Counterion activity in dilute salt-free solutions of some anionic polyelectrolytes

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This paper presents experimental data on sodium ion activities obtained by two methods in salt-free solutions for four anionic polyelectrolytes in their completely neutralized sodium salt form. Treatment of the data reveals some quantitative disagreement with theoretical predictions although there is considerable qualitative agreement with the main proposition of Manning's counterion condensation theory. A striking disparity between potentiometric and osmometric results is noted and an explanation is offered.

(Keywords: salt-free polyelectrolytes; sodium ion activity; osmotic activity; potentiometric activity; Manning's counterion condensation theory)

INTRODUCTION

In a salt-free solution of a polyelectrolyte of sufficiently high molecular weight, the macro-ion is vastly outnumbered by the counterions, and any colligative property, such as osmotic pressure, is found to be almost entirely due to the counterions. Such a system affords a relatively rare opportunity to study single ion activity. For an ideal solution of a completely neutralized salt-free polyelectrolyte the osmotic pressure Π is given by

$$\Pi = kT(n_p + n_p P) \tag{1}$$

where n_p is the number density of polymer molecules and P is the number of ionic charges in a molecule of contour length L. For $P \gg 1$, $\Pi = kTn_pP$, or

$$\Pi = kTn_c \tag{2}$$

where n_c is the concentration of the polymer in equivalents. Since for the sodium salts Na^+ is the only species of counterion present, n_c is the total number of sodium ions per cubic metre. For real solutions equation (2) takes the form

$$\Pi = kTa_c \tag{3}$$

where a_c is an operational activity which may be designated as the colligative or osmotic activity. It is obvious that while the osmotic activity is an unambiguous empirical quantity, calculated as Π/kT, there is no unequivocal way of defining the corresponding osmotic coefficient ϕ, which may be a_c/n_c or a_c/n, where n is the actual number density of 'free' counterions which only may for some reason be considered relevant to the observed property. The well-known counterion condensation theory developed principally by Manning[1] emphasizes the existence of free or mobile ions alongside bound or condensed ions. For univalent counterions, Manning's theory gives the relation

$$n = n_c/\xi \tag{4}$$

where the charge-density parameter $\xi = e^2/(\varepsilon_0\varepsilon_r kTb)$, where e is the protonic charge, ε_0 is the permittivity of a vacuum, ε_r is the relative permittivity of the solvent, and $b = L/P$, provided that $\xi > 1$. For $\xi < 1$, $n = n_c$.

The counterion activity can be defined alternatively through some property specifically sensitive to the counterion. One such property is the electrochemical potential E, which is given by the Nernst equation for a univalent counterion:

$$E = E^0 + (RT/F)\ln a_p \tag{5}$$

where E^0 is the standard potential, a_p is the counterion activity, to be called the potentiometric activity, and the other symbols have the usual meanings. Because of the ambiguity in the meaning of the standard potential of a single electrode potential, and hence the single ion activity a_p (a_{Na^+} in this case), Nagasawa *et al.*[2,3] and Satoh *et al.*[4] have been followed and a_p has been determined by comparison with the electrode potential of a Na^+ selective electrode immersed in standard NaCl solutions of known mean activity $a_\pm$ values. The underlying assumption is that the following transitive chain of correspondences:

$$a_{Na^+}\,(\text{electrochemical}) \leftrightarrow E \leftrightarrow a_\pm\,(\text{NaCl})$$

leads to

$$a_p = a_{Na^+}\,(\text{electrochemical}) = a_\pm\,(\text{NaCl}) \tag{6}$$

It should be noted that the coefficient corresponding to a_p is generally called the activity coefficient, γ, which also suffers from the same uncertainty as the osmotic coefficient, ϕ.

The main aim of this work was to measure the above-mentioned activities and use them to test some interesting predictions deduced from the theoretical

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Table 1 Physicochemical properties of the polyanionic materials used

Macromolecules	M_v	ξ	ν^a	Eq. wt
NaCMC 4M	244 000	0.623	0.415	470
NaCMC 9M	207 000	1.425	0.95	250
NaPA	230 000	2.85	1	94
NaAM	200 000	3.46	1.27	89

(Ludox: diameter 18 nm; charge density 0.062 C m^{-2})

[a] Number of ionizable groups per monomer unit

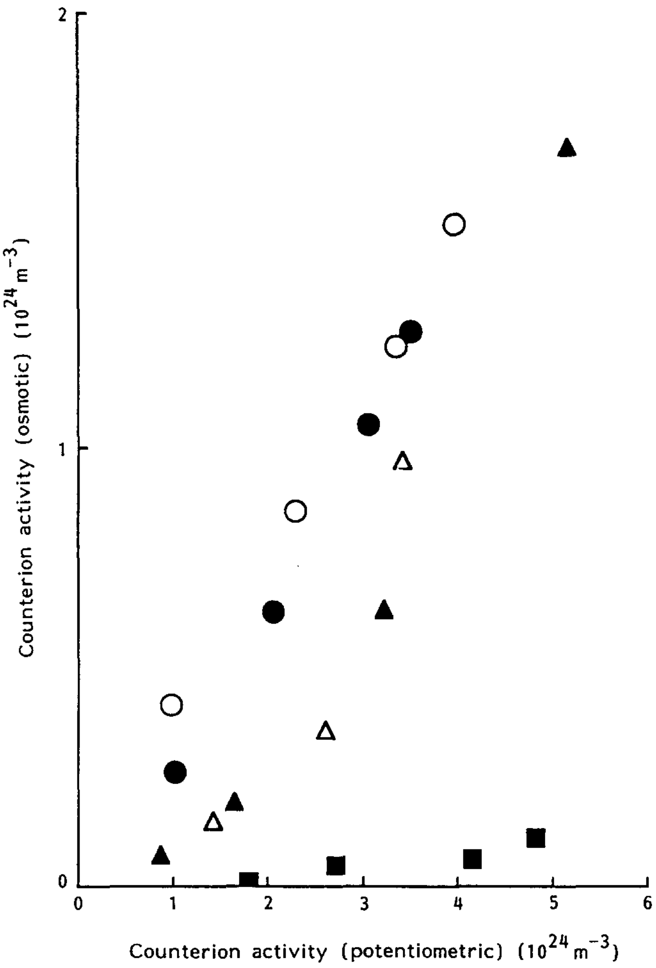

Figure 1 Counterion activity (osmotic) a_c *versus* counterion activity (potentiometric) a_p: (●) CMC 4M; (○) CMC 9M; (▲) NaPA; (△) NaAM; (■) Ludox

models of Katchalsky *et al.*[5] and Manning[1]. The cylindrical cell model of the former gives the result

$$\gamma/\phi = 1 \qquad (7)$$

Manning[1], on the other hand, obtained

$$\gamma/\phi = 1.21 \qquad (8)$$

for $\xi > 1$. Although the individual coefficients cannot be determined with certainty, their ratio should be so determinable since we can reasonably assume that

$$\gamma/\phi = a_p/a_c \qquad (9)$$

For $\xi < 1$, Manning obtains

$$\phi = 1 + \ln \gamma \qquad (10)$$

Apart from these quantitative relations, the really interesting conclusion of the theories is that the ratio a_p/a_c should have a global character, that is, the same value for all polymers irrespective of charge density.

In addition to the above objective, the results were also used to test the validity of the main feature of Manning's theory, namely the partitioning of the counterions into two phases: condensed and mobile.

EXPERIMENTAL

Materials

Commercial samples of sodium carboxymethyl cellulose (CMC 4M and CMC 9M) kindly donated by Aqualon U.K. Ltd were used. Sodium polyacrylate (NaPA) and sodium acrylate–maleate copolymer (NaAM) were obtained from Unilever Research Laboratories. The polyelectrolytes were neutralized to pH 10 and dialysed until the pH was 9. Properties of the polyelectrolytes are given in *Table 1*. Ludox was kindly donated by du Pont.

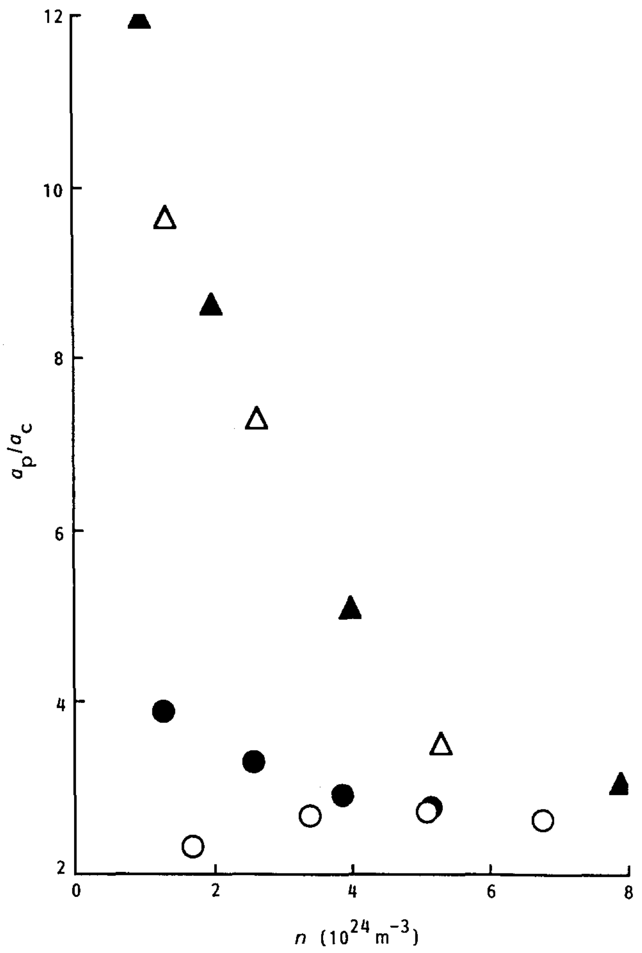

Figure 2 Activity ratio a_p/a_c *versus* mobile counterion density n: (●) NaCMC 4M; (○) NaCMC 9M; (▲) NaPA; (△) NaAM

Table 2 Activity ratio for Ludox

Concentration (%)	a_p/a_c
4	169.5
8	69.5
12	68.9
16	43.8

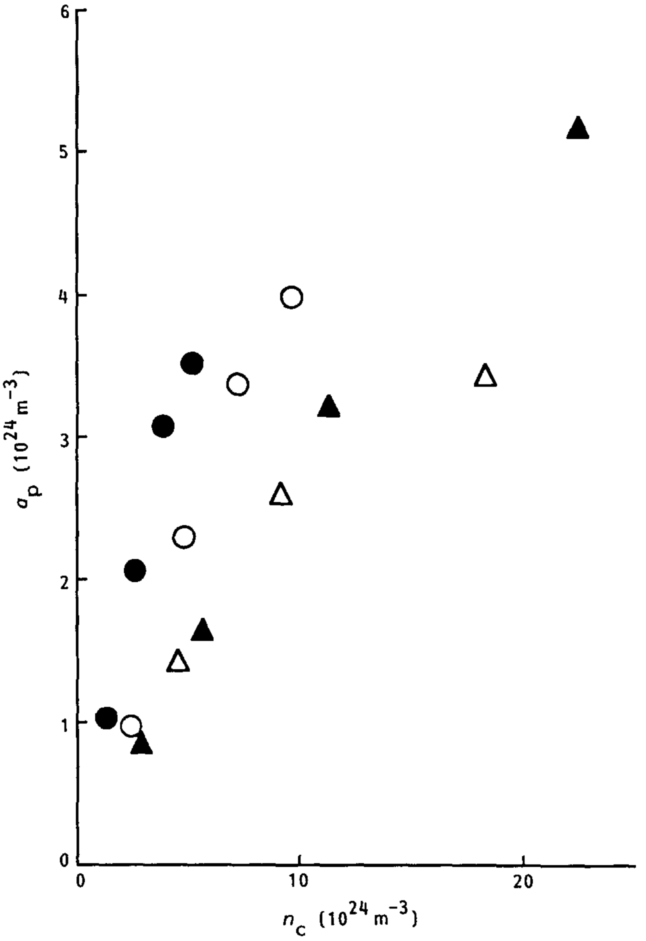

Figure 3 Potentiometric activity a_p *versus* total counterion density n_c: symbols as in *Figure 2*

Measurements

Osmotic pressure was measured with a Knauer Membrane Osmometer at 25 ± 0.1°C, to within ±3%.

Potentiometry was carried out with an EIL 6070 potentiometer with a sodium ion selective electrode at 25 ± 0.1°C, to within ±5%.

RESULTS AND DISCUSSION

The experimental data (not reported here) comprise (1) equivalent concentrations of the polymers as the number of sodium nuclei per m^3, n_c, which included condensed counterions in any state of binding or association; (2) the osmotic activity, a_c, which was calculated as Π/kT and expressed as number per m^3; and (3) the potentiometric activity, a_p, also expressed as number density. The number of 'free' or 'mobile' counterions, denoted by n, was calculated from n_c by using equation (4).

Plots of a_c *versus* a_p (*Figure 1*) and of a_p/a_c *versus* n (*Figure 2*) enabled some theoretical predictions to be tested as stated in the Introduction. The expected global relationship between the two activities is not borne out in *Figure 1*. As shown in *Table 2*, Ludox shows the maximum departure from expectation. This anionic particulate colloid does not of course fall within the scope of the theories mentioned, and is included here only to show the remarkable trend for polyanionic materials of this kind away from the relatively flexible polymers. In *Figure 2* there is a distinct trend of the activity ratio for the polymers towards a constant value at higher concentrations, although this value is approximately 2.7, rather than 1 or 1.21.

Usually the activity coefficient and osmotic coefficient receive great attention in solution thermodynamics. In polyelectrolyte systems, however, it is more expedient to approach the same problem through a functional relationship between activity and solute concentration. The difficulty is that whereas activity is an operational quantity, the 'true' solute concentration is not. It is now universally agreed that counterions are distributed between at least two phases: a condensed phase and a relatively mobile phase. Although activity is the same in all phases, the activity coefficient and hence counterion concentration cannot be. Actually, in all probability, the concentration must vary continuously in the diffuse mobile layer with distance from the polymer backbone. Although Manning[1] attributes translational freedom to the condensed counterions as well as the mobile ones. Satoh *et al.*[4] attribute translational freedom to the mobile ions only. Here the view is taken that only the mobile ions have enough translational freedom to be relevant to thermodynamic properties associated with mixing.

To test this view, a_p and a_c are plotted against the total counterion density n_c in *Figure 3* and against the mobile counterion density n in *Figure 4*. It is interesting to note that in *Figure 4* the points for all the polymers lie nearly on one curve, which clearly is not the case in *Figure 3*. Statistically fitted regression curves were drawn using the

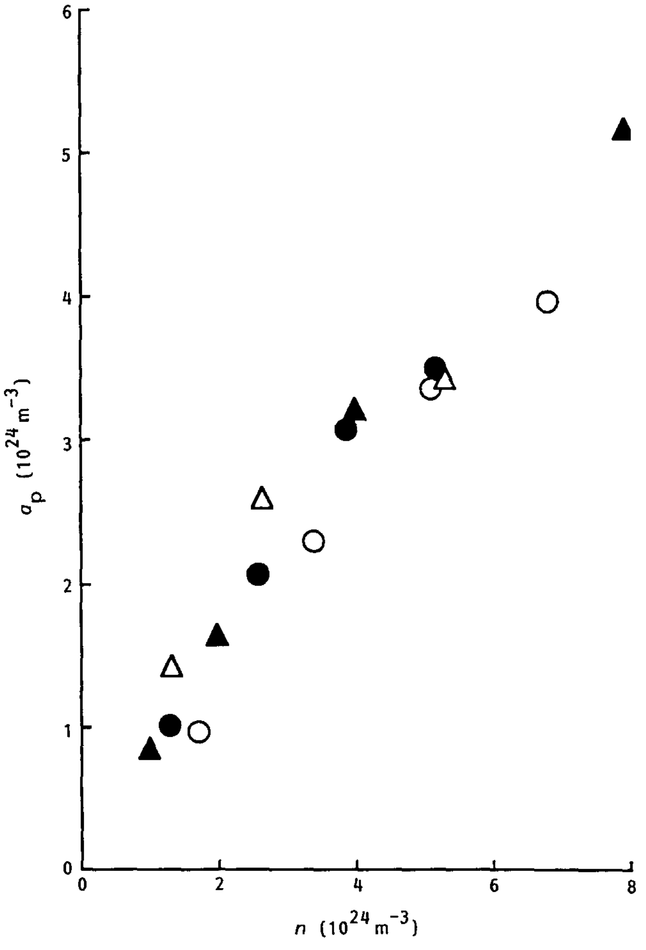

Figure 4 Potentiometric activity a_p *versus* mobile counterion density n: symbols as in *Figure 2*

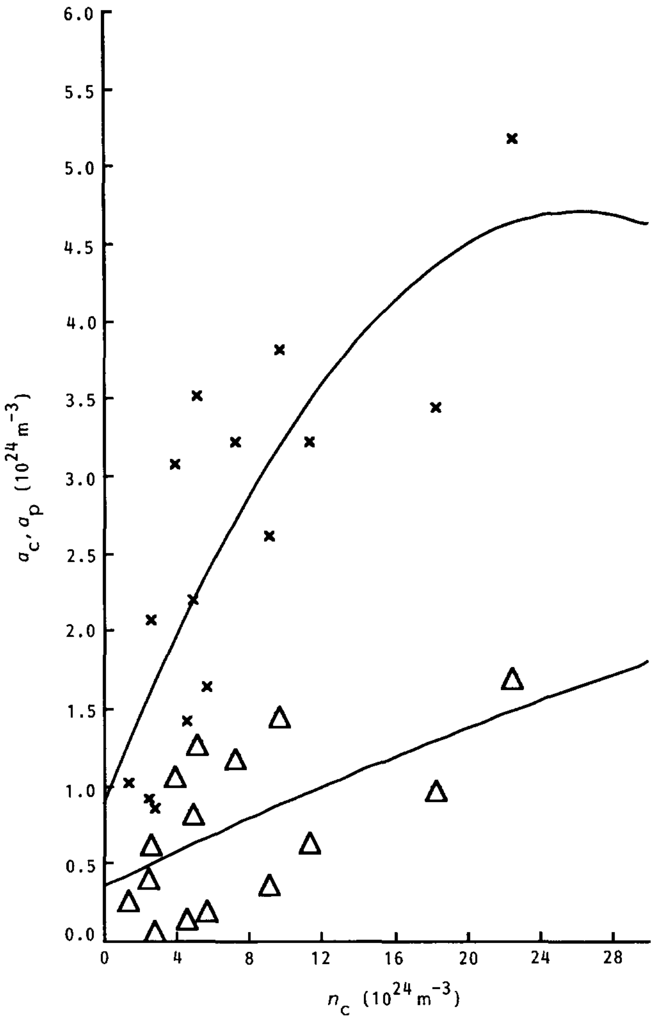

Figure 5 Counterion activities a_p and a_c for all four polymers *versus* total counterion density n_c, with computer-fitted curves: (×) a_p; (△) a_c

Table 3 Correlation coefficients (R^2) for all polymers

	n_c	n
a_p	0.66	0.93
a_c	0.35	0.93
	ln n_c	ln n
ln a_p	0.65	0.91
ln a_c	0.28	0.88

Cricket Graph V1.2 software for collections of points for all four polymers, as shown in *Figures 5–8*. From the values of the correlation coefficients R^2 given in *Table 3*, it is clear that the mobile ion density n relates much better than does n_c to the measured activities. For instance, R^2 is 0.432 for the population (a_c, n_c) and 0.956 for (a_c, n). This may be taken as good support for the Manning theory.

After allowances are made for condensation as above, some departure from the ideal value is expected as a result of interion attraction. According to Manning the counterion condensation is a self-limited process that always leaves a constant charge density on the polymer backbone corresponding to $\xi = 1$, and the mobile ions reorganize themselves in the resulting potential field, which must have its effect on the solution free energy and therefore on the activity coefficient. However, the departure from the ideal value of unity is small for γ and quite appreciable for ϕ. This disparity is difficult to explain. Higher activity values were also obtained from studies[6] on transport phenomena such as conductance, diffusion and transference number. The ratio of activity coefficient to osmotic coefficient in those experiments lies between 2.7 and 2.8, remarkably close to the approximate value of 2.7 for a_p/a_c indicated in *Figure 2*.

Katchalsky[7] considered that all non-condensed ions take part in an irreversible process such as diffusion, whereas only a fraction of them are active in a thermodynamic process. On the basis of the agreement in the value of the activity ratios it may be reasonably suggested that the potentiometric activity is probably kinetic in nature. The fundamental process involved in this measurement is electron transfer from a metal body finally to a sodium ion in solution across potential barriers, possibly involving tunnelling (Bockris *et al.*[8]). A small cathode current in a steady-state experimental condition could depress the energy barrier in a rate-determining step. One other possibility is that at a low ionic concentration, such as obtained in a salt-free

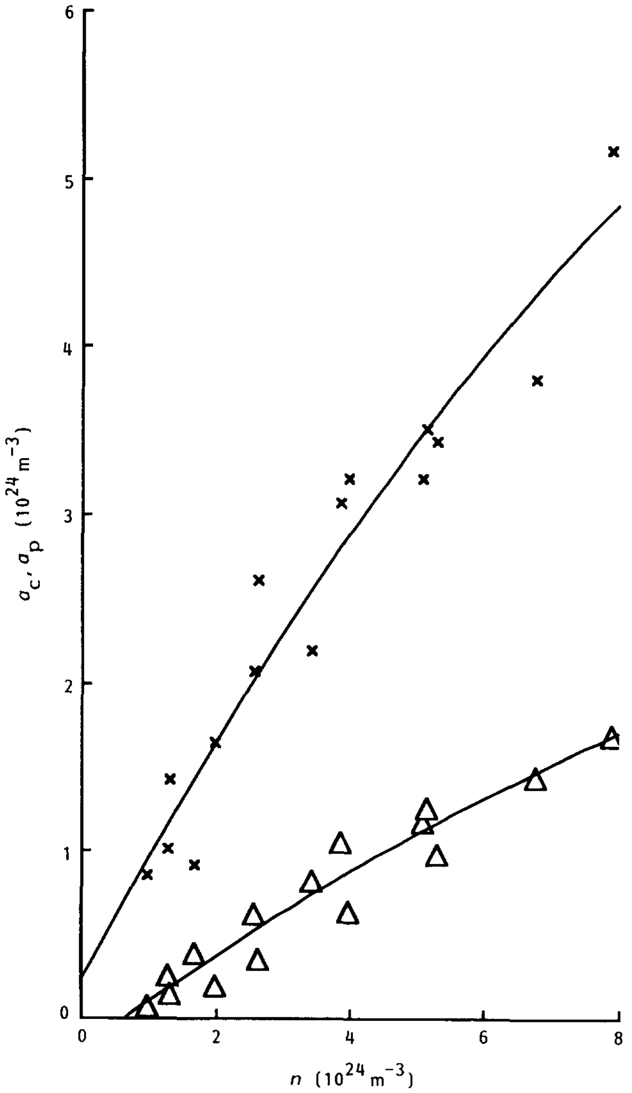

Figure 6 Counterion activities a_p and a_c *versus* mobile counterion density n, with computer-fitted curves: symbols as in *Figure 5*

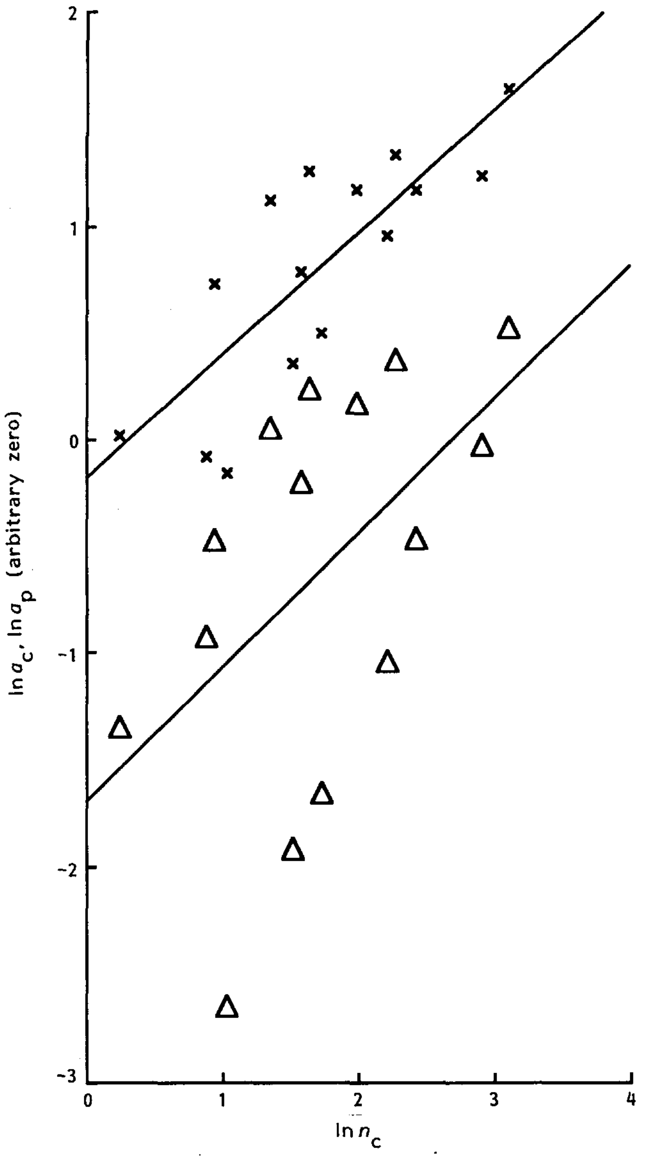

Figure 7 Plots of $\ln(a_p/10^{24}\,\mathrm{m}^{-3})$ and $\ln(a_c/10^{24}\,\mathrm{m}^{-3})$ *versus* $\ln(n_c/10^{24}\,\mathrm{m}^{-3})$, with fitted lines: symbols as in *Figure 5*

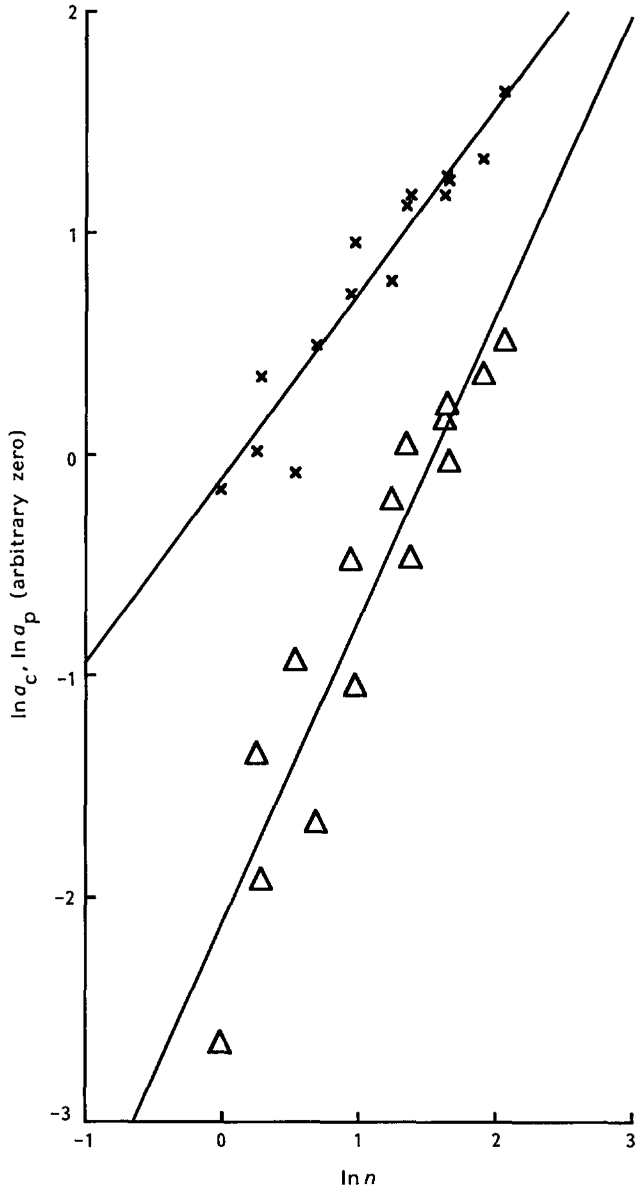

Figure 8 Plots as in *Figure 7*, but *versus* $\ln(n/10^{24}\,\mathrm{m}^{-3})$

solution in the present work, one decisive step may be diffusion-controlled and therefore subject to considerations raised by Katchalsky[7]. Against this, an osmotic pressure measurement takes place in a genuinely equilibrium set-up.

CONCLUSION

From a study of two operational activities of four polyelectrolytes, covering a good range of values of the charge-density parameter ξ, good qualitative agreement is seen with the Manning theory of counterion condensation. The condensed ions do not seem to contribute to either of the activities and hence it is doubtful if these have sufficient translational freedom. The remarkable disparity between the two activities can be explained on the assumption that the potentiometric activity is basically a kinetic quantity.

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