

Donnan Equilibria in Polyelectrolyte Solutions

MEMBRANE equilibria, involving a macromolecule, impermeable through the membrane, and a permeable salt, were first investigated by Donnan¹. He found that at equilibrium the salt was unevenly distributed between the two sides of the membrane, and he advanced a theory to explain the effect. Since then this effect has been intensively examined, first especially with proteins, later even with linear polyelectrolytes.

In recent years numerous theoretical²⁻⁶ papers on the subject have appeared whereas much less attention has been given to the experimental side of the problem, and accurate data are, in general, lacking. In the work recorded here precision measurements on a linear polyelectrolyte and a non-electrolyte polymer are reported. It is shown that the classical Donnan theory alone does not explain the behaviour of linear polyelectrolytes and that in addition an 'excluded volume' effect is present. In this it is assumed that the permeable salt is partly excluded from the interior of the polyelectrolyte molecule. The excluded volume effect has also been considered by Strauss and Ander⁷ in an investigation of polyphosphate solutions.

The polymers used in the present experiments were poly-methacrylic acid (PMA) and poly-oxy-ethylene (POE (CH₂CH₂O)_n). The permeable electrolytes were sodium hydroxide and sodium hydroxide in the presence of sodium chloride. The dialysis cell was essentially an enlarged block-type osmometer cell, made of polyethylene and with a membrane of 'Collophane'. The equilibration of the solutions was carried out at 25° C for 24 h. This was well in excess of the actual time necessary for the equilibrium to be established.

The concentration of sodium hydroxide was determined by titration with hydrochloric acid. In solutions containing PMA a sharp equivalence point was found near pH 10, where the excess sodium hydroxide was neutralized, but the PMA was still in the form of its sodium salt. This point could be accurately determined with thymolphthalein as indicator. In the actual experiments 25 ml. of the equilibrated solutions were transferred with a pipette to glass stoppered flasks and weighed. Most of

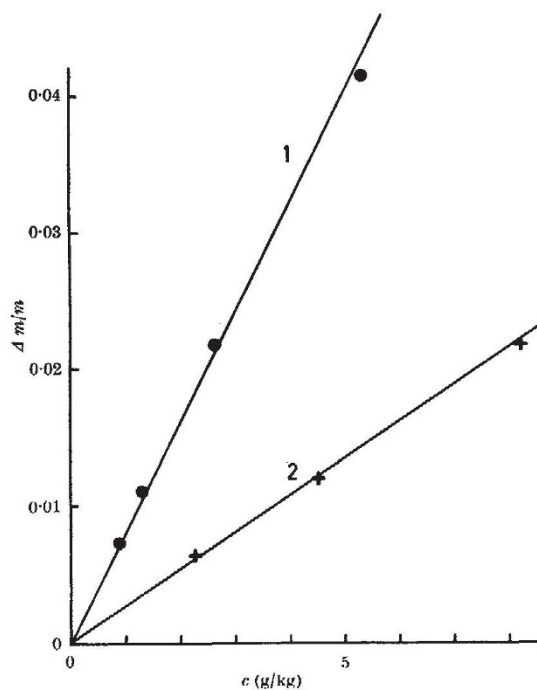


Fig. 1. Measurements at constant sodium hydroxide concentration. Curve 1 for PMA with $m = 0.25$ M/kg; curve 2 for POE with $m = 0.5$ M/kg

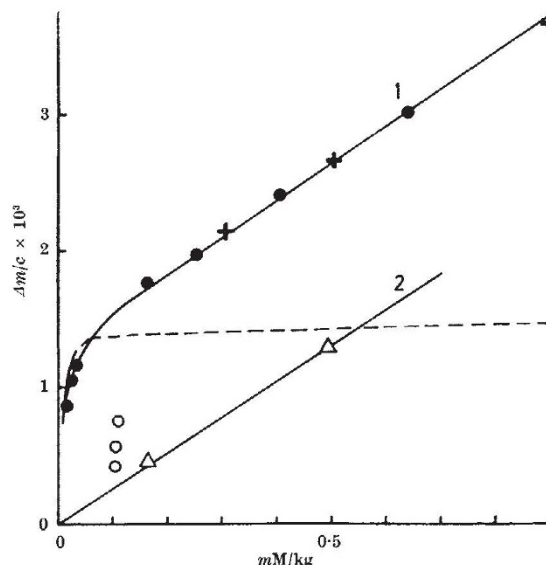


Fig. 2. Measurements at constant polymer concentration. Curve 1 for PMA with $c = 5.2$ g/kg; curve 2 for POE with $c = 4.5$ g/kg. Open circles represent Δm for sodium hydroxide in PMA solutions in the presence of sodium chloride; from top to bottom $m_{\text{NaCl}} = 0.20, 0.40$ and 0.80 M/kg. The crosses on curve 1 represent the corresponding Δm values referring to the total permeable electrolyte concentration. The dotted curve represents equation (1) with $c = 5$ g/kg and with $\epsilon = 0.25$

the alkali in the solutions was then neutralized by adding to each flask 25 ml. of a standard hydrochloric acid solution with a precision pipette. The final neutralization of the alkali was carried out by titrating with a 0.05 M hydrochloric acid solution using a microburette and thymolphthalein as indicator. By this method the concentrations of sodium hydroxide in the two solutions could be determined with a relative accuracy of about 0.01 per cent. The concentrations were expressed in weight units with the following designations:

permeable electrolyte: m moles per kg of solution
polymer: c g per kg of solution.

The results are shown in Figs. 1 and 2. They are expressed in terms of $\Delta m = m - m_1$, where m_1 and m are the m -values for the solution containing the polymer and for the solvent respectively. Fig. 1 shows some results from measurements at constant sodium hydroxide concentration and varying polymer concentrations. We see that with both polymers Δm is very nearly proportional to the polymer concentration. In Fig. 2 the polymer concentration is kept constant and the concentration of the permeable electrolyte varied. With PMA some measurements were carried out with sodium hydroxide in the presence of varying amounts of sodium chloride. We see that Δm for sodium hydroxide is depressed by the presence of sodium chloride. However, if we assume that sodium chloride is displaced to the same extent as sodium hydroxide, and we calculate Δm for the total amount of permeable electrolyte, we find that the points fall on the curve for pure sodium hydroxide. This indicates that both electrolytes behave similarly in this connexion.

The classical Donnan theory gives for Δm the following formula:

$$\Delta m = \frac{c\epsilon}{M} \frac{1}{1 + \sqrt{1 + \frac{c\epsilon}{Mm_1}}} \quad (1)$$

where ϵ is the degree of dissociation of the polyelectrolyte and M its equivalent weight. In Fig. 2, together with the experimental results, a curve representing equation (1) for PMA with $c = 5$ g/kg and with $\epsilon = 0.25$ is shown. We see that equation (1) cannot be made to fit the experimental results.

For the excluded volume effect we have in the first approximation:

$$\Delta m = \alpha m c \quad (2)$$

where α determines the excluded volume (in the present units it equals the mass of solution in kg/g polymer, from which the permeable electrolyte is excluded).

Comparing equation (2) with the experimental results, we see that with POE the agreement is excellent. From both diagrams we obtain $\alpha = 0.0027$ kg/g. As the polymer mass itself is included in α this means that for each gram of the polymer there are 1.7 g of (solvating) water from which sodium hydroxide is excluded. With PMA the situation is more complicated. A comparison of the experimental results in Fig. 2 with the predictions of the Donnan theory and the excluded volume effect reveals that the experimental curve may be obtained by a superposition of these two effects. It is interesting to note that the excluded volume effect for PMA happens to be of the same magnitude as for POE.

I may conclude by stating that the experiments recorded here indicate that in linear polyelectrolyte solutions two effects are present, namely, the classical Donnan effect and the excluded volume effect. The latter occurs even with non-electrolyte polymers. These matters are treated further in a paper to be published in *Acta Chemica Scandinavica*.

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² Harris, F. E., and Rice, S. A., *J. Phys. Chem.*, **58**, 725 (1954).

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⁴ Stigter, D., and Hill, T. L., *J. Phys. Chem.*, **63**, 551 (1959).

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⁷ Strauss, U. P., and Ander, P., *J. Amer. Chem. Soc.*, **80**, 6494 (1958).

Partial Differentiation, with Special Reference to Thermodynamics

FROM time immemorial savants and scholars have taken liberties with well-known words and phrases and by 'new definitions' have imparted highly specialized meanings to familiar expressions. While in some cases such actions can be justified on the grounds of greater clarity of meaning and greater precision of definition, as a general practice the imparting of specialized meanings to well-known words and phrases tends to obscure any language, even the language of mathematics, particularly when the specialized meanings involve largely meaningless 'new definitions'.

In a recent communication, Elliott¹ has suggested a new definition for the partial derivatives occurring in thermodynamics. The approach is based on the form:

$$dz = a dx_1 + b dx_2 + c dx_3 \quad (1)$$

and it is stated that a , b , and c in the limit of small displacement dx_1 , dx_2 , dx_3 are to be identified with the new partial derivatives and indicated as $\frac{\partial z}{\partial x_1}$, etc.

No restrictions are imposed on the manner in which the limit is to be taken and, in our opinion, the failure to do this renders the definition meaningless.

As an illustration of our criticism let us introduce the symbols Z_1 , Z_2 , Z_3 to represent the 'old' derivatives of z , that is, Z_1 is the rate of change of z with respect to x_1 keeping x_2 and x_3 constant. Then to a first order of small quantities:

$$dz = Z_1 dx_1 + Z_2 dx_2 + Z_3 dx_3 \quad (2)$$

Evidently by keeping x_2 and x_3 constant we can deduce from (1) and (2) that:

$$a = \frac{\partial z}{\partial x_1} = Z_1$$

On the other hand, for $dx_1 = dx_2$ and x_3 kept constant

$$\frac{\partial z}{\partial x_1} = Z_1 + Z_2$$

and so on. The symbol $\frac{\partial z}{\partial x_1}$ can have an infinity of values depending on how we approach the limit.

Dr. Elliott implies that the freedom from restrictions in taking the limit is one of the merits of his definition. We believe it can only lead to confusion in a field where precise definitions are essential.

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¹ Elliott, G. A., *Nature*, **198**, 1191 (1963).

THE preceding communication shows that if the partial differential indicated by $\partial z/\partial x_1$ is defined as the limiting value of the rate of change of z with respect to x_1 , and if we include changes due to the variation of x_2 (which is dependent on x_1) then the result obtained depends on the relation between x_1 and x_2 and in particular if $dx_1 = dx_2$ the expression is:

$$\partial z/\partial x_1 = Z_1 + Z_2$$

This 'definition' is therefore quite useless, and on this point there is no dispute.

On the other hand, if we define the partial differential in the way proposed in my previous communication we always obtain the result $\partial z/\partial x_1 = a$ and no other answer is possible. The symbol $\partial z/\partial x_1$ is to be regarded simply as a rather clumsy but time-honoured method of indicating the coefficient a or rather its limiting value when the neglect of differentials of higher order than the first in forming equation (1) above is strictly justified. The new definition is strictly independent of any relations between the variables.

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BIOCHEMISTRY

Enzymatic Evidence for the Configuration of *d*-Isocitric Acid

THE configuration of the α -carbon atom of the *d*-isocitric acid of the Krebs tricarboxylic acid cycle was designated L_3 on the basis of an application of the Lovene displacement rule¹, but subsequent chemical²⁻⁴ and X-ray⁵ studies indicated the D_3 configuration. Other investigations have shown that the α - and β -asymmetric centres of *d*-isocitric acid possess opposite configurations^{6,7}. Although *d*-isocitric acid may be distinguished by the action of isocitric dehydrogenase from the three isomeric isocitric acids, none of the isomers of α -aminotricarballylic acid, the α -amino analogue of isocitric acid, has thus far been found to be attacked by enzymes. Greenstein and Winitz¹, who prepared both DL- α -aminotricarballylic and DL-*allo*- α -aminotricarballylic acids, were unable to find an enzyme capable of resolving these and therefore resorted to the use of brucine. They thus obtained the corresponding four optical isomers, which they converted to the respective isocitric acids by treatment with HNO₂.

Application of the Clough-Lutz-Jirgensons rule permitted assignment of configuration to the *D*- and *L*-isomers of *allo*- α -aminotricarballylic acid, but assignment of the configurations of the isomers of α -aminotricarballylic