

IONIC CONDUCTANCE OF POLYELECTROLYTES IN SALT-FREE SYSTEMS

STUDIES IN POLYELECTROLYTES XXXIII

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I. Introduction

A considerable number of contribution on the electrical conductance of polyelectrolyte solutions have been made by different authors during the past several years. However, so far there has been no satisfactory agreement concerning abnormal behavior of polyelectrolyte solutions within the range of lower concentrations.^{1) 2) 3) 4)} Such difference seems to have its origin in the fact that extrapolations of observed equivalent conductance to infinite dilution were obliged to be based on assumptions, each one different in every paper, because there is no theory predicting the concentration dependency of the electric conductance of polyelectrolyte solutions.—

In the present experiment, without the extrapolation which would lead to an ambiguous conclusion, the ionic conductances of counter ion and polyion were obtained by measuring both the transport number of each ion and the equivalent conductance of polyelectrolyte in solutions of the same concentration. The transport number was calculated from the data of diffusion potential appearing between two solutions of polyelectrolyte having different concentrations.

In general, diffusion potential is given by the following Nernst equation:

$$-dE = RT/F \sum_i (t_i/Z_i) d \ln a_i \quad (1)$$

where E denotes diffusion potential, R gas constant, T absolute temperature, F Faraday constant, t_i transport number of ion of i -specy, Z_i its ionic valency, and a_i its ionic activity. If transport number t_i indicates no remarkable variation with the variation of concentration, Eq. (1) can be integrated under the condition that t_i is constant and becomes

$$E = RT/F \sum_i (t_i/Z_i) \ln (a_{iII}/a_{iI}) \quad (2)$$

Eq. (2) is generally used for calculating transport numbers of simple electrolyte.

However, in the polyelectrolyte solutions where t_i varies remarkably with its concentration, Eq. (2) cannot be used without some sacrifice of accuracy of concentration dependency of t_i . Therefore, in the present paper the transport number of each ion in polyelectrolyte solutions at a certain concentration was calculated on the basis of Eq. (1) by graphically determining the value of $dE/d \ln a_i$ from the

relationship between concentration and diffusion potential. From Eq. (1) the transport number for NaCl and Na₂SO₄ are respectively

$$t_{\text{Na}^+}(\text{NaCl}) = \frac{1}{2} \left[\frac{d \ln a_{\text{Cl}^-}}{d \ln a_{\pm \text{NaCl}}} - \frac{F}{RT} \frac{dE}{d \ln a_{\pm \text{NaCl}}} \right] \quad (3)$$

$$t_{\text{Na}^+}(\text{Na}_2\text{SO}_4) = \frac{2}{3} \left[\frac{1}{2} \frac{d \ln a_{\text{SO}_4^{--}}}{d \ln a_{\pm \text{Na}_2\text{SO}_4}} - \frac{F}{RT} \frac{dE}{d \ln a_{\pm \text{Na}_2\text{SO}_4}} \right] \quad (4)$$

where a_{\pm} denotes mean activity of salt. As the values of $d \ln a_{\text{Cl}^-}/a_{\pm}$ etc. can be calculated from the data already given in previous literature, only $dE/d \ln a_{\pm}$ is necessary to obtain the value of t_{Na^+} .

Moreover, for the polyelectrolyte (Na_zP^{-z}) Eq. (1) is expressed as follows:

$$-dE = \frac{RT}{F} \left[t_{\text{Na}^+} d \ln a_{\text{Na}^+} - \frac{t_{\text{P}^{-z}}}{Z} d \ln a_{\text{P}^{-z}} \right] \quad (5)$$

As Z is a very large value for polyion, the second term of Eq. (5) is neglected when compared with the first term, except when t_{Na^+} is much less than $t_{\text{P}^{-z}}$. Therefore, Eq. (5) becomes

$$t_{\text{Na}^+}(\text{Na-PVS}) = - \frac{F}{RT} \frac{dE}{d \ln a_{\text{Na}^+}} \quad (6)$$

Making use of Eq. (6), the transport number of Na⁺ in polyelectrolyte solutions can be easily obtained from the relationship between E and $\ln a_{\text{Na}^+}$.

As the transport number of Na⁺ (t_{Na^+}) means $I_{\text{Na}^+}/I_{\text{Na}^+} + I_{\text{P}^{-z}}$ and the equivalent conductance of polyelectrolyte ($A_{\text{Na-PVS}}$) means $I_{\text{Na}^+} + I_{\text{P}^{-z}}$, the ionic conductance of counter ion and polyion (I_{Na^+} , $I_{\text{P}^{-z}}$) can easily be calculated from the values of t_{Na^+} and $A_{\text{Na-PVS}}$.

II. Experimental

Samples: The polyelectrolyte samples used in the present experiment are of three different kinds of sodium polyvinyl sulphate each of which is prepared by esterifying polyvinyl alcohol in pyridine using chlorosulfonic acid, and purified by alcohol coagulation.

The degrees of esterification and degrees of polymerisation of these samples are shown in Table 1. These samples were selected because they have almost the same degree of esterification but have different degree of polymerisation.

TABLE 1. Degree of polymerisation and degree of esterification of each sample in present experiment

No.	Degree of polymerisation	Degree of esterification
1	1440	0.71
2	470	0.74
3	1200	0.75

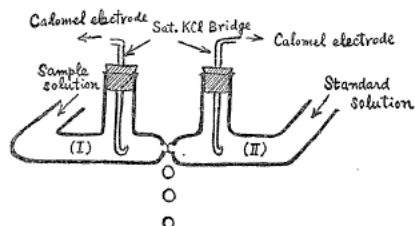


FIG. 1. Cell used for measuring diffusion potential.

Measurement of diffusion potential: The cell⁵⁾ used for measurement of diffusion potential is designed as shown in Fig. 1.

The standard solution and the sample solution come in contact with each other at the cell outlet. The potential difference appearing between the standard solution and the sample solution is conducted through saturated KCl agar bridges and calomel electrodes, and measured by ordinary potentiometer.

The reproducibility of measurements for simple electrolyte solutions was within ± 0.1 mV, but unexpected deviations of potential differences sometimes appeared when dilute solution of polyelectrolyte was used as the standard solution.

Measurements of electric conductivity: The electric conductivity was determined by means of a well adjusted Kohlrausch bridge. We checked the accuracy and found it to be about 0.01% by measuring a solid resistance having a definite value and the conductivity of NaCl solution. Considering that in polyelectrolyte solutions the observed electric conductivity varies with time because of adsorption of polyion on the surface of platinized Pt plate, the observed curve of electric conductance against time was extrapolated to the origin of time to obtain the true value without adsorption of polyion.

III. Results

Results obtained for NaCl and Na₂SO₄ are shown in Fig. 2 to illustrate the accuracy of the diffusion potential method. The variation of transport number of these simple salts with concentration is so slight that the results calculated from Eq. (2) shows the concentration dependency of transport number of simple salt more clearly than do the results calculated from Eqs. (3) and (4). The discrepancy of about 2% between the values obtained by diffusion potential method and those found in published articles⁶⁾ is not very important considering the fact that the latter values are results of different procedures.

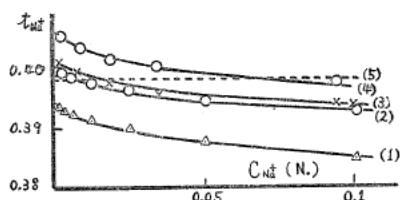


FIG. 2

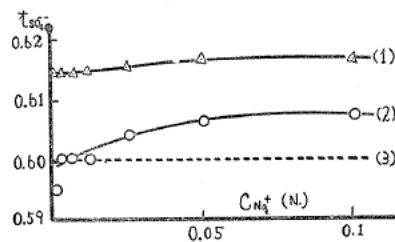


FIG. 3

FIG. 2. Transport number of NaCl.

- (1) By moving boundary method⁶⁾
- (2) Calculated from Eq. (2); standard solution = 1.00×10^{-1} N NaCl
- (3) *ibid.*; standard solution = 9.32×10^{-2} N NaCl
- (4) *ibid.*; standard solution = 3.47×10^{-2} N NaCl
- (5) Calculated from Eq. (3) using the same experimental results as those of Exps. (2), (3) and (4).

FIG. 3. Transport number of Na₂SO₄.

- (1) By Hittorf's method⁶⁾
- (2) Calculated from Eq. (2); standard solution = 1.00×10^{-1} N Na₂SO₄
- (3) Calculated from Eq. (3) using the same experimental results as those of Exp. (2).

The diffusion potentials for Na-PVS are given in Fig. 4. The concentration of standard solution differed in each series of experiments. An inspection of Fig. 4

shows that all of these curves possess quite similar features so that they can be superimposed on each other by vertical shifting. Fig. 5 illustrate the best fitting of all plots found in the entire series of experiments conveniently based on the scale of Exp. (1). It is worthy of special attention that the values of $dE/d\ln C_{Na}$ are independent of both concentration of standard solutions and degree of polymerisation of samples.

However, transport numbers should be calculated from the relationship between diffusion potential and ionic activity. Therefore, we converted the concentration in Fig. 5 into the activity as shown in Fig. 6. The values of Na^+ activity coefficient employed for calculation were determined by using sodium amalgam electrode and ion exchange membrane; for lack of space here the details concerning determination of sodium ion activity will appear in a separate paper. The transport number of Na^+ (t_{Na^+}) was calculated from the slope of tangential lines of curves in Fig. 6 using Eq. (6) as shown in Fig. 7. In Fig. 7 the values of transport

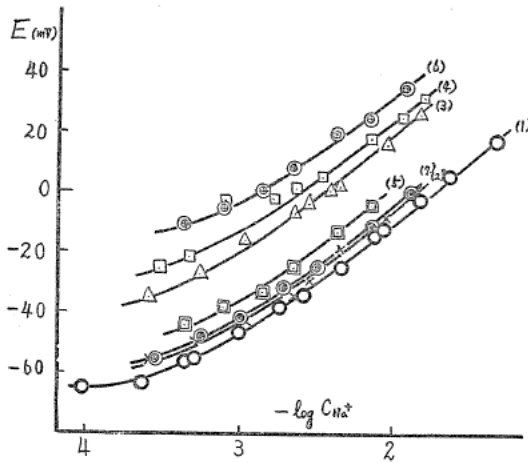


FIG. 4. Diffusion potentials of Na-PVS. (plotted against sample concentrations).

Standard solutions are as follows:

- (1) Sample No. 1 $1.725 \times 10^{-2} N$
- (2) *ibid.* $1.409 \times 10^{-2} N$
- (3) *ibid.* $3.710 \times 10^{-3} N$
- (4) *ibid.* $2.157 \times 10^{-3} N$
- (5) Sample No. 2 $1.153 \times 10^{-2} N$
- (6) *ibid.* $1.343 \times 10^{-3} N$
- (7) Sample No. 3 $1.292 \times 10^{-2} N$

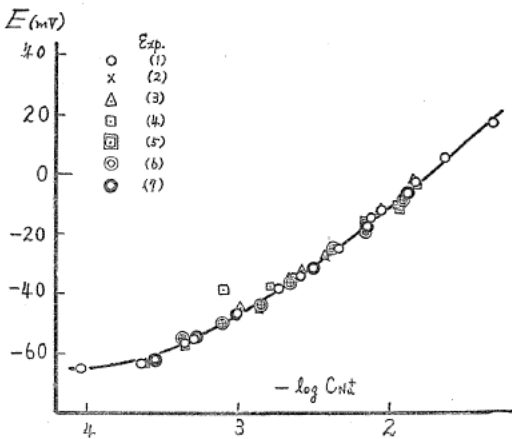


FIG. 5. Diffusion potentials of Na-PVS (Coordinates of curves in Fig. 4 were shifted vertically).

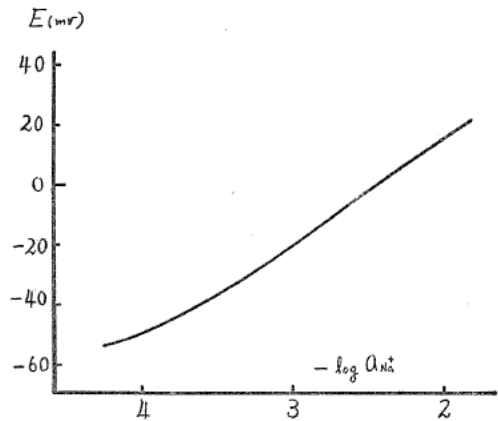


FIG. 6. Diffusion potentials of Na-PVS (plotted against sample activities).

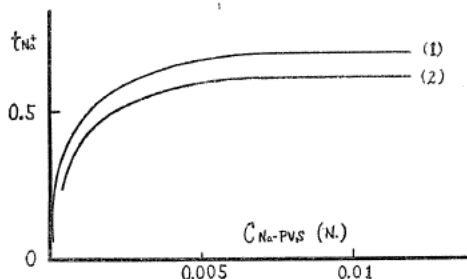


FIG. 7. Transport numbers of Na^+ in Na-PVS solutions.

- (1) Calculated from Fig. 5.
 (2) Calculated from Fig. 6.

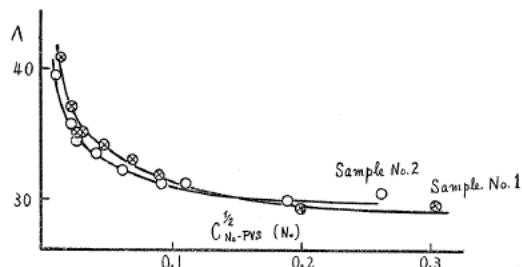


FIG. 8. Equivalent conductance of Na-PVS.

numbers calculated from the curves in Fig. 5 are also shown for reference.

The equivalent conductances obtained for the Na-PVS solutions are shown in Fig. 8, where there can be observed a slight difference between the equivalent conductance of each sample. This slight difference seems to be based on the difference of degree of esterification between samples rather than on the difference of degree of polymerisation.

By combining the values of electrical conductivity and the values of transport number, we can easily obtain the values of ionic conductance of the counter ion l_{Na^+} and $l_{\text{P-Z}}$ as shown in Fig. 9. The slight difference of electrical conductance between two samples, shown in Fig. 8, does not produce the observable difference in the curves of l_{Na^+} , $l_{\text{P-Z}}$.

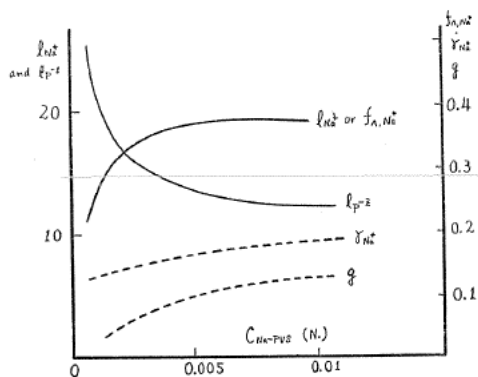


FIG. 9. Ionic conductances of Na-PVS.

IV. Discussion

The accuracy of the experimental results we describe in the present paper depends upon the accuracy of the method of determining the slope of tangential line of the curves in Figs. 5 and 7. It is difficult to draw the exact tangential line of these curves and for that reason we cannot conclusively decide whether or not there is a difference in the transport numbers of the three samples used in the present experiment. However, considering the fact that sample No. 1 has a degree of polymerisation three times greater than sample No. 2, it is reasonable to conclude that transport numbers of polyelectrolyte do not depend upon degree of polymerisation. If it were possible to calculate the transport number of polyelectrolyte from Eq. (2) as is usually done for simple electrolyte, the relationship between transport number and degree of polymerisation could be more precisely determined.

However, Eq. (2) cannot be used to calculate transport numbers which vary remarkably with concentration variations for the following reason, briefly stated in the Introduction: Because the transport numbers (\bar{t}_i) obtained by using Eq. (2) are related to the values (t_i) calculated from Eq. (1) as in

$$\bar{t}_i = \int_1^{\text{II}} t_i \, d \ln a_i$$

we can say that \bar{t}_i is a kind of average value. Therefore the remarkable variations of transport numbers (t_i) of polyelectrolyte with concentrations are not found when using Eq. (2), and also \bar{t}_i varies with concentrations of standard solutions.

The decreasing tendency of l_{Na^+} with the decrease of the concentration of polyelectrolyte solution cannot be explained by any theory of polyelectrolyte so far published. Nevertheless this abnormal behavior of l_{Na^+} as shown in Fig. 9 is doubtless a remarkable feature of counter ion in polyelectrolyte solution, since the decreasing tendency of other characters (i.e. activity coefficient and osmotic pressure coefficient) of counter ion with dilution of the solution can be independently observed in the same sample solution. The observed values of activity coefficient (r_{Na^+}) and osmotic pressure coefficient (g), as will be described in a paper to be published, are shown in Fig. 9 along with the curves of l_{Na^+} and $l_{\text{P-Z}}$. There f_{Λ, Na^+} is the conductivity coefficient of counter ion, i.e., the ratio of the observed ionic conductance l_{Na^+} to the limiting value $l_{\text{Na}^+}^0$ in simple electrolyte solution. Fig. 9 shows that there is a relationship between f_{Λ, Na^+} , r_{Na^+} and g , as follows:

$$f_{\Lambda, \text{Na}^+} > r_{\text{Na}^+} > g$$

On the contrary, it is well known that the relationship observed in simple electrolyte solution is as follows:

$$g > f > r$$

It seems to us that one of the most important problems in the study of polyelectrolyte solution is to make clear the origin of this feature of polyelectrolyte.

Because of the impossibility of neglecting the second term of Eq. (5) in the very dilute solution where t_{Na^+} is very small, it is extremely difficult to predict the behavior of l_{Na^+} and $l_{\text{P-Z}}$ in a more dilute solution than used in the present experiment. Naturally, the prediction of their limiting values extrapolated to the infinite dilution is also impossible despite their importance to the progress of the theory.

Experiments on the influence of different kinds of counter ion or charge density of polymer ion upon the transport number of polyelectrolyte are now being planned.

V. Summary

The ionic conductances of polymer ion and counter ion in sodium polyvinyl sulphate solutions were determined by combining the equivalent conductance and the transport number of the polyelectrolyte measured by the diffusion potential method. It was observed that the ionic conductance of the counter ion decreased with dilution of the polyelectrolyte solution, in absolute contrast to the behavior of simple electrolyte.

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