_2-$, with only two carbon atoms between adjacent nitrogen atoms. In these circumstances, it is clearly unrealistic to apply the polyelectrolyte theory in which the charge is treated as uniformly distributed over the segments of a coil situated in a medium having a dieletric constant of 80. Instead, the interaction between neighbouring groups must be considered.

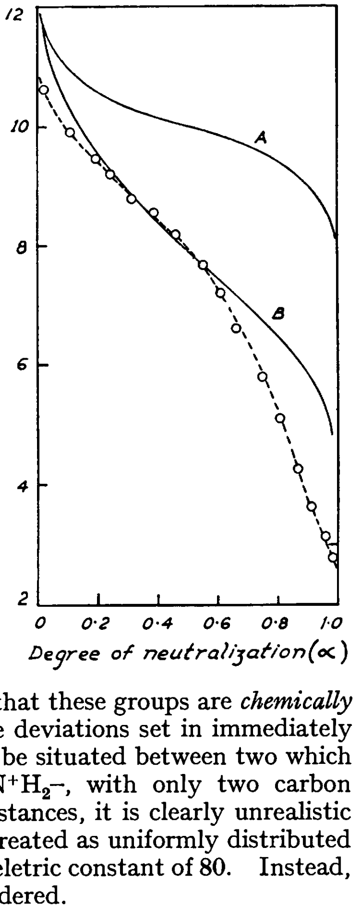

FIG. 3. *Titration of polyethyleneimine in* 0·1N-KCl. *Points experimental. Curve A, Henderson–Hasselbach equation with* pK = 10. *Curve B, polyelectrolyte theory, giving* pK_0 = 10.

TABLE 2.

No. of C atoms between ionic sites	Dibasic acids				Diacidic bases			
	Acid	pK_1	pK_2	ΔpK	Base	pK_1	pK_2	ΔpK
2	Oxalic	1·2	4·2	3·0	Ethylenediamine	10·0	7·0	3·0
3	Malonic	2·7	5·4	2·7	Trimethylenediamine	10·6	8·6	2·0
4	Succinic	4·0	5·3	1·3	Tetramethylenediamine	10·4	9·3	1·1
5	Glutaric	4·3	5·4	1·1	Pentamethylenediamine	11·0	9·7	1·3
6	Adipic	4·4	5·4	1·0	Octamethylenediamine	11·0	10·1	0·9

Table 2 gives some examples of the magnitude of the electrostatic influence of neighbouring acid or base groups separated by only a few carbon atoms. The value of ΔpK (= pK_2 − pK_1) is proportional to the electrostatic energy required to remove a proton from the second ionization centre against the field exerted by the first. It is well known that the magnitude of such ΔpK values is approximately accounted for by the theory of Kirkwood and Westheimer[7] which allows for the fact that the medium between the two centres is partly composed of paraffinic matter of low dielectric constant.

Electrostatic interaction in a number of simple polyamines has been shown by Rometsch, Marxer, and Miescher[10] to be an approximately additive effect when two or more ionized groups are within range. The *average* increments of pK found for different numbers of intervening carbon atoms were 3·1 for 2C, 2·0 for 3C, 1·1 for 4C, 1·0 for 5C, 1·0 for 7C, 0·9 for 8C. In the present work, the thickness of the diffuse double layer of counter-ions was about 10 Å and the N–N distance about 3·7 Å. Consequently, only near-neighbour sites will interact strongly, with possibly a small contribution from next-but-one sites, as the effect of more distant sites will be largely cancelled by their counter-ions. Hence, one would estimate the displacement of pK to be about $2 \times 3{\cdot}1 \approx 6$ pH units. This is precisely the displacement (from the Henderson–Hasselbach line) found with polyethyleneimine at high degrees of ionization ($\alpha \approx 0{\cdot}9$).

The conclusion is therefore reached that the titration curve of polyethyleneimine can be regarded as consisting of three regions. (*a*) At very low degrees of ionization ($\alpha = 0$—$0{\cdot}06$) a constant apparent pK of 9·0 is obtained from the Henderson–Hasselbach equation. This is almost certainly due to the presence of a few primary NH_2 end-groups. There is then a transition into a middle region, (*b*) ($\alpha = 0{\cdot}3$—$0{\cdot}5$), where the intrinsic strength of the groups is $pK_0 = 10{\cdot}0$ (corresponding to isolated $\cdot[CH_2]_2\cdot NH\cdot[CH_2]_2\cdot$ groups) and interaction of the polyelectrolyte type is present. This region is well represented by Katchalsky's theory. (*c*) At high degrees of ionization the predominant effect is the action of the two near-neighbour $-NH_2^+-$ groups. The order of magnitude of this effect is accounted for by the Kirkwood–Westheimer theory.

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[9] Kirkwood and Westheimer, *J. Chem. Phys.*, 1938, **6**, 506—513; cf. Westheimer and Shokoff, *J. Amer. Chem. Soc.*, 1938, **61**, 555.

[10] Rometsch, Marxer, and Miescher, *Helv. Chim. Acta*, 1951, **34**, 1611.