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[389]

ON THE HYDRATION OF SIMPLE IONS AND POLYIONS

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CONTENTS

Hydration of polymeric ions is investigated by examination of salting-out behaviour in relation to dielectric saturation effects and to the significance of partial molal volumes of polysalts.

The validity of previous distribution theories of salting-out is examined and limitations are shown to arise from an unjustified expansion of an exponential distribution factor, and neglect of solvent dielectric saturation effects in the primary solvation shell of the ion where, relatively, the maximum salting-out effect is developed. A new theory is proposed, as a basis for extension to the case of polyions, in which the calculation of the salting-out behaviour is carried out over two regions: (*a*) in the primary hydration shell where a high degree of solvent dielectric saturation prevails and the exponential distribution function must be retained, and (*b*) beyond the primary region where weaker polarization occurs and Kirkwood's theory of dielectrics can be applied. Comparison of the predictions of various forms of the salting-out equation with experimental data is made.

Comparative calculations of the variation of solvent dielectric constant with distance from ions of various geometries have been carried out. The cases examined are those for simple spherical ions, linear polyions and planar colloidal ions having various charge densities. The dependence of solvent dielectric constant on distance from the ions enables a semi-empirical primary hydration radius r_d to be evaluated.

Values of r_d for various simple and polymeric ions are examined in relation to salting-out by polyions and their corresponding monomers and in relation to hydration radii deduced by other methods. In the case of the polyions and planar ions, the extent to which increasing charge density causes increased dielectric saturation can be evaluated.

Experimental studies on hydration of polyions and corresponding monomer salts have been carried out by examination of the salting-out of selected non-electrolytes by the polysalts, and by partial molal volume measurements. The effect of variation of the degree of neutralization or charge density has been examined; in general, it is found that the salting-out and partial molal volume behaviour varies with degree of ionization in the expected manner but differs from the corresponding behaviour of the monomer salts owing to stronger electrostriction effects due to condensation of the ionic charge into a chain configuration.

The results are examined in relation to the dielectric saturation calculations for polyions, and theoretical salting-out equations are developed for the polyion case, and applied to the present experimental results. The partial molal volume data for the same materials lead to complementary information on the effective hydration radius and solvation numbers of the polysalts.

1. INTRODUCTION

The subject of hydration of simple ions has been previously examined in many papers (e.g. Bernal & Fowler 1933; Frank & Evans 1945; Stokes & Robinson 1948; Conway & Bockris 1954; Azzam 1960) and by ourselves (Desnoyers & Conway 1964) with reference to the significance of hydration numbers and radii deduced from partial ionic volumes and ionic mobilities. The subject is of some general importance with regard to (a) the thermo-dynamics of electrolytes at moderate and high concentrations; (b) the kinetics of ionic reactions; and (c) the properties of the partially ionic transition state involved in most solvolytic reactions.

Very little work has been done with regard to examination of the hydration of polyions, although the statistical electrostatic problem of polyion configuration and gegen-ion inter-action has been extensively studied. Hydration effects will be important in interactions of polyions with counter-ions and small molecules and with regard to the ionization of polyacids and polybases.

In the present paper, we first examine new aspects of the role of hydration in salting-out by simple ions and use the principles developed to formulate a theory of salting-out for polymeric ions, the behaviour of which is studied experimentally with regard to: (a) partial molal volumes and (b) salting-out of selected non-electrolytes. A complementary theoretical approach is also made through calculation of dielectric saturation effects at simple and polymeric ions.

2. CRITICAL APPRAISAL OF PREVIOUS THEORIES OF SALTING-OUT

In thermodynamic terms, the equilibrium saturation solubility of a non-electrolyte is changed from a value S_0 in the absence of a salt to S in the presence of a salt, if the activity coefficient γ of the non-electrolyte is changed. Thus, in general,

$$\gamma_0 S_0 = \gamma S. \tag{2.1}$$

Usually γ_0, corresponding to S_0, is taken as unity so that $\gamma = S_0/S$. The problem is hence the evaluation of γ, or of the corresponding electrostatic non-ideal free-energy contribution, $RT \ln \gamma$. Usually γ is greater than unity since the solvent activity is decreased by interaction with the ions of the dissociated salt. Electrostatic theories of salting-out have been given previously by Debye & McAulay (1925) in terms of the dielectric increments for salt and non-electrolyte and by Butler (1929a) in terms of molecular polarizabilities and volumes of non-electrolyte and solvent. Subsequent theories (Debye 1927; Belton 1937; Gross 1933;

Albright & Williams 1937; Bockris, Bowler-Reed & Kitchener 1951) are modifications or improvements of these basic approaches. A more thermodynamic approach has been given by McDevit & Long (1952). None of these theories is entirely satisfactory. The equations deduced below are derived formally by the method of Debye (1927), but important improvements will be introduced by taking into account the following factors not previously examined or treated in quantitative detail:

(a) dielectric saturation effects;

(b) the existence of a discrete primary hydration shell about the ions, and

(c) relation between dielectric constant and molecular parameters (dipole moment, polarizability, molar volume) according to Kirkwood's theory of dielectrics.

3. New aspects of the theory of salting-out by simple ions

The energy U stored in an element of volume dV of a medium of dielectric constant ϵ, subject to the action of an electrical field E is given (Böttcher 1952) by

$$dU = (\epsilon E^2/8\pi)\, dV. \tag{3·1}$$

The distribution of solute and solvent about the ion is calculated by using a distribution equation

$$dn_2 = S_0 \exp{-[\varDelta U/kT]}\, 4\pi r^2\, dr, \tag{3·2}$$

where n_2 is the number of non-electrolyte molecules in a spherical volume element of thickness dr at a distance r from the ion, and S_0 is the solubility in the absence of the salt; the energy $\varDelta U$ arises from the difference of the energy of the ion when the dielectric constant is changed from ϵ_0 in the absence of non-electrolyte to ϵ when it is present. From electrostatic theory (Debye 1927), $\varDelta U$ is obtained as

$$\varDelta U = \frac{1000 z^2 e^2}{8\pi r^4}\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_0}\right)\frac{1}{NS}\ \text{ergs molecule}^{-1}. \tag{3·3}$$

Integration of (3·2) over spherical volume elements from $r = a$, the ionic radius, to $r = R$ (a critical radius corresponding to the volume available per ion in the solution, and defined by

$$R = (3000/4\pi Nm)^{\frac{1}{3}}, \tag{3·4}$$

where m is the g. ionic concentration) then gives the relative change of solubility $(S_0 - S)/S_0$ as

$$\frac{S_0 - S}{S_0} = \frac{4\pi Nm}{1000}\int_a^R (1 - \exp{[-\varDelta U/kT]})\, r^2\, dr. \tag{3·5}$$

Usually (Butler 1929a; Bockris et al. 1951) the exponential in $\varDelta U$ is expanded to its linear term and a simple result is obtained for the salting-out ratio* defined as $(S_0 - S)/S_0 m$. This procedure is, however, quite unjustified since with small ions in water $\varDelta U$ is usually not small in comparison with kT near the ions where relatively the biggest salting-out effect is to be expected. The linear expansion causes the calculated value of the salting-out ratio to be seriously in error as we shall show subsequently. $\varDelta U$ is difficult to evaluate satisfactorily and for many simple solutes, e.g. gases, the dielectric decrement $\epsilon_0 - \epsilon$ is not easily obtained. Butler's treatment (1929a) is easier to use since the $\varDelta U$ is expressed in terms of more accessible

* When $m \to 0$, the salting-out ratio, which is normally a function of ionic concentration, is termed the salting-out constant and will be represented by k_s.

392 B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

molecular quantities. However, the theory formulated is really only applicable to the idealized situation of salting-out of non-polar solutes in a non-polar solvent.

In the present treatment, we shall relate $\epsilon_0 - \epsilon$ to the molecular properties of the system following the method discussed by Long & McDevit (1952) but Kirkwood's theory of dielectrics will be used rather than Onsager's as they suggested.

Equation (3·3) may be written in terms of the ionic field $E(= -ze/\epsilon_0 r^2)$ as

$$\Delta U/kT = \frac{1000E^2}{8\pi kT} (\epsilon_0 - \epsilon) \frac{1}{NS} \tag{3·6}$$

assuming $\epsilon_0 \epsilon \doteqdot \epsilon_0^2$.

When the dielectric constant ϵ of a solution is high compared with the optical dielectric constant of the solvent ϵ_∞, it may be shown (Edsall & Wyman 1958), by using a limiting case of Kirkwood's theory of dielectrics, that

$$1000(\epsilon_0 - \epsilon)/S = V_2 \epsilon_0 - \tfrac{9}{2} P_2, \tag{3·7}$$

where V_2 is the molar or partial molar volume of the non-electrolyte and P_2 is the total molar polarization of the non-electrolyte, defined by

$$P_2 = \tfrac{4}{3}\pi N(\alpha_0 + \mu\bar{\mu}/3kT). \tag{3·8}$$

In this equation, α_0 is the polarizability and μ the moment of the individual non-electrolyte molecules in solution and μ the vector sum of the moment of the central molecule plus that of all the neighbours which may affect its orientation. For non-associated polar molecules, $\mu\bar{\mu}$ may be related to μ_0, the moment of the molecule in the gaseous state, by Onsager's theory as

$$\mu\bar{\mu} = \tfrac{1}{9}(n^2 + 2)^2 \mu_0^2, \tag{3·9}$$

where n is the refractive index of the molecule.

When the left-hand side of equation (3·7) is substituted in equation (3·6), the energy function becomes

$$\Delta U/kT = (E^2/8\pi kTN)(V_2 \epsilon_0 - \tfrac{9}{2} P_2). \tag{3·10}$$

The salting-out of a non-electrolyte by an ion may hence be predicted if the size of the ion, the molar volume and the polarization of the non-electrolyte are known. However, it must be noted that the approximate form of the Kirkwood theory used in this derivation is only valid when the electric field is low, so that equation (3·10) cannot be applicable close to the ions, as will be discussed further below.

A relation similar to equation (3·5) with the energy ΔU given by equation (3·10) can predict (see McDevit & Long 1952) the correct dependence of the salting-out constant k_s on the nature of the non-electrolyte but fails to explain the marked variation of k_s for different types of ions. Such a theory represents fairly well the situation existing at intermediate distances and far from the ion but cannot be at all reliable in the immediate vicinity of most simple ions for the following reasons:

(a) The dielectric constant near the ion is usually much lower than that of the pure solvent, owing to saturation effects to be examined in §8.

(b) Equation (3·7) is not valid in the region near the ion where the field intensity is very high.

(c) Important interactions in the vicinity of the ion (ion-dipole, ion-quadrupole, dipole-dipole) are not considered in detail, i.e. the primary hydration of the ion by the solvent near the ion should preferably be taken into account. Primary solvation effects (Bockris 1949) may be introduced by correcting the field in the salting-out equation for the effect of dielectric saturation.

In the first case, let us assume that $\Delta U/kT$ is small compared with unity; then, as in Butler's treatment (1929), the salting-out ratio is obtained approximately as

$$\frac{S_0-S}{S_0 m} = \frac{4\pi N}{1000}\int_a^R (\Delta U/kT)\, r^2\, \mathrm{d}r, \qquad (3\cdot11)$$

and substituting for E in equation $(3\cdot10)$ gives

$$\frac{S_0-S}{S_0 m} = \frac{4\pi N}{1000}\int_a^R \frac{z^2 e^2}{8\pi k T N \epsilon^2}\left(V_2\epsilon_0 - \tfrac{9}{2}P_2\right)\frac{1}{r^2}\,\mathrm{d}r, \qquad (3\cdot12)$$
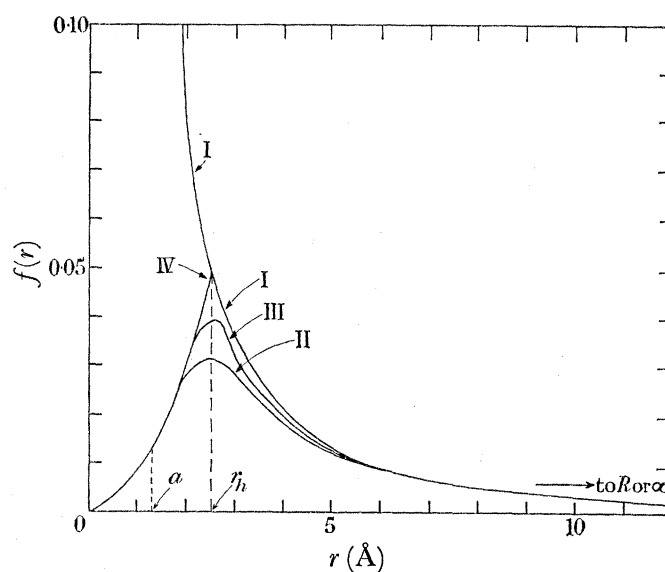

FIGURE 1. The salting-out function $f(r)$ for various equations and models. Curve I, approximate equation $(3\cdot13)$; II, equation $(3\cdot14)$; III, equation $(3\cdot14)$ with dielectric saturation effects considered; IV, finite limit $(2\cdot6\ \text{Å})$ of primary hydration shell taken into account.

If a graphical solution is required (e.g. when a field-dependent dielectric constant is considered) it is necessary to plot $f(r)$ against r, where

$$f(r) = \frac{z^2 e^2}{2000\epsilon^2 kT}\left(V_2\epsilon_0 - \tfrac{9}{2}P_2\right)\frac{1}{r^2}\ \text{l. mole}^{-1}\,\text{cm}^{-1}. \qquad (3\cdot13)$$

This function is plotted as curve I in figure 1 for the case of salting-out of benzene by a monovalent ion. Benzene was chosen as a typical non-electrolyte for this calculation because it is large [molar volume $89\cdot4\,\text{ml. mole}^{-1}$, McDevit & Long (1952)] compared with the solvent, is spherical and non-polar. The polarization term P_2 is small for this molecule (and most non-polar solutes) in comparison with $V_2\epsilon_0$ for the water solvent. The term $(S_0-S)/S_0 m$ is then equal to the area under the curve from $r=a$ to $r=R$, or from a to infinity when $m\to 0$ and $[(S_0-S)/S_0 m]_{m=0} = k_s$.

From figure 1 it is easy to see why the approximate equation (3·12) fails with small ions. This equation* (cf. Butler 1929 a; Bockris *et al.* 1951) predicts that an infinitesimally small ion would be associated with an infinite salting-out constant. If this equation was corrected for the effect of dielectric saturation near the ion, the situation would be even worse since the field would be higher at small values of r. This equation is thus satisfactory only for quite large ions and cannot be valid for most inorganic ions with crystal radii less than *ca.* 3 Å.

If we do not expand the exponential in the salting-out equation, then $f(r)$ is given by

$$f(r) = (4\pi N/1000)\,(1 - \exp\,[-\varDelta U/kT])\,r^2 \qquad (3\cdot14)$$

instead of by (3·13), and is represented as curve II in figure 1; $f(r)$ does not tend to infinity but rather to zero as the distance r tends to zero. Hence, the main objection to the approximate equations used in previous work is now removed. In addition, if we take the dielectric constant as a function of the field intensity (see § 8) instead of as a constant everywhere, i.e. if we use the integral dielectric constant as a function of distance in the field relation, the maximum in the function $f(r)$ is raised to higher values and shifted to larger values of r (see curve III, figure 1), so that k_s will be increased. This correction is in the right direction since the theory of Debye (1927) usually predicts values of k_s which are too small. It is clear that dielectric saturation will usually be an effect of primary importance in aqueous salting-out since if the field due to the ion is strong enough to cause appreciable salting-out, it must also usually cause appreciable dielectric saturation. This important fact has not been recognized in previous theories of salting-out.

The maximum in the function $f(r)$ is a result of two effects: $f(r)$ increases as the volume around the ion increases with increasing r and decreases exponentially due to the Boltzmann distribution assumed. The maximum in curve III of figure 1 corresponds to a distance of about 2·6 Å from the centre of the ion. It is apparent from this graph that the region between the radius a of the ion and the distance where the maximum in $f(r)$ occurs can contain only solvent molecules, i.e. the non-electrolyte molecules are completely salted-out in this region. Hence the distance at which $f(r)$ has a maximum value should approximately correspond to the radius r_h of the primary hydration shell of the ion; we have, in fact, shown elsewhere (Desnoyers & Conway 1964) from density and mobility data that the radii of hydrated monatomic univalent ions vary between 2·3 and 2·8 Å, i.e. in agreement with the distance associated with the maximum in figure 1.

This theoretical treatment implies that the maximum in $f(r)$ should be relatively independent of the nature (except for the charge) of the ions, but should vary to some extent with the nature of the non-electrolyte. This follows since the dielectric saturation corrections do not take into account the specific properties of the ions or the finite size of the water molecules in the immediate vicinity of the ions. More exactly the maximum would depend to some extent on the specific nature of the ion-solvent interactions and hence vary somewhat from ion to ion. Therefore the model and assumptions made in the derivation of

* Similar difficulties arise in Butler's theory (1929 b) of adsorption of molecules at electrodes where the main polarization term is associated with the orientation of the solvent in the case of aqueous solutions. However, this theory gives quite good agreement with experiment for adsorption of organic substances at the mercury electrode.

equation (3·5) do not allow us to calculate in general the extent of primary hydration from salting-out data. However, the salting-out equation can be improved by taking into account the primary hydration shell around the ions, as follows.

Two regions may be considered in the vicinity of an ion. In the primary hydration shell only field-oriented water molecules are present, so that the dielectric constant may be assumed small. Consequently $\Delta U/kT$ is large and $\exp(-\Delta U/kT)$ is small compared with unity in equation (3·5) or (3·14). Beyond the primary hydration shell $\Delta U/kT$ is small compared with unity owing to the rapid rise of ϵ with increasing distance from the ion (see §8); hence the exponential in equation (3·14) may be expanded, retaining only the first term of the series. Thus, the integration of the salting-out equation may be carried out conveniently over two integrands; from a to r_h where $\epsilon \ll \epsilon_0$ and from r_h to R where $\epsilon \approx \epsilon_0$ (or to $r = \infty$ when $m \to 0$); equation (3·14) then becomes

$$f(r) = \frac{4\pi N}{1000}\left\{[r^2]_a^{r_h} + \left[\frac{\Delta U}{kT}r^2\right]_{r_h}^R\right\}, \tag{3·15}$$

from which it can be seen that the limit r_h of the primary hydration shell is one of the critical factors determining k_s and a close relation should hence exist between the geometry of the primary hydration shell and the degree of salting-out caused by the ions.

The salting-out equation corresponding to equation (3·15) is

$$\frac{S_0 - S}{S_0 m} = \frac{4\pi N}{1000}\left\{\int_a^{r_h} r^2\, \mathrm{d}r + \int_{r_h}^R (\Delta U/kT)\, r^2\, \mathrm{d}r\right\}. \tag{3·16}$$

The field term in ΔU may be taken as $-ze/\epsilon_0 r^2$ for $r > r_h$ ($\epsilon \to \epsilon_0$) and, after integration, equation (3·16) becomes

$$\frac{S_0 - S}{S_0 m} = \frac{4\pi N}{3000}(r_h^3 - a^3) + \frac{z^2 e^2}{2000 kT\epsilon_0^2}(V_2\epsilon_0 - \tfrac{9}{2}P_2)\left[\frac{1}{r_h} - \frac{1}{R}\right]. \tag{3·17}$$

This equation eliminates the difficulty of using Kirkwood's relation (3·7) in a region ($r < r_h$) of high field intensity where it would be invalid. Thus, the second term in (3·17), derived from Kirkwood's theory, refers to the salting-out effect beyond $r = r_h$ where the field is relatively low on account of the appreciable distance from the ion and because the dielectric constant is much nearer its bulk value than in the region $a < r < r_h$ (see §8).

The first term of equation (3·17) is proportional to the amount of water held in the primary hydration shell, i.e. the volume of the hydrated ion less that of the ion itself. We have shown elsewhere (Desnoyers & Conway 1964) that the correct effective volume of a dissolved spherical ion is only the geometrical spherical volume if the radius r of the sphere is much larger than that of the solvent molecules (or the solvent is 'continuous'), otherwise the dead space around the particles must be taken into account. The volume of most ions is comparable with that of water molecules so that the first term of equation (3·17) will underestimate the effect of the primary hydration term in k_s. This difficulty may be avoided by expressing the first term of equation (3·17) in a different but equivalent way. Salting-out by ions can be regarded as essentially determined by the extent of primary hydration of the ions, in so far as the water involved in the primary hydration shell is

effectively removed from its normal solvent role. Therefore, ignoring electrostatic considerations for the time being, the solubility of the non-electrolyte is proportional to the amount of 'free water' available to dissolve it (Eucken & Herzberg 1950), i.e.

$$\frac{S}{S_0} = \frac{55 \cdot 5 - nm}{55 \cdot 5}, \tag{3.18}$$

where n is a primary hydration number (Conway & Bockris 1954) and m the molality. If the concentration is expressed in terms of molarities then the salting-out equation, corresponding to solvent removal in the primary hydration shell only, becomes

$$\frac{S_0 - S}{S_0} = \frac{18nm}{1000d - mW}, \tag{3.19}$$

where d is the density of the salt solution and W the molecular weight of the dissolved salt. The term on the right-hand side of this equation is equivalent to the first term of equation (3.17) but has the advantage of not involving any assumption about the particular extent (in terms of r_h) of the primary hydration shell. The salting-out equation may therefore be rewritten in the form

$$\frac{S_0 - S}{S_0 m} = \frac{18n}{1000d - mW} + \frac{z^2 e^2 [V_2 \epsilon_0 - \frac{9}{2} P_2]}{2000kT\epsilon_0^2} \left[\frac{1}{r_h} - \frac{1}{R} \right], \tag{3.20}$$

which gives k_s as $m \to 0$, $R \to \infty$ and $d \to d_0$ the density of pure solvent.

The present treatment clarifies the molecular picture of salting-out; the first term of equations (3.17) or (3.20) takes into account strong ion-solvent interactions associated with the primary solvation shell of the ion, where dielectric saturation effects are important, and is, to a first approximation, independent of the nature of the non-electrolyte. For most ions, this term would always contribute a salting-out effect. The second term depends mostly on the nature of the non-electrolyte and may lead *either* to salting-out *or* salting-in, depending on V_2 and P_2.

The relative salting-out $(S_0 - S)/S_0$ evaluated from equation (3.17), where the primary hydration term is expressed as a function of r_h rather than of n, leads to values of k_s that are all smaller than those calculated from equation (3.20) by a quantity which is constant for each pair of ions. The reason for this discrepancy is probably associated with the neglect of the finite size of the solvent molecules in the derivation of the salting-out equation, in comparison with the size of the ion, as discussed above (p. 395). If the finite size of the solvent molecules around the hydrated ions were taken into account in the derivation of equation (3.17), a term approximately equal to $3 \cdot 15 r^2 / 1000$ would have to be added to allow for dead space in the primary hydration sphere. For most alkali halides, this contribution to k_s is of the order 0·025 to 0·035 and is approximately equal to the difference between the predictions of the two theoretical equations (3.17) and (3.20) for a given ion. Since in equation (3.20) this problem is avoided, equation (3.20) is to be preferred to equation (3.17).

4. COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES OF k_s

In order to examine the validity of equation (3.17), we have calculated values of k_s (tables 1 and 2) for the salting-out of rare gases and other neutral molecules by the alkali halides. The values of r_h and n required for the theoretical evaluation of k_s were obtained

TABLE 1. THEORETICAL AND EXPERIMENTAL SALTING-OUT CONSTANTS

system	eqn. (3·12) (linear approx.)	eqn. (3·17) (density data*)	eqn. (3·20) (density data*)	eqn. (3·20) (mobility data*)	eqn. (5·1) (McDevit & Long)	expt.	ref.*
helium ($V_2 = 7\cdot7$)							
NaCl	0·056	0·079	0·116	0·185	0·082	0·186	1
LiCl	0·066	0·062	0·091	0·207	0·059	0·115	1
NaBr	0·044	0·076	0·111	0·176	0·075	0·200	1
KCl	0·044	0·063	0·091	0·152	0·065	0·157	1
KI	0·033	0·051	0·071	0·132	0·037	0·191	1
helium ($V_2 = 26$)							
NaCl	0·180	0·129	0·166	0·235	0·276	0·186	1
LiCl	0·216	0·112	0·141	0·257	0·200	0·115	1
NaBr	0·144	0·126	0·161	0·226	0·250	0·200	1
KCl	0·144	0·113	0·141	0·202	0·220	0·157	1
KI	0·108	0·101	0·121	0·182	0·125	0·191	1
neon ($V_2 = 16\cdot8$)							
NaCl	0·096	0·106	0·142	0·202	0·18	0·223	1
LiCl	0·133	0·093	0·122	0·223	0·13	0·136	1
KI	0·074	0·081	0·100	0·152	0·08	0·184	1
argon ($V_2 = 24\cdot2$)							
LiCl	0·192	0·118	0·145	0·239	0·19	0·221	1
NaCl	0·139	0·128	0·165	0·220	0·27	0·306	1
KI	0·105	0·104	0·124	0·170	0·11	0·249	1
KF	0·129	0·138	0·191	0·232	0·38	0·330	2
krypton ($V_2 = 38\cdot8$)							
LiCl	0·308	0·165	0·193	0·275	0·31	0·267	1
NaCl	0·223	0·172	0·208	0·256	0·43	0·336	1
KCl	0·181	0·161	0·189	0·228	0·33	0·285	1
KBr	0·175	0·158	0·183	0·220	0·27	0·276	1
KI	0·168	0·151	0·170	0·208	0·15	0·276	1
NH$_4$Cl	0·158	0·159	0·171	0·217	—	0·150	1
xenon ($V_2 = 48\cdot6$)							
NaCl	0·278	0·201	0·236	0·281	0·53	0·343	1
KI	0·210	0·182	0·200	0·233	0·22	0·260	1
benzene ($V_2 = 89\cdot5$)							
LiCl	0·708	0·332	0·357	0·396	0·70	0·325	4
NaCl	0·512	0·325	0·358	0·382	0·98	0·449	4
KCl	0·416	0·321	0·346	0·359	0·77	0·382	4
RbCl	0·392	0·321	0·334	0·352	0·73	0·322	4
CsCl	0·365	0·330	0·333	0·344	0·58	0·203	4
NaBr	0·499	0·320	0·352	0·374	0·83	0·357	4
KBr	0·403	0·316	0·340	0·351	0·78	0·274	4
NaI	0·482	0·316	0·342	0·362	0·63	0·219	4
NH$_4$F	0·450	0·348	0·383	0·384	—	0·237	4
NaF	0·570	0·329	0·388	0·418	1·63	0·585	4
naphthalene ($V_2 = 112$)							
NaCl	0·643	0·402	0·425	0·437	1·23	0·599	3
biphenyl ($V_2 = 131$)							
NaCl	0·879	0·406	0·482	0·483	1·43	0·636	3

Notes on table

1. References: (1) Morrison & Johnstone (1955). (2) The present work. (3) Paul (1952). (4) Saylor, Whitten, Clairborne & Gross (1952).

2. Source of molar volume data in column 1 is referred to in text.

3. Values of the parameters r_h and n required for calculations by means of equations (3·17) and (3·20) are listed in table 3 from the paper by Desnoyers & Conway (1964).

398 B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

from partial molal volume and mobility data by principles developed elsewhere (Desnoyers & Conway 1964; see §12). The values of the parameters used are recorded in table 3. In the present calculations, the molar volumes of the non-electrolytes were taken from the

TABLE 2. COMPONENT TERMS IN THE SALTING-OUT CONSTANTS FOR
SELECTED IONS AND NON-ELECTROLYTES (SEE ALSO TABLE 1)

(Calculations based on equation (3·17))

ion*	non-electrolyte	$(k_s)_1$	$(k_s)_2$
Li^+	helium ($V_2 = 7\cdot7$)†	0·026	0·011
Na^+		0·043	0·011
K^+		0·027	0·011
Cl^-		0·012	0·011
Br^-		0·009	0·011
I^-		0·0	0·011
Li^+	argon ($V_2 = 24\cdot2$)	0·026	0·040
Na^+		0·043	0·033
K^+		0·027	0·037
F^-		0·041	0·033
Cl^-		0·012	0·039 (5)
I^-		0·0	0·040
Li^+	benzene ($V_2 = 89\cdot6$)	0·026	0·148
Na^+		0·043	0·124
K^+		0·027	0·136
Rb^+		0·023	0·140
Cs^+		0·017	0·155
NH_4^+		0·006	0·180
F^-	benzene ($V_2 = 89\cdot6$)	0·041	0·121
Cl^-		0·012	0·146
Br^-		0·009	0·144
I^-		0·0	0·149

Notes on table

* Ionic component values are additive at infinite dilution and give the overall values listed in table 1.
† The $(k_s)_2$ values are given for $V_2 = 7\cdot7$. Corresponding values for $V_2 = 26$ ml. will be 3·37 times larger.

TABLE 3. VALUES OF THE PARAMETERS r_h AND n USED IN TABLE 1
(FROM DESNOYERS & CONWAY 1964)

ion	r_h (density) (Å)	n (density)	r_h (mobility) (Å)	n (mobility)
Li^+	2·18	2·6	3·28	7·1
Na^+	2·61	4·0	3·04	5·9
K^+	2·36	2·6	2·72	4·1
Rb^+	2·30	2·1	2·73	3·6
Cs^+	2·27	1·6	2·74	3·2
NH_4^+	1·79	0·6	2·77	3·5
F^-	2·65	4·1	2·96	5·4
Cl^-	2·21	1·1	2·75	3·0
Br^-	2·23	0·8	2·73	2·5
I^-	2·16	0	2·74	1·9

literature whenever possible (e.g. Hildebrand & Scott 1950). When these values were not available, they were calculated from the molecular weight and density of the compound in the solid state since this will give a molecular volume most relevant to the condition of the molecule in solution. The case of helium presents a difficulty. The molar volume from critical data is 7·7 ml. mole⁻¹ (Moelwyn-Hughes 1947) while the volume in the solid is

26 ml. mole^{-1} (Moelwyn-Hughes 1957). The latter value is abnormally large and is *greater* than that for neon in a corresponding state; the anomaly may be associated with quantum effects in the solid. We believe the smaller value will be most relevant since the individual helium atom should be small enough to enter cages in the water structure without much expansion of the lattice. However, calculations for $V_2 = 26$ ml. will also be included. Helium has no permanent dipole moment and its polarizability is small, so that the second term of the salting-out equation (3·17) is small since it depends on the magnitude of the term $(\epsilon_0 V_2 - \frac{9}{2} P_2)$. If the 'atomic volume' of helium were used, the second term would be negligible and the salting-out determined by the primary hydration term only in equation (3·17)

Examination of table 1 shows that the approximate equation (3·12) gives low values for k_s for helium (for $V_2 = 7·7$ ml.), somewhat low values for the other rare gases and predicts, for naphthalene and biphenyl, values which are too large. It is also not very satisfactory with small ions, e.g. Li$^+$, or large ions, e.g. I$^-$. However, for the salting-out of benzene by ions of intermediate sizes, k_s is predicted fairly well. This apparently good agreement is a result of the fact that the error introduced by expanding the exponential in the salting-out equation (3·5) nearly balances that caused by the neglect of effects associated with the primary hydration shell around the ions (see figure 1).

Equation (3·20) predicts the dependence of k_s on the size of the non-electrolyte molecule fairly well (see table 1) although the calculated values are all about 20 to 25 % lower than the experimental ones. The dependence of k_s on the nature of the ions is predicted satisfactorily when the non-electrolyte is small. Individual ionic contributions calculated from equation (3·17) and expressed in terms of component values $(k_s)_1$ and $(k_s)_2$ corresponding to the two terms in equation (3·17) for primary and secondary hydration regions are given in table 2. For large non-electrolytes, the predicted k_s values vary only slightly for different salts while the experimental values differ quite significantly, particularly for large non-electrolytes. The discrepancy may arise from the assumption that primary hydration and electrostatic interactions beyond the primary hydration shell are independent effects; this of course is only valid as a first approximation. Also non-electrostatic 'iceberg' effects may be most important for large non-polar solutes.

The k_s values predicted using hydration parameters (n and r_h) obtained from mobility data are in better agreement with experiment than those calculated from density data. However, the density data predict that k_s values for the lithium salts should be smaller than those for corresponding sodium salts. It is therefore difficult to say which set of data should be preferred in these calculations.

Experimentally, salting-out may also be associated with some non-electrostatic effects. It has been shown by Eley (1939, 1944) and Frank & Evans (1945) that the solubility of non-electrolytes is associated with strong entropy effects; a cage or 'iceberg' can be formed around the neutral molecules in water. The presence of a region around the ions in which the water structure is locally modified—'structure breaking' (Gurney 1953; Frank & Wen 1957) —could affect the formation of such cages and result in a change of solubility of the dissolved gas on account of entropy effects. Thus, the few data available on the solubility of rare gases in the presence of tetra-alkyl ammonium salts (Morrison & Johnstone 1955) indicate a small degree of salting-in. Since these large cations can be assumed to have no primary hydration,

the salting-in must be caused by some non-electrostatic effects. The general explanation offered by Bockris *et al.* (1951) that salting-in is a result of van der Waals forces between large ions and large non-electrolytes is inapplicable here since the non-electrolytes concerned are small rare gases. A systematic study of the solubility of rare gases in the presence of tetra-alkyl ammonium ions would be required to elucidate this point. Fortunately these non-electrostatic interactions are not too important for ordinary salts since electrostatic and hydration effects can account for at least 75% of the observed salting-out effect.

5. Comparison with the theory of McDevit & Long

We now compare equations (3·17) or (3·20) with the following equation obtained by McDevit & Long (1952), based on the internal pressure concept

$$k_s = \frac{\bar{V}_2(V_s - \bar{V}_s)}{\beta_0 RT}, \tag{5·1}$$

where $\bar{V}_2$ and $\bar{V}_s$ are the partial molar volumes of the non-electrolyte and salt, respectively, V_s is the molar volume of the (liquid) salt and β_0 the compressibility of water.

The comparison (table 1) of predicted values of k_s, from McDevit & Long's theory, with the experimental data, shows that their theory generally over-estimates the dependence of k_s on the volume of the non-electrolyte. Their relation also fails to take into account the polarization of the non-electrolyte and consequently would not apply to polar non-electrolytes. The advantage of this theory, however, is that it predicts the dependence of k_s on the nature of the salt much better than do other previous theories, a fact which arises because $V_s - \bar{V}_s$ is related to the degree of hydration of the salt; this factor is included in our theory in the first term of equation (3·17) or (3·20).

6. Dependence of k_s on concentration

The only general effect which we have not yet discussed is the concentration dependence of k_s. Qualitatively, from equations (3·17) or (3·20), a curve and not a straight line is predicted for $\Delta S/S_0 m$ as a function of m. The limiting k_s ($m \to 0$) is only obtained when the

Table 4. Theoretical salting-out of benzene by potassium chloride:
equation (3·17) with r_h from mobility data

m (mole l.$^{-1}$)	$(S_0 - S)/S_0 m$ (l. mole^{-1})	m (mole l.$^{-1}$)	$(S_0 - S)/S_0 m$ (l. mole^{-1})
0·00	0·36	0·5	0·29
0·05	0·33	1·0	0·28
0·25	0·30	—	—

term mW can be neglected in comparison with $1000d$, and $1/R$ in comparison with $1/r_h$ as $m \to 0$. The work on dielectric saturation effects near simple and polymeric ions, to be described in §8, indicates that the effective radius of a hydrated ion does not change very significantly with concentration up to $m = 1$ molar. Correspondingly we may assume that the hydration number is constant. The variation of the radius R with m [equation (3·4)] is the main concentration dependent effect so that the second term of equation (3·17) decreases as m increases. The salting-out ratio hence decreases with increasing m as can be seen from

table 4 where theoretical values of $(S_0 - S)/S_0 m$ have been calculated as a function of concentration for the salting-out of benzene by potassium chloride. Equation (3·17) thus leads to non-linearity in the salting-out relation with increasing concentration of salt as is observed experimentally.

7. DISCUSSION OF RECENT THEORIES OF SALTING-OUT

We shall now examine critically some of the theories, or improvements to previous salting-out theories, that have been proposed since the publication of the review by Long & McDevit (1952). Wada & Ito (1957) and Nakajima (1953) have substituted the free ion electrostatic field by the Debye–Hückel field in the Debye & McAulay salting-out theory (1925) in their attempt to explain deviations from linearity of the log (S_0/S) plot at high concentrations. Baranoski & Sarnowski (1958), in addition to using the above field correction, have tried to explain these deviations at high concentrations by introducing a correction for the 'extent of hydration' of the ions. Their correction is similar to that suggested by Stokes & Robinson (1948) for extension of the Debye–Hückel (1923) theory. This type of correction is mostly empirical and is of such a form that it becomes important only at high concentrations; however, we have shown above that the discreteness of the primary hydration shell of ions must be recognized, even at infinite dilution, in explaining salting-out ratio values more quantitatively. In addition, all the above authors have used the Debye–McAulay theory which gives a result similar in form to that from the approximate equation (3·11) which is erroneous in principle, particularly for small ions. These authors are thus attempting to correct for the statistical electrostatic distribution of ions while they are failing to take into account the correct distribution of solvent and neutral molecules around the ions. Actually, the reverse should be done; in very dilute solutions, the distribution of ions is not important and the ions may be considered isolated, but the proper exponential distribution of solvent and non-electrolyte molecules should always be retained and must be a primary basis for any satisfactory theory.

It was realized by Altshuller & Everson (1951) that solvation and the related degree of dielectric saturation must be an important factor in determining salting-out effects. They therefore made corrections to an equation similar to that of Debye & McAulay, but in order to remove the difficulty of the prediction of an infinite k_s as a tends to zero, they proposed that the radius of the ion should be taken as the hydration radius and not the crystal ionic radius. This implies that the more the ion is hydrated the *lower* would be the salting-out constant, while we have shown that the opposite must be the case, and in fact the extent of primary hydration is a *principal factor* determining the k_s values. The authors also attempted to correct the theory of Debye & McAulay by taking into account the effect of dielectric saturation near the ion. This is the same as correcting curve I of figure 1 for this effect. Since this correction led to even larger values for k_s in the case of very small ions, they concluded that dielectric saturation was *not* an important effect. We have shown that this conclusion certainly cannot be correct and that, in fact, consideration of dielectric saturation effects which we examine in the following section leads to improved theoretical values of k_s and is a necessary factor to be taken into account in any complete theory of salting-out.

8. Dielectric saturation and hydration

(a) Method of approach

We have shown above that interpretation of salting-out data requires information concerning the limit of primary hydration r_h to be used, for example, in equation (3·17). In the present section, we examine the dielectric constant profiles near various kinds of ion, including linear polyions such as we have examined experimentally in the present work (see § 9).

In a polar associated solvent such as water, there is a clear relation between the dielectric saturation of the solvent in the high field within one or two molecular radii of the ions, and the extent of primary hydration and the energy of solvation of the ion by the primary layer.

We now present calculations which allow an estimate to be made of the effective limit of appreciable dielectric saturation near ions of various geometries. Such limits may be compared with the estimates of the radii r_h of hydrated ions obtained from mobility and density data (Desnoyers & Conway 1964) which have been used in the theory of salting-out presented above (see table 3). In the case of a polyion, not only the local charge but the first, second and further neighbouring charges on the chain will contribute to the local field intensity so that the extent of hydration and dielectric saturation can be much larger, as will be shown below, than that for a corresponding simple electrolyte at the same ionic concentration.

Theoretical studies of hydration are possible with simple electrolytes since an isolated ion can always be considered. In the case of polyions, however, no matter how dilute a solution is considered, the ion will still retain some ionic atmosphere of gegen-ions. Also, the shape, charge density, concentration and size of the polyions will determine the overall hydration of these molecules. Therefore, such absolute calculations of hydration by methods which have previously been used, e.g. by Bernal & Fowler (1933) and Eley (1939, 1944) for simple ions, cannot be carried out for polyions with the same degree of rigour as for the case of simple ions.

However, for the study of hydration of polyions, it will be sufficient, for the purposes of obtaining initial quantitative data, to make comparisons of the relative degree of hydration of the polyions with that of corresponding simple monomeric ions. In this approach, it will be considered satisfactory to compare the degrees of *primary* hydration (Bockris 1949), since the largest differences between polymeric and simple ions should occur in this primary shell. The primary hydration depends to a large extent on the field intensity in the immediate vicinity of the ion, so that relations which depend on this field may be used to compare hydration of different molecules. As will be shown here, dielectric saturation relations provide a suitable basis for such comparisons. Also, since the effects to be considered are largely short-range ones (i.e. within $10\,\text{Å}$ from the polyion axis), the calculations will not depend to any important extent on details of the overall macromolecular configuration except in the case of closely coiled polyions at low degrees of ionization.

It will be the purpose of these calculations to give a theoretical basis for assignment of the *relative* extents of primary hydration of polyions and corresponding simple ions as a function of symmetry, charge density, concentration, etc., estimated in terms of a distance corresponding to an arbitrarily chosen dielectric constant in the region where the solvent

dielectric constant changes rapidly from its minimum value (optical dielectric constant) to its bulk value ϵ_0 (static dielectric constant at zero field intensity). These extents of primary hydration will be used in § 9 in the interpretation of the salting-out constants and apparent molal volumes of these charged polymeric particles.

The relation between the dielectric constant of the solvent and the distance from an ion is obtained by solution of the Poisson–Boltzmann equation for the relevant model (spherical ion or cylindrical ion) taking into account the dependence of the dielectric constant on field strength (Booth 1951 a, b, c, 1955). The Poisson–Boltzmann relation is a differential equation of the second order and may be solved numerically, e.g. by Milne's method which can be easily programmed for a digital computer. The method, as applied to the present problem, will not be described in detail since the principles involved have been adequately referred to elsewhere (Milne 1953). Computations have been carried out by means of an I.B.M. 650 digital computer.

(b) Simple electrolyte case

The first case to be investigated is that of a simple ion in aqueous solution, so that a basis for comparisons with polyions will be available.

(i) Model

An exact solution for the dependence of the dielectric constant of the solvent upon distance r from a simple ion has previously been obtained (see, for example, Collie, Hasted & Ritson 1948; Laidler 1959; Laidler & Pegis 1957) assuming the ion of charge ze to be an *isolated* point and using the electrostatic field intensity E given by

$$E = -ze/\epsilon_i r^2, \tag{8.1}$$

where ϵ_i is the integral dielectric constant defined by the ratio of the dielectric displacement D to the field. However, if we use the above model as a basis for comparison with the results obtained for the polyion case where the gegen-ion atmosphere of the polyion is normally considered (Alfrey, Berg & Morawetz 1951; Fuoss, Katchalsky & Lifson 1951), we are in effect comparing the behaviour of a monomeric ion without an atmosphere with that of a polymeric ion with an atmosphere. Hence, in the treatment below, we consider a model for the simple ion case in which a central reference ion is surrounded by a quasi-lattice arrangement of ions of the same charge, similar to that discussed by Frank & Thompson (1959 a, b). Such a model for moderate concentrations is in any case better than the Debye–Hückel (1923) diffuse ionic atmosphere picture which ceases to have any clear physical significance above 0·001 M (Frank & Thompson 1959 b). Also, this model is formally exactly analogous in spherical symmetry to that for the polyion in cylindrical symmetry, previously considered for the case of constant solvent dielectric constant (Alfrey *et al.* 1951; Fuoss *et al.* 1951).

The field function for this model at short distances from a simple ion at finite concentration does not differ to any significant extent from the Debye–Hückel field at similar distances and, consequently, the dielectric saturation effects obtained should be essentially the same for either model.

Let us assume that, on a time-average basis, the ions of the same valence z_j are equidistantly spaced (figure 2). The volume of solution available to each ion j is then $\frac{4}{3}\pi R^3$ for

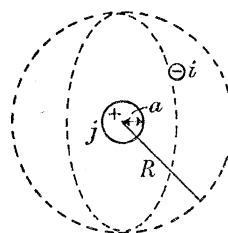404 B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

spherical symmetry (see equation (3·4)). Also, let the gegen-ion of valency z_i be a point charge free to occupy any position in the volume $\frac{4}{3}\pi(R^3 - a^3)$, where a is the radius of the ion j or the distance of closest approach (a is to be taken as the radius of the central reference ion when properties like dielectric saturation or salting-out are considered but is the distance of closest approach when properties such as the activity coefficient, depending on ionic interaction, are considered).* The charge density σ in the region bounded by the two

(a) *Simple ion*

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} = \frac{1}{\epsilon_d}\left\{ K\mathrm{e}^{-z_i e\psi/kT} - \frac{2\epsilon_i}{r}\frac{\mathrm{d}\psi}{\mathrm{d}r} \right\},$$

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_R = 0, \quad \left(\epsilon_i\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_a = -\frac{z_j e}{a^2},$$

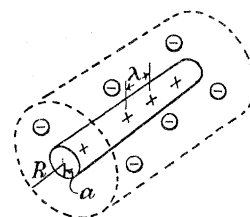$$R = \left(\frac{3000}{4\pi m N}\right)^{\frac{1}{3}}.$$

(b) *Polyion*

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} = \frac{1}{\epsilon_d}\left\{ K'\mathrm{e}^{-z_i e\psi/kT} - \frac{\epsilon_i}{r}\frac{\mathrm{d}\psi}{\mathrm{d}r} \right\},$$

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_R = 0, \quad \left(\epsilon_i\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_a = -\frac{2\alpha e}{a\lambda},$$

$$R = \left(\frac{1000}{\pi m N\lambda}\right).$$

(c) *Planar colloidal ion*

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} = \frac{1}{\epsilon_d}\{ K''\mathrm{e}^{-z_i e\psi/kT} \},$$

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_R = 0, \quad \left(\epsilon_i\frac{\mathrm{d}\psi}{\mathrm{d}r}\right)_a = -\frac{4\pi e}{\lambda^2},$$
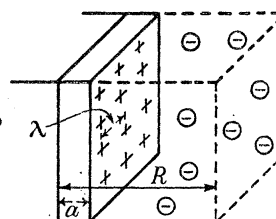
$$R = a + \frac{1000}{m N\lambda^2}.$$

Figure 2. Comparison of models, Poisson–Boltzmann equations and boundary conditions for the cases considered: (a) simple ion, (b) linear polyion, (c) planar colloidal ion.

radii a and R (therefore depending only on the ion i) is given by the usual Boltzmann expression

$$\sigma = n_{\mathrm{av.}}\,z_i e \exp\left(-z_i e\psi/kT\right), \tag{8·2}$$

where $n_{\mathrm{av.}}$ is the average concentration of ions i per cm^3 and ψ is the electrostatic potential at the distance where the space charge density is σ.

The two boundary conditions are

(i) $$(\mathrm{d}\psi/\mathrm{d}r)_R = 0 \tag{8·3}$$

and (ii) that the total charge in the region from a to R is equal but opposite in sign to the charge on the ion j, i.e.

$$\int_a^R 4\pi r^2 \sigma\,\mathrm{d}r = -z_j e. \tag{8·4}$$

* The a quantities mentioned here are, of course, only identical in the case considered above where the gegen-ions are regarded as 'point charges' so that the ionic radius of the central ion is then also the distance of closest approach.

The second boundary condition may be simplified by combining equations (8·3), (8·4) and the Poisson equation*

$$\nabla^2\psi = \frac{1}{r^2}\frac{d}{dr}\left(\epsilon_i\frac{d\psi}{dr}\right) = -4\pi\sigma,\tag{8·5}$$

which then reduces to

$$(\epsilon_i\,d\psi/dr)_a = -z_i e/a^2.\tag{8·6}$$

The parameter R is defined by equation (3·4) with m in mole l.$^{-1}$.

The above model is not without justification. Recently, Frank & Thompson (1959 a, b) have shown that the Debye—Hückel ion cloud model ceases, in principle, to be a valid description of the behaviour of electrolyte solutions above concentrations of about 0·001 mole l.$^{-1}$ for a 1:1 electrolyte, and that the properties of such solutions, e.g. the activity coefficients, will be determined mainly by the nearest neighbour interactions, i.e. the solution behaves like a disordered ionic lattice.

(ii) *Computation procedure*†

From equations (8·2) and (8·5), we may write the Poisson–Boltzmann equation for an ion in an electrolyte solution at finite concentration in the form

$$\frac{d^2\psi}{dr^2} = \frac{1}{\epsilon_d}\left\{-\frac{4\pi e z_i m N}{1000}\exp\left(-\frac{z_i e\psi}{kT}\right) - \frac{2\epsilon_i}{r}\frac{d\psi}{dr}\right\}.\tag{8·7}$$

The complete differential equation is then obtained from equation (8·7) by using the relations discussed below for ϵ_i and ϵ_d.

The theories of Onsager (1936) and Kirkwood (1939) have been extended by Hasted, Ritson & Collie (1948) and by Booth (1951 a, b, c, 1955) to give complex expressions for the integral dielectric constant at high field strengths. Grahame (1950, 1953) was able to show, however, that Booth's relation may be represented very accurately by the simpler empirical relation

$$\epsilon_d = \frac{dD}{dE} = \frac{\epsilon_0 - n^2}{1 + b(E^2)} + n^2,\tag{8·8}$$

where ϵ_0 is taken as 78·5 at 25 °C. The square of the optical refractive index n^2 is equal to 1·78 and the constant b is found to be equal to $1·08 \times 10^{-8}$ e.s.u.$^{-2}$.

If the integral dielectric constant is desired, equation (8·8) may be integrated (Laidler 1959) to give

$$\epsilon_i = \frac{D}{E} = \frac{\epsilon_0 - n^2}{b^{\frac{1}{2}}E}\tan^{-1}(b^{\frac{1}{2}}E) + n^2.\tag{8·9}$$

Therefore, provided the field strength near an ion or polyion is known, the dielectric constant may be obtained as a function of the distance from the charged particle by the procedure discussed by Conway, Bockris & Ammar (1951) and by Laidler (1959). The validity of the above relation for the dielectric saturation effect can only be checked experimentally (Malsch 1928) up to field strengths of about 10^4 e.s.u. Within this limit, the theoretical results are in satisfactory agreement with the experimental ones and probably

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* Here we write the Poisson equation in terms of the integral dielectric constant (Buckingham 1956). For the ionic double-layer case at electrodes, Grahame (1950) has used the differential dielectric constant ϵ_d. However, for this one-dimensional problem use of either ϵ_i or ϵ_d gives identical results. This is not, however, the case for the three-dimensional problem for which ϵ_i must be used.

† Compare also Guggenheim's (1959) numerical calculations.

remain reasonably valid to higher fields. Since we are primarily interested here in the relative effect of hydration for different types of electrolytes, it is sufficient to compare degrees of dielectric saturation for different models in the range of fields for which Booth's theory is applicable.

We require, for numerical computation, the starting values ψ, $d\psi/dr$, $d^2\psi/dr^2$ and $d^3\psi/dr^3$ at $r = R$. From the first boundary condition, $(d\psi/dr)_R = 0$ and consequently from equation (8·7)

$$\left(\frac{d^2\psi}{dr^2}\right)_R = -\frac{4\pi e z_i mN}{1000\epsilon_0} \exp\left(-\frac{z_i e\psi_R}{kT}\right). \tag{8·10}$$

Differentiating equation (8·7) with respect to distance r and writing the result at $r = R$ gives

$$\left(\frac{d^3\psi}{dr^3}\right)_R = -\frac{2}{R}\left(\frac{d^2\psi}{dr^2}\right)_R. \tag{8·11}$$

Hence the only parameter required, which is still unknown, is ψ_R. This value is initially guessed and the equation is integrated numerically by means of the computer until the point $r = a$ is reached. The quantity $(\epsilon_i d\psi/dr)_a$ is then evaluated and compared with the right-hand side of equation (8·6). From the difference between $(\epsilon_i d\psi/dr)_a$ and the value of the second boundary condition given by equation (8·6), the initial value ψ_R is corrected and the integration is then repeated. After the second run, a third value for ψ_R is obtained by linear interpolation and the procedure repeated until the correct starting value is obtained.

The starting value for ψ_R was evaluated by the method indicated above and it was found that ψ_R, when the dielectric constant was assumed uniform throughout the solution, was in fact negligibly different from the value of ψ_R when ϵ_i was assumed to be a function of the field intensity. It was hence sufficient to evaluate the starting values for ψ_R assuming $\epsilon_i = \epsilon_0$ and then to use the same values for the regular differential equation. Physically, the reason for this conclusion is that, except in very strong solutions, the dielectric saturation effects are negligible at appreciable distances (e.g. at $r = R$) from the ions.

(iii) Computational error

The size of each step in the integration was chosen so that the total number of steps would be between 18 and 50. To ensure that the iterative computational error would remain less than 1 %, the initial values were calculated to five significant figures* and the remaining values to four. A few check runs were made in which the number of steps and the number of significant figures were increased and only the fourth significant figure was affected. Errors are cumulative, so that if a large number of steps is used, the errors in the last steps can become appreciable. For this reason, data for very dilute solutions are not so reliable as those for stronger solutions.

The overall computational accuracy of the numerical results of the calculations is estimated to be better than 1 %. Various methods have been devised to estimate the error in numerical integrations (Kunz 1957) but, since the parameters used in our differential equation are often not known to better than 1 to 10 % (for example b, in equation (8·8)) a more rigorous evaluation of the error was not attempted.

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* This procedure is used simply to minimize build-up of error in the computation itself. The initial data and constants on which the calculation is based obviously cannot be specified to this degree of accuracy.

The largest source of error in the computations probably arises from the calculation of the integral dielectric constant which involves the evaluation of arctan $(b^{\frac{1}{2}}E)$ by means of a power series. This series converges fairly rapidly except in the region where x is close to unity so that at least six terms must be retained in the numerical evaluation of this function. In the latter case, the error is as large as 5%. Fortunately, this error occurs only at very high field strengths and, as will be shown below, does not affect our results since we use the dielectric constant at lower field strengths (where the error in evaluating ϵ_i is small) in the comparison of the relative degree of primary hydration of different types of charged particles.
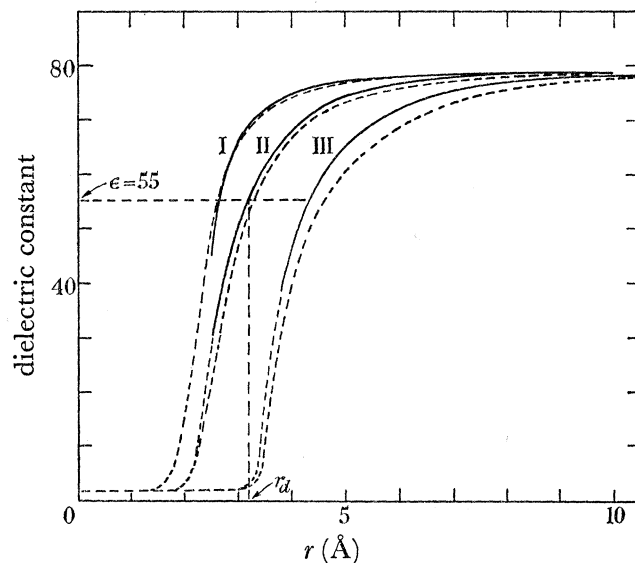

FIGURE 3. Differential and integral dielectric constants of the solvent near monovalent and divalent ions. Curve I, ϵ_i near monovalent ion; II, ϵ_d near monovalent ion; III, ϵ_d near divalent ion. ———, $a = 2 \times 10^{-8}$ cm; – – –, isolated ions.

(iv) *Results for the simple electrolyte case*

The Poisson–Boltzmann equation was solved for various values of the parameters a, m and z_j, with ϵ_d and ϵ_i being used both as constants and as functions of the field intensity. The values for ϵ_i and ϵ_d as a function of r are plotted in figure 3 for $a = 2\cdot0$ Å and $m = 0\cdot1$ mole l.$^{-1}$ Complete tabulations of ψ, $d\psi/dr$, ϵ_i and ϵ_d are available in a thesis (Desnoyers 1961). For this case, it was not possible to solve the differential equation from R all the way to a since the values of $d\psi/dr$ and $d^2\psi/dr^2$ become too large for the computer to handle at distances less than about $2\cdot2$ Å from the ion. The starting values were obtained from a previous run where the dielectric constant was assumed to be equal to ϵ_0 throughout the solution. The integrand was then evaluated numerically at each step until the computer stopped. The low values of the dielectric constant in figure 3 are obtained by extrapolation and are represented by broken lines. The exact solutions were compared with the solutions which neglect the distribution of ions, i.e. for the case of an *isolated* ion. The differential and integral dielectric constants were evaluated for this case by the method suggested by Laidler (1959). It is interesting to note that the differential dielectric constants calculated by both methods agree fairly well. The small deviation between the two solutions is certainly expected since the field obtained from the Poisson–Boltzmann equation (i.e. considering

the ionic atmosphere) is always slightly smaller than the simple electrostatic field except at $r = a$ where they are equal.

The values of ϵ_i calculated by both methods do not, however, agree so well as those of the differential dielectric constant at shorter distances from the ion. This is probably due to errors involved (*ca.* 5 %) in the series expansion of the arctan ($b^{\frac{1}{2}}E$) as we have mentioned above; this also explains why ϵ_i calculated from the Poisson–Boltzmann equation suddenly becomes smaller than the value calculated for the isolated ion.

The dielectric saturation effect has also been evaluated for a 2:1 electrolyte and the differential dielectric constant is plotted in figure 3 as a function of the distance from the divalent ion. The solution obtained in the present calculations from the Poisson–Boltzmann equation was again compared with the one obtained for an isolated ion and the difference between the two solutions is much larger than in the case of monovalent ions. This is expected since Coulombic distribution effects become more important with increasing valency of the ions in solution.

(v) *Comparison with hydration radii*

The principles involved in the estimation of the radii r_h of hydrated ions from partial molal volumes and mobility data (Desnoyers & Conway 1964; see §12) indicate that a close relation between hydration and dielectric saturation effects may be expected. Thus, the radii r_h from partial molal volumes were found to cover the range 2·2 to 2·6 Å for monatomic univalent ions and 3·2 to 3·6 Å for bivalent ions. This corresponds to the region where the differential dielectric constant ϵ_d lies between 5 and 30 (see figure 3) and is rapidly changing. The radii r_h deduced from mobility data vary between 2·7 to 2·9 Å for univalent ions and 3·6 to 3·9 Å for bivalent ions and this corresponds to a region where ϵ_d is between 35 and 45 (figure 4). In the case of oxyanions, the hydration radii are a little higher and consequently the corresponding values of ϵ_d will also be somewhat higher.

The good agreement between the determination of hydration radii from experimental density and mobility data Ulich (1927), and their theoretical prediction in terms of the distance at which the theoretically calculated dielectric constant suddenly drops indicates that hydration effects can be dealt with in a satisfactory quantitative way by the methods discussed in this section. Thus, there is a region near the ion, corresponding to the distance at which both ϵ_d and ϵ_i fall rapidly to their minimum values, within which the water molecules are bound fairly strongly, move with the ion as one entity and are compressed to some extent. Beyond this limiting distance lies another region where ϵ_d has intermediate values (see figure 4) and the water molecules are held loosely, still move with the ion as one entity but are not compressed to any significant extent (Desnoyers & Conway 1964). From the dielectric saturation calculations, no sharp boundary to this second layer of water is expected since ϵ_d increases smoothly to its bulk value ϵ_0 as r increases from 2·5 to 5 Å and beyond. However, the presence of a 'disordered structure' region near the ion (Gurney 1953; Frank & Wen 1957), not taken into account in dielectric saturation calculations, makes the limit of this second layer more definite. This is the one normally deduced from interpretations of mobility data. Therefore the profile of dielectric saturation as a function of distance can serve as a guide for the prediction of the extent of hydration, in terms of an effective geometrical limit of 'primary' hydration and supports deductions from other experimental data.

The purpose of the present calculations is to use the dielectric saturation profiles to predict the hydration of cylindrical polyions and the dependence of hydration on variables such as concentration, size, shape and charge density. This method cannot be expected to predict absolute values of the extent of hydration but should provide a satisfactory basis for the comparison of relative degrees of hydration of ions of different geometries and charge densities, e.g. in the case of polyions and ions of the corresponding monomer. Thus, a critical value of ϵ_d was chosen and the distance from the charged particle at which the dielectric constant has this value ϵ_d is defined as r_d. The choice of this ϵ_d is arbitrary and not too critical since the plots of ϵ_d versus distance are essentially parallel below $\epsilon_d = 55$ for different parameters such as concentration, radius and charge density. We have chosen the
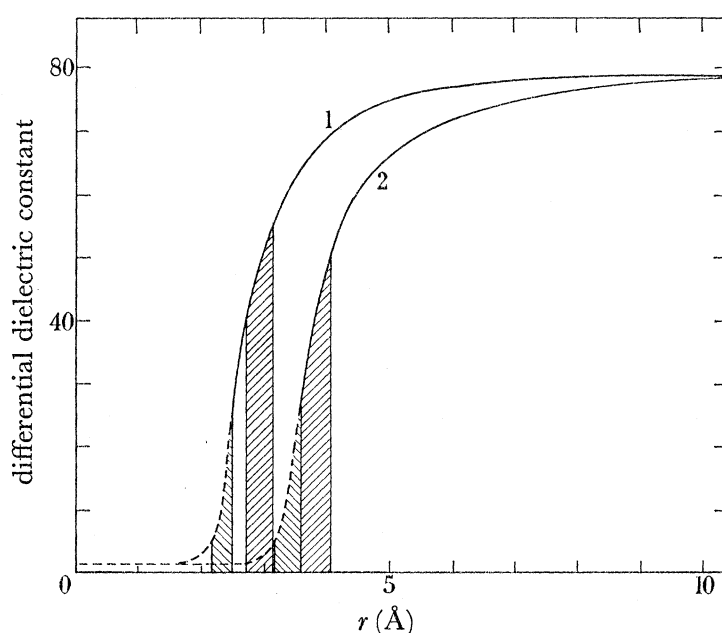

FIGURE 4. Values of r_h for (1) mono- and (2) divalent ions in relation to the corresponding dielectric saturation profiles. (r_h data calculated from partial ionic volumes ◩ and mobility data ◨; Desnoyers & Conway 1964).

value $\epsilon_d = 55$ for the following reasons: at this relatively high ϵ_d the theory of dielectric saturation (Booth 1951 a) is more reliable than in regions near the ions where the field intensity is much higher; the error introduced in the present calculations by expanding arctan $(b^{\frac{1}{2}}E)$ (see equation (8·9)) is small in this region; finally, the value of r_d for a univalent simple ion is similar to the radii of the larger monomeric ions involved in the present work and to the radii of the corresponding polymeric ions studied. The evaluation of the critical distance parameter r_d can therefore be used as a satisfactory basis for prediction of the relative degrees of hydration of polyions, colloidal ions and corresponding monomeric ions.

The dependence of the degree of dielectric saturation on concentration was investigated and it was found that r_d for monovalent ions increases slightly with increasing dilution but the effect is rather small. The difference in r_d when the concentration m changes from 1 to 0·01 M is only approximately 0·05 Å, i.e. the extent of 'saturation' primary hydration of an ion is independent of concentration below 1 M, and it is then sufficient to choose one

concentration, say one molar, for investigation of the effects of variation of the other parameters, e.g. ionic radius and charge.

The dependence of the degree of dielectric saturation on the radius of the ion will be shown in figure 9. These results indicate a small increase in effective hydration radii with increasing crystal radii. This is actually observed experimentally for large ions: thus, examination of hydration parameters obtained from mobility data (Desnoyers & Conway 1964) for Br^-, I^- and $(CH_3)_4N^+$ shows that although the hydration number is decreasing, the hydration radius is increasing as the size of these ions increases. For smaller ions the opposite effect is observed; the limit of primary hydration tends to increase with decreasing ion size. This is probably due to structural effects and stronger interaction between the ion and the solvent.

(c) Linear polyelectrolyte case

(i) Charged rod model

The charged rod model is probably the most satisfactory one for most simple polyelectrolytes at high degrees of extension and would be particularly applicable to linear polyphosphates and polymines. An exact solution of the Poisson–Boltzmann for this model has been given independently by Alfrey *et al.* (1951) and Fuoss *et al.* (1951) with the assumption that the dielectric constant is uniform throughout the solution. The same model will be used here, except that the dielectric constant will be, more correctly, assumed to be a function of the field intensity, since we are specifically interested in the behaviour at short distances from the polyions in relation to their hydration and salting-out behaviour (see §9). Since only short range ion-solvent interactions are to be considered, the limitations of the linear charged rod model (e.g. those due to random coiling effects and finite length) are minimized.

It is assumed that the polyelectrolyte molecules are long thin rods, uniformly charged and parallel to each other (Alfrey *et al.* 1951; Fuoss *et al.* 1951), the radius of the cylindrical volume element of solution available to each polyion being R (see figure 2). The gegen-ions, taken as point charges, are regarded as being distributed statistically in the annular cylindrical region between the limits of the radii a and R. Again a is defined as either the radius of the polyion or the distance of closest approach, depending on the function investigated. Comparison of this model with that for the simple ion case is given in figure 2. The Poisson equation for such a model is

$$\nabla^2(\psi) = \frac{1}{r}\frac{d}{dr}\left(\epsilon_i r \frac{d\psi}{dr}\right) = -4\pi\sigma. \tag{8·12}$$

In the region between a and R, the charge density is associated with the counter-ions, and if these are univalent anions, the space charge density is

$$\sigma = -\frac{\alpha e m N}{1000}\exp\left(\frac{e\psi}{kT}\right), \tag{8·13}$$

where α is the degree of ionization and m the concentration (mole l.$^{-1}$) of the counter-ions.

Combining equations (8·12) and (8·13) gives (cf. equation (8·7))

$$\frac{d^2\psi}{dr^2} = \frac{1}{\epsilon_d}\left\{\frac{4\pi e\alpha m N}{1000}\exp\left(\frac{e\psi}{kT}\right) - \frac{\epsilon_i}{r}\frac{d\psi}{dr}\right\}, \tag{8·14}$$

where ϵ_i and ϵ_d have been defined previously.

The first boundary condition is that the field at R is equal to zero, as in the simple ion case, where R is defined (cf. equation (3·4)) for the cylindrical system as

$$R = (1000/\pi m N \lambda)^{\frac{1}{2}} \tag{8·16}$$

and λ is the distance between ionizable groups on the polymer chain.

The second boundary condition is analogous to that defined by equation (8·4) but written for the cylindrical case, i.e.

$$\int_a^R 2\pi r \sigma \, dr = -\alpha e/\lambda \tag{8·17}$$

which, with σ obtained from equation (8·12), gives the second boundary condition as

$$\left(\epsilon_i \frac{d\psi}{dr}\right)_a = -\frac{2\alpha e}{a\lambda}. \tag{8·18}$$

The starting conditions for the numerical integration are

$$\begin{aligned}
\left(\frac{d\psi}{dr}\right)_R &= 0, \\[6pt]
\left(\frac{d^2\psi}{dr^2}\right)_R &= \frac{4\pi e m N \alpha}{1000\epsilon_0} \exp\left[e\psi_R/kT\right], \\[6pt]
\left(\frac{d^3\psi}{dr^3}\right)_R &= -\frac{1}{R}\left(\frac{d^2\psi}{dr^2}\right)_R.
\end{aligned} \tag{8·19}$$

and

The starting value ψ_R was obtained in the same way as that described for the case of the simple ion, and the computation procedure was similar.

(ii) *Results for the charged rod model*

The variables in the problem for rod-shaped particles are the concentration m, the degree of ionization α and the radius a of the polyion. The distance between ionizable groups, λ, was taken as 2·5 Å in the series of calculations (the value used by Alfrey *et al.* 1951), and is the approximate effective value for vinyl polyions. The temperature was taken as 298 °K and ϵ_0 as 78·5.

The computational procedure was checked by comparing the numerical results obtained without considering dielectric saturation with those obtained from the equation of Alfrey *et al.* (1951) and the results agreed within the computational error estimated as 1 %.

The calculated values for $d\psi/dr$, ϵ_i and ϵ_d are shown as a function of r for selected conditions in figures 5, 6 and 7. Complete tabulations including those of ψ are available in a thesis (Desnoyers 1961). As in the case of the simple ion, the distance at which the differential dielectric constant is equal to 55 will again be defined as r_d for the purposes of comparing degrees of dielectric saturation and the relative extents of the primary hydration layer for simple and corresponding polymeric ions.

The extent of dielectric saturation increases slightly with dilution. The distance r_d changes from 4·25 Å at 1 M to 4·5 Å at 0·05 M for a molecule for which $a = 3\cdot2$ Å and $\alpha = 0\cdot6$. Since the degree of dielectric saturation was found not to vary very much with concentration, most of the runs were carried out for unit normality (i.e. for 1 M concentration of

412   B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

'monomer' units in the polyion); we hence proceed to make comparisons for different degrees of ionization—a more important and interesting variable.

The variation of the differential dielectric constant with distance for different values of α is compared with the results obtained for the case of the corresponding simple ion in
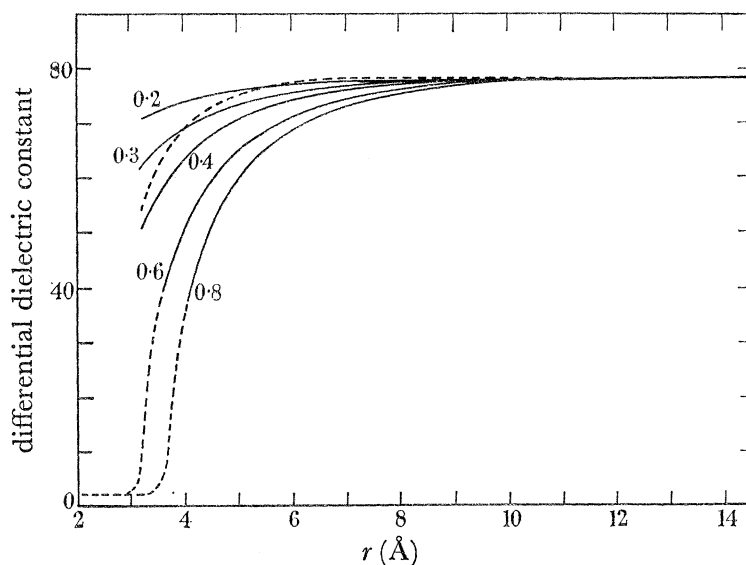

FIGURE 5. Dielectric saturation effects near a linear polyion for different degrees of dissociation, α. $a = 3 \cdot 2 \times 10^{-8}$ cm; $m = 1 \cdot 0$ M. ——, Polyion for various values of α; – – –, corresponding simple ion.
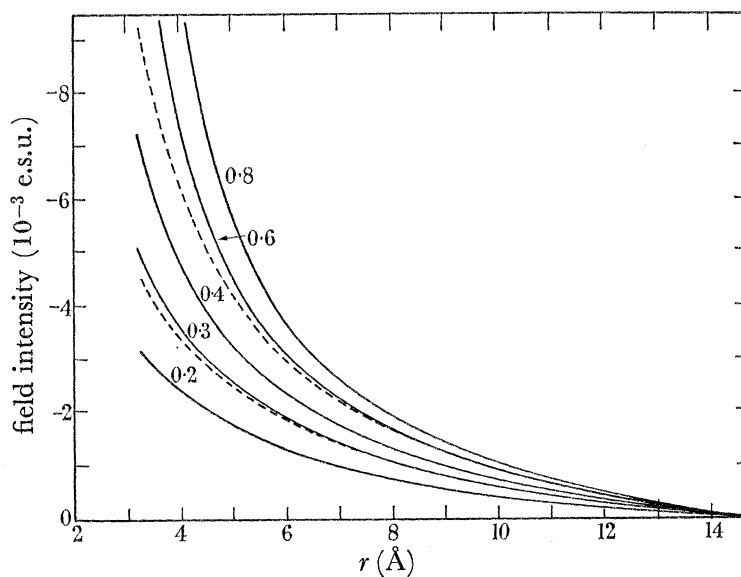

FIGURE 6. Field intensity near a linear polyion for different degrees of dissociation. $a = 3 \cdot 2 \times 10^{-8}$ cm; $m = 1 \cdot 0$ M. ——, $\epsilon = f(E)$; – – –, $\epsilon = \epsilon_0$.

figure 5. It is seen that the dielectric saturation near a polyelectrolyte is quantitatively similar to that near a simple electrolyte only when the degree of dissociation of the polyelectrolyte (or absolute degree of ionization) is about 0·35.

In order to investigate the dependence of the dielectric saturation effect on the degree of ionization, the parameter r_d, as defined previously, has been plotted comparatively in

figure 10 (see below) as a function of the effective distance between the charges on the charged cylinder. Since λ was taken as $2{\cdot}5\,\text{Å}$, the charge separation is simply $2{\cdot}5/\alpha\,\text{Å}$. Therefore, a polyion and a corresponding simple ion with the same radius will have the same value of r_d, and consequently the same average hydration radius, when the charge separation on the polyion chain is equal to approximately $7\,\text{Å}$. Figure 10 (see below) and figure 5 both indicate that the degree of hydration of a polyion depends to a large extent on this charge separation or on the degree of ionization of the polyelectrolyte; if the charge separation is less than $7\,\text{Å}$, the degree of hydration of the polyion should be much larger than that of the corresponding simple ion, a prediction which is verified by experiments to be described in §9.
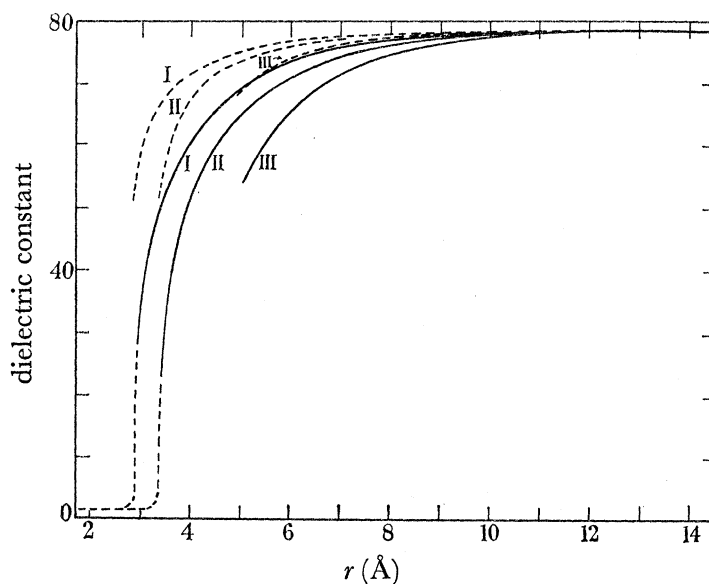

FIGURE 7. Dielectric saturation effects near a linear polyion for different values of a. Curve I, $a = 2{\cdot}2 \times 10^{-8}$ cm; II, $3{\cdot}2 \times 10^{-8}$ cm; III, $5{\cdot}0 \times 10^{-8}$ cm. $\alpha = 0{\cdot}6$; $m = 1{\cdot}0$ M. ——, ϵ_d; ----, ϵ_i.

The effect of dielectric saturation on the field functions is shown in figure 6 from which it can be seen that neglect of dielectric saturation effects can lead to rather serious errors in these functions in some cases.

The effect of the radius of a 'time-average' cylindrical element of the polyion on the degree of dielectric saturation in terms of ϵ_d and ϵ_i, as demonstrated in figures 7 and 9 (see below) shows that a significant increase in the 'saturation' hydration radius of the polyion occurs with increasing 'crystal' radius.

At quite low degrees of ionization ($\alpha < 0{\cdot}1$) most polyions adopt the configuration of a random coil. The electrostatics of this case have been considered by Wall & Berkowitz (1957) for constant dielectric constant. We have made computational runs for field-dependent dielectric constant and found that the results for reduced field and potential (Wall & Berkowitz 1957) as a function of r are almost unaffected by taking into account field dependence of the dielectric constant, and the latter has values near that of ϵ_0 at the periphery of the random coil where the overall field is highest. However, local effects inside the coil are still existent but are best considered in terms of a solution of localized ion sites

at a concentration determined by α and the volume density of the coil. When the coil becomes more open ($\alpha > 0.25$), the linear model is then applicable for evaluation of *short-range* effects such as are involved in primary hydration.

(iii) *Comparison with experiment*

Very few previous experimental studies exist which can be used for examination of the above theoretical conclusions on dielectric saturation and hydration. Jacobson (1954, 1955) appears to be the only worker who has attempted to study the hydration of polyelectrolytes but these were confined to nucleic acids which have such a complicated structure that it is almost impossible to draw any more than very qualitative conclusions about their hydration. By measurements of the dielectric constant of aqueous solutions of these macromolecules by a streaming method, Jacobson (1954, 1955) concluded that the hydration shells of some nucleic acids could be as large as one-quarter (namely *ca.* 5000 Å) of the length of the macromolecules. Our results definitely show that the field near the polyion can never account for such a large degree of hydration, and it is most doubtful if hydrogen bonding between the polyion and the water, as suggested by Jacobson (1955) and discussed by Klotz (1958), can increase the structure of water in an ice-like manner over such a range and to such an extent. A similar conclusion regarding Jacobson's interpretation was reached by O'Konski (1960) on the basis of dielectric polarization studies (cf. de Brouckere & Vos 1955). Qualitatively, their evidence confirms the theoretical conclusions presented here and the experimental results to be discussed in §9.

In view of the lack of direct measurements on the degree of hydration of polyions, an important part of the present work will be concerned with the *experimental evaluation* of extents of hydration of polysalts and the correlation of this extent of hydration with other properties of the polyelectrolytes such as the salting-out behaviour.

(d) *Colloidal electrolyte case*

(i) *Model*

It is convenient for us also to consider the case of an impenetrable colloidal electrolyte since the method of solution of the problem is similar to that considered in §§ 8 (*b*) and 8 (*c*) above. On account of their large dimensions, these particles may be treated *locally* (i.e. for short distances from their surfaces) as charged plates. This problem has been studied by Verwey & Overbeek (1948) and Levine & Bell (1960), and it is possible to solve the Poisson–Boltzmann equation exactly in this case. This case is also of interest because of its relation to the problem of the double layer at colloidal particles and at planar electrodes. Calculations have already been carried out on the improvement of the Poisson–Boltzmann equation for the double-layer at electrodes with regard to such effects as dielectric saturation first by Conway (1949), and by Conway *et al.* (1951) and later by Grahame (1950) in relation to the properties of the double-layer (Sparnaay 1958).

We assume, by analogy with the polyion case, that two charged parallel plates of infinite dimensions are separated by the distance $2R$ as in the model of Verwey and Overbeek (1948) for interaction of two double-layers. Between the two plates there are enough counterions* to neutralize the charges on the two plates (see figure 2).

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* This situation could, for example, arise by ionization of a protein particle, or occur near a large micellar ion.

(ii) Calculations

The Poisson–Boltzmann equation for this model is

$$\frac{d\psi}{dr}\left(\epsilon_i \frac{d\psi}{dr}\right) = -\frac{4\pi z_i e N m}{1000} \exp\left(-\frac{z_i e \psi}{kT}\right), \tag{8.20}$$

where m is the average concentration of the counter-ions of valency z_i.

The two boundary conditions are similar to the ones in the previous problems

$$\left(\frac{d\psi}{dr}\right)_R = 0, \quad \left(\epsilon_i \frac{d\psi}{dr}\right)_a = -4\pi\sigma_s = -\frac{4\pi e}{\lambda^2}, \tag{8.21}$$

where a is the distance between the point where the charge resides and the surface of the plate (or is the distance of closest approach), σ_s the surface charge density of the plate and λ the nearest neighbour charge separation on the plate. The concentration m is related to R by

$$m = \frac{1000}{N\lambda^2(R-a)}. \tag{8.22}$$

The starting values for this case are

$$\left(\frac{d\psi}{dr}\right)_R = 0, \tag{8.23}$$

$$\left(\frac{d^2\psi}{dr^2}\right)_R = -\frac{4\pi z_i e N m}{1000\epsilon_0} \exp\left(-\frac{z_i e \psi_R}{kT}\right), \tag{8.24}$$

$$\left(\frac{d^3\psi}{dr^3}\right)_R = 0, \tag{8.25}$$

and ψ_R is obtained by guessing, and correcting repetitively by equation (8.21) on the computer, as in the previous problem discussed.

The main difference between the present model and the ones used in the theory of the diffuse double-layer for hydrophobic colloids is that we assume that only counterions are present between the two plates in concentrations corresponding stoichiometrically to the charge on the plate. The model is thus analogous to the linear polyelectrolyte case in the absence of added salt, and is therefore applicable to both colloidal particles stabilized by strongly adsorbed simple ions, and to actual colloidal electrolytes in the presence of their counterions only, which have arisen by chemical ionization of the plate or particle.

(iii) Results for the colloidal electrolyte case

The Poisson–Boltzmann equation was solved for different values of the parameters m, a and λ, with and without corrections for the effect of dielectric saturation. As for the cases of simple and polymeric electrolytes, the degree of dielectric saturation increases slightly with dilution, i.e. with distance between the plates. The dielectric saturation (expressed again in terms of r_d) is also found to be directly proportional to the parameter a, i.e. $r_d - a$ is independent of a, as required by equation (8.21).

The dependence of the extent of dielectric saturation on the charge density on the plate is shown in figure 8 where ϵ_d is plotted against the charge separation on the plate for R fixed at 50 Å. In the polyion model, the concentration was constant for a constant R, but this is not so in this case since we are varying the charge separation λ and the concentration is a

416   B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

function of λ (equation (8·22)). For example, when $\lambda = 15\,\text{Å}$ the free ion concentration is equal to 0·58 M and when $\lambda = 8\,\text{Å}$ then m is 0·15 M. However, it was shown by keeping λ constant and varying R that the concentration has little effect on the degree of dielectric saturation over the chosen range of concentrations (as also found for the polyion case). Therefore the comparison made in figure 10 of r_d for the three models as a function of the charge separation is valid.

As expected from the comparison with the results for the previous models, the saturation effect can be important in the plate model to distances much further away from the surface of the plate than in the polyion or simple ion cases. For comparable proximities of charges beyond 6 or 7 Å the dielectric constant can be taken as its normal static value for an average polyion, but in the case of colloidal ions the distance beyond which the dielectric constant may be taken as uniform and having its normal value can be appreciably greater (figure 8).
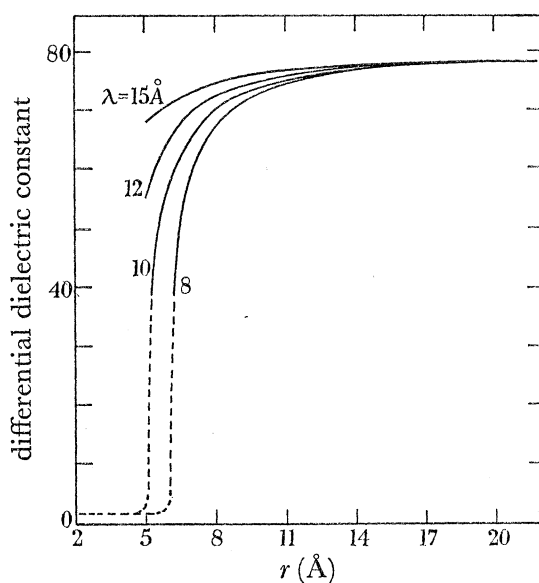

FIGURE 8. Dielectric saturation effects near a charged plate colloidal ion model for different charge separations on the plate. $R = 50 \times 10^{-8}$ cm; $a = 5 \times 10^{-8}$ cm.

(e) *Conclusions and comparison between the results for the three cases*

Relative extents of hydration of ions of various geometries can be estimated by comparison of the distance r_d at which appreciable dielectric saturation of the solvent occurs. For polyions and planar colloid ions, the r_d depends on charge separation, i.e. on degree of ionization, or the linear or surface charge density, respectively. The effects of the ions on the local dielectric constant of the solvent increase in the order: simple ions < linear polyions < planar colloid ions for a given degree of ionization at a given concentration. This comparison is shown quantitatively in figure 10. There is a significant dependence of the limit of dielectric saturation r_d on the size of the ion, and the effect depends on the geometry of the ion. The relation, based on the results presented above, is shown in figure 9.

If the geometrical extent of primary hydration of a charged particle with definite shape and charge density is required, the present results indicate that an estimate of this hydration can be obtained by considering the theoretical dielectric saturation limit. From the symmetry, charge density, radius and concentration (important in some cases), it is possible by

suitable interpolations to obtain a value for the parameter r_d, which as a first approximation may be identified with the radius of the primary hydration shell.

In §9, we examine the hydration of some polyelectrolytes and corresponding monomeric analogues by two experimental approaches and obtain parameters which can be compared with the calculated r_d values. In relation to these results, we also discuss the limitations of the calculations, e.g. with regard to 'discreteness of charge' effects.
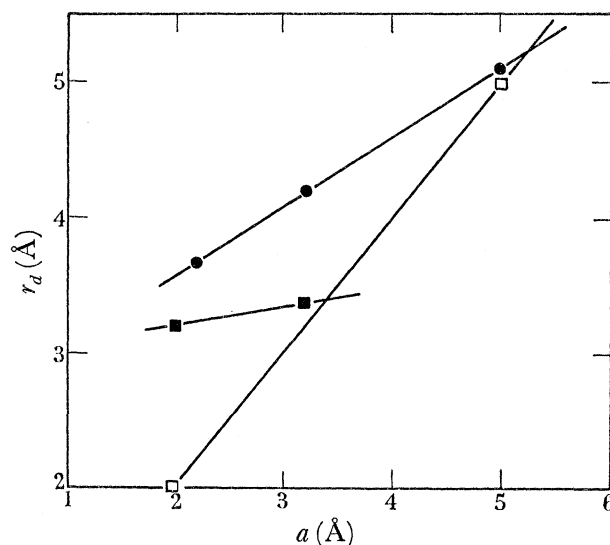

FIGURE 9. Comparison of the dependence of r_d on a for the three models: simple ion ($\blacksquare$, $z_i = 1$, $m = 1$ M), charged rod ($\bullet$, $\alpha = 0.6$, $m = 1$ M) and charged plate ($\square$, $R = 50$ Å, $\lambda = 12$ Å).
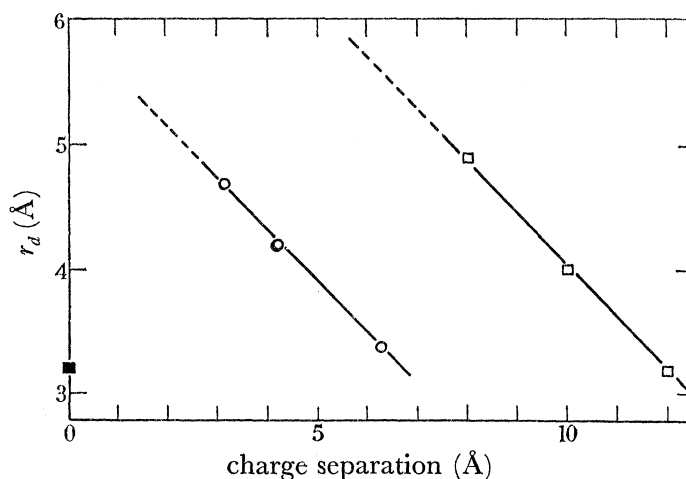

FIGURE 10. Comparison of the dependence of r_d on the charge separation for the three models: simple ion ($\blacksquare$, $a = 3.2 \times 10^{-8}$ cm, $m = 1$ M), charged rod (—o———, $a = 3.2 \times 10^{-8}$ cm, $m = 1$ M) and charged plate (—$\square$———, $a = 3.2 \times 10^{-8}$ cm, $R = 48.2 \times 10^{-8}$ cm).

9. HYDRATION AND SALTING-OUT BY POLYELECTROLYTES

In the final section of this paper, we report and discuss experimental measurements of the salting-out constants for several polyelectrolytes as a function of degree of ionization and molecular weight, using gaseous and solid non-electrolytes. Complementary measurements

on partial molal volumes are also described, and related to the salting-out data by the principles discussed elsewhere (Desnoyers & Conway 1964), and in the preceding sections on the theory of salting-out and dielectric saturation.

(a) Experimental

(i) Choice and preparation of substances examined

Three polyelectrolytes were studied: sodium polyphosphate (NaPP), potassium poly-methacrylate (KPMA) and poly-4-vinyl-N-n-butyl-pyridinium bromide (PBPB). The polyphosphates were used since it was possible to obtain various fractions having different molecular weights, so that effects of increasing chain length on the salting-out constant could be examined. Polyphosphates also approach most closely the model assumed in the theoretical calculations given above. The two other polyelectrolytes were chosen since they are typical polyanionic and polycationic salts, whose degree of ionization can be varied.

Sodium polyphosphates (NaPP). Linear polyphosphates were obtained from Albright and Wilson Ltd and had the following molecular weights: 800, 2800 and 6800. Phosphates of higher molecular weight are difficult to study owing to their limited solubility.

The polyphosphates were prepared by quenching sodium phosphate melts containing different proportions of P_2O_5 between water-cooled rollers. The polymer of molecular weight 6800 was obtained by melting anhydrous sodium trimetaphosphate in platinum at 900 to 1000 °C in an electric furnace and rapidly quenching the poured melt between steel plates.

Molecular weights were determined by 'end group' titration. All the above samples are believed to be somewhat polydisperse* linear polyphosphates, although paper chromatography showed that they contained up to 7·5 % of cyclic tri- and tetrametaphosphates.

Polymethacrylic acid (PMA). A 10 % aqueous solution of practical grade methacrylic acid (Matheson, Coleman and Bell) containing 0·1 to 0·2 % of hydrogen peroxide was kept at $60 \pm 0·2$ °C for about 3h. The polymer was fractionally precipitated out of aqueous solution by adding successive aliquots of a mixture of hydrochloric acid and acetone. The precipitated fractions were removed from the solution and dried on a steam bath. The polyacid was then purified further by dissolving it in the minimum amount of alcohol and pouring this solution in a fine stream into cool ethyl acetate with vigorous stirring. The fluffy white polyacid was then filtered, washed with ether and dried at 100 °C.

The weight average molecular weights of the polyacid preparations were determined by viscosity measurements in benzene (Jordan, Mathieson & Porter 1956) after conversion of the acid to the methyl ester (Katchalsky & Eisenberg 1951).

The potassium salt of the polyacid at the required degree of neutralization was prepared by titration of the polyacid. The percentage of free acid in the polymethacrylic acid (PMA) samples was 96 to 97 % as determined by means of a potentiometric titration.

Poly-4-vinyl-N-n-butylpyridinium bromide (PBPB). A 5 % solution of 4-vinyl-pyridine freshly distilled under reduced pressure with a nitrogen leak was prepared in oxygen-free toluene containing 0·2 % benzoyl peroxide (Fuoss & Strauss 1948). The polymer precipi-

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* The small degree of polydispersity present is probably unimportant in relation to the salting-out and hydration studies, since we will show later that the salting-out constant and apparent molal volume per monomer unit of a polyelectrolyte are essentially independent of chain length except for very short polymers.

tated out of solution after about a week at 25 °C, and was then removed from the solution, washed with toluene and dried *in vacuo*. The quaternary salt was prepared by the procedure of Fuoss & Strauss (1948) and purified by fractional precipitation in ethanol-ethyl acetate solutions. Varying degrees of neutralization were obtained by changing the amount of *n*-butyl bromide used in the quaternization.

The molecular weight of the poly-4-vinyl-pyridine preparation was estimated from its intrinsic viscosity in alcohol for values of using the constant $K = 1.51 \times 10^{-5}$ and $a = 0.52$ (Jordan *et al.* 1956) in the usual viscosity equation. The degree of neutralization of the salt was determined by potentiometric titration with silver nitrate.
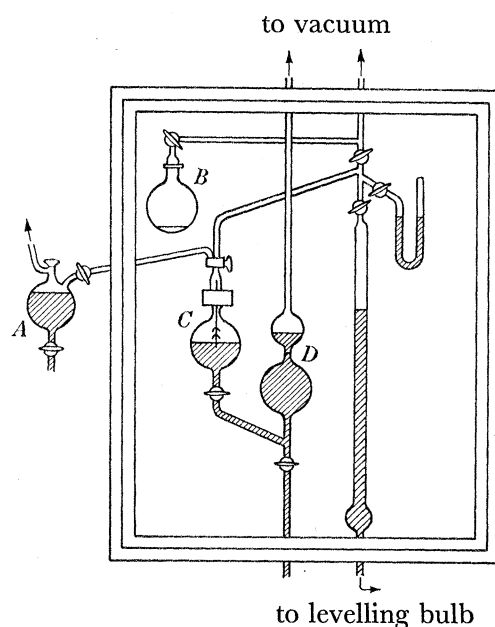

FIGURE 11. Apparatus for measuring gas solubilities.

Simple electrolytes. The simple electrolytes used (NaH_2PO_4, NaH_2PO_3, NaH_2PO_2 and KF) were the analytical reagent grade salts and were used without further purification. The salt 4-ethyl-*N*-*n*-butylpyridinium bromide, the monomer analogue to *PBPB*, was prepared in the same manner as *PBPB* and potassium isobutyrate was taken as the monomeric analogue of K*PMA*.

Non-electrolytes. In the work on salting-out, argon and ethylene were chosen as typical non-polar gases on account of their structural simplicity and spherical geometry in the case of argon, and because of their moderate solubilities. The two gases were the cylinder reagent pure materials.

The two solid polar non-electrolytes used were reagent grade *d-l*-leucine and benzamide, which could be determined directly by the Kjeldahl method.

(ii) *Solubility of the gases*

Techniques have been reviewed elsewhere (Zimmerman 1952; Mader, Vold & Vold 1960); in the present measurements, the amounts of gas dissolved at equilibrium were determined at 30.0 (± 0.1) °C by a volumetric method in an apparatus (figure 11) and by a technique similar, in principle, to that of Åkerlof (1935).

The total pressure of gases used inside the glass vacuum system was kept constant by reference to the pressure in a sealed manometer (see figure 11); volumes of gas dissolved were corrected to s.t.p. The relative solubility $S/S°$ can be shown to be in error by only 0·1 % if corrections are not made for the presence of solvent vapour in the pressure measurements, provided that the salt solutions are not so excessively strong that the vapour pressure over the salt solution is much less than that over the pure solvent at the same temperature. In the present work, the correction factor for $S/S°$ was only 1·001 and this correction is well inside experimental error. Effective agitation of the liquid for maintenance of equilibrium was achieved by operation of a magnetically activated shaker. Equilibrium was reached in 20 to 30 h when no more dissolution of the gas could be detected over a further period of 2 to 3 h. The equilibrium condition was checked in several runs by dissolving more gas (by increasing the pressure) and letting the equilibrium be reached again at the same initial pressure. Very little difference in solubility was detected, thus confirming the initial equilibration.

Solutions and pure solvent were carefully degassed by periodic evacuation. Concentration changes arising from loss of solvent by evaporation were allowed for by weighing the evaporated solvent which was collected in a trap. Any errors involved in this procedure can be avoided completely by determining the exact electrolyte concentration after the solubility measurement.

(iii) *The gas solubility measurements*

The vessel C (figure 11) was first filled with mercury and the degassed liquid from vessel A was introduced into vessel C by displacement of mercury into a calibrated vessel D until D was filled. Thus, the volume of solution in vessel C was equal to the calibrated volume of bulb D. The gas, stored in vessel B and saturated with the solution vapour, was now introduced into the calibrated gas burette where its volume was measured accurately. The gas was then introduced into vessel C by displacement of mercury as before. Agitation of the solution was commenced and the pressure maintained constant by periodic adjustment. The amount of dissolved gas was determined by returning the gas to the gas burette by raising the mercury in the vessel C and measuring the difference in volume. This procedure was repeated until equilibrium was attained.

(iv) *Accuracy and reproducibility*

The solubilities of the gases in pure water measured in the above apparatus agreed quite well with those recorded in the literature. The solubilities in ml. of gas per 100 ml. of water at 30·0 °C and 1 atm of gas pressure (corrected for the vapour pressure of water) were found to be 2·90 for argon and 9·86 for ethylene. The corresponding values taken from the literature (Lannung 1930) were 2·89 and 9·04. Because of the excellent agreement between the present results and the literature value for the case of argon, and since the present results were reproducible to within one percent, it seems that the value quoted in the literature for ethylene may be slightly in error.

The total error in the measurement of solubilities of argon in simple salt solutions was estimated as 1·5 %, so that the maximum error in the salting-out measurements will be 3 % if we neglect the error in the electrolyte concentration.

The experimental errors in the measurements of salting-out by polyelectrolytes are significantly larger than those estimated above owing to difficulties involved in: (i) the degassing of solutions, since foaming tends to occur, and (ii) attainment of solubility equilibrium on account of the high viscosity of the polyelectrolyte solutions. The exact error introduced by these effects is difficult to evaluate but the overall error in the measurements of the salting-out constant for polyelectrolytes should, we estimate, not exceed 7 %.

(v) *Solubility of solid non-electrolytes*

In the present experiments, an amide and an amino acid were chosen as solid non-electrolytes, since their solubility could be determined readily by means of the Kjeldahl method. The solubilities were determined in an insulated, constant temperature water bath maintained at 30.4 ± 0.1 °C.

By means of an automatic shaker, 50 ml. of the salt solution and excess non-electrolyte were mixed continuously. The equilibration time varied with the viscosity of the solutions, but in all cases equilibrium was reached after shaking for 48 h. This was confirmed by repeating some experiments under conditions where the equilibrium was approached from an initial temperature of 45 °C with the solution later placed in the thermostat at 30.4 °C. Analysis of the solution after 24 h gave the same result as in the first experiments.

After equilibrium had been reached, the solution was filtered through a sintered glass funnel completely enclosed so that it could be placed inside the constant temperature bath during the filtration, thus always maintaining the solution at the same temperature. Samples of 10 ml. were then analyzed in duplicate for nitrogen by the standard Kjeldahl method.

(vi) *Accuracy and reproducibility*

The accuracy of the analytical procedure was checked on known standard solutions of *d-l*-leucine and benzamide and gave results correct to better than 1 %. The absolute values of the solubilities were also reliable to 1 %, being in agreement with the data of Cohn & Edsall (1943). The overall errors in the salting-out measurements (arising from errors in analytical results, concentration of salt used, temperature, etc.) were estimated to be not greater than 3 %.

(vii) *Density of the polyelectrolyte solutions*

The apparent molal volume ϕ_v of a solute in solution can be obtained directly from the density d of the solution, and the accuracy of ϕ_v depends almost entirely on the accuracy of the term $d - d_0$ where d_0 is the density of the pure solvent and d that of the solution.

Relative densities of solution and solvent were determined by the differential buoyancy method which has been described in detail elsewhere (Bauer & Lewin 1960; Wirth 1937) and gives the required accuracy in $d - d_0$ to six decimal places with floats of about 200 ml. in volume. Suspension wires were black-platinized at the points of contact with the liquid surfaces in order to minimize surface tension effects. Temperature was measured to 0.02 degC by means of a calibrated thermometer having a scale of 12 in. for 6 degC, and all measurements were conducted at 30.00 ± 0.02 °C.

(viii) *Accuracy and reproducibility of the density measurements*

A given density measurement could be obtained to six decimal places although, in most cases, the last decimal place was uncertain to ± 2 units. The densities of potassium chloride solutions were measured at $30 \cdot 00 \,°C$ and agreed with the values given in the *International critical tables* for different concentrations in the fifth decimal place. The apparent molal volume of KCl at infinite dilution was also calculated and was found to be $26 \cdot 6$ ml./g mole at $30 \cdot 00 \,°C$. The value given in the literature (Fajans & Johnson 1942) is $26 \cdot 5$ ml./g mole at $25 \,°C$ so that the agreement is quite satisfactory. The density measurements were reproducible to about 5 in the *sixth* decimal place.

If we neglect small errors due to temperature fluctuations, wetting of the platinum wires, etc., the overall error in the estimation of the apparent molal volume ϕ_v will be the sum of the errors in m and $d - d_0$. The relative error on these two terms varies with concentration but it is found that above $0 \cdot 01$ M both these terms are accurate to within 1%. Therefore ϕ_v and also ϕ_v^0, are reliable to within about 2%. At concentrations lower than $0 \cdot 01$ M, the error increases significantly and the values of ϕ_v in this region are not so reliable for the evaluation of ϕ_v^0 by extrapolation.

(b) Experimental results

The measured salting-out ratios, $\Delta S / S_0$, of the non-electrolytes are given as a function of concentration of the simple and polymeric electrolytes in figures 12, 13 and 14* for the temperatures indicated above. The electrolyte concentrations are in moles per litre m for the simple salts and in terms of the molarity of the counterions or neutralized monomer units in the case of the polysalts.

(i) Salting-out by sodium polyphosphates (NaPP)

The salting-out data for ethylene, argon and *d-l*-leucine by the sodium polyphosphates are shown in figures 12 and 13. Sodium dihydrogen phosphate was taken as the reference monomer electrolyte corresponding to these polysalts. The salting-out constants k_s were obtained from the limiting slope of the plot of $(S_0 - S)/S_0$ against m (see, for example, figure 12). In figure 13, k_s is plotted as a function of the molecular weight of the polyphosphates for the different systems. From this graph the following conclusions can be drawn:

(α) The salting-out constant depends on the nature of the non-electrolyte and decreases in the order ethylene, argon and *d-l*-leucine.

(β) The dependence of k_s on the molecular weight of the polyelectrolyte seems to be independent of the nature of the non-electrolyte. The constant k_s decreases rapidly at first as the molecular weight increases and beyond a certain molecular weight, approximately 3000, k_s becomes nearly independent of the molecular weight.

(γ) The polyelectrolyte (NaPP) salts-out *less* than the corresponding simple electrolyte (NaH_2PO_4).

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* The numerical solubility data on which these figures and k_s values are based are available in tabular form in a thesis (Desnoyers 1961).

(ii) *Salting-out by potassium polymethacrylate* (K*PMA*) *and poly*-4-*vinyl*-N-n-*butylpyridinium bromide* (*PBPB*)

The salting-out data for argon and benzamide by K*PMA* (molecular weight 43 000) and for argon by *PBPB* (molecular weight 180 000) are shown in figure 14. Potassium isobutyrate was chosen as the reference simple electrolyte for K*PMA*, and both 4-ethyl-*N*-*n*-butyl-
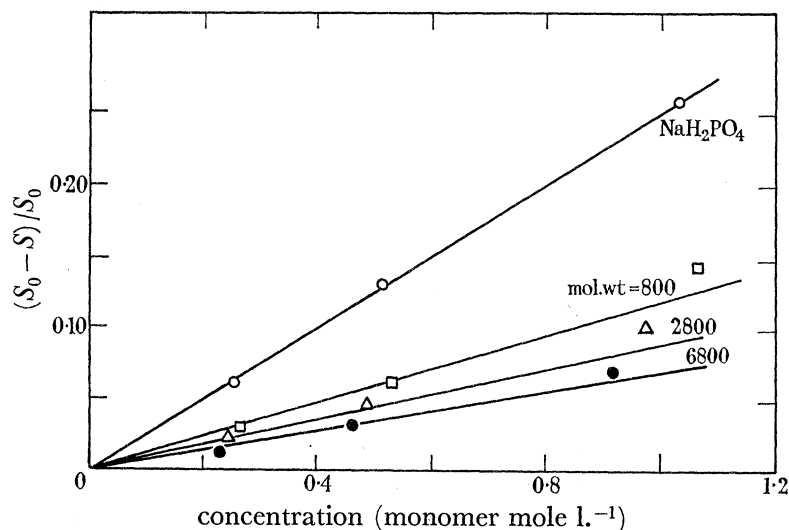

FIGURE 12. Salting-out ratio for *d-l* leucine by Na*PP*, as a function of concentration.
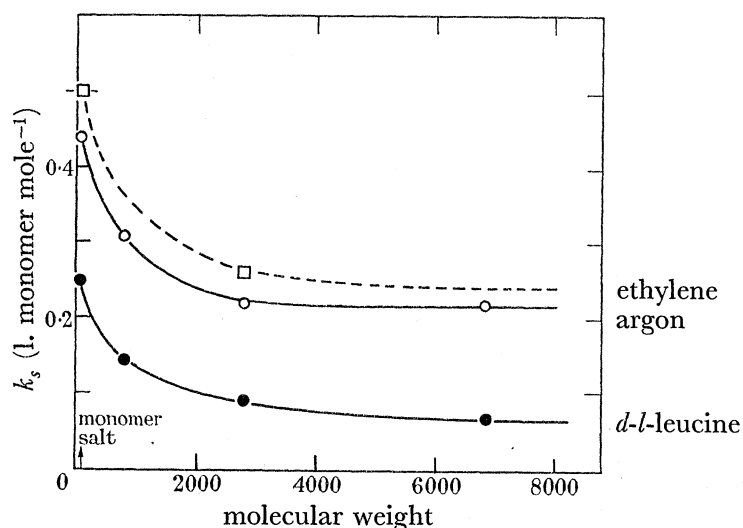

FIGURE 13. Salting-out constants for three different non-electrolytes as a function of the polymer (Na*PP*) molecular weight.

pyridium bromide and 4-vinyl-*N*-*n*-butylpyridinium bromide for *PBPB*. The values of k_s as a function of degree of neutralization are compared in figure 14 for the different systems. The main conclusions to be drawn from these results are as follows:

(α) The constant k_s depends appreciably on the degree of neutralization. In the case of K*PMA*, k_s is approximately equal to, or lower than, that of the corresponding simple salt when α is low, but is much larger when $\alpha \doteqdot 0.5$ and finally decreases as $\alpha \to 1$. The data

424 B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

available for *PBPB* indicate that k_s in this case is less dependent on α than in the case of K*PMA*.

(β) The dependence of k_s on α appears to be also dependent on the non-electrolyte. The maximum value of k_s for argon salted-out by K*PMA* occurs when $\alpha = 0.4$ to 0.5 while in the case of benzamide the maximum occurs at $\alpha \doteqdot 0.8$.

(γ) At intermediate values of α, the degree of salting-out by both K*PMA* and *PBPB* at a given normality is larger (as expected theoretically) than that observed with the corresponding simple salt; this result is thus the *opposite* of that found in the Na*PP* case.
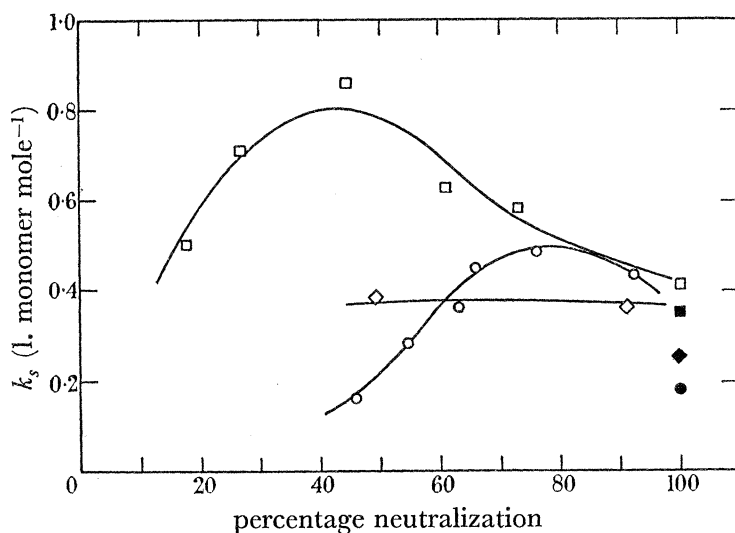
(δ) Argon is salted-out more than benzamide.

FIGURE 14. Salting-out constants for argon by K*PMA* ($\square$) and *PBPB* ($\lozenge$) and benzamide by K*PMA* ($\circ$) as a function of the percentage neutralization of the polyacid or polybase. $\blacksquare$, $\blacklozenge$ and $\bullet$ are the points for the corresponding monomeric salts.

In order to examine the possible effect of the undissociated part of the polyacid in determining k_s when $\alpha < 1$, the salting-out by potassium isobutyrate was determined in the presence of an excess of isobutyric acid; the undissociated organic acid has little effect on the degree of salting-out. This was also found for the salting-out of argon by pure polymethacrylic acid for which k_s is less than 0.02.

In order to examine the effect of polymer dispersity, further fractionation of *PMA* was carried out by differential precipitation but the fractionated material (as the potassium salt) gave the same salting-out behaviour as the initial preparation. Molecular weight and monodispersity are hence not critical in the salting-out. Molecular weight is only important for short chains, as in the case of polyphosphates, where end-group effects can become significant.

(iii) *Apparent molal volumes of* K*PMA and* Na*PP*

The densities of the Na*PP* and K*PMA* salts were measured in aqueous solution and the results together with the calculated ϕ_v and extrapolated ϕ_v^0 values are given in tables 5 and 6.

For the range of Na*PP* oligomers studied (see §9(a), (i)), the apparent molal volume contribution ϕ_v per monomer unit was evaluated from the observed densities of the solutions

using the molecular weight of the repeating unit [$NaPO_3$], end effects due to the presence of OH instead of O groups thus being neglected in the calculations.

In the case of KPMA, the apparent molal volume of the neutralized monomer unit on the chain was evaluated by assuming additivity of contributions from the neutralized and unneutralized monomer units with respect to change of density resulting from the presence of the polysalt in solution, i.e. the total change in density $d-d_0$ due to introduction of polysalt into the solvent water was corrected for contributions associated with the presence of neutral groups in the polymer chain in the evaluation of the ϕ_v contribution for the *ionic* groups in the chains. This correction term can be obtained by plotting $d-d_0$ as a function of concentration for the unneutralized *PMA*. The densities of the corresponding simple salt solutions were also evaluated for comparing the electrostriction effects (in terms of ϕ_v^0 values) of the polysalts with those of corresponding monomeric salts. The apparent molal volumes of KPMA at different degrees of neutralization are plotted as a function of the square-root of concentration (Harned & Owen 1958) in figure 15 and the extrapolated values of ϕ_v^0 at infinite dilution are given as a function of the degree of neutralization in figure 16; similar data for the NaPP oligomers are shown in figure 17 as a function of molecular weight. The values for the corresponding simple electrolytes are given for comparison.

TABLE 5. DENSITIES AND APPARENT MOLAL VOLUMES OF NaPP AT 30·00 °C

$d_0 = 0.995646$ g/ml.

salt	m (mole/l.)	d (g/ml.)	ϕ_v (ml./g-ion)	ϕ_v (ml./g-ion)
NaH_2PO_4	0·10086	1·005927	17·9	—
	0·03839	0·999587	17·4	—
	0·01321	0·997002	17·4	—
	0·00674	0·996336	17·7	—
	0·00569	0·996225	18·2	17·0 ± 0·3
NaH_2PO_3	0·16400	1·006835	35·9	—
	0·08833	1·001699	35·6	—
	0·04521	0·994043	35·6	35·2
NaH_2PO_2	0·07178	0·999516	36·2	—
	0·03437	0·997499	36·2	—
	0·02031	0·996741	36·2	—
	0·01164	0·996296	34·2	36·2
800 mol. wt. NaPP	0·13665	1·006514	22·5	—
	0·07361	1·001475	22·9	—
	0·03084	0·998126	21·7	—
	0·01618	0·996938	22·2	—
	0·00809	0·996300	20·9	20·2
2800 mol. wt. NaPP	0·15235	1·007396	25·0	—
	0·04790	0·999384	24·0	—
	0·02842	0·997906	22·8	—
	0·02277	0·997439	23·3	—
	0·01776	0·997047	23·2	—
	0·10517	0·996852	22·5	21·8 ± 0·2
6800 mol. wt. NaPP	0·13766	1·006207	25·4	—
	0·07064	1·001083	25·1	—
	0·01525	0·996839	23·8	22·8

In these tables, extra significant figures were carried in the concentration and density data in order to minimize the error in calculating ϕ_v. The concentrations are actually reliable only to four decimal places and the densities to five.

TABLE 6. DENSITIES AND APPARENT MOLAL VOLUMES OF $KPMA$ AT 30·00 °C

Molecular weight of PMA is 43000: $d_0 = 0.995646$ g/ml.

salt	m (acid) (mole/l.)	m (base) (mole/l.)	d (g/ml.)	ϕ_v (ml./g-ion)	ϕ_v^0 (ml./g-ion)
potassium isobutyrate	0·20979	0·20979	1·005422	79·9	—
	0·17398	0·17398	1·003790	79·7	—
	0·08291	0·08291	0·999586	78·9	—
	0·04590	0·04590	0·997862	78·3	76.0 ± 0.5
isobutyric acid	0·06326	—	0·995813	85·8	—
	0·04822	—	0·995710	87·2	—
	0·02588	—	0·995695	87·4	89·0
95 % neutralized PMA	0·10124	0·08160	1·002194	52·5	—
	0·06098	0·05795	1·000021	50·7	—
	0·03689	0·03504	0·998373	48·8	—
	0·01980	0·01827	0·997041	50·9	47·8
75% neutralized PMA	0·14941	0·11207	1·004823	55·1	—
	0·08339	0·06256	1·000795	53·7	—
	0·05469	0·04102	0·999011	53·8	—
	0·03159	0·02369	0·997632	50·4	50·0
60 % neutralized PMA	0·18298	0·10978	1·005476	61·6	—
	0·09564	0·05740	1·000821	59·6	—
	0·04495	0·02696	0·998068	57·7	54·0
40% neutralized PMA	0·14164	0·05653	1·001851	74·9	—
	0·05519	0·02208	0·998076	70·8	—
	0·03037	0·01214	0·996982	66·8	61·8
20% neutralized PMA	0·17266	0·03453	1·001232	132·6	—
	0·08944	0·01790	0·998682	120·4	—
	0·06294	0·01259	0·997728	114·9	—
	0·04883	0·00976	0·997296	107·9	85·5
0% neutralized PMA (pure polyacid)	0·18773	—	1·000118	62·7	—
	0·07370	—	0·997158	66·0	—
	0·03413	—	0·996235	69·0	—
	0·02025	—	0·995992	69·4	72·5

See note to table 5.
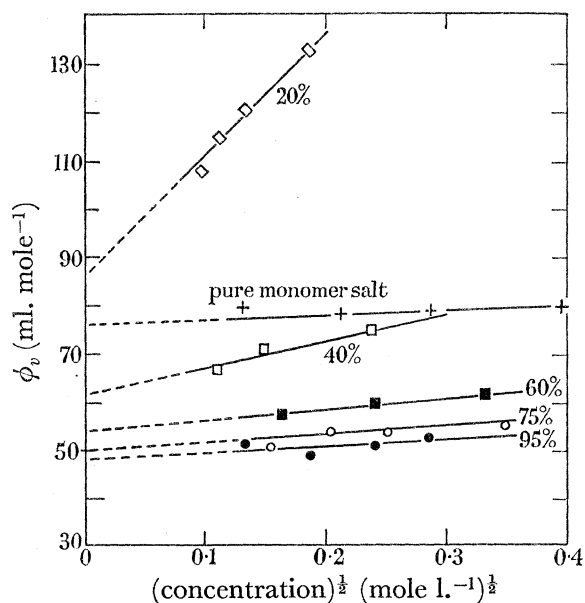
FIGURE 15. Square-root dependence of the apparent molal volumes ϕ_v of $KPMA$ on concentration for different percentage neutralization.

From figures 17 and 13, it is clear that there is a close relationship between ϕ_v^0 and k_s values for the polysalts. It can be seen from figure 13 for the k_s values and from figure 17 for the ϕ_v^0 values, that the relation of these values for the polysalt NaPP to those for the corresponding simple salt NaH_2PO_4 is anomalous compared with the analogous relationship
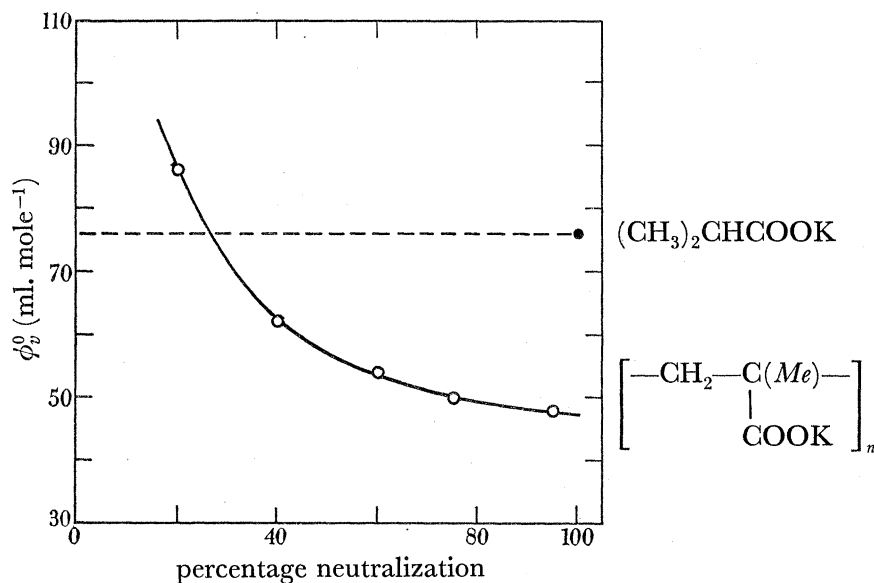

FIGURE 16. Apparent molal volumes of KPMA at infinite dilution as a function of the percentage neutralization.
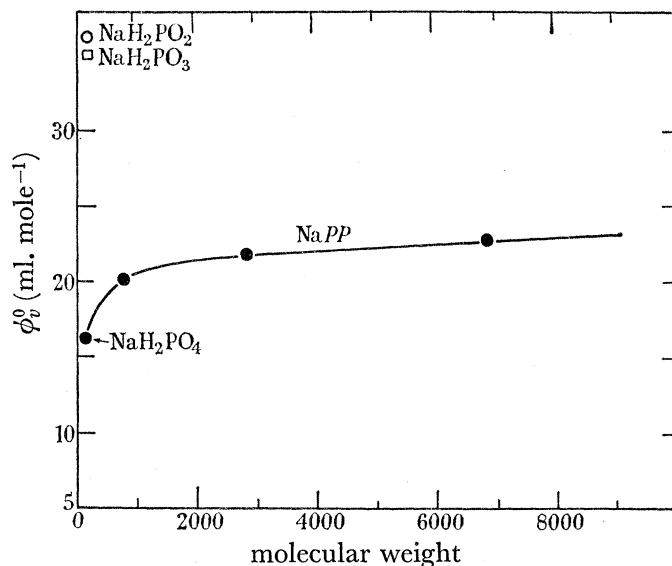

FIGURE 17. Apparent molal volumes of NaPP at infinite dilution as a function of molecular weight.

for ϕ_v^0 and k_s values for KPMA and $PBPB$. However, the trends of both k_s and ϕ_v^0 with molecular weight in the NaPP series are mutually consistent; thus the smaller electrostriction associated with the larger ϕ_v^0 values, as the molecular weight increases, is consistent with the diminishing k_s values. In order to establish the cause of the apparent abnormally high degree of hydration of sodium dihydrogen phosphate which, as we shall see, must be

assumed in order to explain these experimental results, the apparent molal volumes of sodium hydrogen phosphite and of sodium hypophosphite were also measured. It was

suspected that the anomalous results arose because the salt $Na^+ HO$—P—OH was being

compared with NaPP in which the repeating group is, in fact,

—P—O—. Hence, the salts $Na^+ H$—P—OH and $Na^+ H$—P—H
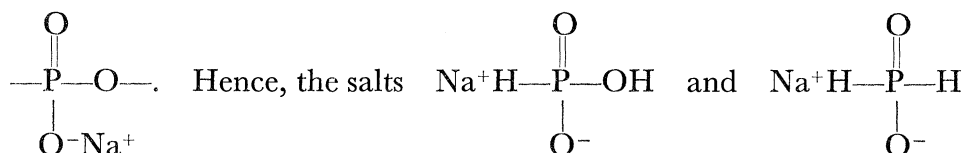
may be a preferable basis for reference. As expected by comparison with the case of KPMA and theoretically, the apparent molal volumes of these two salts (see table 5) are *larger* than that of the polymeric salt NaPP. The result which is anomalous is therefore that for NaH_2PO_4 rather than that for the polymer and we shall show below that this is probably a result of hydrogen bonding which also plays an important role in the hydration of the polyphosphates of low molecular weight, through end-group effects.

10. Salting-out equation for polyions

We now extend the treatment of salting-out for simple ions given in §3 to the polyion case using the model shown in figure 1.

For cylindrical symmetry, equation (3·5) becomes

$$\frac{S_0 - S}{S_0} = \frac{\overline{C}N}{1000} \int_a^R [1 - \exp(-\Delta U/kT)]\, 2\pi l r\, dr, \tag{10·1}$$

where $\overline{C}$ is the molar concentration of the polyion of length l and the terms a and R have been defined previously. Now $l\overline{C} = \lambda \overline{m}$, where $\overline{m}$ is the molar concentration of ionizable groups and λ is the distance between the ionizable groups on the polymer chain; also $\alpha \overline{m} = m$, where m is the monomer mole concentration of free charges on the polyion chain when the degree of dissociation is α.

The energy term ΔU can be obtained from equation (3·10) but the choice of a suitable field function in this equation is somewhat more difficult. Normally, the field obtained from the solution of the Poisson–Boltzmann equation, e.g. as calculated by Alfrey *et al.* (1951), should be used since the central polyion cannot be separated from its atmosphere of gegen-ions even at high dilution. Unfortunately, owing to the complexity of the field function derived by Alfrey *et al.* (1951), such calculations are very tedious. It was found easier in most cases simply to use the proper field intensities obtained numerically on the computer (see §8(c)) and solve the salting-out equation graphically. Alternatively, the field function for an isolated charged rod can be used in the salting-out equation. It will be shown later that the value of k_s predicted for this case is not too different from the solutions where the ionic atmosphere is taken into consideration. For example, the effect of concentration on k_s is still taken into account since the parameter R is concentration dependent.

The field intensity at a distance r from an infinitely long charged rod is given by

$$E = -2\alpha e/\epsilon \lambda r. \tag{10·2}$$

The energy term hence becomes

$$\Delta U/kT = \frac{\alpha^2 e^2}{2\pi\lambda^2\epsilon^2 NkT}\frac{1}{r^2}(V_2\epsilon_0 - \tfrac{9}{2}P_2) \tag{10.3}$$

If we now substitute equation (10·3) into equation (10·1) and otherwise treat the polyion case in the same manner as the simple ion case (see equations (3·17) and (3·20)), we obtain

$$\frac{S_0-S}{S_0 m} = \frac{18n}{1000d-mW} + \frac{\alpha e^2}{1000\lambda\epsilon^2 kT}(V_2\epsilon_0 - \tfrac{9}{2}P_2)\ln\frac{R}{r_h}, \tag{10.4}$$

where R has been defined by equation (8·16), W is the molecular weight per ionized group, r_h the radius of the cylindrical primary hydration shell and n is the hydration number per charged unit on the polymer chain. For the cylindrical polyion case, the equation corresponding to (3·17) simply has the term $(\pi\lambda N/1000\alpha)$ $(r_h^2-\alpha^2)$ instead of the first term on the right-hand-side of equation (10·4).

The unknown parameters in equation (10·4) are r_h and n. The parameter r_h can either be evaluated (as r_d) from the calculated dielectric saturation curves or r_h and n can be calculated from the apparent molal volume of the polyion to be discussed below.

11. Comparison of salting-out by simple and polymeric ions

We shall assume that the simple ion and polyion can both be represented closely by the idealized models discussed previously (see figure 1). We shall first solve the two salting-out equations (3·5) and (10·4) above, taking the ionic atmosphere and dielectric saturation effects into account. This is done by replacing the field function in the salting-out equation by the numerical values obtained in §8 (e). The results are summarized in figure 18 where $f(r)$, obtained for the polyion in the same way as the corresponding function (equation (3·13)) for the spherically symmetric simple ion, is plotted as a function of the distance from the centre of the polyion for different values of the parameters m and α, with and without dielectric saturation corrections.

The equation was solved for the salting-out of benzene by a polyion of radius $3\cdot2\,\text{Å}$, of degree of ionization $0\cdot6$ and at an equivalent monomer concentration of 1 M. Benzene was chosen since effects of changing variables, e.g. concentration, degree of ionization, etc., are quite large in this case and can be shown clearly in the comparative plot (figure 18). From this graph, it is clear that dielectric saturation corrections are much more important in the case of salting-out by linear polyions than for the simple ion case for the same non-electrolyte; these corrections are important out to distances much farther from the centre of the polyion than from centres of corresponding simple ions.

The salting-out equation was also solved for the same case as above but taking the concentration as $0\cdot1$ M. The salting-out ratio $\Delta S/S_0 m$ increases quite significantly with dilution. The extreme case occurs when the electrostatic field given by equation (10·2) is used and R is taken as infinity (infinite dilution). In this case, $f(r)$ never tends to zero and an infinite value of $(S_0-S)/S_0 m$ would be obtained at infinite dilution. This also follows from equation (10·4), since $(S_0-S)/S_0 m$ is proportional to $\log R$. The same situation would occur with the more exact field function of Alfrey et al. (1951) since all these equations result in a

430   B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

logarithmic dependence of $(S_0 - S)/S_0 m$ on R; this mathematical difficulty arises from the fact that the models used all assume the polyions to be infinite in length. It should be realized, however, that an extrapolation to infinite dilution is not very realistic, since the minimum concentration for the polyions must be when only one polyion is present in the volume of solvent, and this corresponds to an order of a thousand gegen-ions present in the region of the polyion if the molecular weight were of the order of 10^5. The theoretical salting-out equation (10·4) can, however, be used to calculate $(S_0 - S)/S_0 m$ for polyions in the range of finite concentrations (0·1 → 1M) used experimentally.

1, $\epsilon = \epsilon_0$ (other conditions as for curve 3)

2, $\alpha = 0·6$, $m = 0·1$ M, $a = 3·2 \times 10^{-8}$ cm

3, $\alpha = 0·6$, $m = 1·0$ M, $a = 3·2 \times 10^{-8}$ cm

4, $\alpha = 0·6$, $a = 3·2 \times 10^{-8}$ cm electrostatic field $E = -2\alpha e/\epsilon \lambda r$

5, $\alpha = 0·3$, $m = 1·0$ M, $a = 3·2 \times 10^{-8}$ cm

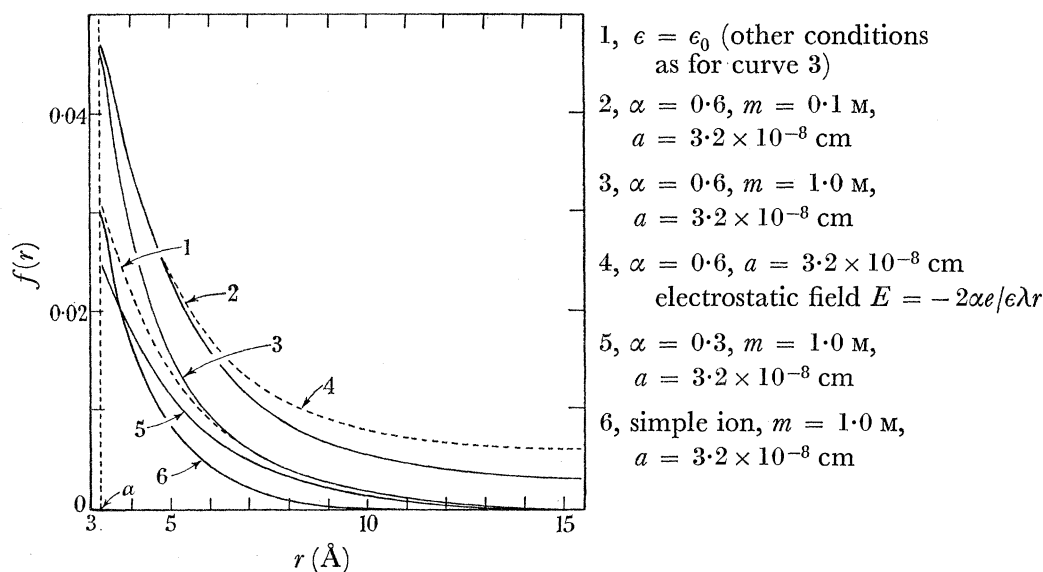6, simple ion, $m = 1·0$ M, $a = 3·2 \times 10^{-8}$ cm

FIGURE 18. Theoretical salting-out functions (see text) for benzene by polyions.

Because of the difficulty arising from the dependence of $(S_0 - S)/S_0 m$ on R, it is clear that evaluation of R is considerably more important than the choice of the field function. It is for this reason that we have neglected the ionic atmosphere in the present theory of salting-out for polyions but have retained the parameter R; a small error in the absolute evaluation of $(S_0 - S)/S_0 m$ (see figure 18) will hence be introduced but should not affect too much the relative values of $(S_0 - S)/S_0 m$, e.g. with regard to their dependence on α and the comparison with values for corresponding simple ions, etc.

It can also be seen from figure 18 that $(S_0 - S)/S_0 m$ depends in an important way on the *degree of ionization* of the polyion as indicated experimentally (see figure 14).

12. EVALUATION OF THE EFFECTIVE RADIUS OF THE PMA ION

In order to use equation (10·4), we require r_h which can be evaluated from the work on dielectric saturation discussed in §8 (c). For a given radius a and degree of dissociation α, we can evaluate the parameter r_d derived from the dielectric saturation calculations by double interpolation (r_d depends on both a and α (see figures 9 and 10)) and assume that r_d is approximately equal to r_h. This approach will be approximate since many polyions (except perhaps polymine ions) bear their charges near the surface of a cylinder or at extremities, and the charges are discrete.

In another publication (Desnoyers & Conway 1964), we have shown that the hydration number n or hydration volume v_h of an ion of radius a can be evaluated from the partial molal volume ϕ_v^0 by means of the equations (Conway & Bockris 1954)

$$n = \frac{v_a - \phi_v^0}{v_0 - v_0^h}, \quad \text{and} \quad v_h = \frac{v_a v_0 - \phi_v^0 v_0^h}{v_0 - v_0^h}, \tag{12.1}$$

where v_a is the effective ionic volume. The term v_a must include any dead-space which arises from the packing of ion and solvent molecules of finite sizes (radii r_w) in the primary hydration shell. The dead-space effect can be taken into account empirically by writing (Desnoyers & Conway 1964)

$$v_a = \frac{4\pi N}{3}\left\{1 + \left(\frac{3 \times 8}{4\pi} - 1\right)\frac{r_w}{a}\right\}a^3 \tag{12.2a}$$

for spherical ions or

$$v_a = \pi\lambda N\left\{1 + \left(\frac{4}{\pi} - 1\right)\frac{r_w}{a}\right\}a^2 \tag{12.2b}$$

for cylindrical polyions. Similarly, the effective hydration radius r_h can be obtained from the effective hydration volumes v_h by equations analogous to (12.2a) and (12.2b) but with r_h taken instead of a.

The term $v_0 - v_0^h$ is the difference of molar volume v_0 of normal water in the bulk and that (v_h^0) of water in the primary hydration shell, and is hence a measure of the electrostriction Δv per mole of primary hydration water. The quantity Δv was estimated (Desnoyers & Conway 1964) as 2·7 ml. mole^{-1} from electrostatic calculations of effective pressure (Frank 1955) in the primary hydration shell taking into account dielectric saturation and using compressibility data of Gibson (1934) and Bridgeman (1935) for high pressures.

For the polyions used in the present work, the ionic volumes are not available by the usual methods but can be estimated indirectly from the apparent molal volumes of the corresponding un-ionized acids determined in the present work. The partial or apparent molal volume of a weak, and hence undissociated, acid, e.g. isobutyric acid and *PMA*, is probably fairly close to its molar volume. Therefore, the actual molar volume of the anion can be obtained from the ϕ_v^0 of the pure acid, corrected for the H atom contribution of 3·1 ml. mole^{-1} (Traube 1891). The values found are

$$v_a \text{ (isobutyrate ion) } 72\cdot5 - 3\cdot1 = 69\cdot4 \text{ ml.,}$$

and

$$v_a \text{ (}PMA\text{-monomer unit) } 89\cdot0 - 3\cdot1 = 85\cdot9 \text{ ml.}$$

so that a can be obtained by means of equation (12.2a).

In order to find the contribution of the anion to the experimentally determined ϕ_v^0, it is necessary to subtract from this value ϕ_v^0 for the counter-ion K^+ in the present case. The assignments of ionic contributions in partial molal volumes of salts have been considered elsewhere (Stern & Amis 1959; Mukerjee 1961; Desnoyers & Conway 1964) where values of ϕ_v^0 for K^+ and Na^+ equal to 4·5 and −5·7, respectively, were obtained.

With these values, we have calculated the volumes and radii of the hydrated *PMA* and isobutyrate ions and the results are given in table 7 and figure 19 where values of $r_h - a$ are plotted as a function of the degree of neutralization of the *PMA*. Comparison is also made in this diagram with the result for the corresponding monomer ion, isobutyrate, and with

the values of $r_d - a$ obtained from the dielectric saturation calculations (§8(c)). Quite good agreement is seen to be obtained between the values of r_h and r_d over most of the range of degrees of ionization. The effective extent of primary hydration $r_h - a$ for the polyion becomes the same as that of the free monomer ion when $\alpha = 0.25$. The entirely theoretical

TABLE 7. EFFECTIVE IONIC AND HYDRATION RADII OF POLYMETHACRYLATE
AND ISOBUTYRATE IONS

Isobutyrate ion

$v_a = 85.9$ ml., $a = 2.88$ Å (obtained from v_a).
$\phi_v^0 = 71.5$ ml. (for a value of ϕ_v^0 for K^+ of 4.5 ml.; Mukerjee 1961).
$v_h = 167.0$ ml.; $r_h = 3.68$ Å (from equations (12.1) and (12.2a)).
$n = 5.3$.

Polymethacrylate ion (molecular weight = 43000).

$v_a = 69.4$ ml.; $a = 3.65$ Å (using equation 12.2b).

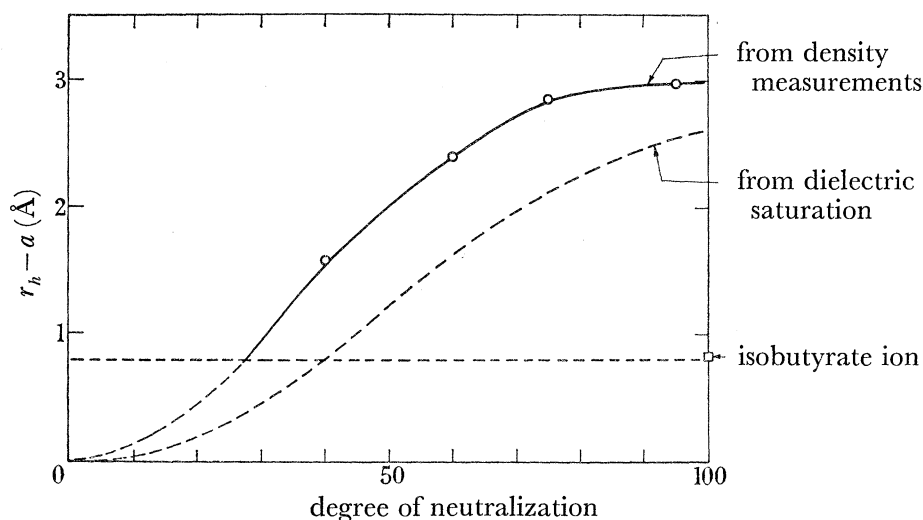| α	ϕ_v^0 (ml.)	v_h (ml.)	n	r_h (density) (Å)	r_h (dielectric saturation) (Å)
0.95	43.3	217.8	9.1	6.6 (0)	5.9 (0)
0.80	—	—	—	—	—
0.75	45.5	210.1	9.2	6.4 (9)	—
0.60	69.5	182.6	7.4	6.0 (3)	5.35
0.40	57.3	138.2	4.5	5.2 (2)	4.45
0.30	—	—	—	—	4.00
0.20	81.0	—	—	—	3.84

FIGURE 19. Evaluation of the effective hydration radii of *PMA* for different degrees of neutralization.

calculations predict this identity of hydration (in terms of r_d) at $\alpha \doteq 0.35$. These two approaches, therefore, give satisfactory agreement and provide a basis for regarding the theoretical treatments developed as leading to meaningful conclusions on the degree of hydration of polyions in relation to that of corresponding simple ions. The principal difference between the experimentally and theoretically determined variation of $(r_h - a)$ with α is that $(r_h - a)$ found from the density measurements becomes effectively constant as $\alpha \to 1$ while the theoretical curve increases more continuously with degree of ionization. This difference is probably due to identification of the degree of neutralization with the

degree of ionization, and arises from ion pair formation (Wall & Hill 1960; Wall, Huizenga & Grieger 1950; Wall & Doremus 1954). An estimate of the hydration numbers n calculated from the equation for n in (12·1) is given in table 7.

13. INTERPRETATION OF THE PRESENT EXPERIMENTAL RESULTS ON SALTING-OUT BY $KPMA$

We can now calculate k_s values theoretically from equation (10·4) with the r_h and n values estimated above in table 7 from data in table 5; a fixed value of R (46·2 Å) corresponding to $m = 0·1$ M will be taken, which is about the lowest concentration used in the experimental evaluations of k_s. Values of k_s for the salting-out of argon by $KPMA$ are plotted as a function of the degree of neutralization in figure 20 and compared with k_s for potassium isobutyrate calculated from equation (3·20).
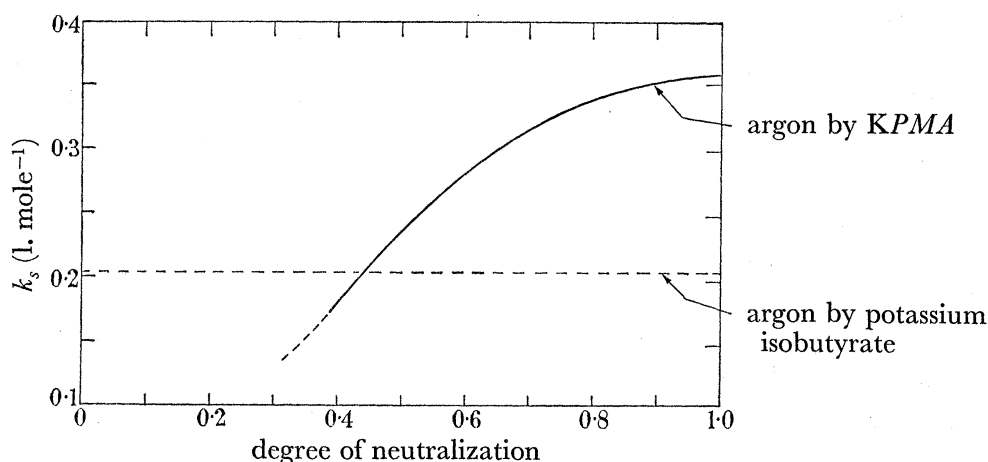

FIGURE 20. Theoretical dependence of the salting-out constant k_S for argon on the degree of neutralization of PMA by KOH.

The theoretical dependence of k_s on the degree of neutralization is in fair agreement with experiment (see figure 14). At low degrees of neutralization, k_s for $KPMA$ is comparable with that for potassium isobutyrate, while at high degrees of neutralization it is much larger. However, the experimental k_s reaches a maximum value at about $\alpha = 0·45$, while theoretically it is predicted that k_s should reach a limiting value as the degree of neutralization tends to unity. We suggest that the maximum in k_s is a result of ion association between K^+ and the PMA ion. The first term of equation (10·4) is effectively corrected for local ion association effects since the values used are obtained from experimental ϕ_v^0 data, but the second term is not corrected for any association effects. The error introduced by assuming that the degree of neutralization is equal to the degree of dissociation is much more important in the second term of equation (10·4) than in the first, e.g. an electrostatically bound K^+ may still have a significant primary hydration but its long-range influence on the non-electrolyte and solvent will be largely attenuated. Therefore the position and shape of the maximum in k_s will depend on the non-electrolyte salted-out since the second term of equation (10·4) is a function of the volume and polarization of the non-electrolyte. It is for this reason that the maximum in k_s for the salting-out of benzamide by $KPMA$ is lower and occurs at about $\alpha = 0·8$.

The interpretation of the salting-out behaviour of benzamide is more complex owing to the structure of the molecule. Experimentally it is salted-out less than argon yet the simple electrostatic theory predicts a greater k_s value than that for argon. It is clear that the dipole of benzamide resides principally in the highly polar amide group and will be preferentially attracted to the ion. This salting-in effect will be counteracted by a salting-out of the relatively non-polar phenyl residue. A combination of these opposing effects may lead to the low value of k_s compared with that for the smaller argon atom.

Although the relative k_s values for KPMA can be accounted for, the absolute value of k_s is more difficult to explain. Figure 20 indicates a maximum k_s of 0·35 while the experimental value is about 0·80. We have shown previously that k_s is determined by the choice of a value for R but it does not seem reasonable to use a value of R corresponding to lower concentrations than 0·1 M, since few experimental results were obtained at such concentrations. The discrepancy between the experimental and theoretical values of k_s could be associated with the fact that the electrical charges on the PMA ion are not in the centre of the molecule but distributed near the surface of the hypothetical cylinder so that the polyion could influence the solvent and non-electrolyte to greater distances since the effective radius of each ionic species on the polymer chain is rather smaller than the averaged radius of the molecule and the degree of salting-out is larger for smaller ionic radii. A further factor introducing error is the use of the Poisson–Boltzmann equation for a system which in reality involves discrete charges (Levine, Bell & Calvert 1962; Grahame 1958; Ershler 1946). However, this approach has been used in several previous calculations of the electrostatic behaviour of colloids and polyions, and for the *comparative* hydration calculations carried out in the present work, it is probably an adequate approximation.

In the case of $PBPB$, the actual polyion must have a local structure rather different from that of a charged rod, so that it is difficult to attempt to predict k_s or its dependence on degree of neutralization. All we can say is that the polyion salts-out more than the corresponding simple ion which is what the calculations predict.

14. Evaluation of hydration parameters and k_s for polyphosphates and monomer analogues

The evaluation of hydration parameters for simple and polymeric phosphates is more difficult that with PMA ions since there is no simple experimental method available to evaluate the volume v_a. Mukerjee (1961) has estimated this volume from bond lengths to be 57 ml. for $H_2PO_4^-$. The corresponding v_a for $H_2PO_3^-$ and $H_2PO_2^-$ may be taken as 54·7 and 52·4 ml. if we assume that the effective contribution of an hydroxy oxygen atom to volume is about 2·3 ml. (Edsall & Wyman 1958; cf. Traube 1891). The volume v_a for the repeating unit in the polyphosphate ion was taken as 55 ml. and the repeating distance λ was estimated as 3 Å. The contribution of the Na^+ ion to the ϕ_v^0 of the phosphate salts was taken as $-5·7$ ml. The parameters n and r_h were evaluated from these data as described previously and are summarized in table 8. In the case of the PP^- ion, only the data for the 6800 mol. wt. polymer were considered since end-effects are significant for the smaller oligomers.

The hydration parameters for $H_2PO_3^-$ and $H_2PO_2^-$ are reasonable since they are of the same order of magnitude as the hydration data for other oxyanions (Desnoyers & Conway

1964). The data for the PP^- ion also fall in the same range as those for the PMA^- ion. Therefore the only anomalous result is that for $H_2PO_4^-$ which has a hydration number larger than that of PP^- and most simple ions (the effective hydration radius however is smaller than that of PP^-).

Correspondingly, k_s for $H_2PO_4^-$ is also anomalously high (figure 13). However, the value ϕ_v^0 for $H_2PO_4^-$ (Couture & Laidler 1957) calculated from recorded density measurements is 33·6 ml. mole^{-1} compared with 17·0 ml. mole^{-1} obtained in the present work. This agreement is poor but since the density measurements involved were made to only four decimal places compared with six in our work and since they were made more than 75 years ago it is reasonable to assume that our values are more correct.

TABLE 8. HYDRATION PARAMETERS FOR MONOMERIC AND POLYMERIC PHOSPHATES

ion	ϕ_v^0 (ml.)	v_a (ml.)	n	r_h (Å)
$H_2PO_4^-$	22·7	57	12·7	4·3
$H_2PO_3^-$	41·1	54·7	5·4	3·4
$H_2PO_2^-$	41·9	52·4	4·2	3·2
PP^- (mol. wt.6800)	28·5	55	10·6	6·0

An explanation for this anomalously high degree of hydration of the phosphate ion is that hydrogen bonding is enhancing the normal hydration due to the field of the ion. Normally hydrogen bonding alone is not sufficient to cause significant electrostrictive hydration, e.g. as found in the case of undissociated PMA and isobutyric acid which have little hydration (very small 'salting-out' constants). However, it is possible that a hydrogen bonding effect which can occur at both —OH groups in $H_2PO_4^-$, when added to the normal effect of the electrical field of the ion, may increase the bonding interaction between water and the $H_2PO_4^-$ ion sufficiently to account for the anomalously high degree of hydration.*

The dependence of ϕ_v^0 (see table 5) and k_s (see figure 13) on chain length of NaPP can also be explained in these terms. If end-groups are more hydrated than the monomer units within the chain because of the presence of —OH groups, the relative contribution of the end-groups to the hydration properties of the complete polyion will decrease with increasing molecular weight or chain length.

The salting-out constants can be evaluated from these hydration parameters. For example, k_s for argon salted-out by NaH$_2$PO$_4$ may be calculated to be 0·35 which agrees fairly well with the experimental value of 0·44. The case of NaPP is more difficult, owing to counter-ion association. If we assume no association (and take the parameter R corresponding to $m = 0.1$) then $k_s = 0.40$ which is much larger than the experimental value of 0·22. However, Wall & Doremus (1954) have shown that the degree of gegen-ion association in polyphosphates is about 0·5, and this value for α in equation (10·4) would then lead to a value of k_s for the polyelectrolyte substantially lower than for the simple phosphate.

* Second dissociation to HPO_4^{2-} is insignificant at the pH's of these solutions.

436 B. E. CONWAY, J. E. DESNOYERS AND A. C. SMITH

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