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SALTING-OUT AND SALTING-IN OF NON-ELECTROLYTES

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The problem of the effect of electrolytes on the solubility of non-electrolytes is of great theoretical and practical importance. A great deal of work[1-57] has shown that electrolytes can either decrease or increase the solubility of neutral substances in water, the phenomenon being termed *salting-out* or *salting-in* respectively.

Processes associated with salting-out are widely used in the production of dyes, amines, soaps, etc. At the present time the employment of salting-out agents in extraction is becoming especially important[58-74]. On the other hand, substances which increase the solubility of non-electrolytes in water (hydrotropic substances) are beginning to find application in industry.

McKee[75] reported the employment of alkanesulphonates of the alkali and alkaline earth metals in papermaking, and referred to the possibility of replacing organic solvents by solutions of hydrotropic salts in the electrolysis of organic substances. The presence of a second phase in the system is known to diminish the rate of many organic reactions. By the use of hydrotropic salts the system can be made homogeneous, and the rate of the process thereby increased. In addition, salts influence the course of a reaction[76-79].

The behaviour of salts in aqueous solutions of non-electrolytes is a complicated phenomenon owing to the occurrence in the water–electrolyte–non-electrolyte system of various types of interaction: water–electrolyte, water–non-electrolyte, and electrolyte–non-electrolyte.

Systematic study of the effect of salts on the solubility of neutral substances in water has revealed several regularities, which have subsequently formed a basis for theories of salting-out and salting-in. The influences of some substances on the solubility of others has been investigated by various methods — by direct measurement of solubilities, determination of partition coefficients, determination of

freezing-point depression, and measurement of partial vapour pressures. The results obtained can be summarised briefly as follows:

1. In the overwhelming majority of cases, electrolytes diminish the solubility of non-electrolytes in water.

2. The smaller an ion having a given charge, the greater its salting-out action.

3. The sequence of salts remains the same for their action on many but not all non-electrolytes.

4. Increase in ionic radius (of cation or anion) results in a decrease in the salting-out effect and a change to salting-in.

5. The salting-out constant can be calculated from Sechenov's equation

$$\log\frac{S_0}{S} = K_S C_S, \qquad (1)$$

where S_0 and S are the solubilities of the non-electrolyte in water and in the aqueous salt solution, C_S is the concentration of the salt, and K_S is the salting-out constant.

6. The change in the logarithm of the activity coefficient of the non-electrolyte is found to be proportional to the salt concentration expressed in moles or equivalents per litre.

Sechenov's equation has been tested many times[80-84], and, although the constant varies with the electrolyte concentration, especially at high values of the concentration, the equation has so far found wide application for assessing the effects of different salts.

Rendall and Failey[5-7] proposed as measure of the salt effect the ratio of the logarithm of the activity coefficient of the non-electrolyte f_S to the ionic strength of the solution μ_{soln}. In their view this quantity $(1/\mu_{soln})\log f_S$ has the advantage that it does not involve the valencies of the ions, and it remains constant in solutions of different ionic strength. Rendall and Failey's results for benzoic acid in solutions of sodium chloride at 25° may serve as illustration (Table 1).

Rendall and Failey give the following sequence for the action of the ions

$$OH^- > SO_4^{2-} > CO_3^{2-} > ClO_3^- > BrO_3^- > Cl^- > CH_3COO^- > IO_3^- > ClO_4^- > Br^-,$$
$$I^- > NO_3^- > Na^+ > K^+ > Li^+ > Ba^{2+} > Ca^{2+} > Ni^{2+} > Co^{2+} > Mg^{2+} > Fe^{2+} >$$
$$> Zn^{2+} > Mn^{2+} > Al^{3+} > NH_4^+ > H^+$$

This sequence is approximately maintained for many non-electrolytes, but investigations of the effect of 0.5 M NaCl solution on the solubility of various substances in water at 30° showed that the salting-out effect depends also on the nature of the non-electrolyte (Table 2).

TABLE 1. Activity coefficient and values of $(1/\mu_{soln})\log f_S$ in solutions of different ionic strengths[5].

μ_{soln}	f_s	$(1/\mu_{soln})\log f_s$
0.01982	1.007	0.153
0.02502	1.010	0.173
0.03320	1.014	0.182
0.05010	1.023	0.197
0.1002	1.045	0.191
0.2009	1.092	0.190
0.3356	1.154	0.185
0.5022	1.231	0.180

It is difficult from the data in Table 2 to establish a relation between the polarity of the non-electrolyte and the salting-out effect of the given electrolyte. Although the percentage salting-out is greatest for substances which possess no dipole moment μ, it is also high with ethyl iodide (μ = 1.7) and low with chlorobenzene (1.56).

We can also examine Long and McDevit's data[4] in Table 3, in which the dipole moments and the salting-out constants of organic compounds are compared (with potassium chloride as electrolyte).

No very clear parallelism is observed on comparing the variation in salting-out constant with dipole moment. Thus nitrobenzene and benzene, which differ greatly in their polar properties, have the same salting-out constants, but if nitrobenzene and *p*-phenylenediamine are excluded, an increase in dipole moment entails a decrease in salting-out constant. Where the tables give no indication of salt concentration, the values of K_S relate to infinite dilution, and have been calculated from the slope of the linear dependence of $\log f_S$ on salt concentration.

Interesting observations were made by Linderstrøm-Lang[86] on the effect of substituted ammonium chlorides on the solubility of benzoquinone and quinol in water. That of quinol increases and the salting-in constant changes with change in size of the cation, whereas benzoquinone is salted-out by all these salts, and the salting-out constant is small and unchanged.

Long and McDevit[87] examined the difference in the action of salts on acidic and basic non-electrolytes. If the non-electrolyte is basic in character, sensitivity to the charge on the anion is observed, and lithium salts cause salting-in. The salting-out of weak acids increases with the charge on the cation, and cations show the normal sequence in their action: i.e. salting-out is more intense with lithium than with sodium salts. In the view of these workers the difference in the action of salts on non-electrolytes of acidic and basic character is associated with the orientation of water

TABLE 2. Effect of 0.5 M NaCl solution on the solubility of various substances in water at 30°.[85]

Compound	Salting out, %	$10^{18}\mu$	Compound	Salting out, %	$10^{18}\mu$
p-Nitroaniline	3.0	7.1	Methylene diiodide	11.6	1.1
m-Dinitrobenzene	3.0	3.8	Propyl bromide	11.9	1.9
Nitrobenzene	3.1	4.0	n-Butyl bromide	12.3	1.9
Bromobenzene	4.1	1.50	Propyl iodide	13.2	1.7
Chlorobenzene	5.6	1.56	Ethyl iodide	13.5	1.7
Bromoform	8.2	1.0	Ethylene dibromide	13.7	1.0
Methylene dibromide	9.1	1.4	Carbon tetrachloride	16.7	0
Chloroform	9.7	1.2	Benzene	19.1	0
Ethylene dichloride	11.3	1.8	Toluene	24.3	0

TABLE 3. Dipole moment and salting-out constant[4].

Compound	μ	K_s	Compound	μ	K_s
p-Nitroaniline	6.5	0.049	Benzoic acid	1.7	0.144
p-Nitrophenol	5.0	0.050	Phenol	1.6	0.133
m-Nitroaniline	4.7	0.077	Aniline	1.5	0.130
Nitrobenzene	4.0	0.166	*p*-Phenylenediamine	1.5	0.018
Salicylic acid	2.6	0.126	Benzene	0	0.166

molecules in the hydration sphere of the ion. Water molecules hydrating a cation are oriented with the protons on the outside, non-electrolyte molecules of basic character being attracted to them, while those of acidic character are repelled. In studying the phenomenon of salting-out, many workers have noted that the effect diminishes with increase in size of the ions, and a change to salting-in is observed [88-94].

Neuberg [95] established that aqueous solutions of many salts, such as benzoates, benzenesulphonates, and their homologues, are able to bring into solution substances of various classes which are insoluble in water (hydrocarbons, alkaloids, aldehydes, ketones, nitro-compounds, proteins, fats, etc.). Numerous experiments have shown the widespread occurrence of this phenomenon, which is termed hydrotropism.

Hydrotropic substances are usually saltlike in character, containing COOM, SO_3M, SO_2M, or OSO_3M groups. They can have either a chain or a ring structure, and may also contain halogeno-, amino-, nitro-, or hydroxy-groups.

Neuberg [95] noted that hydrotropic salts are specific in their action: sulphonates bring proteins and alkaloids into solution, but not essential oils, higher alcohols, or ketones. Table 4 shows the change from salting-out to salting-in with increase in size of the ions in the electrolyte.

Interesting results were obtained by Bockris et al. in a study of the effect of the radius of the cation on the solubility of benzoic acid in water [97]. Table 5 shows that the salting-in action increases with increase in radius of the cation.

Licht and Wiener [98] studied phase equilibria in the water–benzoic acid system containing sodium salts of benzene-, toluene-, and xylene-sulphonic acids. They noted that all the salts increase the solubility of benzoic acid in water, and that the hydrotropic effect increases as the alkyl group becomes longer, i.e. with increase in molecular weight of the salt. Introduction of a bromine atom (sodium *p*-bromobenzenesulphonate) gives the same result as increasing the size of the alkyl group. It is curious that introduction of a second sulpho-group (sodium benzene-*m*-disulphonate) destroys the salting-in property of the salt for benzoic acid, and a slight salting-out is observed. These workers remarked that the phase diagrams which they obtained give no indication of the formation of chemical compounds.

Booth and Everson [99] studied the effect of sodium *o*-, *m*-, and *p*-xylenesulphonates on the aqueous solubility of acetophenone, aniline, benzaldehyde, *o*-cresol, cyclohexanone, and diethyl ether, and found that all three salts increase the solubility of these substances to the same extent. Another paper by these workers [100] describes the action of the

TABLE 4. Constants for the salting-in of non-electrolytes by large ions at 25°. [96]

Salt	Benzene	Benzoic acid	Aniline
LiCl	0.148	0.189	0.070
NaCl	0.195	0.182	0.136
C_6H_5COONa	—0.052	—0.218	—0.043
$C_6H_5SO_3Na$	—0.090	—0.170	—0.062
p-$CH_3C_6H_4SO_3Na$	—0.070	—0.355	—0.093
$(CH_3)_4NBr$	—0.149	—0.140	—0.185
$(C_2H_5)_4NI$	—0.248	—0.360	—0.308

TABLE 5. Effect of quaternary ammonium salts on the solubility of benzoic acid in water at 25°. [97]

Salt	K_s
NH_4I	+0.021
$N(CH_3)_4I$	—0.256
$N(C_2H_5)_4I$	—0.633
$N(C_3H_7)_4I$	—0.970
$N(C_4H_9)_4I$	—1.32

sodium salts of benzene-, toluene-, xylene-, and cymene--sulphonic acids on the solubility of various kinds of substances in water. They found that hydrotropic salts, which increase the solubility of benzoic acid, behave altogether differently towards some non-electrolytes. Thus the solubility of benzene, carbon tetrachloride, cottonseed oil, and n-hexane is not increased in solutions of these salts, whereas that of *o*-cresol and cyclohexane is greatly increased.

Larsson [101-104] and Kolthoff and Bosch [105] studied the effect of sodium and potassium benzoates on the solubility of benzoic acid in water. It would appear from the law of mass action that salts containing the same ion as the acid should diminish the solubility of benzoic acid, but the opposite results were obtained: the presence of salts of benzoic acid in water led to an increase in the solubility of the acid. Similar effects were found by Ross et al. [106] in a study of the influence of salts of mandelic acid on the solubility of this acid, and by Osol and Kilpatrick [107,108] with *o*-chlorobenzoic acid and the corresponding sodium salt.

Kolthoff and Bosch [105] attribute this action of salts on the solubility of weak acids to interaction between the ion of the salt and a molecule of the acid according to the equation

$$HB + B^- \rightleftarrows HB_2^-.$$

Observations of salting-in effects were accompanied by attempts to explain this phenomenon. Some authors assumed it to result from chemical interaction between electrolyte and non-electrolyte [18,106,109], but Neuberg [95] did not regard this as the sole cause, since in many cases the observed increase in solubility is not the result of a chemical process.

Gross [85] suggested that cations and anions have opposite effects, the former salting-out and the latter salting-in, and the overall action of a salt being the net effect of cationic and anionic components.

Gross [85] and Larsson [101-104] suggested that the constant of the salt effect is an additive function of two constants characteristic of the anion and the cation:

$$\log f_s = K_s C_s = (K_K + K_A) C_s.$$

Larsson assumed that $K_{K^+} = K_{Cl^-}$, and since $K_{KCl} = 0.14$, it follows that $K_{K^+} = K_{Cl^-} = 0.07$. This hypothesis was used as a basis for calculating salting-out constants for other ions.

It is seen from the data for benzoic acid in Table 6 that the ionic salting-out constants for many large anions are negative, showing that these ions have a salting-in action. Further investigation established that not only bulky anions but also large cations (quaternary ammonium halides) exert a salting-in effect [97,108].

TABLE 6. Ionic salting-out constants for benzoic acid[85].

H^+	0.02	Cs^+	−0.08	Cl^-	0.07	$OCOCH_3Cl^-$	−0.14
Li^+	0.12	Mg^{2+}	0.10	Br^-	0.00	$OCOCCl_3^-$	−0.12
Na^+	0.11	Ca^{2+}	0.10	I^-	−0.02	$OCOC_6H_5^-$	−0.32
K^+	0.07	Sr^{2+}	0.09	NO_3^-	0.03	$OSO_3C_6H_5^-$	−0.23
Rb^+	0.02	Ba^{2+}	0.08	ClO_4^-	0.06	$OSO_3C_{10}H_7^-$	−0.86

All these investigations led to the development of theories to explain the action of salts on the solubility of non-electrolytes. The earliest of these was the hydration theory. During the 1890's a study of the solubility of carbon dioxide in water and salt solutions led Sechenov[1] to the conclusion that the gas was always less soluble in the presence of salts than in pure water. He put forward the hypothesis that "Salt solutions are compounds of the salt and water. On this basis we could regard the solution as if only the solvent, water, were the absorbing medium for the gas, while the salt combines with water, and weakens its absorbing power". Thus Sechenov was the first to express the opinion that the decrease in solubility of the non-electrolyte is due to hydration of the salt.

Rothmund[2], Philip[110-112], and later Glasstone[113-116] as well as Eucken and Herzberg[117] have assumed that the salting-out action of electrolytes is due to ions binding water molecules and diminishing the quantity of free solvent, so that the solubility of neutral molecules decreases. But this apparently extremely plausible view cannot explain the dependence of the hydration numbers of the ions during salting-out on the nature of the non-electrolyte. Moreover, the hydration theory cannot explain the increase in solubility of a non-electrolyte caused by the addition of certain electrolytes.

Another attempt to provide a theoretical basis for salting-out phenomena is due to Debye and McAulay[118,119], who take into account only the effect of one type of forces, the coulombic forces. Ions are regarded as spheres having a definite radius. The work done in discharging ions is calculated for the pure solvent of dielectric constant D_0 and for a medium of dielectric constant D, which medium may be the solution containing both electrolyte and non-electrolyte. This leads to the appearance of an additional component of the chemical potential, and thus the activity coefficient of the neutral molecules was found to be given by the equation

$$\log f_s = \log \frac{S_0}{S} = \frac{\beta}{2KTD_0} \sum \frac{n_j l_j^2}{r_j}, \qquad (2)$$

where K is Boltzmann's constant, T the absolute temperature, n_j the number of ions of a given kind, l_j the ionic charge, r_j the ionic radius, D_0 the dielectric constant of water, D that of the solution, and n the number of moles of the non-electrolyte.

The constant β, characterising the non-electrolyte, can be found from the equation

$$D = D_0(1 + \beta n). \qquad (3)$$

This equation shows that, if the dielectric constant is smaller than that of the pure solvent, β will be positive, indicating salting-out. If, however, the value of D for the solution is greater than that for water, β will be negative, and salting-in will occur. A single example satisfying this condition has been reported in the literature: the experiments of Gross[120] on the distribution of hydrogen cyanide and acetone between benzene and aqueous solutions of salts show that acetone is salted-out, since it decreases the dielectric constant of water, whereas hydrogen cyanide is salted-in, because hydrocyanic acid possesses a higher dielectric constant than water, and its addition to the latter increases the value of D for the solution.

According to the equation of Debye and McAulay, $\log f_s$ should vary linearly with electrolyte concentration, as is also observed in most cases. Figs. 1 and 2 show as example the effect of various electrolytes on the solubility of hydrogen and benzoic acid[4]. It is noteworthy that this equation is similar in form to the empirical equation of Sechenov. Furthermore, the equation of Debye and McAulay gives the dependence of the salting-out action of an electrolyte on the radius of its ions: the smaller the radius of the cation, the greater the diminution in solubility of the non-electrolyte produced by a given electrolyte. Later Debye developed a more exact theory of salting-out, which was further developed in papers by Gross[121-124], Butler[125], Kirkwood[126], and others[127-132].

Long and McDevit[44] compare the effect of salts on the solubility of benzene in water with values calculated from the equations of Debye and of Kirkwood. It is seen from Table 7 that values calculated by means of the two equations differ little between themselves. They predict the general order of change on passing from one salt to another, but give an inadequate idea of the specific action of salts observed experimentally. This is understandable, since the

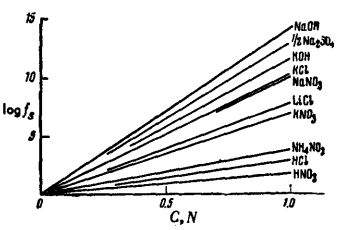


Fig. 1. Action of salts on the solubility of H_2.[4]

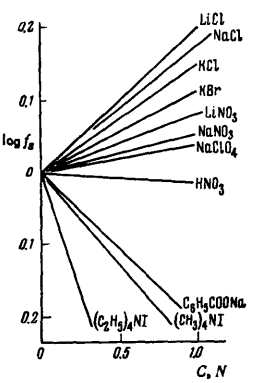


Fig. 2. Effect of salts on the solubility of benzoic acid in water at 25°.[4]

TABLE 7. Comparison of calculated and experimental salting-out constants for benzene[44].

Salt	K_{obs}	K_{Debye}	$K_{Kirkwood}$
NaF	0.254	0.130	0.133
NaCl	0.195	0.126	0.125
NH_4Cl	0.103	0.124	0.109
LiCl	0.141	0.127	0.143
NaI	0.095	0.122	0.120
CsCl	0.088	0.121	0.105
$(CH_3)_4NBr$	—0.24	0.110	0.093

whole specific action of an electrolyte is contained, in these equations, in the ionic radii, which differ little among themselves, so that the salting-out constants calculated from these equations vary insignificantly, and differ appreciably from the observed values. It is noteworthy that neither equation provides for salting-in.

Mikhailov[133] has attempted to refine the Debye equation by introducing the concept of a salting-out sphere of finite radius. A new term appears in the equation, which takes into account both the actual volume of the ion and the change in the salting-out sphere with increase in electrolyte concentration. Agreement between calculated and observed values is unsatisfactory. Thus for the water–benzene–sodium chloride system the calculated coefficient is 0.114, while the actual value is 0.260. The discrepancy between calculated and experimental values is attributed by the author to disregard of non-electrostatic interactions in the solution.

The defects of the Debye theory are not removed by refinements of a different type. As before, experimental activity coefficients differ substantially from the calculated values, and the Debye–McAulay equation gives no transition from salting-out to salting-in. It was mentioned above that several authors found an increase in solubility of a non-electrolyte to be produced by electrolytes having large ions, and it was therefore suggested that salting-in by large ions is due to the action of van der Waals forces. On this basis Bockris[97,132] put forward a theory which took into account the action of both coulombic and dispersion forces. If the latter predominate, salting-in is observed; if coulombic forces are predominant, salting-out occurs. Bockris has shown that, with ions of high polarising power, ion–non-electrolyte dispersion interaction may predominate over ion–water coulombic interaction. Large ions, of high polarisability, interact more strongly with non-electrolyte molecules than with the small water molecules, and therefore salting-in is observed.

The proposed equation is[97,132]

$$\frac{\Delta S}{S_0} = m_i\left(P_C - P_B\frac{v_C}{v_B}\right)\frac{2\pi l_0^2 N_A}{1000\epsilon_s^2 KT}\left(\frac{1}{a_+}-\frac{1}{a_-}\right)+\left(\frac{\alpha_C\nu_C}{\nu_{A\pm}+\nu_c}-\frac{\alpha_B\nu_B}{\nu_{A\pm}+\nu_B}\,\frac{v_C}{v_B}\right)\times$$
$$\times\frac{2\pi\times N_A h}{1000\epsilon_0^2 KT}\left(\frac{\alpha_{A+}\nu_{A+}}{a_+^2}+\frac{\alpha_{A-}\nu_{A-}}{a_-^2}\right), \qquad (4)$$

where A represents the electrolyte, B the solvent, C the non-electrolyte, a ionic radii, P total molecular polarisations, γ characteristic frequencies, α electron polarisabilities, v molecular volumes, ϵ dielectric constants, m_i the electrolyte concentration in g-ions litre^{-1}, l_0 the ionic charge, h Planck's constant, and N_A Avogadro's number. The first term in this equation represents coulombic interaction, and the second term dispersion interaction. Only these two types of forces are considered in this theoretical approach, other components of the van der Waals forces being ignored, since calculations by Bockris and his co-workers showed them to constitute, e.g. for the tetraethylammonium ion, less than 1% of the total dispersion energy.

Results calculated from Eqn. (4) are compared with experimental data in Table 8. Bockris et al.[97] comment on the table that, in view of the approximate character of the equation, it shows a certain agreement, giving the correct sign and sequence of change. In contrast to the Debye–McAulay equation, the possibility of two effects — salting-in and salting-out — is predicted by the present equation. Thus according to the views of Bockris[97] the increase in solubility of a non-electrolyte in the presence of a salt containing large ions results from the predominance of dispersion interaction between the non-electrolyte molecule and the large ion of the salt. Similar views had been expressed earlier by Kruyt and Robinson[86], Gross[85], etc. Thus Gross writes: "The reason for aggregation about the anion is more difficult to see, at least for the simple spherical ions such as the halogens. For the complex ions it is not so difficult. An ion like the benzoate ion consists of a large non-polar phenyl group and a small polar carboxy-group. The field around such an ion is highly unsymmetrical, and water molecules can accumulate around the carboxy-group, with non-electrolyte molecules at the other end. The size of the ion, the distribution of polar portions, and the possibility of orientation inherent in the non-electrolyte molecule should result in a highly specific character in the solubility effect".

Albright and Williams[134] concluded, from a comparison of experimental results for the action of various salts on the solubility of ethyl acetate in water with values calculated by means of various equations, that salt constants calculated on the basis of electrostatic theories disagree most with experimental data, and therefore dispersion interactions must be taken into account.

Work on other lines links the action of salting-in and salting-out agents with structural changes in the solvent (water) itself. At the end of the past century Tammann[135–140] pointed out that, if a substance which dissociates into ions is dissolved in water, the water behaves as if it were under an additional pressure, and the volume of the solution decreases owing to compression of the water itself.

Using this hypothesis, Gibson[141–143] suggested an extrapolation equation representing the property of water as a function of pressure and taking into account the change in volume of pure water when a salt is dissolved in it.

TABLE 8. Comparison of experimental salting-out with values calculated from Eqn. (4).[97]

System	$\frac{\Delta S}{S_0 m}$ coulombic	$\frac{\Delta S}{S_0 m}$ dispersion	$\frac{\Delta S}{S_0 m}$ total	$\frac{\Delta S}{S_0 m}$ expt.
$N(C_2H_5)_4I$–ethylene glycol–benzoic acid	—0.480	+0.536	+0.06	+0.26
$N(CH_3)_4Br$–water–benzene	—0.283	+0.864	+0.58	+0.72
$N(CH_3)_4I$–water–benzoic acid	—0.279	+1.224	+0.95	+0.80
$N(C_2H_5)_4I$–water–benzoic acid	—0.257	+1.224	+0.97	+0.22
$N(C_3H_7)_4I$–water–benzoic acid	—0.242	+1.224	+0.98	+8.3
$N(C_4H_9)_4N$–water–benzoic acid	—0.231	+1.224	+0.99	+2.0

Euler [144-146] was the first to point out the link between the decrease in solubility of a neutral substance and the magnitude of the compression produced by the added electrolyte. He states that a certain parallelism exists between the compression of the solvent and the diminution in solubility, but no quantitative relations have yet been found. Euler then compares the surface tension of the solution with the solvent power of the salt solutions, and shows that only a qualitative relation exists between decrease in surface tension and change in solubility.

Geffcken [147] also concluded, from determinations of the solubility of H_2, O_2, N_2O, and CO_2 in aqueous acids and bases, that the cause of the decrease in solubility of the gases must be sought in compression of the water itself.

Long and McDevit [44] measured the activity coefficients of benzene in aqueous salt solutions. This non-electrolyte was chosen as having a non-polar molecule, which almost completely excludes any type of interaction between the solution components and simplifies explanation of the results. These workers obtained for univalent anions the following salting-out sequence

$$OH^- > Cl^- > Br^- > NO_3^- > ClO_4^- > I^-,$$

and for alkali-metal cations

$$Na^+ > K^+ > Li^+ > Rb^+ > Cs^+.$$

Compounds containing large ions, such as $(CH_3)_4NBr$ and C_6H_5COOK, increase the solubility of benzene in water. These results were explained on the basis of Tammann's views: compression of the solvent under the influence of the ions impedes entry of neutral molecules into the solution, as a result of which the solubility diminishes; and conversely, large ions loosen the structure of water and thereby facilitate dissolution of neutral molecules.

In order to assess quantitatively the action of electrolytes on the solubility of non-electrolytes, Long and McDevit [44] proposed an equation of the form

$$K_s = \lim \frac{d \ln f_s}{dC_s} = \lim \frac{v_i^0 dP_e}{RTdC_s} = \frac{v_i^0 (v_s - v_s^0)}{RT\beta_0}, \qquad (5)$$

where v_S^0 is the partial molar volume of the salt at infinite dilution, C_S the molar concentration of the salt, β_0 the compressibility of water, v_S the molar volume of the liquid salt, v_i the partial molar volume of the non-electrolyte, and P_e the effective pressure. The quantity v_S cannot be found directly, and therefore data on compression are mostly used and the quantity dP_e/dC_S is employed.

Table 9 gives a comparison of salting-out constants for benzene, hydrogen, and oxygen from aqueous solutions of various salts as calculated by means of Eqn. (5) and found experimentally. With oxygen and hydrogen satisfactory agreement is observed between calculated and experimental values of the salting-out constants, but in the case of benzene the calculated value exceeds the experimental value by factors of 2–3. It was supposed [44] that, if a correction is introduced into Eqn. (5) to allow for the closest distance of approach of an ion and a non-electrolyte molecule, the equation would become

$$\lim \frac{d \ln f_s}{dC_s} = \frac{v_i^0 (v_s - v_s^0)}{RT\beta_0} \cdot \frac{a}{a+b}, \qquad (6)$$

where a and b are the radii of the ion and the neutral molecule. With this correction better agreement is obtained between experiment and calculation for benzene molecules.

TABLE 9. Comparison of calculated and experimental salting-out constants [44].

Salt	Hydrogen		Oxygen		Benzene	
	K_{obs}	K_{calc}	K_{obs}	K_{calc}	K_{obs}	K_{calc}
Na_2SO_4	0.278	0.46	—	—	0.548	1.33
NaOH	0.140	0.25	0.179	0.29	0.256	0.85
NaCl	0.114	0.12	0.141	0.15	0.198	0.42
NaBr	—	—	0.110	0.12	0.155	0.34
LiCl	0.076	0.09	0.100	0.11	0.141	0.31
KCl	0.102	0.10	—	—	0.166	0.34
RbCl	—	—	—	—	0.140	0.31
$NaNO_3$	0.100	0.09	—	—	0.119	0.31
KNO_3	0.070	0.07	0.100	0.08	0.095	0.27
$NaClO_4$	—	—	—	—	0.106	0.26
CsCl	—	—	—	—	0.088	0.26
NH_4Cl	—	—	—	—	0.103	0.15
HCl	0.030	0.03	0.031	0.03	0.048	0.09
$HClO_4$	—	—	—	—	—0.041	—0.05
$(CH_3)_4NI$	—	—	—	—	—0.24	—0.54

A characteristic feature of Eqn. (5) is its prediction of salting-in by such substances as tetramethylammonium bromide and perchloric acid. According to the equation a linear dependence of $\log f_S$ on salt concentration corresponds to a linear dependence of P_e on C_S (Fig. 3), and the sequence of salting-out effects of the salts is approximately the same as that of the effective pressure.

This theory is in essence the same as the view expressed earlier by Bernal and Fowler [148] that in liquid water the molecules tend to form a tetrahedral structure, with the oxygen atoms at the corners. When a substance which dissociates into ions is introduced, the water molecules begin to orient themselves around these ions. The number of water molecules surrounding an ion depends on the relative size of ion and water molecule, the charge on the ion, and hence on the force field at the surface of this ion. These factors will determine the degree of hydration of ions in aqueous solution and the extent to which the water structure is compacted or loosened.

Small ions carrying a high charge will make the water structure more rigid, produce compression of the solvent or increase its internal pressure, and thereby impede penetration of non-electrolyte molecules into the solution:

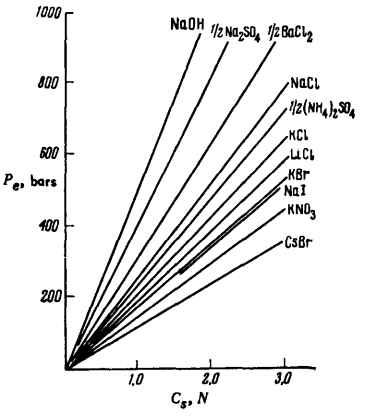


Fig. 3. Dependence of effective pressure P_e on salt concentration [142,143].

they will diminish the solubility of the non-electrolyte, i.e. salt it out. Large ions having the same charge, on the other hand, will loosen the structure of water, diminish its internal pressure, and thereby favour the passage of molecules of non-electrolyte into the solution: they will salt it in.

The effect of ions on the structure of water is shown in many papers [149-159]. Gurikov [160], for example, links the salting-out action of ions with changes in the structure of water itself. The passage of water into a condensed state is accompanied by the formation of hydrogen bonds. This leads to a redistribution of electron density in the molecule and in the hydrogen bond, resulting in the appearance of a dipole possessing its own moment. In estimating the salting-out effect of electrolytes, therefore, we must take into account the structural correction produced by the action of "hydrogen dipoles" on the structure of water in the electrostatic field of the ions. The complete salting-out coefficient is made up of two terms: $K = K_S + \Delta K_S$, where K is the salting-out constant calculated from Eqn. (5) and ΔK_S a structural correction which can be calculated from an equation suggested by Gurikov. Calculations made for singly charged ions give satisfactory agreement with experimental values of the salting-out constants of benzene at 20° (Table 10).

Samoilov and his coworkers [161-164] have examined the influence of the nature of the salting-out agent on the extraction of certain mineral salts from aqueous solution. The process of extraction involves complete or partial replacement of water molecules by molecules of the organic solvent. The role of the salting-out agent is in effect to facilitate this process. Regarding the thermal motion of the solvent molecules as consisting of vibrations and rotational oscillations about temporary equilibrium positions, together with intermittent displacements from one state of equilibrium to another, Samoilov considers that a molecule must have a certain activation energy in order to accomplish such a jump. This activation energy is affected by the salting-out agent, and may either decrease, which results in salting-out, or increase, which leads to salting-in.

In a study of the influence of various substances on the solubility of benzoic acid in water, alcohols, and water–alcohol mixtures [165-168] the reviewer and her collaborators have observed both salting-in and salting-out. If alkali-metal halides and perchlorates, biphenyl, phenanthrene, resorcinol, and diphenylamine are used as additives, the solubility of benzoic acid is diminished; whereas methylpyridinium, ethylpyridinium, and tetraalkylammonium iodides and urea increase the solubility of benzoic acid in water.

On the basis of these results we have put forward a hypothesis which enables the salting-in and the salting-out of non-electrolytes to be considered from a unified viewpoint. The essence of this hypothesis is that salting-in will be observed if the added solid dissolves the salted-in substance better than does the solvent (water, alcohol, or a mixture thereof) in which the solubility is determined; and conversely, if the added substance dissolves the non-electrolyte less well than does the solvent, salting-out will be observed. Similar views were put forward, but in a more general form, by Bancroft [169].

In order to test our hypothesis experimentally, we have made direct determinations of the solubility of benzoic acid in the substances added as electrolyte. Sodium and lithium chlorides, sodium iodide, lithium perchlorate, etc. do not lower the melting point of benzoic acid: i.e. they do not dissolve in it, and salt it out from any solvent (water or alcohol). Such salts as methylpyridinium and ethylpyridinium iodides and quaternary ammonium salts, which dissolve benzoic acid many times better than water, increase its solubility in water. For example, the solubility of benzoic acid in water at 100° is 0.108 mole fraction, whereas in tetraethylammonium iodide under the same conditions it is 0.680. On the other hand, these same substances salt out benzoic acid from ethanol, which, as is evident from Fig. 4, dissolves benzoic acid better than do the above electrolytes.

These results led us to study the effect of methylpyridinium, ethylpyridinium, and tetraethylammonium iodides on the solubility of benzoic acid in water–alcohol mixtures, since it should then be possible to observe the interesting phenomenon of a gradual transition from salting-out to salting-in. The experiments confirmed the correctness of this suggestion (Fig. 5). In aqueous–alcoholic solutions a change from salting-out to salting-in is observed, and in a mixture containing ~ 50% of alcohol the salt effect is zero [170-172]. Nevertheless, lithium perchlorate salts-out benzoic acid from water, alcohol, and water–alcohol mixtures (Fig. 5).

A study of the effect of electrolytes and non-electrolytes on the solubility of naphthalene in methanol has yielded similar results [173,174]. Substances which do not dissolve naphthalene (sodium iodide and bromide, lithium chloride and perchlorate, urea, etc.) salt it out from methanol. Biphenyl and phenanthrene form with naphthalene an ideal system obeying the Schröder–Le Châtelier equation, but nevertheless they salt naphthalene into methanol, since it is less soluble in this solvent than in phenanthrene and

TABLE 10. Comparison of calculated and experimental values for the salting-out of benzene [160].

Salt	K	K_{calc}	K_{exp}
NaCl	0.42	0.245	0.195
NaBr	0.34	0.175	0.155
NaI	0.27	0.095	0.095

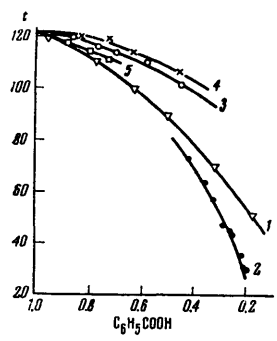


Fig. 4. Solubility of benzoic acid (mole fraction) in: 1) ideal solubility; 2) ethanol; 3) $C_5H_5NCH_3I$; 4) $(C_2H_5)_4NI$.

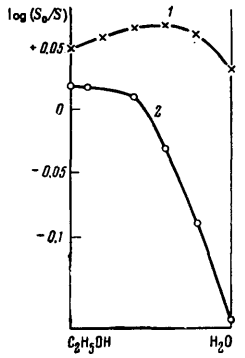


Fig. 5. Variation of logarithm of activity coefficient for benzoic acid with composition of binary solvent: 1) $LiClO_4$; 2) $C_5H_5NCH_3I$.

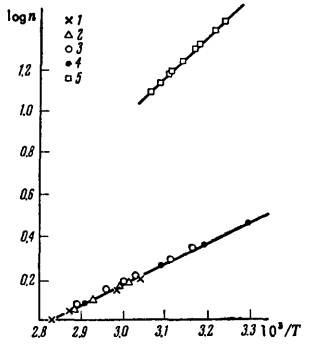


Fig. 6. Dependence of logarithm of mole fraction of benzoic acid ($\log n$) on reciprocal of absolute temperature for: 1) naphthalene–biphenyl; 2) naphthalene–phenanthrene; 3) naphthalene–diphenylamine; 4) ideal straight line; 5) naphthalene–methanol.

TABLE 11. Salting-out constants for naphthalene and benzoic acid in methanol.

Compound	C, M	$C_{10}H_8$ $K_{35°}$	C_6H_5COOH $K_{35°}$
LiCl	0.1	0.185	0.245
$LiClO_4$	0.1	0.073	0.123
$(C_6H_5)_2$	0.1	—0.512	0.630
$(C_6H_5CH)_2$	0.1	—0.512	1.34
$(C_6H_5)_2NH$	0.1	—0.403	0.033
$(NH_2)_2CO$	1.0	0.051	—0.056
$C_6H_4(OH)_2$	2.0	0.006	0.049
$C_5H_5NC_3H_5I$	0.1	—0.155	—0.512

biphenyl (Fig. 6). Benzoic acid is salted-out of methanol by these substances, because it is more soluble in methanol than in them.

Table 11 shows the effect of various substances on the solubility of naphthalene and of benzoic acid in methanol. The salting-out constant was calculated from Sechenov's equation. Experiments on the effect of biphenyl and phenanthrene on the solubility of naphthalene in methanol show that chemical interaction between these substances is not a necessary condition for a salting-in action.

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STEPWISE REACTIONS IN ELECTROCHEMICAL KINETICS

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I. INTRODUCTION

A cathodic process is usually divided into stages — (*a*) supply of the ion to the electrode surface, (*b*) reduction of the ion, and (*c*) desorption of the reaction product or its interaction with the electrode material — and an anodic process consists correspondingly of the reverse sequence of analogous stages. The departure of the electrode potential from the equilibrium value is governed by the rate of the slowest stage.

During 1930–1933 Erdey-Grúz and Volmer[1] and also Frumkin[2] linked the polarisation accompanying the discharge and ionisation of hydrogen with the stage actually involving reduction of the ion and oxidation of a neutral atom of hydrogen.

The concept of discharge–ionisation as the slow stage proved to be extremely fruitful, and led to a theory of so-called electrochemical kinetics which in several cases provided a quantitative account of experimental results. In this theory reduction or oxidation was usually regarded as a process occurring in a single act. In other words, it was assumed that an ion undergoing reduction added on at once all the electrons required to form the final product, and that in oxidation simultaneous removal of electrons at once yielded an ion of the required valency.

Recently, however, it has become clear that this simplest form of the theory is not always consistent with the experimental data. This has led to attempts to develop