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APPARENT MOLAL VOLUMES OF POLYETHYLENIMINE HYDROCHLORIDE AND ITS OLIGOMERS IN DILUTE AQUEOUS SOLUTION

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The apparent molal volumes of polyethylenimine hydrochloride and its low-molecular-weight analogues have been measured as a function of concentration at 25°C. The partial molal volume of monomer unit increases with increasing the molecular weight of the polysalts. This has been interpreted in terms of two types of the overlapping of the electrostrictional effect on water molecules.

The volumetric behavior of polyelectrolytes in aqueous solution can provide information concerning polyion-water interactions. In order to make clear the nature of this interactions in detail, it may be important to compare the volumetric behavior of polyelectrolytes with that of simple electrolytes. Recently the apparent molal volumes of polyethylenimine hydrobromides and its low-molecular-weight analogues have been measured by Lawrence and Conway.1)

In this communication we describe some results of the apparent molal volumes of polyethylenimine hydrochloride (PEI·HCl) and its oligomers, i.e., hydrochlorides of ethylenediamine (ED·2HCl), diethylenetriamine (DT·3HCl), triethylenetetramine (TT·4HCl) and tetraethylenepentamine (TP·5HCl), in dilute aqueous solution at 25°C. The molecular weight of PEI·HCl is about 4000. The densities of the solutions were obtained by a float method2) similar to that used by Desnoyers and Arel.3) The volume of the float is about 100 ml, and the temperature of the solution cell was controlled to 25 ± 0.001°C. The precision of the densities determined by this apparatus is believed to be better than 1 part in 10^6. All measurements were made under nitrogen atmosphere.

The apparent molal volume, φ_v, was calculated from the equation

$$\varphi_v = \frac{1000}{mdd_o}(d_o - d) + \frac{M}{d} \qquad (1)$$

where d_o is the density of water, d is that of the solution, M is the molecular weight of the solute and m is its molality.

In Figs. 1 and 2 the values of φ_v of PEI·HCl and its oligomers were plotted as a function of molar concentration, c (open circles). These substances tend to hydrolyze to some extent in dilute solutions except for ED·2HCl. For its correction φ_v was calculated by the following equation;

$$\varphi_V(\text{salt}) = \varphi_V(\text{exp}) + h\{\overline{V}^o(\text{salt}) - (\overline{V}^o(\text{base}) + \overline{V}^o(\text{HCl}))\}$$
$$= \varphi_V(\text{exp}) + h\Delta V \qquad (2)$$

where φ_V(salt) is the apparent molal volume of completely dissociated polyimine hydrochloride, φ_V(exp) is that of the hydrolized polysalt measured directly, $\overline{V}^o$(salt), $\overline{V}^o$(base) and $\overline{V}^o$(HCl) are the partial molal volumes of the polysalt, free polyimine and hydrochloric acid respectively at infinite dilution, h is the degree of hydrolysis, and ΔV represents a volume change accompanying the ionization reaction at infinite dilution. The values of h were determined by the pH measurements of the solutions. The values of φ_V(salt) and $\overline{V}^o$(salt) were estimated by a successive approximation method as follows. At first $\overline{V}^o$(salt) was obtained roughly from the extrapolation of φ_V(exp) values to an infinite dilution by neglecting the rapidly increasing region of φ_V(exp) in very low concentration. From this $\overline{V}^o$(salt) value and the values of $\overline{V}^o$(base) and $\overline{V}^o$(HCl) found in the literatures, ΔV was calculated, and φ_V(salt) can be obtained from Eq.(2). The calculated values of φ_V(salt) were plotted as a function of concentration and then $\overline{V}^o$(salt), therefore ΔV, were obtained more accurately. By repeating this process until the constant value of ΔV is obtained, one can estimate the plausible values of φ_V(salt) and $\overline{V}^o$(salt). The error in the determination of $\overline{V}^o$(salt) seems to be ±0.5 ml/mole because of the uncertainty in h at very low concentration and because of the obscurity of the concentration dependence of φ_V as will be mentioned later. The filled circles in Figs. 1 and 2 represent φ_V(salt) values estimated by this method.

Table 1. The volume change for the ionization reaction (ml/mole)

$H_2N(CH_2CH_2NH)_{n-1}H + nHCl \longrightarrow ClH_3N(CH_2CH_2NH_2Cl)_{n-1}H$

	$\overline{V}^o$(salt)	$\overline{V}^o$(base)[a]	n × $\overline{V}^o$(HCl)[b]	ΔV	$\Delta V/n$
ED·2HCl	80.3±0.5	63.1±0.4	35.6	− 18.4±0.9	− 9.2
DT·3HCl	125.8±0.5	101.2±0.4	53.4	− 28.8±0.9	− 9.6
TT·4HCl	177.6±0.5	137.6±0.5	71.2	− 31.2±1.0	− 7.8
TP·5HCl	232.3±0.5	175.9±0.6	89.0	− 32.6±1.1	− 6.5
PEI·HCl	56.3±0.5[c]	38.0[c]	17.8	+ 0.5±0.5[c]	

a) Reference 1. b) Reference 4. c) values in ml/monomole

The calculated values of $\overline{V}^o$(salt) and ΔV are summarized in Table 1. The values of $\Delta V/n$ in the last column of this table refer to the volume changes accompanying the ionization reactions of the monomer units of the polysalts. Therefore these values may indicate the extent of the volume contraction per monomer unit by the electrostriction of water around the oligomeric polyelectrolytes. In the case of ED·2HCl and DT·3HCl, $\Delta V/n$ values are larger than those of ammonium chloride (−6.8 ml/mole) or ethylamine hydrochloride

(3)

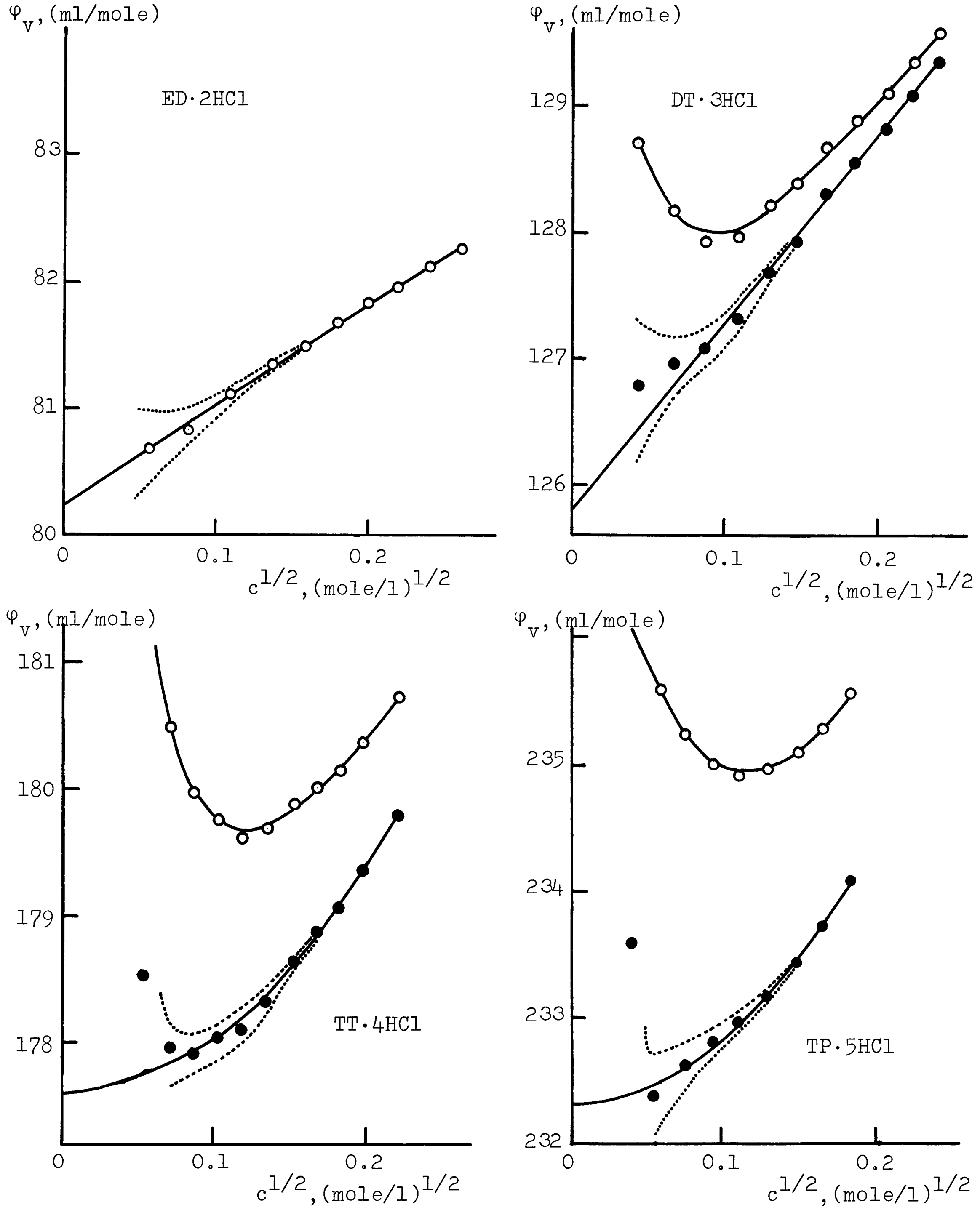

Fig. 1. $\varphi_v(c^{1/2})$ plots for ED·2HCl, DT·3HCl, TT·4HCl and TP·5HCl at 25°C. In these figures and in Fig. 2, the dotted lines are the range of uncertainties in φ_v values corresponding to the errors of ±1 p.p.m. in density measurements.

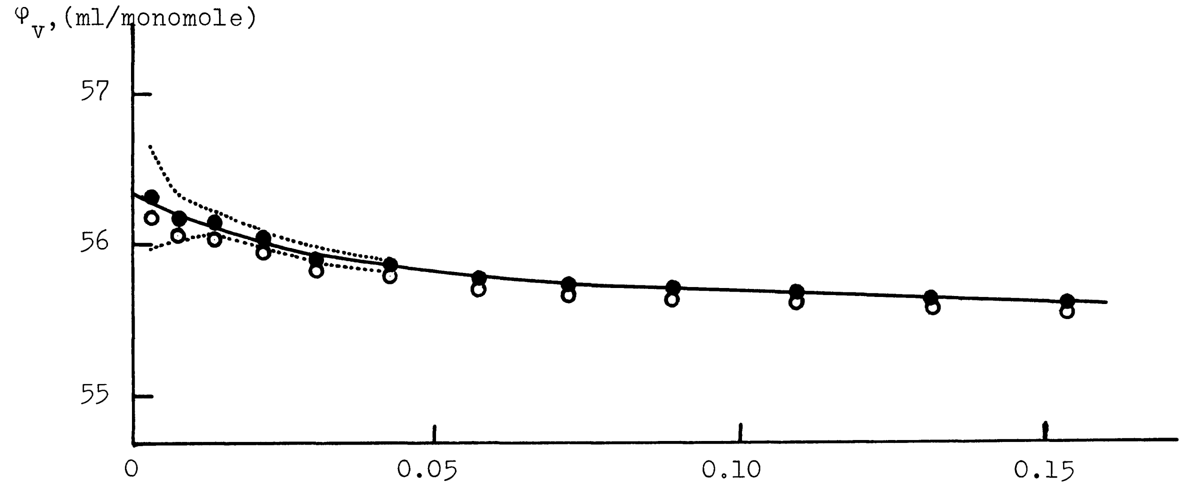

Fig. 2. $\varphi_v(c)$ plot for PEI·HCl at 25°C.

(− 3.6 ml/mole).5) As the molecular weight of the polysalts increases, the volume change accompanying the ionization decreases, and finally reaches almost zero in the case of PEI·HCl. This result may suggest that the electrostriction reduces with increasing the molecular weight of these salts.

In order to obtain further information concerning the solvation of polyelectrolytes, the partial molal volume of the monomer unit at infinite dilution, $\overline{V}^o(CH_2CH_2NH_2Cl)$, was obtained as the difference of $\overline{V}^o$(salt) values of successive homologues. This result is given in Table 2. It is shown that $\overline{V}^o(CH_2CH_2NH_2Cl)$ values are much smaller than $\overline{V}^o$ of ethylamine hydrochloride (70.4 ml/mole7)). This may indicate that these polysalts exhibit much larger electrostrictional effect than the simple 1-1 electrolytes. On the other hand, the fact that $\overline{V}^o(CH_2CH_2NH_2Cl)$ increases with the increase in the molecular weight may suggest the decrease of the extent of the volume contraction by the electrostrictional effect. These results are consistent with the result of volume change in the ionization reaction.

Table 2. The partial molal volume of $CH_2CH_2NH_2Cl$ group (ml/mole)

$\overline{V}^o$(PEI·HCl)	56.3±0.5[a]
$\overline{V}^o$(TP·5HCl) − $\overline{V}^o$(TT·4HCl)	54.9±1.0
$\overline{V}^o$(TT·4HCl) − $\overline{V}^o$(DT·3HCl)	51.8±1.0
$\overline{V}^o$(DT·3HCl) − $\overline{V}^o$(ED·2HCl)	45.5±1.0
$\overline{V}^o$(ED·2HCl) − $\overline{V}^o(NH_4Cl)$[b]	44.0±0.5

a) value in ml/monomole b) Reference 6.

Thus the following two remarks are deduced from our volumetric study;

(1) If two or more charges are fixed to a hydrocarbon chain separated each other by an appropriate distance, it is recognized that the extent of the volume contraction by the effect of electrostriction is much larger than that in the simple 1-1 electrolytes.

(2) The increase in the degree of polymerization brings about the expansion of the volume of the monomer unit of the polyelectrolyte.

The effect (1) has been examined in detail by Kauzmann, et al.,$^{5)}$ who attributed this effect to the overlap of the electrostatic field and stated it as the "reinforcing effect" on the electrostriction.

For the effect (2), we propose a tentative interpretation in terms of counterion binding. The fractions of counterions bound to PEI·HCl and TP·5HCl are about 0.5 and 0.1 respectively according to the measurements of the tracer diffusion coefficient of the counterion by Lapanje, et al.$^{9)}$ There is no direct evidence of the counterion binding in the case of the other oligomeric salts. It can, however, be expected that the counterions are bound in some sense to these cations, if we remember the fact that the degree of counterion binding determined by such a diffusion method is usually much smaller than that estimated by thermodynamic methods (e.g., activity coefficient). When anions approach to a polycation, the overlap of the electrostriction may also here take place. In this case, however, the overlapping of the electrostriction by anion and polycation may not produce the "reinforcing effect" but may tend to weaken each electrostriction, because the circumstance of the orientation of water molecules around anion may be different from that around cation. Thus the occurrence of counterion binding cancels out to some extent the large volume contraction due to the reinforcing effect on electrostriction.

It is interesting to compare the concentration dependence of φ_v of these polysalts. In Fig. 1 φ_v values are plotted against $c^{1/2}$ for four oligomeric salts. Good linearities with positive slopes were obtained for ED·2HCl and DT·3HCl solutions. This indicates that the φ_v behavior of these salts in water accords apparently with the results of the Debye-Hückel theory, though the slopes (7.4 and 14.6 for ED·2HCl and DT·3HCl respectively) are smaller than the limiting slopes for 2-1 and 3-1 electrolytes (9.706 and 27.453 at 25°C respectively$^{4)}$). For TT·4HCl or TP·5HCl, however, it seems that a linear behavior is observed when φ_v values are plotted against c rather than against $c^{1/2}$. Therefore the values of $\overline{V}^o$(salt) for these salts were determined by the extrapolation of $\varphi_v(c)$ to an infinite dilution.

It is noticeable that φ_v decreases gradually with increasing concentration for PEI·HCl. As a rule, φ_v values of many polyelectrolytes have been found to be almost independent of the concentration by Ise and Okubo.$^{10)}$ They interpreted this behavior as a result of a delicate balance of two counteracting effects, that is the hydrophobic effect, which tends to decrease φ_v with the increase of concentration and the electrostrictional effect, which tends to increase φ_v when concentration increases. The latter effect is due to the reduction of the constrictive effect per ion with increasing concentration because of the overlapping of already electrostricted region of water around ions. This consideration is analogous to the one which was given above in discussing the effect (2), and therefore one should bear in mind that in polyelectrolyte solutions these overlapping of the electrostriction may take place more or less even in very dilute solutions owing to the counterion binding. On the other hand the hydrophobic effect may not be observed in such solutions as PEI·HCl, since the appearance of this effect in electrolyte solutions is limited to such a case that the charge is completely masked by large hydrophobic groups, as in tetraalkylammonium halide solutions. Thus the concentration dependence of φ_v of polyelectrolytes may not necessarily be interpreted along the theories proposed in the cases of simple electrolytes.

At present, we can not explain thoroughly the concentration dependence of φ_v of PEI·HCl solution. We consider that the φ_v behavior of polyelectrolyte solutions is largely influenced by the overlap of the electrostrictional effect, as was described above. Therefore it is proposed that the concentration dependence of φ_v is related to the configurational change of the polymer chain and also to the change of the degree of counterion binding with increasing concetration, since both are accompanied by the change of the overlapping of the electrostriction of water around the polymer chain.

In order to elucidate these points, we are now preparing to measure φ_v of the other polyelectrolytes as a function of concentration, degree of neutralization and temperature.

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