

SOLUBILIZATION OF POLY (2-HYDROXYETHYL METHACRYLATE) WITH AQUEOUS SALT SOLUTIONS; SWELLING OF GELS

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The effect of a number of salts possessing the salting-in and salting-out effects on the equilibrium swelling of loosely crosslinked poly(2-hydroxyethyl methacrylate) in water has been studied. The decisive role is played by the anion, particularly at low salt concentrations. Perchlorates, thiocyanates or iodides are typical salting-in anions, while sulphates, fluorides and most chlorides are typical salting-out anions. The salting-in salts are frequently preferentially sorbed in the gel phase, but positive sorption is not a condition sufficient for an increase in the degree of swelling. In dilute solutions the increase in the degree of swelling can be correlated with the entropy of hydration of the anions. The influence of the cations is considerably weaker. Generally, both the salting-in and the salting-out effect become smaller with increasing salt concentration. However, the salting-in effect may appear or become stronger, for some salts capable of forming ion pairs or complex low-hydrated ions at higher concentrations. The salt effects are explained not only by a change in the water structure (hydrophobic interactions), but also by specific interactions between the polymer and the ions.

The importance of interactions of water with hydrophobic parts of protein molecules is generally admitted, and the denaturing effect of various low-molecular weight compounds is generally brought into relation with their effect on these interactions. To shed more light on these phenomena, a number of studies have been carried out with low-molecular protein models (review in ref.¹) and with synthetic polymers (review in ref.²). Poly(2-hydroxyethyl methacrylate) is a suitable simple model for the investigation of such interactions, because its molecule bears hydrophobic groups and undissociated hydrophilic groups. The polymer is insoluble in water, but dissolves in aqueous solutions of urea³ and of some salts. These compounds also increase the degree of swelling of loosely crosslinked gels.

It is known that salts can markedly and according to their nature variously affect the solubility of hydrophilic undissociable polymers in water⁴. The introduction of salt ions may improve the conditions for the mixing of the polymer and aqueous phase (salting-in), or may impair them (salting-out). The overall effect results from partial effects of nonspecific character. One of the partial effects is the electrostatic effect⁵ (the ions preferentially attract more polar components of the solution, *i.e.* predominantly water molecules). Other effects are the influence of ions on the water structure and the association of the hydrophobic parts of the polymer molecule⁶⁻¹², and formation of complexes of the polymer with the cation¹³ or with the anion¹¹. It is obvious that in the salting-in those effects must prevail which may destroy the association of the hydrophobic groups.

On the whole, the existing knowledge about the behaviour of undissociating polymers in aqueous solutions is rather scarce². The choice of salts has been — especially in earlier works — rather random, the effect of temperature has almost not been investigated, and the sorption of ions on the polymer has been neglected. All this stimulated an investigation of the properties of poly(2-hydroxyethyl methacrylate) in aqueous salt solutions. We believe that they may be useful in interpreting the effect of salts on the conformational changes of biological polymers and in modelling the structure and functions of biological membranes. In this paper we report a study of the swelling of gels of the loosely crosslinked polymer; the forthcoming two communications^{14,15} will be dealing with the results of viscosity measurements carried out with the soluble polymer.

EXPERIMENTAL

Crosslinked gels used in the swelling were prepared by bulk copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate (0.32 wt. %) in Teflon moulds in the shape of plates, 1–1.5 mm thick. The monomer mixture was bubbled through with nitrogen. The polymerization was initiated with 0.1% isopropyl percarbonate and lasted 6 h at 60°C. The samples were cut into strips, extracted with boiling water and dried to constant weight under reduced pressure at 100°C.

The degree of equilibrium swelling was measured gravimetrically in most cases. The samples swollen to equilibrium were dried with filter paper and weighed in closed weighing bottles. The weight degree of swelling, W , was determined by the weight ratio of the swollen and dry sample. In some series the dry weight was checked after swelling by drying samples swollen in water; no weight loss could be observed. All measurements were performed at $24 \pm 1^\circ\text{C}$. The temperature dependence of the equilibrium degree of swelling, V , was measured dilatometrically (*cf.*³).

As a rule, the salt content in swollen gels was determined after mineralization of the gel with sulphuric acid. Usually, the content of the respective sulphate was determined gravimetrically. If the sulphate was not sufficiently defined, the usual analytical methods suited for one of the salt ions were employed. The weight fraction of salt in the aqueous solution present in the gel phase, $w_s^{(g)}$, was calculated from

$$w_s^{(g)} = W(c_i/100) (M_i/M_s)/(W - 1) \quad (1)$$

where c_i is the ion content in the gel in % by weight, M_i and M_s respectively are molecular (atomic) weights of the ion and salt, and W is the weight equilibrium degree of swelling.

The solutions of salts were prepared from analytically pure chemicals. Their concentrations are given in molarities at 25°C. In some cases the salt concentration was determined by the chemical analysis of the content of the respective ion. The densities of the salt solutions were determined pycnometrically.

RESULTS

If the dependence of the degree of swelling, W , on the salt concentration in the external solution, C_s (mol/l), is concave to the x -axis (Fig. 1), it could be successfully linearized by plotting $C_s/(W - W_0)$ vs C_s (Fig. 2) and described by

$$W = W_0 + k_1 C_s / (1 + k_2 C_s), \quad (2)$$

where W_0 is the weight degree of swelling in pure water. The parameter k_1 (Table I) gives the initial slope of the dependence $W-C_s$:

$$k_1 = (dW/dC_s)_{C_s \rightarrow 0}. \quad (3)$$

With nitrates of metals of higher groups of the periodical system, or of transition metals, and with LiBr and $MgBr_2$ the $W-C_s$ dependences have a shape convex to the x -axis (Fig. 3). The initial slope $(dW/dC_s)_0$ was in these cases determined by extrapolating the dependence $(W - W_0)/C_s$ vs C_s (Fig. 4) based on the equation

$$W = W_0 + k'_1 C_s + k'_2 C_s^2, \quad (4)$$

where

$$k'_1 = (dW/dC_s)_{C_s \rightarrow 0}. \quad (5)$$

The sorption of salts in the gel phase was estimated from the difference between the weight fraction of the salt in solution in the gel $w_s^{(s)}$ (determined from the analytically determined salt (ion) concentration in the gel and from the equilibrium degree of swelling, W , using Eq. (1)) and in the external solution (in equilibrium with

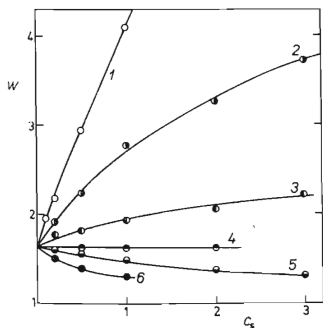


FIG. 1

Dependence of the Weight Degree of Swelling on Salt Concentration (25°C)

1 $Mg(ClO_4)_2$; 2 NaSCN; 3 $Ca(NO_3)_2$;
4 NaBr; 5 NaCl; 6 Na_2SO_4 .

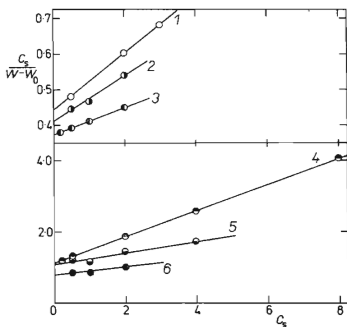


FIG. 2

Determination of the Parameters of Eq. (2) for Perchlorates (25°C)

Cations: 1 Ba^{2+} ; 2 Ca^{2+} ; 3 Mg^{2+}
4 Na^+ ; 5 Li^+ ; 6 Ag^+ .

TABLE I
Parameters of Eqs (3), (5) and (6)

Cation	k_1	k_2	m_1	m_2	m'_2	$(C_s)_{\max}^a$
Sulphates						
Li ⁺	-0.89	1.53	-0.26	-7.4 ^d	-0.81	2.0
Na ⁺	-1.00	1.93	-0.42	-6.3 ^d	-0.89	1.0
Be ₂ ⁺	-0.55	1.53	-0.58	-3.0 ^d	-0.32	1.0
Mg ²⁺	-0.74	1.56	-0.55	-10 ^d	-1.2	1.0
Sulphites						
Na ⁺	-1.0	1.95	-0.47	-3.0	-0.38	1.0
Carbonates						
Na ⁺	-0.74	1.18	—	—	—	0.5
Iodates						
Na ⁺	-0.45	— ^b	—	—	—	0.2
Bromates						
Na ⁺	-0.32	0.68	-0.52	0.6	0.09	1.0
Chlorates						
Na ⁺	c. 0.07	— ^b	0.34	0.5	0.05	4.0
Nitrites						
Na ⁺	c. 0.15	— ^b	0.3	0.4	0.03	4.0
Formates						
Na ⁺	-0.35	+0.40	-0.51	-1.3	-0.09	1.0
Acetates						
Na ⁺	-0.38	+0.34	-0.52	-0.3	-0.03	2.0
Propionates						
Na ⁺	-0.37	+1.07	-0.59	+1.0	0.10	2.0
Nitrates						
Li ⁺	0.17	0.11	0.06	0.1	0.01	2.0
Ca ²⁺	0.35	0.26	-0.15	0	0	4.0
Mg ²⁺	0.32	0	-0.67	0.6	0.09	4.0
Cu ²⁺	0.34 ^c	0.053 ^c	-0.37	0.8	0.15	3.3
Cd ²⁺	0.70	0.028	—	—	— ^a	4.0
Mn ²⁺	0.15 ^c	0.019 ^c	—	—	— ^a	4.8
Ni ²⁺	0.37 ^c	0.057 ^c	—	—	— ^a	3.7
Co ²⁺	0.52 ^c	0.04 ^c	0.01	0.2	0.04	3.0
Al ³⁺	0.95	0.16	—	—	— ^a	1.5
Fe ³⁺	0.16 ^c	0 ^c	-0.14	0.6	0.15	1.6
Cr ³⁺	0.15 ^c	0.001 ^c	-0.02	0.8	0.19	1.6
Perchlorates						
Li ⁺	0.90	0.13 ₅	—	—	— ^d	4.0
Na ⁺	0.88	0.32	0.06	0.06	-0.07	8.0
NH ₄ ⁺	1.25	0.79	0.52	-3.4	-0.40	1.0

TABLE I
 (Continued)

Cation	k_1	k_2	m_1	m_2	m'_2	$(C_s)_{\max}^a$
Mg ²⁺	2.68	0.100	—	—	— ^d	2.0
Ca ²⁺	2.46	0.154	0.52	-1.6	-0.38	2.0
Ba ²⁺	2.27	0.719	0.45	-1.0	-0.24	3.0
Ag ⁺	1.30	0.16	—	—	—	2.0
			Fluorides			
Na ⁺	-0.56	1.17	-0.45	-8.6	-0.36	1.0
			Chlorides			
Li ⁺	-0.21	1.18	-0.45	-1.4	-0.06	2.0
Na ⁺	-0.21	0.26	-0.40	-1.4	-0.08	3.0
K ⁺	-0.22	0.37	-0.36	-1.4	-0.11	2.0
Rb ⁺	-0.21	0.35	—	—	— ^b	1.0
Cs ⁺	-0.17	0.50	-0.64	+0.2	0.03	1.0
NH ₄ ⁺	-0.15	0.21	—	—	—	2.0
Mg ²⁺	-0.36	1.15	-0.87	1.2	0.11	2.0
Ca ²⁺	-0.33	0.96	-0.53	1.5	0.17	4.0
Sr ²⁺	-0.32	0.54	—	—	— ^b	1.0
Ba ²⁺	-0.18	0.18	-0.49	0	0	1.0
Zn ²⁺	-0.09 ^{c,d}	0.044 ^{c,d}	-0.80	+3.1	0.42 ^d	5.0
Cu ²⁺	-0.20	0.70	-0.54	1.0	0.17	1.0
Co ²⁺	-0.21	1.00	-0.39	-2.1	-0.27	1.0
Ni ²⁺	-0.22	0.82	-0.69	0.1	0.01	1.0
Al ³⁺	-0.40	0.52	-0.50	0.3	0.04	1.0
Fe ³⁺	0.1 ^c	— ^b	-0.70	4.8	0.78	1.0
			Bromides			
Li ⁺	0.055 ^c	0.05 ^c	-0.13	0.6	0.05	6.0
Na ⁺	-0.30	— ^b	-0.30	-0.2	-0.02	2.0
K ⁺	0.10	— ^b	—	—	— ^b	2.0
Ca ²⁺	0.20 ^c	0.08 ^c	-0.40	0.5	0.10	2.0
			Iodides			
Li ⁺	0.86	0.043	0.20	-1.5	-0.20	4.0
K ⁺	0.75	0.051	-0.02	0	0	5.7
			Thiocyanates			
Na ⁺	1.43	0.39	—	—	— ^d	6.0
NH ₄ ⁺	1.49	0.46	—	—	— ^d	4.0
			Cyanides			
Na ⁺	0.12	— ^b	0.36	—	—	2.0
			Tetrafluoroborate			
Na ⁺	-0.66	3.25	—	—	—	1.0

^a Highest salt concentration used. ^b Not given because of a large scattering of data. ^c Parameters k'_1 , k'_2 of Eq. (5). ^d Strongly curved dependences (Fig. 5).

the gel), $w_s^{(1)}$. The difference $\Delta w_s = w_s^{(g)} - w_s^{(1)}$ indicates whether the polymer adsorbs the salt or whether its presence excludes the salt from the aqueous solution in the gel (negative sorption). At zero sorption, $\Delta w_s = 0$. The difference Δw_s usually depends on the salt concentration non-linearly, but for the majority of cases the plot

$$\Delta w_s/w_s^{(1)} = m_1 + m_2 w_s^{(1)}, \quad (6)$$

in which m_1 , m_2 were constants, was quite satisfactory. The plot $\Delta w_s/w_s^{(1)}$ for some typical cases is given in Fig. 5; the m_1 , m_2 values (if they could be determined) are summarized in Table I; m_1 does not change on passing from weight to molar concentrations, but the constant m_2 must be recalculated using

$$m'_2 = m_2 M_s / 1000 \quad (7)$$

to molal m'_2 , which then has the dimension kg/mol.

All parameters of Eqs (2)–(7) hold only for samples used in this work. For other samples, differing on the degree of crosslinking, they would assume somewhat different values. Qualitative differences are rather unlikely.

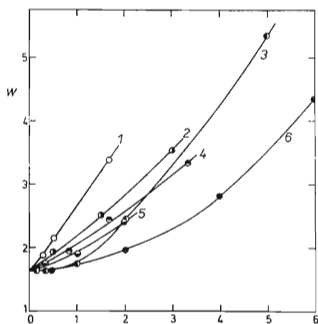


FIG. 3

Dependence of the Weight Degree of Swelling on Salt Concentration (25°C)

1 $\text{Cr}(\text{NO}_3)_3$; 2 $\text{Co}(\text{NO}_3)_2$; 3 ZnCl_2 ;
4 $\text{Cu}(\text{NO}_3)_2$; 5 CaBr_2 ; 6 LiBr .

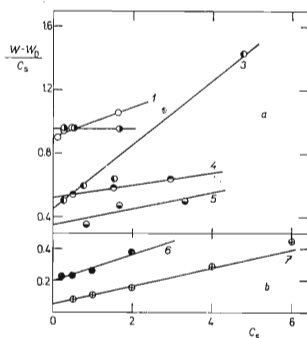


FIG. 4

Determination of the Parameters of Eq. (4)

a) Nitrates: 1 Cr^{3+} ; 2 Fe^{3+} ; 3 Mn^{2+} ;
4 Co^{2+} ; 5 Cu^{2+} ; b) Bromides: 6 CaBr_2 ;
7 LiBr .

DISCUSSION

Very Dilute Solutions

As shown by Eqs (2) to (7), the parameters k_1 , k'_1 , m_1 characterize the behaviour of the polymer at an extreme dilution of the salt solution, and thus under conditions when the average distances between the ions are so large that the mutual interaction of ions in solution need not be considered. Under such conditions the ions may be regarded as acting independently, and the role of anions and cations can be evaluated separately.

Univalent anions arranged with respect to the increasing values of the sorption parameter m_1 of the sodium salts (-0.47 to $+0.5$) form a series

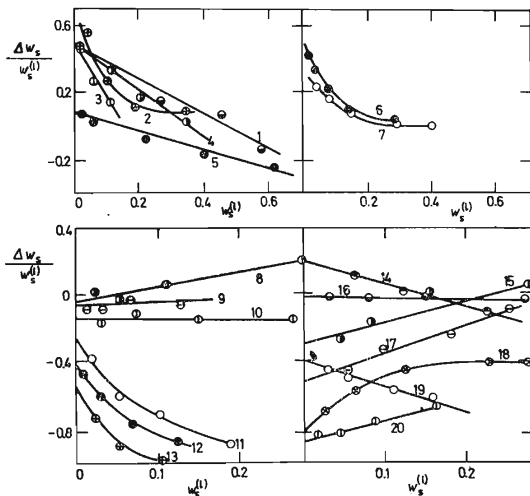
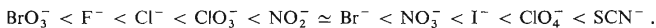


FIG. 5

Determination of the Parameters of Eq. (6)

1 $\text{Ba}(\text{ClO}_4)_2$; 2 $\text{Mg}(\text{ClO}_4)_2$; 3 NH_4ClO_4 ; 4 $\text{Ca}(\text{ClO}_4)_2$; 5 NaClO_4 ; 6 NH_4SCN ; 7 NaSCN ;
 8 $\text{Cr}(\text{NO}_3)_3$; 9 LiNO_3 ; 10 $\text{Ca}(\text{NO}_3)_2$; 11 Li_2SO_4 ; 12 Na_2SO_4 ; 13 MgSO_4 ; 14 LiI ; 15 LiBr ;
 16 KI ; 17 CaCl_2 ; 18 ZnCl_2 ; 19 NaCl ; 20 MgCl_2 .

A similar order (though consisting of a smaller number of data) is found for the Li^+ and Ca^{2+} salts. The k_1 values vary in a similar order. A question then emerges as to the degree of correlation between the sorption of the salt into the gel and its degree of swelling. Indeed a correlation (Fig. 6) between k_1 and m_1 (for a common cation) exists and is comparatively narrow with a positive slope. However, positive

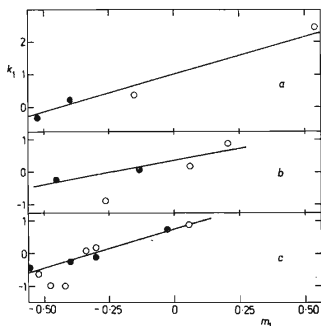


FIG. 6
Correlation of the Parameters k_1 and m_1 in Eqs (2) and (6)
a) Sodium salts; b) lithium salts; c) calcium salts. Oxygen-containing anions \circ , halides \bullet .

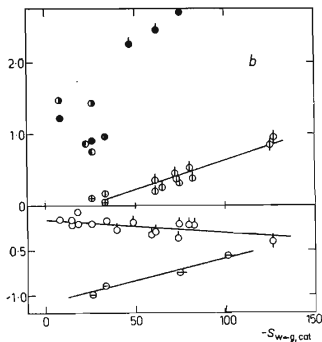
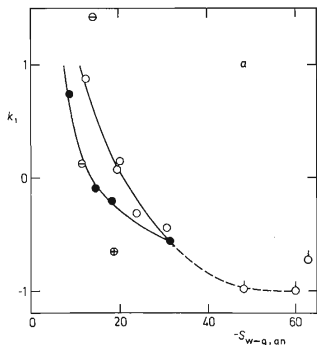


FIG. 7

Correlation of the Parameter k_1 with the Entropy of Hydration S_{w-g} .

a) with a common cation (Na^+): \bullet halides, \circ oxygen-containing anions, \oplus BF_4^- , \ominus SNC^- ;
b) with a common anion: \circ Cl^- , \oplus Br^- , \bullet I^- , \ominus NO_3^- , \bullet ClO_4^- , \ominus SO_4^{2-} , \bullet SCN^-
Bivalent ions with a pip, trivalent ions with two pips.

sorption of the salts is not a condition of their salting-in effect. The majority of salts are sorbed negatively, even if they possess the salting-in effect. Positive sorption ($m_1 > 0$) is found only with salts exhibiting the strongest salting-in effect (perchlorates, thiocyanates). The positive m_1 indicates a specific bond between the ions of these salts and the polymer. The results of electrophoretic measurements¹⁶, in which poly(2-hydroxyethyl methacrylate) in a solution of magnesium perchlorate behaves as a polyanion, allows to infer that the bond of the anion is stronger.

In this connection one should notice that the degree of exclusion of the anions from the water-air and water-hexane interface decreases in a virtually the same order in which the parameters k_1 and m_1 (and the viscometric parameter a_1 (ref.¹⁴)) increase^{17,18}. The cause is seen in the decreasing hydration of the anions¹⁹. In Fig. 7a we correlate the parameter k_1 of the sodium salts of various anions with their entropy of hydration, S_{w+g} . The data needed for this purpose were taken from Table II, ref.²⁰, or calculated from the data given in the same paper. We obtain two smooth dependences, one for anions of halides (including CN^-), the other for univalent oxygen-containing anions. The dependences have an ascending tendency. The salting-in ability is obviously exhibited by salts of anions whose S_{w+g} is higher than -15 to -20 gibbs/mol. On the other hand, the salting-out activity is highest for anions possessing a high negative S_{w+g} . The data for SCN^- and BF_4^- lie beyond these dependences. We have doubts as to whether the correlation for oxygen-containing anions may be extended to include bivalent anions (CO_3^{2-} , SO_3^{2-} and SO_4^{2-}), because in these cases the concentration of cations is higher than in the case of salts of univalent anions.

We were unsuccessful in trying to find out what rules controlled the effect of cations on the swelling of poly (2-hydroxyethyl methacrylate), because of the lack of data and of the low accuracy of some of them. The scheme in Fig. 8 shows that the most negative sorption is exhibited by salts of the alkali earth metals, with magnesium(II)

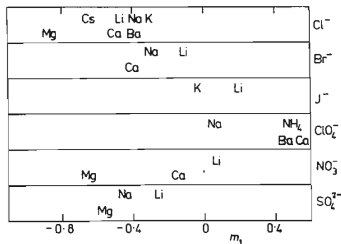


FIG. 8
Comparison of the Parameters m_1 of Salts

salts in the first place (salts of the cation with strongest hydration). On the other hand, in the case of perchlorates, where we have a positive sorption of the salt into the gel, the Ba^{2+} and Ca^{2+} salts possess higher m_1 values than the sodium salt; Li^+ , Na^+ and K^+ chlorides have virtually identical m_1 values, while $CsCl$ (salt with the least hydrated cation) exhibits the most negative m_1 . In the other cases, more positive values are usually found for Li^+ salts than for Na^+ and K^+ salts, although the lithium cation is more strongly hydrated. No correlation was found between k_1 and m_1 for different cations and the same anion. The points lie in wide bands the width of which considerably exceeds the errors of determination and the position of which depends on the character of the anions. Only with perchlorates ($m_1 > 0$) can one talk (in rough features) about a parallel increase in both parameters.

The correlation of the parameter k_1 with the entropy of hydration of the cations is similarly vague. Even though it seems, judging by Fig. 7b, that there is a relation between k_1 and S_{w-g} (though less close than in the case of the anions), it could be an artefact for the same reasons as those given in connection with bivalent anions. Since the role of the anions appears to be more important, the possibility of an artefact is even stronger in this case. We shall therefore restrict ourselves to comparing cations of the same valency. For salts of univalent cations the k_1 values are identical or very close. Li^+ (for which always higher values of both parameters are found) and in some cases also NH_4^+ (higher k_1 values) are exceptions. For bivalent cations the k_1 vs S_{w-g} dependence has a tendency opposite to that of the anions: higher k_1 values are observed with cations having a higher absolute entropy of hydration. The dependence is however much weaker than for the anions. The scatter of points is larger and it cannot be ascribed to experimental errors. Obviously, S_{w-g} is suitably used here as a correlation variable only in the first approximation.

As has been pointed out in the introduction, the effect of inorganic salts on the solubility of undissociated organic salts is related, among other things, also to their effect on the supermolecular water structure "in bulk", even in the closest vicinity of molecules of the dissolved compound. Compared with the polymer, gels are a comparatively concentrated system. The volume fraction of the polymer in the absence of salt is c. 0.5; there are about 5 molecules of water per one 2-hydroxyethyl methacrylate repeat unit. It is difficult to imagine that in such system the water molecules would be arranged to form a long-range structure. On the other hand, the importance of the interaction of ions, particularly of anions, with the polymer-water interface in the case of poly(2-hydroxyethyl methacrylate), is documented by the results of electrophoretic measurements carried out earlier¹⁶, as well as by the sorption data presented here.

Anions adsorbed on the polymer molecules charge them negatively; these charges repel each other, thus expanding the chain dimensions (increase in the degree of swelling and in specific viscosity). The adsorption of anions (probably in the nonpolar

part of the chain) further reduces the hydrophobic character of the polymer chain and restricts the association of the hydrophobic groups which takes place in water. Moreover, anions adsorbed on the surface attract electrostatically cations together with their hydration layers, so that strongly hydrated cations raise the amount of water in the polymer coil or network.

In the case of poly(2-hydroxyethyl methacrylate) the cations may also become operative by interacting directly with the polar groups of the polymer (*e.g.*, OH), coordinating the latter instead of water molecules into their own hydration sphere the stronger, the longer is the range of cation of their charge (that is, the more negative their entropy of hydration) and the higher the dipole moment of the polar groups. The latter hypothesis need not be only speculative, taking into account the solubilities of Li, Be, Mg salts and of some Ca salts in alcohols and other oxygen-containing organic compounds. This effect could also be responsible for the higher k_1 values of the Li salts and with bivalent cations for the correlation of the k_1 values with the entropy of hydration.

In the case of organic cations, the affinity of the hydrophobic groups to the non-polar parts of the chain could also play a decisive role. Thus, *e.g.*, tetraethylammonium bromide exhibits a comparatively good salting-in effect: $k'_1 = 0.75$, $k'_2 = 0$, $m_1 = 0.36$, $m'_2 = 0.66$ compared with *e.g.* LiBr ($k'_1 = 0.055$, $k'_2 = 0.05$, $m_1 = -0.13$, $m'_2 = 0.05$).

Salt Solutions of Higher Concentration

A model calculation²¹ shows that in 1M solution of a uni-univalent electrolyte the distance between the ions is three times at utmost that of the dimensions of the molecules of water. This means that the water molecules lie within the spheres of action of both ions. With solutions of such concentration one must bear in mind interactions between the ions, which are undoubtedly dependent in their individuality. The knowledge of these interactions is unsystematic, and the views about the structure of concentrated solutions are not sufficiently clear. Some authors consider a structure similar to that of crystalline hydrates (especially at very high concentrations)²², others suggest ion pair formation, ion association or complex ion formation²¹. The interaction between ions will also depend on the composition and properties of the medium in which the ions are present *i.e.* on the polymer/water ratio. Interactions of ions with the polymer chain will also increase in number, while on the other hand the "solvent structure mediated effect" will gradually become unimportant. Such a variety of forms makes it quite understandable that ions which possess the same k_1 values at extreme dilution can exhibit different concentration dependences of sorption, swelling and specific viscosity,

The sorption parameter m_2 (Table I) is negative in most cases, predominantly with sulphates, somewhat less with chlorides and perchlorates. The negative sign

means that with increasing salt concentration either the negative sorption becomes stronger (sulphates, chloride), or the positive sorption becomes weaker (perchlorates). The m_2 values observed with all nitrates, Li and Ca bromides and with chlorides of some bivalent (Mg, Ca, Zn, Cu, Ni) or trivalent (Al, Fe) metals are positive; the positive sorption becomes stronger at higher concentrations. Particularly high m_2 values are found with zinc and ferric chlorides.

The results obtained by measuring the degree of swelling were discussed by evaluating the effect of concentration with respect to the magnitude of the ratio y_{sw} defined by

$$y_{sw} = (d^2W/dC_s^2)_0 / (dW/dC_s)_0, \quad (8)$$

It can be calculated from the parameters of Eqs (2) or (4)

$$y_{sw} = -2k_2, \quad y_{sw} = 2k_2/k_1'. \quad (9, 10)$$

The ratio y_{sw} is predominantly negative; this means that with increasing concentration both salting-out and salting-in become weaker. Positive values were found with nitrates of bi- and trivalent metals (Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{3+} , Al^{3+}), some chlorides (Zn^{2+} , Fe^{3+}) and bromides (Li^+ , Ca^{2+}). The increasing concentration of these salts leads to a more intensive salting-in. The parameters m_2 and y_{sw} are obviously qualitatively similar, but no quantitative correlation could be established (also due to the lack of data).

The ratio y_{sw} (at a constant cation) is comparatively well correlated with the entropy of hydration of the anions (Fig. 9a). The lowest concentration changes in the degree of swelling are also observed with salts possessing a low entropy of hydration of the anion. On the other hand, y_{sw} of salts with strong hydration demands of the anion is high, and the dependence of the degree of swelling on salt concentration is strongly curved. If the y_{sw} values for the same anion are compared with each other (Fig. 9b), the result is similar to that obtained with the parameter k_1 . Obviously, the dependence of the degree of swelling on salt concentration is determined predominantly by the anions, even at higher concentrations.

Some anomalies do exist, however, indicating some further factors. Nitrates are the first example. According to the spectroscopic²³ and conductivity measurements²¹, they are supposed to form readily ion pairs of the "solvent separated pair" type (especially at medium concentrations), or of the "contact pair" type (in very concentrated solutions). For several nitrates used in our work the data on the structure of aqueous solutions are missing (Ni, Mn, Cu). In spite of this, however, it seems of interest to compare the y_{sw} values with respect to the information on the ion pair formation. The parameter y_{sw} is negative for the Li^+ salts (where no ion pairs have been proved²¹), Al^{3+} salts (where the pair formation is very weak^{21,23}), and

Ca^{2+} salts (where the dissociation constant of the salt²¹ is $\text{p}K = 0.28$). It becomes almost zero for the Fe^{3+} salt ($\text{p}K = 1.0$) (ref.²¹) and assumes positive values for the Cd^{2+} ($\text{p}K = 0.4$) (ref.²¹), Cr^{3+} and Co^{2+} salts, the Raman spectra of which suggest the ion pair formation²³. No pair formation has been proved for the Mg^{2+} salts, but $y_{\text{sw}} = 0$.

Other anomalies are exhibited by solutions of Zn^{2+} and Cd^{2+} halides:

1) The $W-C_s$ dependence for ZnCl_2 at $C_s < 0.3\text{M}$ has a negative slope, which could be compared *e.g.* with LiCl (and thus with the salt of a strongly hydrated cation), and a minimum at $C_s = 0.3\text{M}$ (Fig. 10). Further course is concave to the Y -axis and is very steep. The same is true for the $\eta_{\text{sp}}-C_s$ dependence¹⁴.

2) Zinc chloride (as the only one of the chlorides) can dissolve poly(2-hydroxyethyl methacrylate), if its molar concentration is higher than 2.8M . Of bromides, only LiBr (at $C_s \geq 4\text{M}$) and CdBr_2 (at $C_s \geq 1.5\text{M}$) dissolve the polymer. Dissolution in aqueous solutions of iodides of alkali metals and magnesium takes place at $C_s \geq 2\text{M}$, while with CdJ_2 it occurs already at $C_s = 0.4\text{M}$ (*cf.*¹⁴).

3) The salting-in activity determined for cadmium iodide by viscosity measurements is higher by 50% than for alkali metal iodides, while the activity of perchlorates of all these cations is virtually the same¹⁴.

4) The sorption parameter m_2 found with zinc chloride is positive and exceptionally high.

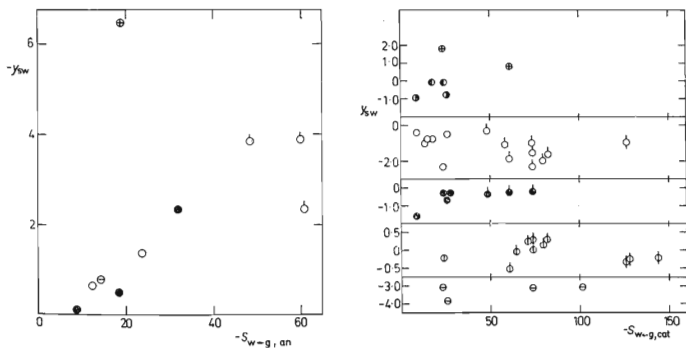


FIG. 9

Correlation of the Parameter y_{sw} with the Entropy of Hydration of Ions

a) with common cation; b) with common anion. Designation as in Fig. 7a, b.

There exists an ample experimental evidence provided by spectroscopic, conductivity and other measurements²¹ that zinc and cadmium halides form ion pairs already at low concentrations, and complex cations (MeX^+) and anions (MeX_3^- , MeX_4^{2-}) at higher concentrations, and that a great part of the molecules remains undissociated. The number of complex ions increases with increasing salt concentration. The tendency towards complex ion formation increases in the following order: $\text{CdCl}_2 < \text{CdBr}_2 < \text{CdJ}_2$ and $\text{ZnJ}_2 < \text{ZnBr}_2 < \text{ZnCl}_2$. Complex ions are less hydrated than simple ions.

The results obtained by us and referred to above allow the following conclusion to be drawn: At extreme dilutions, *i.e.* at a high degree of dissociation of the salt, zinc chloride behaves towards poly(2-hydroxyethyl methacrylate) like other chlorides, *i.e.* salts it out. At higher concentrations, when complex ions and undissociated salt molecules appear to an increasing extent, the salting-in effect sets in. Of chlorides, besides ZnCl_2 , FeCl_3 also raises the degree of swelling while exhibiting an extremely high and positive parameter m_2 . In solutions of this salt complexes have been detected²⁴, of which the FeCl_6^{3-} predominate at the highest concentrations. Consequently, the salting-in effect of ferric chloride could be explained similarly to the zinc salt.

It seems that a hypothesis could be accepted that the salting-in effect of some salts (nitrates, halides of Zn^{2+} , Cd^{2+} , or Fe^{3+}) is related to the fact that unhydrated or low-hydrated particles (undissociated molecules, ion pairs, complex ions) increase in number with increasing concentration; they bind the water molecules much less than simple ions, are not squeezed out from the polymer-water interface, destroy the water structure owing to their bulkiness (if this structure can still exist) and "release" water molecules for the interaction with the hydrophilic polymer

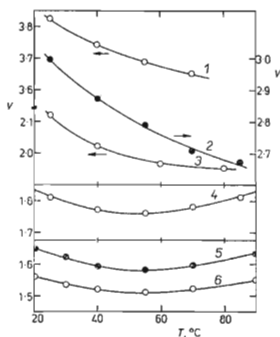


FIG. 10
Temperature Dependence of the Degree of Swelling in Solutions of $\text{Mg}(\text{ClO}_4)_2$, NaCl and in Water

1 1M- $\text{Mg}(\text{ClO}_4)_2$; 2 0.5M- $\text{Mg}(\text{ClO}_4)_2$;
3 0.1M- $\text{Mg}(\text{ClO}_4)_2$; 4 water; 5 0.54M- NaCl ;
6 0.93M- NaCl (concentration related to 25°C).

groups. It should be pointed out, in this connection, that perchlorates (including $\text{Zn}(\text{ClO}_4)_2$) exhibit only a very weak tendency towards associations^{21,23} and that no ion pair formation could be proved for alkali metal iodides²¹. Unfortunately, such information about thiocyanates of the above cations is lacking.

Temperature Dependence of the Degree of Swelling

Typically salting-in and typically salting-out salts, $\text{Mg}(\text{ClO}_4)_2$ and NaCl were chosen for the investigation of the temperature dependence of the equilibrium volume degree of swelling, V . Examples of the dependences (Fig. 10) show that the minimum of the degree of swelling in water at $\sim 55^\circ\text{C}$ is quickly shifted towards higher temperatures and cannot be perceived any more in the temperature range studied. The temperature coefficient of the degree of swelling is then negative. A similar effect is exhibited by urea³, but $\text{Mg}(\text{ClO}_4)_2$ is much more effective: while with urea the minimum disappears only at $C_s = 4 \text{ mol/l}$, with $\text{Mg}(\text{ClO}_4)_2$ it cannot be perceived already at a concentration of 0.1 mol/l . On the other hand, the constants of the concentration dependence analogous to Eq. (4) for the volume degree of swelling (k'_1 and k'_2) decrease with increasing temperature: for 25, 40, 55 and 70°C k'_1 is 3.08, 2.60, 2.22 and 1.82, k'_2 is 0.43, 0.32, 0.15 and -0.02 . The qualitative interpretation of the temperature behaviour is similar to urea³: with increasing salt concentration the hydrophobic interactions become weaker, and the "aqueous" character of the system is extended to higher temperatures.

The effect of NaCl on the shape of the temperature dependence is small, which means that the character of the interactions in the swollen gel does not change too much by salting-out effects.

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