

# CONCENTRATION GRADIENT AND DIFFUSION POTENTIAL IN COLLOIDAL ELECTROLYTE SOLUTIONS

BY C. BOTRÉ, V. L. CRESCENZI, A. M. LIQUORI AND A. MELE  
Laboratorio Ricerche sulla Struttura e l'Attività di Composti Chimici,  
Istituto di Chimica Farmaceutica, Università di Roma;  
Istituto di Chimica Generale, Università di Bari

*Received 1st August, 1958*

It is shown that measurements of diffusion potential along linear concentration gradients may be considered a useful new method to study some electrochemical properties of solutions of polyelectrolytes and colloidal electrolytes. Ionic transference numbers have been obtained both for anionic polyelectrolytes and anionic synthetic detergents. In the latter case the method has also given the possibility to determine the critical micelle concentration. The potential interest of this new type of experimental approach in the study of interaction phenomena in colloidal electrolytes of biological importance is pointed out.

The anomalous electro-chemical behaviour of polyelectrolytes and colloidal electrolyte solutions has been widely studied in recent years by several experimental techniques. Binding of counterions or added ions by the highly charged macro-ions has been recognized as a very important factor. Determinations of the transference numbers of a few typical polyelectrolyte salts<sup>1, 2, 3</sup> have shown that a very large fraction of counterions moves towards the anode with the macro-ion. This interesting effect is readily explained by considering the intense electrostatic field arising from the high charge density on the macro-ions which tends to attract the small counterions.

A more direct investigation of binding phenomena in both polyelectrolytes and detergent solutions has been carried out in this laboratory by determining the activity coefficients of counterions by means of membrane-potential determinations.<sup>4, 5</sup> For highly charged polyelectrolytes and for detergent solutions above the critical micelle concentration, the activity coefficients have been found anomalously low in agreement with the generally accepted views of the large extent of binding in these systems. An approximate theory was found to explain the results on an almost quantitative basis. With the aim to investigate further some electrochemical properties of polyelectrolytes and colloidal electrolytes, an attempt has been made to combine the data previously obtained on counterions activity with those from diffusion-potentials determinations.

It is known that, owing to the different mobilities of the ionic species present in solution, an electrical potential gradient is set up along a concentration gradient with an electrolyte solution. The diffusion potential (along a continuous gradient of concentration) may be readily derived from the thermodynamics of irreversible processes.<sup>6</sup> For the isothermal case the expression for the electrical potential gradient for an electrolyte which dissociates in solution into two ionic species, with no external forces acting on the diffusing species, is

$$\frac{d\phi}{dx} = - \frac{1}{F} \left( \frac{t_1 d\mu_1}{Z_1 dx} + \frac{t_2 d\mu_2}{Z_2 dx} \right), \quad (1)$$

where  $d\phi/dx$  is the diffusion potential gradient along the direction  $x$  of the concentration gradient, and  $d\mu_1/dx$  and  $d\mu_2/dx$  are the chemical potential gradients of the ionic species of charge  $Z_1$  and  $Z_2$ , the transference numbers of which are  $t_1$  and  $t_2$  respectively.

We have succeeded in setting up linear and stable electrolytic concentration gradients. Along them, e.m.f. measurements have been carried out. This technique has allowed the study of transference properties of polyelectrolytes and detergent solutions without encountering the well-known difficulties involved in the conventional procedures based on electrolytic transference. In fact, by a suitable choice of experimental conditions, the gradient of diffusion potential may be derived from the e.m.f. measurements along a concentration gradient, often to a good degree of approximation. From such potentials, the transference numbers of the ionic species may be obtained provided that ionic activities along the gradient are known.

## EXPERIMENTAL

### MATERIALS

Sodium chloride and lithium chloride were both of analytical grade. (The solutions of lithium chloride have been titrated according to Volhard.)

Sodium dodecylsulphate (NaLS) was prepared according to Dreger<sup>7</sup> and purified by repeated crystallization from ethyl alcohol and continuous extraction with ether for 36 h to remove traces of unreacted lauryl alcohol. The value of the critical micelle concentration of the product—as tested by conductivity measurements—was of  $8.0 \times 10^{-3}$  mole/l.

Sodium polyacrylate (NaPA) was obtained by neutralizing a commercial polyacrylic acid with a standard NaOH solution.

Sodium maleate + vinyl acetate copolymer (NaMa—Va) was obtained from maleic anhydride + vinyl acetate copolymer as described elsewhere.<sup>4</sup>

Graham's salt (NaPP) was prepared from  $\text{NaH}_2\text{PO}_4$  which was kept in a platinum crucible for 7 h at 220°C and for 13 h at 900°C in a furnace. The phosphate glass was obtained by rapid chilling of the melt on a cold metal plate.

### CONCENTRATION GRADIENT

In fig. 1 the arrangement used to set up stable and linear concentration gradients is shown. The vessel *a* containing an aqueous solution (150 ml) of the electrolyte under study has an inlet for the solvent and an outlet which goes to a graduated cylinder. The solvent is contained in vessel *b* and through a tube with a stopcock *c* goes to the mixing bottle *a* where the electrolyte is continuously diluted under stirring.

Before starting the experiment, the stopcock *c* is closed, the levels of the liquids in the two vessels are brought to the same height and stirring is started in vessel *a*. Then the two stopcocks *c* and *d* are opened and the rate of flow of the liquid is regulated, generally to 2–3 ml/min. It has been shown theoretically<sup>8</sup> that such an arrangement provides the conditions whereby the density and hence the concentration of the solution filling the graduated cylinder is a linear function of the collected volume. The linearity of the gradient was checked by direct determination of the concentration of a number of fractions collected from vessel *a*, either by chemical titration or by conductivity measurements.

### E.M.F. MEASUREMENTS ALONG CONCENTRATION GRADIENTS

**ELECTRODES.**—The e.m.f.s were measured along the concentration gradients by means of three types of electrodes, namely:

- (i) conventional Ag—AgCl electrodes for the chloride solutions (see fig. 1);
- (ii) Ag—AgCl electrodes whose tip was immersed in a 0.1 M NaCl solution contained in a tube ending with a small orifice (see fig. 1). This latter arrangement was devised for e.m.f. measurements in detergent solutions in order to avoid the use of calomel electrodes with agar bridges since these were found not suitable. In fact, due to the high KCl concentration in the agar, flocculation of detergent occurs at the tip of the bridge, thus interrupting electrical contact.
- (iii) Calomel electrodes with long agar bridges for the polyelectrolyte solutions (see fig. 1).

The common feature of these electrodes is their thinness. In each case the diameter of the tubes or bridges did not exceed about 0.5 cm. This was necessary to avoid connection or stirring when the electrodes had to be dipped into the gradients for the measurements.

PROCEDURE.—After setting up the concentration gradient, the e.m.f.s were measured at given heights along the gradient by slowly dipping one electrode into the cylinder, the other being clamped at a certain level, usually a few cm below the free surface of the solution in the cylinder.

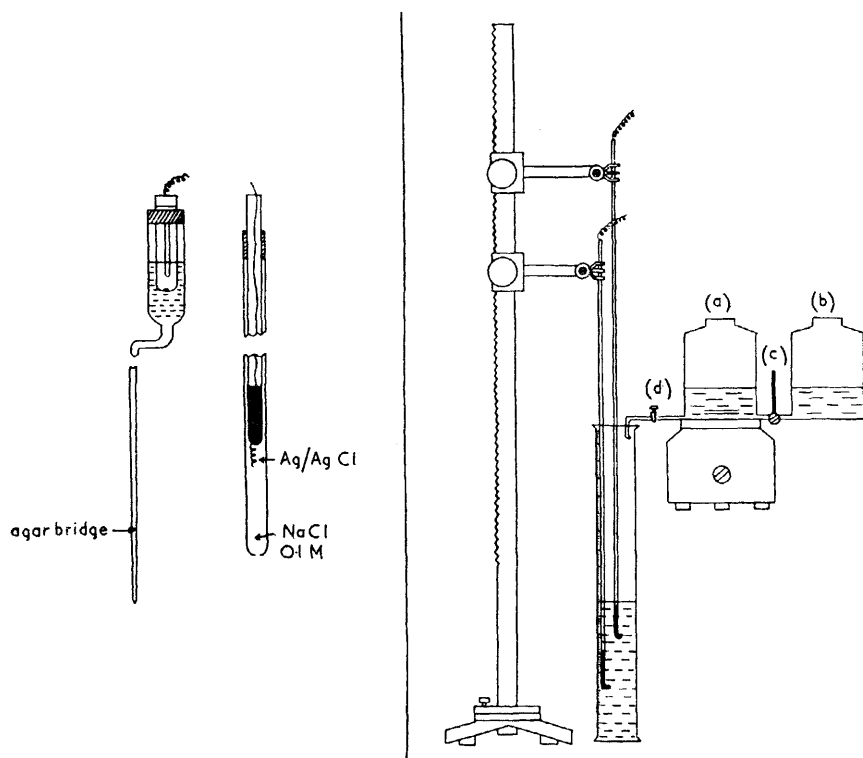


FIG. 1.—Arrangement for the construction of a concentration gradient and electrodes used for the measurements of the e.m.f.s  $E$ .

## RESULTS AND DISCUSSION

### E.M.F.S IN SIMPLE ELECTROLYTES SOLUTION GRADIENTS

The results of the measurements are reported in fig. 2, where the e.m.f.  $\Delta E$  has been plotted against the logarithm of the mean ionic activity for both NaCl and LiCl. These measurements have been carried out in order to check the validity of the technique employed throughout the entire investigation.

In this case, eqn. (1) for the diffusion potential reduces to

$$\left(\frac{d\phi}{dx}\right) = -\frac{RT}{F} \left( t_+ \frac{d \ln a_1}{dx} - t_- \frac{d \ln a_2}{dx} \right), \quad (2)$$

which may be integrated between any two values of  $x$ , provided that they are close enough that the transference numbers may be considered constant.

With this assumption,

$$\phi = -58 (t_+ \Delta \log a_+ - t_- \Delta \log a_-);$$

since the electrodes are reversible to anions, the expression for the total e.m.f. is

$$\Delta E = -2t_+ 58 \Delta \log a_{\pm}.$$

The transference numbers for sodium and lithium ions have been calculated from the plots of fig. 2 and are reported in table 1. In the last column of this table, the range of concentration investigated is also shown.

TABLE 1

compound	$t_+$ , expt.	$t_+$ , literature	range of conc.
NaCl	0.37	0.386 *	0.166-0.062
LiCl	0.31	0.318 †	0.145-0.069

\* ref. (9);                      † ref. (10).

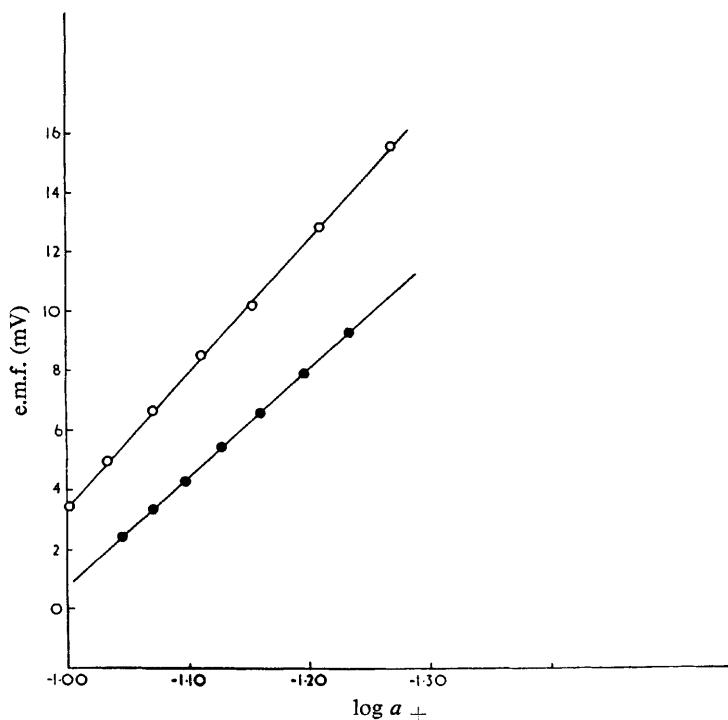


FIG. 2.— $\Delta E$  in mV against the logarithm of the mean ionic activity in a LiCl and NaCl gradient respectively. ● LiCl; ○ NaCl.

#### E.M.F. IN POLYELECTROLYTES-SOLUTION GRADIENTS

Concentration gradients have been set up with three polyelectrolytes solutions, namely sodium polyacrylate, sodium maleate + vinyl acetate copolymer and sodium polyphosphate. In fig. 3 (*a*, *b* and *c*) the e.m.f., in mV, is reported against the logarithm of the concentration for these three polyelectrolytes.

The approximate analytical expression for the diffusion potential is given in this case by

$$\phi = -58[t_+ \Delta \log a_+ - (t_-/n), \Delta \log a_-],$$

where  $n$  is the charge of the macro-ion. Since  $n \gg t_-$  we may assume that the second term on the right-hand side of the above equation can be omitted. With the usual assumption that the two junction potentials at the bridge tips + solution contacts may be neglected, the total e.m.f. may be approximated to the diffusion potential.

With these assumptions, the transference number of sodium ions may be calculated from

$$t_+ \cong - \frac{\Delta(E)}{58 \Delta \log \gamma_+ C_+},$$

where  $C_+$  and  $\gamma_+$  are concentration and activity coefficient of sodium ions respectively. The activity coefficients of sodium counterions in solutions of the

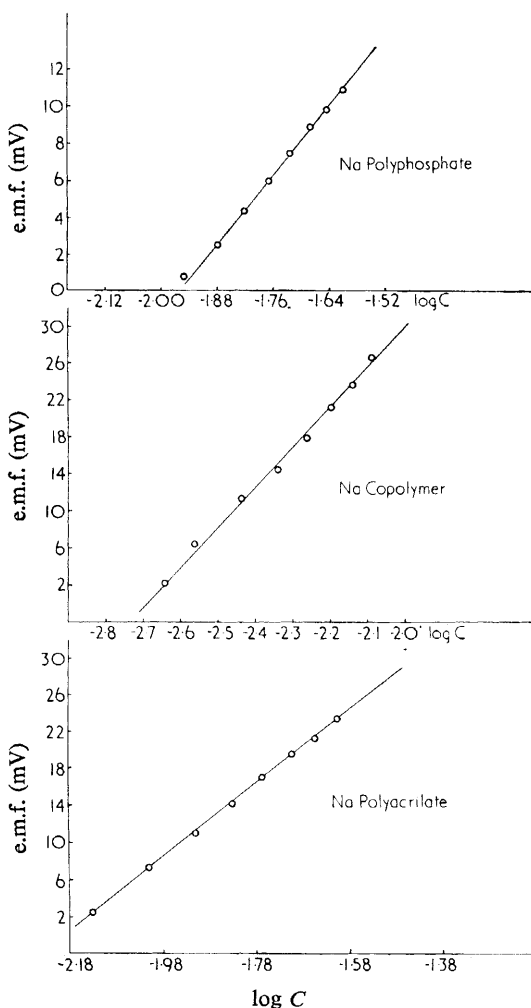


FIG. 3.— $\Delta E$  in mV against the logarithm of  $\text{Na}^+$  ions concentration as measured along the gradients: (a) sodium polyacrylate (NaPA), (b) sodium maleate + vinyl acetate copolymer (NaMA—VA), (c) Graham's salt (NaPP).

three polyelectrolytes have been obtained by means of membrane-potential measurements as described elsewhere,<sup>4</sup> and have been found to be practically invariant with concentration. The transference numbers of sodium ions have therefore been calculated from the slopes of the experimental curves shown in fig. 3 (a, b, c) and are reported in table 2 with the range of concentration studied.

TABLE 2

compound	$t_+$	range of concentration mole/l. $\times 10^{-2}$
Na polyacrylate	0.69	0.70-3.20
Na copolmer	0.72	0.25-0.81
Na polyphosphate	0.54	0.85-4.51

A value of 0.60 for the transference number of sodium ions in solution of polyacrylate is reported in the literature.<sup>1</sup> Wall and Doremus have found a value of 0.56 for the transference number of sodium ions in Graham's salt solution.<sup>2</sup>

#### E.M.F. IN A DETERGENT-SOLUTION GRADIENT

Sodium laurylsulphate (NaLS) has been chosen as a typical example of colloidal electrolyte. In fig. 4, the e.m.f.s measured along the concentration gradient set up with NaLS is plotted against the logarithm of concentration. As may be seen from this plot, the experimental points lie on two straight lines, which intersect at a concentration of detergent of  $0.78 \times 10^{-2}$  M. This value of the concentration has been identified with the critical micelle concentration, which is found by conductivity measurements to be  $0.8 \times 10^{-2}$  M (see experimental part).

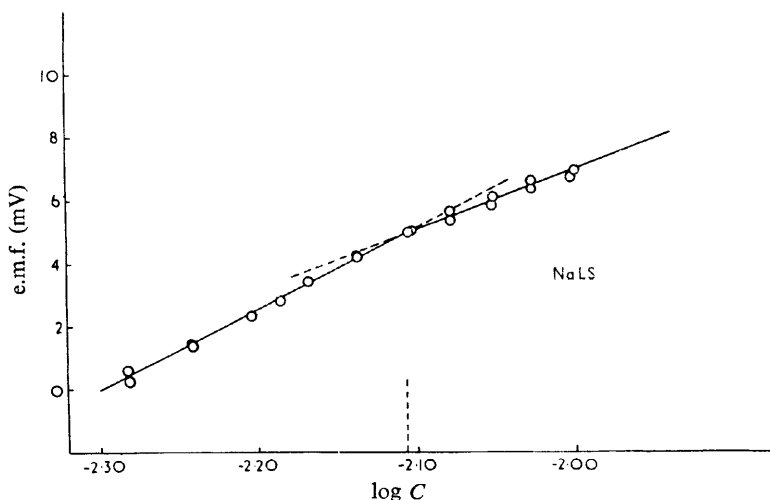


FIG. 4.— $\Delta E$  in mV against the logarithm of  $\text{Na}^+$  ions concentration of Na laurylsulphate. The dotted line on the abscissa indicates the critical micelle concentration.

We have made an attempt to evaluate the transference numbers of  $\text{Na}^+$  ions and  $\text{LS}^-$  ions for sodium laurylsulphate below the critical micelle concentration (c.m.c.). With the same assumptions made for polyelectrolytes,\* one has

$$\Delta E = -58(t_+ \Delta \log a_+ - t_- \Delta \log a_-).$$

Introducing the same values for the activity coefficients of the cation and the anion as a further approximation,<sup>5</sup> mean values for the transference numbers have been calculated. These are  $t_{\text{Na}^+} = 0.76$  and  $t_{\text{LS}^-} = 0.24$ . From the transference number of the anion, an ionic mobility of the laurylsulphate anion of

\* In this case, since the Ag—AgCl, NaCl 0.1 M electrodes were used, neglect of the two electrode + solution junction potential is less justified than with agar bridges. Therefore, we used for the calculations, only e.m.f. values recorded when the two electrodes were close to each other.

about 16 may be derived. This figure agrees with the value of 17 reported by Mysels.<sup>11</sup> For concentrations of detergents above the c.m.c., an evaluation of the transference numbers of all the ionic species present, is more complicated.

As may be noted in fig. 4, the two straight lines intersecting at the c.m.c. show different slopes, i.e. smaller in the region where micelles are present, higher where the detergent molecules are unmicellized. This may be related qualitatively to a sensibly higher transference number of the micelle anions as compared to that of monomer anions. In fact, the micelle may be considered a spherical aggregate of about 80 monomers for NaLS. It may be predicted from simple considerations that the mobility of the charge polyanion should be significantly higher than that of the monomer.

On the basis of these preliminary results, it appears that e.m.f. measurements along concentration gradients in conjunction with other data may provide useful information on various aspects of polyelectrolytes and colloidal electrolytes solutions.

We wish to acknowledge Prof. R. M. Fuoss for critical reading of the manuscript. This work was sponsored and financially supported by the Colgate-Palmolive Company, New York, which is gratefully acknowledged.

<sup>1</sup> Huizenga, Grieger and Wall, *J. Amer. Chem. Soc.*, 1950, **72**, 2636.

<sup>2</sup> Wall and Doremus, *J. Amer. Chem. Soc.*, 1954, **76**, 868.

<sup>3</sup> Fuoss, *J. Polymer Sci.*, 1954, **12**, 185.

<sup>4</sup> Ascoli, Botré, Crescenzi, Liquori, Mele, *J. Polymer Sci.*, in press.

<sup>5</sup> Botré, Crescenzi and Mele, *J. Physic. Chem.*, 1959, **63**, 650.

<sup>6</sup> de Groot, *Thermodynamics of Irreversible Processes* (Interscience Publ., N.Y., 1951).

<sup>7</sup> Dreger, Keim, Miles, Shedlovsky and Ross, *Ind. Eng. Chem.*, 1944, **36**, 610.

<sup>8</sup> Tung and Taylor, *J. Polymer Sci.*, 1956, **21**, 144.

<sup>9</sup> Glasstone, *Introduction to Electrochemistry* (Van Nostrand, New York, 1944), p. 122.

<sup>10</sup> Glasstone, *Introduction to Electrochemistry* (Van Nostrand, New York, 1944), p. 207.

<sup>11</sup> Mysels, *J. Physic. Chem.*, 1955, **59**, 45.