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Salting-out and Salting-in of Gaseous Non-electrolytes in Aqueous Solutions of Electrolytes

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Modern theories of salting-out and salting-in of gaseous non-electrolytes are reviewed and compared with experimental data. We conclude that a strict thermodynamic theory of salting-out and salting-in of non-electrolytes is not yet available. The use of salting-out and salting-in data to determine some physicochemical characteristics of solutions is described. 56 references.

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I. INTRODUCTION

Salting-out and salting-in effects of non-electrolytes in aqueous solutions of electrolytes are of general interest in physical chemistry as well as being used in applied chemistry.

Salting-out and salting-in effects are widely used in extraction. Quantitative data on the salting out of gases such as hydrogen, carbon monoxide, and oxygen are highly relevant to the design of electrochemical generators (fuel cells). Electrochemical generators operate in the diffusion-controlled regime for the supply of gaseous reagents to the electrodes. In electrolyte solutions the concentration of these gases is decreased by salting out, and as a result the diffusional flow to the electrodes and the available current density both decrease. Salting-in and salting out are directly related to changes in the activity coefficients of the gaseous non-electrolytes. A knowledge of the activity coefficients of the non-electrolytes is essential to the calculation of electrode equilibria involving these non-electrolytes. The calculation of the activity coefficients of non-electrolytes in solutions of electrolytes will provide the main stimulus for the development of the theory of salting in and salting out of non-electrolytes.

Allowance for salting-out and salting-in effects is necessary also in the application of polarographic methods and apparatus to the analysis of gases in solutions. This is because some of these methods measure the activity rather than the concentration of the gas. Hence we need to know the activity coefficients of the gases in solution in order to calculate their concentrations.

The fund of experimental data on the salting out and salting in of non-electrolytes has grown very considerably during the last 25 years. Substantial progress has been made in developing the theory of the phenomenon. These achievements are due primarily to progress in the development of the theory of solutions.

II. THE "HYDRATION" THEORY

The "hydration" theory of salting out—the first theory of the phenomenon—was proposed at the end of the 19th century. The first quantitative experimental results on the salting-out of gaseous non-electrolytes from aqueous solutions of electrolytes were published by Sechenov in 1875.[1,2] The result of this work was Sechenov's empirical equation, which is still one of the most successful expressions for describing quantitatively the salting out and salting in of non-electrolytes:

$$\lg \frac{s^0_{ne}}{s_{ne}} = Kc_e, \qquad (1)$$

where s^0_{ne} and s_{ne} are the solubilities of the non-electrolyte in water and in the electrolyte solution respectively, c_e is the concentration of electrolyte, and K is the salting-out coefficient (or constant).

Sechenov first put forward the suggestion that the decrease in solubility of the non-electrolyte is due to the hydration of the electrolyte. Most workers at the turn of the century explained the salting out of non-polar non-electrolytes in terms of hydration of the electrolyte: the non-electrolyte molecules are repelled from the ionic atmosphere of the electrolyte ion by the polar water molecules, and the volume of water available for dissolving the non-electrolyte is less than the total volume of water in the solution.

According to the hydration theory of salting out the quantity s^0_{ne}/s_{ne} is equal to the ratio of the volumes of "free" water in the solution before and after addition of the electrolyte:

$$\frac{s^0_{ne}}{s_{ne}} = \frac{1}{1 - \Sigma c_e V^h_e}, \qquad (2)$$

where V^h_e is the volume of one mole of hydrated molecules of electrolyte.

The hydration theory tried to explain salting-out and salting-in phenomena by considering only the hydration of the electrolyte, and it could not give a physical interpretation of the significance of the salting-out coefficient K in Eqn. (1). More recently, Ruetschi and Amlie [3] obtained an expression for $\ln(s^0_{ne}/s_{ne})$ by a series expansion of the logarithm of the right-hand side of Eqn. (2):

$$\ln\frac{s^0_{ne}}{s_{ne}} = \Sigma c_e V^h_e + \frac{1}{2}(\Sigma c_e V^h_e)^2 + \frac{1}{3}(\Sigma c_e V^h_e)^3 + \ldots \quad (3)$$

For an electrolyte at infinite dilution they retained only the first term of the series to give the approximate linear equation

$$\ln\frac{s^0_{ne}}{s_{ne}} = \sum_{c_e \to 0} c_e V^h_e = \Sigma c_e V^0_e, \quad (4)$$

where V^0_e is the intrinsic volume of one mole of the electrolyte at infinite dilution. For a fully dissociated electrolyte $c_e = \nu_e c^M_e$ (where ν_e is the number of ions produced by the dissociation of the electrolyte and c^M_e is the molar concentration of the electrolyte), and therefore

$$\ln\frac{s^0_{ne}}{s_{ne}} = c^M_e \Sigma \nu_e V^0_e. \quad (5)$$

Thus the empirical Sechenov equation (1) can be interpreted theoretically. In particular, the salting-out coefficient in Sechenov's equation should be given, according to the hydration theory, by the sum of the products $\nu_e V^0_e$ for all the electrolytes present in the solution. In this way the hydration theory can account for the relative insensitivity of the K value of an electrolyte to the nature of the non-polar non-electrolyte. It is also found that the neglect of the higher terms of the series in Eqn. (3) is compensated by the decrease of V^h_e with increasing concentration of electrolyte, so that the parameter K in Sechenov's equation remains constant up to relatively high concentrations of electrolyte. At the highest electrolyte concentrations, or if the electrolyte is not fully dissociated, the quantity c_e is no longer proportional to c^M_e, and as a result the plot of $\lg(s^0_{ne}/s_{ne})$ against c^M_e deviates from linearity.

The hydration theory cannot explain the salting-in effect occasionally observed with non-electrolytes; it follows that the constant K in Sechenov's equation is not determined simply by the intrinsic volume of the electrolyte at infinite dilution and by the number of ions formed by the dissociation of the electrolyte. The difference between the K values for hydrogen and oxygen (~25%) in both NaOH and KOH [4] is another fact which the hydration theory cannot explain.

Thus the hydration theory in its original form has only historical value as the first attempt at a theoretical interpretation of salting-out and salting-in effects of non-electrolytes. Further developments in the theory of this complicated phenomenon had to wait the appearance of the Debye–Hückel electrostatic theory of electrolyte solutions. Even more recently Ruetschi and Amlie [3] introduced the elements of electrostatic theory into the hydration theory, enabling it to take fuller account of all the factors which influence the salting out and salting in of non-electrolytes.

III. ELECTROSTATIC THEORIES

A qualitatively new approach to the salting out and salting in of non-electrolytes in terms of electrostatic interactions in electrolyte solutions was developed in 1925 by Debye and McAuley [5]. Their electrostatic theory of salting out, which treats the electrolyte solution as an ideal solution, allows for the effect of the non-electrolyte on the dielectric constant of the solution. The electrostatic field of the electrolyte ions is altered by the change in the dielectric constant of the solvent from its initial value ϵ_0 to a new value ϵ resulting from the presence of the non-electrolyte, and as a result the activity coefficient f_{ne} of the non-electrolyte is also altered. The quantity f_{ne} is given, according to the Debye–McAuley theory, by the equation [5]

$$\ln f_{ne} = \frac{N\delta_{ne}e^2}{\epsilon_0 bRT}\cdot\frac{\Sigma c_e z^2}{2}, \quad (6)$$

where N is Avogadro's number, δ_{ne} is the decrement in the dielectric constant of the solution produced by dissolution of the non-electrolyte, e and z are the electronic charge and the valency of the electrolyte ion respectively, and b is the ionic radius of the electrolyte.

Debye and McAuley calculated the quantity δ_{ne} in Eqn. (6) by a formula which includes the number of molecules of non-electrolyte per 1 ml of solution (n_{ne}):

$$\epsilon = \epsilon_0(1 - \delta_{ne}\eta_{ne}). \quad (7)$$

The δ_{ne} values for hydrogen and oxygen were determined by Scatchard [6] in 1927 (0.05 and 0.06 respectively). To calculate the ionic radius of the electrolyte Debye and McAuley proposed a formula involving the radii of the cation (r_c) and of the anion (r_a), and ν_e:

$$\frac{1}{b} = \frac{1}{\nu_e}\left(\frac{1}{r_c} + \frac{1}{r_a}\right). \quad (8)$$

The effect of hydration of the electrolyte on salting out is accounted for by the term $\Sigma c_e z^2/2$ in the Debye–McAuley equation. (This term appears also in the Born equation for the hydration energy of the electrolyte.)

Eqn. (6) has the same form as the empirical equation

$$\lg f_{ne} = K\mu, \quad (9)$$

where μ is the ionic strength of the solution. Eqn. (9) is also called the Debye–McAuley equation. In the electrostatic theory the salting-out coefficient is given by the expression

$$K = \frac{N\delta_{ne}e^2}{\epsilon_0 bRT}. \quad (10)$$

Debye and McAuley assumed that the electrolyte solution was ideal, and therefore confined the application of their electrostatic theory to the case of very dilute solutions.

Randall and Failey [7] showed that simple linear expressions such as Eqns. (6), (9), and (10) cannot be strictly correct. In particular, using Eqn. (9) to interpret experimental data on the salting out of hydrogen, oxygen, and other gases, they obtained varying values of K for these gases in the same electrolyte at different concentrations, which is inconsistent with the definition of a salting-out constant.

The salting-out theory of Debye and McAuley correctly predicts an increase in K with increasing charge and decreasing radius of the electrolyte ions. This theory allows for the decrease in the dielectric constant of the solvent caused by the presence of the non-electrolyte. However Debye and McAuley made no allowance for the decrease in the dielectric constant of the solvent caused by the presence of the electrolyte, which can be substantial [8]. The Debye–McAuley theory also fails to allow for specific interactions between the non-electrolyte and the solvent, and therefore it is powerless to explain the

salting-in effect of non-electrolytes. Experimental verification of the Debye–McAuley equation is not easy because the equation applies to very dilute solutions of electrolytes. The effect of non-electrolytes on the activity coefficient of electrolytes was first considered by Born[9]. Somewhat later Debye improved the Debye–McAuley theory[10] by treating the mixture of water and non-electrolyte as a heterogeneous medium. Assuming that the dielectric constant of the solution varies with distance r from the ion in such a way that the overall free energy of the system is a minimum, he showed that

$$f_{ne} = \left(1 - \frac{4\pi N}{1000}\sum_i I_i c_i\right)^{-1}, \qquad (11)$$

where c_i is the molar concentration of the solute. From the spherical structure of the ionic atmosphere he obtained the equation

$$I_i = \int_{r_i}^{\infty}\left[1 - \exp\left(-\frac{\bar{R}}{r}\right)^4\right] r^2\,dr, \qquad (12)$$

where r_i is the radius of the ion of solute i.

Debye's improved electrostatic theory introduces, in addition to the quantity δ_{ne}, also the change in the dielectric constant of the solution caused by the presence of the electrolyte. This leads to the equation

$$\bar{R}^4 = \frac{(ze)^2\,[v_{ne}(\partial\varepsilon/\partial c_w)\,c_{ne} - v_w(\partial\varepsilon/\partial c_{ne})\,c_w]}{8\pi RT\varepsilon^2 v_w}, \qquad (13)$$

where c_w is the molar concentration of water, $v_{ne} = V_{ne}/N$, V_{ne} is the molar volume of the non-electrolyte in the solution, $v_w = V_w/N$, V_w is the molar volume of water. The difference in the numerator of Eqn. (13) determines whether salting out or salting in of the non-electrolyte will take place.

The integration of Eqn. (12) is not taken to infinity. As shown by Ruetschi and Amlie[3], the effect of the electric field of the ion on the dielectric constant of the solution extends over the layer of solution lying between the radius of the hydrated ion (r_h) and the radius of the ionic atmosphere (r_n). Hence the integration of Eqn. (12) can be taken from r_h to r_n. The same workers[3] used the ideas of the improved Debye–McAuley electrostatic theory to develop the hydration theory, and obtained a more accurate form of Eqn. (2):

$$\frac{s^0_{ne}}{s_{ne}} = 1 - \Sigma c_e V^0_e - \Sigma I_i c_i. \qquad (14)$$

For the integral [see Eqn. (12)] which appears in Eqn. (14) Ruetschi and Amlie chose the limits r_h and r_n. At low concentrations of electrolyte they obtained

$$\ln\frac{s^0_{ne}}{s_{ne}} = c^M_e \Sigma v_e V^0_e + \Sigma I_i c_i\ . \qquad (15)$$

The parameter r_n can be calculated by the expression

$$r_n = \left(\frac{3}{4\pi n_e}\right)^{1/3}, \qquad (16)$$

where n_e is the number of ions of electrolyte in 1 ml of solution.

Eqn. (15) combines the concepts of the hydration theory and of the Debye–McAuley electrostatic theory. It is only one of the many salting-out equations.

An equation similar to Eqn. (15) was put forward by Long and McDevit[4] on the basis of an equation given in Ref. 11. For solutions of intermediate concentration, without chemical interaction between the non-electrolyte and the solution and at not too high concentrations of non-electrolyte (the solubility of gaseous non-electrolytes being usually small), Long and McDevit obtained the equation

$$\lg f_{ne} = K_e c^M_e + K_{ne} s_{ne}. \qquad (17)$$

The authors point out[4] that most theories of salting out concentrate the attention on K_e, whereas we also need to know K_{ne} to calculate $\lg f_{ne}$. Since the chemical potentials of the non-electrolyte in solution in equilibrium with the pure non-electrolyte or with the non-electrolyte in the gas phase are the same, we can write

$$f_{ne}s_{ne} = f^0_{ne}s^0_{ne}. \qquad (A)$$

It follows that

$$\lg\frac{f_{ne}}{f^0_{ne}} = \lg\frac{s^0_{ne}}{s_{ne}}, \qquad (B)$$

and

$$\lg f^0_{ne} = K_{ne}s^0_{ne}, \qquad (C)$$

and therefore Eqn. (17) can be re-written[4]

$$\lg\frac{f_{ne}}{f^0_{ne}} = K_e c^M_e + K_{ne}(s_{ne} - s^0_{ne})\ . \qquad (18)$$

The parameter K_{ne} according to Long and McDevit is determined only by internal interactions of the non-electrolyte molecules. If the difference between s^0_{ne} and s_{ne} is not large Eqn. (18) becomes identical to Sechenov's Eqn. (1). The Sechenov equation is often obeyed also when the last term of Eqn. (18) is relatively large. The empirical coefficient K of Eqn. (1) is not equal to the theoretical coefficient K_e of Eqn. (18). Experimental studies of the solubility of non-electrolytes give K_e values. However we need to know also K_{ne} in order to calculate the activity coefficients of non-electrolytes having intermediate or high solubility. Eqn. (15) makes fuller allowance than Eqn. (18) for the effects of various factors on the salting-out process.

Givon and coworkers[12] further developed the ideas of Debye and McAuley. They obtained, by a series expansion, an approximate value of the integral in Eqn. (12) between the limits 0 and the radius of the hydrated electrolyte ion. Assuming that $K = \lim_{c_e \to 0}\dfrac{d\lg f_{ne}}{dc_e}$, and that the solubility of the non-electrolyte is much greater than the concentration of electrolyte (in order to simplify the calculation of the effect of the non-electrolyte on the ϵ value of the solution), they obtained the following equation as a first approximation (for 25 °C):

$$K = 0.025 z^{5/2} V^{3/4}_{ne}\left(\frac{\delta_e}{V^0_e + 18h^0_e} + \frac{\varepsilon_0 - \varepsilon_{ne}}{1000}\right)^{3/4}, \qquad (19)$$

where δ_e is the decrement in the dielectric constant of the solvent due to the presence of the electrolyte, h^0_e is the hydration number of the electrolyte at infinite dilution, and ϵ_{ne} is the dielectric constant of the non-electrolyte.

Eqn. (19) is one of the most accurate equations of the electrostatic theory of salting-out effects of non-electrolytes. All the parameters in the equation can be determined. The δ_e values for many electrolytes are known,[7,13] and V^0_e and h^0_e values are also available[14,15].

Eqn. (19) correctly predicts an increase of K with increasing charge on the electrolyte ion, with the molar volume of the non-electrolyte, and with the decrement $\epsilon_0 - \epsilon_{ne}$. This equation takes account of the hydration of the electrolyte and also (unlike the Debye–McAuley theory) of the correction δ_e due to the electrolyte. As a result Eqn. (19) predicts an increase of K with the

decrement in the dielectric constant of the solvent due to the presence of the electrolyte. This prediction agrees with experimental results. Eqn. (19) also allows the possibility of salting in of the non-electrolyte, which occurs when $(\epsilon_0 - \epsilon)/1000$ is negative and greater than $\delta_e/(V_e^0 + 18h_e^0)$ in absolute value. However Eqn. (19) was obtained from an approximate solution of Eqn. (12). Furthermore, several values, differing by 50–70%, have been reported[14,15] for V_e^0 and h_e^0, suggesting that available data on the hydration of electrolytes have a low precision. A more exact solution of Eqn. (12) and more accurate numerical values of the parameters of Eqn. (19) can be expected to result from a better understanding of the structure of solutions of electrolytes and non-electrolytes.

Frank[16] described a derivation of the basic equation of the electrostatic theory of salting out which is stricter than Debye and McAuley's but equivalent to it. He envisaged the role of the ion as merely to generate an electrostatic field, and he assumed that the non-electrolyte forms an ideal solution. He also assumed that local fluctuations in the concentration of water are negligibly small in comparison to changes in the concentration of the non-electrolyte during salting out, and that the chemical potentials of the electrolyte and of the water are constant. Conway and coworkers[17] calculated the dielectric decrement $\partial\epsilon/\partial c_{ne}$ in Frank's equation in terms of Kirkwood's theory[18] of the polarisation of non-electrolytes in polar liquids:

$$\left(\frac{\partial\varepsilon}{\partial c_{ne}}\right)_{T,p,n_w} = \frac{9}{2}P_{ne} - V_{ne}\varepsilon_0, \qquad (20)$$

where n_w is the number of water molecules in 1 ml of solution, and P_{ne} is the total molecular polarisation of the non-electrolyte.

The integral form of the Frank–Conway equation is

$$K = \frac{V_e^h}{1000} + \frac{(ze)^2}{2000\varepsilon_0 kT}\left(V_{ne}\varepsilon_0 - \frac{9}{2}P_{ne}\right)\left(\frac{1}{r_h} - \frac{1}{r_n}\right), \qquad (21)$$

where k is Boltzmann's constant.

In the case of non-polar non-electrolytes the quantity $\frac{9}{2}P_{ne}$ can be ignored in comparison to $V_{ne}\epsilon_0$.[16] We then have

$$K = \frac{V_e^h}{1000} + \frac{(ze)^2 V_{ne}}{2000\varepsilon_0 kT}\left(\frac{1}{r_h} - \frac{1}{r_n}\right). \qquad (22)$$

V_e^h can be evaluated by the equation[19]

$$V_e^h = V_e + hv_s^h. \qquad (23)$$

Where V_e is the intrinsic molar volume of the electrolyte, h is the hydration number of the ion pair, and v_s^h is the molar volume of the solvent in the hydration shell of the electrolyte. Formulae for the calculation and for the experimental determination of V_e, h, and v_s^h are given in Ref. 19.

However Conway and coworkers[17] in their derivation of the integral equation for K failed to take account of the dielectric decrement of the electrolyte. They also carried out the integration in two steps (from the crystal-chemical radius r to r_h, and from r_h to r_n) because of the difference in dielectric saturation between these two regions. However the maximum of the integrand was not always found at a distance r_h from the centre of the ion: its position is a function of the nature of the electrolyte and of the non-electrolyte. Because of these simplifications the K values calculated by Eqn. (21) differ significantly from experimental values: for example the discrepancy for the noble gases is at least 50%.[17]

According to Kirkwood's theory[18] the parameter P_{ne} in Eqn. (21) is

$$P_{ne} = \frac{4}{3}\pi N[\alpha_0 + (n^2+2)\mu_0^2/27kT], \qquad (24)$$

where μ_0 is the dipole moment of the non-electrolyte in the gaseous state, α_0 is its polarisability, and n is the refractive index. The value of the parameter P_{ne} in the quantitative treatment of salting-in and salting-out phenomena is demonstrated by the good correlation between the K and μ_0 values of different types of non-electrolyte (Table 1).

Table 1. Dipole moments and salting-out coefficients of various non-electrolytes in KCl.[4]

Non-electrolyte	K, litre mole^{-1}	μ_0, D	Non-electrolyte	K, litre mole^{-1}	μ_0, D
O_2	0.132	0.0	NH_3	0.057	1.4
H_2	0.102	0.0	HCN	0.006	2.7
N_2O	0.099	0.1	SO_2	−0.022	1.7
CO_2	0.072	0 0	NH_4NO_3	−0.070	3.6
H_2S	0.067	1.0			

Conway and coworkers[17] have proposed and experimentally confirmed an expression for the quantity V_e^h in Eqns. (21) and (22). The expression was derived from "free-water" considerations adopted from the hydration theory: it can be written

$$V_e^h = \frac{18h_e^n}{1000d - mM}, \qquad (25)$$

where h_e^p is the primary hydration number of the electrolyte, m is the molarity and d is the density of the electrolyte solution, and M is the molecular weight of the electrolyte.

Cohn and Edsell[11] obtained an expression for P_{ne} different from Eqn. (24):

$$P_{ne} = 4\pi N\mu_0^2/9kT. \qquad (26)$$

Using Eqn. (26) they arrived at the following expression for the dielectric decrement of the non-electrolyte:

$$\delta_{ne} = \frac{V_{ne}(\varepsilon_1 - j)}{\varepsilon_0} - \frac{hP_{ne}}{1000\varepsilon_0}. \qquad (27)$$

Cohn and Edsell combined Eqn. (27) with the Debye–McAuley equation (6) in order to facilitate the application of the latter in practical calculations.

Kirkwood's electrostatic theory of the salting-out effect[20,21] is based on the polarisation of the non-electrolyte in solutions of electrolytes. Using his theory[18] of the polarisation of non-electrolytes in polar liquids, Kirkwood calculated the total electrostatic energy of a spherical ion and a neutral molecule, and obtained the following expression for the activity coefficient of the non-electrolyte in an electrolyte solution:

$$\ln f_{ne} = \Sigma K_e z^2 c_e. \qquad (28)$$

The quantity K_e in Eqn. (28) is defined by the expression

$$K_e = \frac{2\pi Ne^2}{2.303\varepsilon_1 kT}\left[\frac{3\mu_0^2}{2\varepsilon akT} - \frac{r_{ne}^3\Gamma(\rho)}{a}\right], \qquad (29)$$

where

$$\Gamma(\rho) = \frac{1}{3\rho^4}[(\rho^3-2)\lg(1+\rho) - (\rho^3-2)\lg(1-\rho) - 2\rho^2], \qquad (D)$$

$$\rho = r_{ne}/a,$$

a is the distance of closest approach between the non-electrolyte molecule and the electrolyte ion, and r_{ne} is the radius of the non-electrolyte molecule.

The salting-out coefficients calculated by Kirkwood's equation (29) agree better with experiment than those calculated by either the Debye–McAuley or the Debye theory. However even the K values given by the Kirkwood equation differ from the experimental values by much more than the experimental error.

Long and McDevit, in an attempt to allow for the Van der Waals forces in the salting-out effect, obtained the equation[4]

$$\lg f_{ne} = A\Sigma z^2 c_e - B\Sigma\alpha_e c_e, \qquad (30)$$

where A and B are parameters depending on the non-electrolyte and (to a lesser extent) on the electrolyte, and constant to a first approximation for a series of similar electrolytes (e.g. halides); α_e is the polarisability of the electrolyte ion. The first term of Eqn.(30) depends on the ion–molecule interaction, the second term depends on the Van der Waals' forces between water molecules opposing the replacement of water molecules by electrolyte ions. The constancy of A and B implies that the distance of closest approach between ions and molecules must be similar to the distance of closest approach between ions.

Bockris and coworkers[22] allowed for the effect of dispersion forces by using the London formula[23] for the dispersion potential, and obtained the equation

$$\frac{\Delta s_{ne}}{s^0_{ne}} = \left(P_{ne} - P_w\frac{V_{ne}}{V_w}\right)\frac{2\pi Ne^2}{1000\varepsilon^2 kT}\sum\frac{z^2c_e^2}{r_i} + \left(\frac{\alpha_{ne}\nu_{ne}}{\nu_{e\pm}+\nu_{ne}} - \frac{\alpha_w\nu_w}{\nu_{e\pm}+\nu_{ne}}\cdot\frac{V_{ne}}{V_w}\right)\frac{2\pi N\hbar}{1000\varepsilon kT}\sum\frac{\alpha_e\nu_{e\pm}c_e}{r_i^3}, \qquad (31)$$

where ν_{ne} and $\nu_e^{\pm}$ are the characteristic frequencies of the non-electrolyte and of the electrolyte respectively, α_{ne} is the polarisability of the non-electrolyte, h is Planck's constant, and P_W is the molar polarisation of water. Eqn.(31) is generally similar to Eqn.(30), but in Eqn.(31) the second term, which determines the salting-in effect, is much less sensitive to the nature of the electrolyte and of the non-electrolyte than is found in practice. This is because of the approximation used in Eqn.(31) for the distance of nearest approach (taken as the ionic radius r_i rather than the sum of the radii of the ion and of the neutral molecule). In practice the factor r_i^3 nullifies the attempt to allow for the change in polarisability of the ions, and as a result the theory predicts far less specificity in the effect of various ions on salting out and salting in than is found in practice. However the theory does predict the experimentally observed salting in of non-electrolytes by large ions such as tetra-alkyl-ammonium ions.

Neither the Kirkwood theory[20,21] nor the equations of Long and McDevit[4] [Eqn.(30)] and of Bockris and coworkers[22] [Eqn.(31)] can explain the anomalously small salting out observed in the presence of electrolytes containing H^+ or Li^+ cations. Because of these shortcomings, and of their theoretical limitations pointed out above, Eqns.(28)–(31) cannot be said to give an adequate representation of the role of dispersion forces in the salting out and salting in of non-electrolytes.

Danckwerts[24] has suggested the use of salting-out coefficients in conjunction with the Henry constants of the non-electrolytes in water (He^0) to calculate the Henry constants of gaseous non-electrolytes in solutions. He obtained an equation similar in form to the Sechenov equation (1) and to the empirical Debye–McAuley equation (9):

$$\lg\frac{He}{He^0} = K\mu. \qquad (32)$$

The salting-out coefficient in Eqn.(32) is defined as

$$K = h_+ + h_- + h_g, \qquad (33)$$

where h_+ and h_- are constants relating to the cation and the anion of the electrolyte (litre g-ion^{-1}), and h_g is a constant relating to the gaseous non-electrolyte (litre mole^{-1}).

Danckwerts considers that the change in K with temperature is due entirely to the change in h_g with temperature. Values of h_g for hydrogen, oxygen, carbon dioxide, hydrogen sulphide, ammonia, and sulphur dioxide are given in Ref. 24 together with h_+ and h_- values for a large number of ions. However Danckwerts does not give any theoretical justification of Eqn.(33), which is merely a sum of empirical constants for the electrolyte and the non-electrolyte and therefore cannot be reconciled with any of the theories of salting out and salting in. Furthermore Danckwerts does not state the considerations used in selecting values for the h_+, h_-, and h_g constants for different ions and non-electrolytes.

IV. THE "EFFECTIVE PRESSURE" THEORY

As its name implies, this theory treats the salting out and salting in of non-electrolytes as a consequence of the internal pressure generated in solutions of electrolytes by the electrostatic interaction between electrolyte and solvent.

Geffcken[25], and later Tammann[26], established a correlation between salt effects in solutions and the relative effects of salts on the compressibility of solutions. On the basis of this work McDevit and Long[27] developed the "effective pressure" theory of salting out and salting in of non-electrolytes. They derived an expression for K by considering the electro-striction effect resulting from the interaction between electrolyte and solvent following the addition of an electrolyte to a solution of a non-polar non-electrolyte. This effect gives rise to an effective pressure p_e within the solution which tends to eject the non-electrolyte molecules from the solution because they are non-polar and they oppose the electrolyte–solvent interaction. Thus according to the "effective pressure" theory the salting in or salting out of a non-electrolyte is determined by the extent to which the solution is compressed or dilated by the addition of the electrolyte.

McDevit and Long based their quantitative conclusions on a calculation of the change in free energy attending the transfer of the non-polar non-electrolyte from water to the electrolyte solution. They found that the change in free energy of the non-electrolyte due to this process is $p_e V_{ne}$, and they obtained the following theoretical equation for K [27]:

$$K = \lim_{c_e\to 0}\frac{V^0_{ne}}{2{,}3RT}\cdot\frac{dp_e}{dc_e} = \frac{V^0_{ne}(V^g_e - V^0_e)}{2.3\beta_w RT}, \qquad (34)$$

where V^0_{ne} is the partial molar volume of the non-electrolyte at infinite dilution in the solution, V^g_e is the hypothetical molar volume of the pure supercooled electrolyte in the liquid state, and β_W is the compressibility of water.

The McDevit–Long equation (34) predicts an increase of K with increasing molar volume of the non-electrolyte at infinite dilution. The main advantage of the "effective pressure" theory is its ability to account for

salting in in terms of the properties of the electrolyte only, in keeping with experimental results. According to Eqn. (34) salting in of non-electrolytes occurs when the difference ($V_e^g - V_e^0$) for the electrolyte is negative.

The K values for a range of structurally different non-electrolytes (hydrogen, oxygen, nitrogen dioxide, benzene) in the same electrolytes are very similar [4]. Hence we may conclude that salting-out and salting-in effects are far more sensitive to the properties of the electrolyte in solution than to the nature of the non-electrolyte or its interaction with the solution. This conclusion is implicit in Eqn. (34), according to which the salting in and salting out of the non-electrolyte is determined mainly by the ion–solvent interaction and by the effect of this interaction on the volume difference $V_e^g - V_e^0$. Values of V_e^g for various electrolytes are given in Ref. 28.

When the electrolyte is added to the water the primary effect is the attraction of the water dipoles towards the electrostatic field of the ions. At ordinary temperatures most of the water molecules are in a quasi-crystalline state with an open structure, and when the water dipoles are attracted towards the field of the ions the rearrangement of this open structure to give a more closely packed structure around the ions is primarily responsible for the compression effect. If the size of the ions added to the solution is increased the electro-striction of the solution decreases for two reasons. Firstly, the electrostatic field of the ion decreases with increase in the ionic radius, and its effect on the breakdown of the water structure is less marked (decrease in the structure factor). Secondly, water molecules are replaced by ions (replacement factor). If the electrolyte ions had been uncharged spheres the replacement would have led to a decrease in the breakdown energy of the system accompanied by an increase in volume. Both the structure factor and the replacement factor make a large contribution to the decrease in the difference $V_e^g - V_e^0$ with increasing size of the electrolyte ion. The "effective pressure" theory indicates that the difference $V_e^g - V_e^0$ may become negative as the influence of both these factors increases, leading to salting in of the non-electrolyte.

The salting-out effects of the very small hydrogen and lithium ions are not quantitatively consistent with the small size of these ions, suggesting that the quasi-crystalline structure of water is stabilised rather than broken down by hydrogen and lithium ions [4]. One possible explanation is that these ions are incorporated in the water structure in sites normally occcupied by hydrogen atoms. The result is the formation of electrostatic bridges between the oxygen atoms of the water molecules, with an energy comparable to the energy of the hydrogen bond [4].

The electrostatic theories of salting in and salting out ignore the structure factor and the replacement factor, which depend on the size of the electrolyte ion. Hence these theories give best results when these terms are small (e.g. in solutions of sodium or potassium chloride [4]).

Gibson showed [29] that the linear plots of p_e against c_e and of lg (s_{ne}^0/s_{ne}) against c_e lie in the same relative sequwnce, indicating a common underlying cause. This observation confirms that the "effective pressure" theory offers, on the whole, a correct description of the main features of the salting out and salting in of non-electrolytes.

One weakness of this theory is its failure to allow for the non-electrolyte–solution interaction of a given non-electrolyte in different electrolytes. Furthermore, the value of Eqn. (34) for calculating K is doubtful as long as published values of V_e^g remain scarce and inaccurate.

V. EFFECT OF TEMPERATURE ON SALTING OUT AND SALTING IN OF NON-ELECTROLYTES

Experimental and theoretical studies of the effect of temperature on the salting out and salting in of non-electrolytes began in 1907. [30] Changes in temperature affect the state of all three components of the non-electrolyte–electrolyte–solvent system. Ion hydration decreases as the temperature increases. At the same time the energy needed to break down the structure of pure water decreases, and exothermic effects in concentrated solutions (formation of ion pairs and of undissociated molecules of electrolyte) also decrease. It was pointed out [31] that the enhanced translational motion of the water and mobility of the electrolyte ions at elevated temperatures may even convert the positive hydration of the ions into negative hydration. Simultaneously, the solubility of the non-electrolyte decreases, both in water and in the electrolyte solution.

Because so many parameters of the three-component system are affected by temperature changes, the theoretical interpretation of the effect of temperature on the salting out and salting in of non-electrolytes is a complex problem. The temperature coefficient of the quantity $\ln (f_{ne}/f_{ne}^0)$ can be obtained (as first pointed out by Rothmund [30]) by differentiating the Gibbs–Helmholtz equation:

$$\Delta G_{ne}^0 = \Delta H_{ne} - T\Delta S_{ne} = RT \ln \frac{f_{ne}}{f_{ne}^0}, \qquad (35)$$

where ΔG_{ne}^0 is the change in standard free energy of the non-electrolyte attending the transfer of one mole of non-electrolyte dissolved in water into the electrolyte solution. From Eqn. (35) Rothmund obtained [30] the following expression for the temperature coefficient of $\ln (f_{ne}/f_{ne}^0)$:

$$\frac{d\left(\ln \frac{f_{ne}}{f_{ne}^0}\right)}{dT} = -\frac{\Delta H_{ne}^0}{RT^2}. \qquad (36)$$

He also derived the equation

$$\frac{d\left(T \ln \frac{f_{ne}}{f_{ne}^0}\right)}{dT} = -\frac{\Delta S_{ne}^0}{R}. \qquad (37)$$

In Eqns. (36) and (37) ΔH_{ne}^0 and ΔS_{ne}^0 are the changes in standard enthalpy and entropy of the non-electrolyte when 1 mole (dissolved in water) is transferred to the electrolyte solution at the same temperature.

Frank and Evans [32] obtained an expression for ΔS_{ne}^0 during the transfer of the non-electrolyte from water into the solution of electrolyte:

$$\Delta S_{ne}^0 = -\left(\frac{\partial \Delta G_{ne}^0}{\partial T}\right)_{p_{ne} m_{ne}} = R \ln f_{ne} + RT \left(\frac{\partial \ln f_{ne}}{\partial T}\right)_{p_{ne} m_{ne}}, \qquad (38)$$

where p_{ne} is the partial pressure of the gaseous non-electrolyte (atm) and m_{ne} is the molar concentration of the non-electrolyte.

Using the Debye–McAuley electrostatic theory Frank and Evans derived the expression [32]

$$\Delta S_{ne}^0 = -RT \ln f_{ne} \left(\frac{\partial \ln \varepsilon_0}{\partial T} - \frac{\partial \ln \delta_{ne}}{\partial T} + \frac{\partial \ln b}{\partial T} + \frac{\partial \ln V}{\partial T}\right), \qquad (39)$$

where V is the volume of the solution.

If the internal interactions of the non-electrolyte molecules are negligibly small, or if the solubility of the

non-electrolyte is very low, Eqn.(18) becomes similar to Eqn.(1) and we can write

$$\lg \frac{s^0_{ne}}{s_{ne}} = \lg \frac{f_{ne}}{f^0_{ne}} = Kc_e. \quad (40)$$

Combining Eqns.(36), (37), and (40) we can evaluate dK/dT from the known quantities ΔH°_{ne} and ΔS°_{ne}. This is because the difference between s^0_{ne} and s_{ne} is small and the internal interactions of the gaseous non-electrolyte molecules can be ignored.

The heat of dissolution of the non-electrolyte in a given solution of electrolyte can be calculated from solubility data at different temperatures. We use an equation analogous to the Clapeyron–Clausius equation

$$\frac{d \ln s_{ne}}{d(1/T)} = -\frac{\Delta H_{ne}}{R}, \quad (41)$$

where ΔH_{ne} is the heat of dissolution of the non-electrolyte. ΔH_{ne} is given by the slope of a plot of ln s_{ne} against $1/T$.

On general grounds we would expect dK/dT to be negative, since the properties of solutions tends towards ideality on raising the temperature, and ideal solutions do not exhibit salting-out effects. Negative temperature coefficients of K were indeed obtained by Long and McDevit[4] for nitric oxide in various electrolytes, and by Yatskovskii [33] and by David and coworkers [34] for oxygen in KOH solutions. Knaster [35] found that in KOH solutions the temperature coefficient of K is negative for oxygen and positive for hydrogen, but this discrepancy is neither discussed nor explained by Knaster [35].

Morrison has pointed out [36] that the Debye–McAuley equation (10) cannot give a negative value of dK/dT, since the product $\epsilon_0 T$ in Eqn.(10) decreases as the temperature increases. However the parameter δ_{ne} in the same equation should also change with temperature, but there are no data on the sign and magnitude of this change.

An expression for dK/dT for non-polar, gaseous non-electrolytes (oxygen, hydrogen, methane, ethane, etc.) was obtained[4] by differentiating the McDevit–Long equation (34):

$$\frac{dK}{dT} = -\frac{V^0_{ne}}{2.3\beta_\infty RT^2} \cdot \frac{dV^0_e}{dT}. \quad (42)$$

Values of dV^0_e/dT for various gases and electrolytes are given in Refs. 37 and 38. However no experimental test of Eqn.(42) has yet been reported.

Knaster [35] combined the Sechenov equation with the thermodynamic equation for the temperature dependence of the solubility of gases in water and in electrolyte solutions, and obtained the expression

$$K = A' + \frac{B'}{T}, \quad (43)$$

where A' and B' are temperature-independent constants:

$$A' = \frac{\Delta S^1_{ne} - \Delta S^2_{ne}}{2.303 c_e R}, \quad (44)$$

$$B' = \frac{\Delta H^1_{ne} - \Delta H^2_{ne}}{2.303 c_e R}. \quad (45)$$

In these equations ΔS^1_{ne} and ΔS^2_{ne} are the entropy changes of the non-electrolyte when dissolved in water and in the electrolyte respectively for the same activity of non-electrolyte in the gas phase; ΔH^1_{ne} and ΔH^2_{ne} are the corresponding enthalpy changes of the non-electrolyte.

Eqn.(43) is obeyed up to 7 N concentration of KOH in the salting out of hydrogen from KOH solutions [35]. The constants A' and B' in this equation are determined (for a given electrolyte and non-electrolyte) by using two known values of K for a non-electrolyte in the electrolyte of interest.

Thus both Eqns.(36), (37) and Eqn.(43) for dK/dT require a separate experimental determination of the relevant thermodynamic quantities (the enthalpy and entropy of dissolution of the non-electrolyte). This is because of the inadequacy of the existing theory of solutions, which does not provide an analytic expression for calculating the change in entropy and enthalpy of gases dissolved in water and in electrolyte solutions.

The K values of highly soluble non-electrolytes are much more sensitive to temperature than those of sparingly soluble non-electrolytes such as non-polar gases [4]. K usually changes in the same sense as the solubility of non-electrolytes in water [36]. For readily soluble non-electrolytes the quantity $K_{ne}(s_{ne} - s^0_{ne})$ in Eqn.(18) changes significantly with temperature even if K is practically temperature-independent, because of the strong temperature dependence of the solubility of the non-electrolyte. As a result $K_{ne}(s_{ne} - s^0_{ne})$ can change sign, and salting in of the non-electrolyte occurs instead of salting out [36].

Experimental information on the effect of temperature on the salting-in and salting-out behaviour of non-electrolytes is still scarce, and the development of a theory of this effect is shown by our review to be only in its initial stages.

VI. EXPERIMENTAL DATA. COMPARISON OF THEORY AND EXPERIMENT

A large body of experimental information on the salting out and salting in of gaseous non-electrolytes in aqueous solutions of electrolytes is available in the published literature. The data appear either as salting-out coefficients or, more often, as tabulations of the solubility of the non-electrolyte for different concentrations of electrolyte.

Salting-out coefficients and solubilities in various electrolytes have been reported for oxygen [4,25,33,34,37,39-45], hydrogen [4,33,41-43,45], carbon dioxide [45,46], hydrogen sulphide [47], and ethylene [45]. Some of the other published data on the salting out of gaseous non-electrolytes are fragmentary and unsystematic, and their reliability is doubtful. The salting-out coefficients for oxygen, hydrogen, carbon dioxide, hydrogen sulphide, and ethylene quoted in the above references or calculated from the published data on the solubility of these gases are listed in Tables 2 and 2'.

The salting-out and salting-in effects of oxygen and hydrogen in solutions of acids, salts, and bases with cations from Group Ia of the Periodic Table have been investigated most fully. In some cases there are discrepancies between the K values reported by different workers or calculated from the published solubilities of the gaseous non-electrolytes. Occasionally the discrepancy between K values from different sources reaches 50–60%.

The solubility of non-electrolytes at different concentrations of electrolytes has been measured [4,25,33,34,37,39-47] by different methods, but the precision of the concentration measurements (2–5%) is quoted in only five of the fourteen papers [33,34,40,41,44]. Only three of these [34,41,44] include evidence that the equilibrium concentration (solubility)

Table 2. Salting-out coefficient of oxygen in aqueous solutions of various electrolytes at 25°C.

Anion	H+	Li+	Na+	K+	Rb+	Cs+	Mg^{2+}	Ca^{2+}	Ba^{2+}	NH_4^+
				Oxygen						
F^-	—	from 0.725 to −0.385[44]	0.284[44]	0.203[44]	0.146[44]	0.114[44]	—			
Cl^-	0.030[43] 0.034[39] 0.029[25] 0.031[4] 0.022[45]	0.096[43] 0.100[4] 0.137 (20°)[37] from 0.112 to 0.070[44]	0.140[37] 0.141[39] 0.145[42] 0.137[43] 0.127[25] 0.141[4] 0.136[44] 0.101[45]	0.142 (20°)[37] 0.132[39] 0.128[43] 0.129[44]	0.120[44]	0.098[44]	0.428[43] 0.516 (20°)[37] 0.456[39]	0.397[43]	0.528[4] 0.520[43]	2.792[39] 2.950[43]
Br^-	—	from 0.252 to 0.084[44]	0.110[4] 0.115[43] 0.131[44]	0.123[43] 0.117[44]	0.104[44]	0.078[44]	—	—	—	—
I^-	—	0.163[44]	0.120[44]	0.090[4] 0.092[43] 0.093[44]	0.086[44]	0.062[44]	—	—	—	—
NO_3^-	0.019[4] 0.016[25] 0.018[26] 0.019[42]	from 0.196 to −0.040[44]	0.124[44]	0.100[4] 0.099[39] 0.100[43] 0.105[44]	0.096[44]	0.066[44]	—	—	—	—
	—	from 0.218 to 0.066[44]	0.160[44]	0.150[44]	0.138[44]	—	—	—	—	—
OH^-	—	from 0.332 to 0.091[44]	0.179[4] 0.178[25] 0.183[39] 0.188[42] 0.179[43] 0.180[44]	0.175[44] 0.172[25] 0.183[39]	0.168[44]	0.158[44]	—	—	—	—
	—	—	—	0.152[40] 0.170[41] 0.176[42] 0.175[24] 0.168[33] 0.176[44]	—	—				
SO_4^{2-}	0.104[4] 0.086[25] 0.089[39] 0.152[43] 0.091[42] 0.081[43]	0.244[44]	0.306[43] 0.323[39] 0.376[44]	0.344[4] 0.334[25] 0.346[42] 0.304[43] 0.323[39] 0.297[44]	0.290[44]	0.255[44]	—	—	—	—
CO_3^{2-}	—	0.254[44]	0.464[44]	0.379[44]	—	—	—	—	—	—
PO_4^{3-}	0.053[38] 0.046[47]	—	0.652[44]	0.507[44]	—	—	—	—	—	—

Table 2′. Salting-out coefficients of hydrogen, carbon dioxide, hydrogen sulphide, and ethylene in aqueous solutions of various electrolytes at 25°C.

Anion	H+	Li+	Na+	K+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Zn^{2+}	Al^{3+}	NH_4^+
				Hydrogen						
Cl^-	0.030[4] 0.027[42] 0.020[45]	0.076[4] 0.075 (15°)[42] 0.095 (15°)[43] 0.066[b]	0.114[4] 0.107 (15°)[42] 0.088[43] 0.094[45]	0.102 (20°)[4] 0.087 (15°)[42] 0.078[45]	—	0.217 (15°)[42] 0.065[45]	0.190[43]	—	0.270 (15°)[42] 0.028[45]	—
NO_3^-	0.022[4] 0.020[42] 0.022[43]	— — —	0.100 (20°)[4] 0.091 (15°)[42] 0.080[45]	0.070 (20°)[4] 0.061[45]	—	—	—	—	—	0.035 (20°)[43] 0.038 (20°)[47]
OH^-	—	—	0.140[4] 0.142[42]	0.130[4] 0.126[42] 0.146[43] 0.123 (21°)[41] 0.127 (21°)[33]	—	—	—	—	—	—
SO_4^{2-}	0.076[43]	—	0.278 (15°)[4] 0.278 (15°)[42]	—	0.302 (15°)[43] 0.057[45]	—	—	0.211 (15°)[42]	—	—
CO^{2-}	—	—	0.293 (15°)[42]	0.273 (15°)[42]	—	—	—	—	—	—
PO_4^{3-}	0.034 (21°)[38]	—	—	—	—	—	—	—	—	—
				Carbon dioxide						
Cl^-	0.006[45]	—	—	0.059[45]	—	—	0.060[45]	−0.008[46]	—	—
Br^-	—	—	—	0.045[45]	—	—	—	—	—	—
I^-	—	—	—	0.032[45]	—	—	—	—	—	—
NO_3^-	—	—	0.053[45]	0.025[45]	—	—	—	—	—	—
SO_4^{2-}	—	—	0.100[45]	—	—	—	—	—	—	—
				Hydrogen sulphide						
Cl^-	−0.013[47]	—	—	—	—	—	—	−0.005±0.002[47]	—	—
				Ethylene						
Cl^-	—	—	0.093[45]	0.062[45]	0.055[45]	0.058[45]	0.067[45]	—	0.044[45]	—
NO_3^-	—	—	0.050[45]	0.030[45]	—	0.028[45]	—	—	—	—
SO_4^{2-}	—	—	0.098[45]	—	0,064[45]	—	—	—	0.043[45]	—
Br^-	—	—	0.077[45]	0.049[45]	—	—	—	—	—	—

of the non-electrolyte was measured, i.e. that the non-electrolyte had come to equilibrium with the electrolyte solution.

Table 2 shows that the agreement between the salting-out coefficients reported by different workers for oxygen and hydrogen in solutions of electrolytes with cations from Group Ia is usually better than 5%. We may conclude that the published K values for oxygen and hydrogen in these electrolytes are reliable.

Differences between experimental K values for hydrogen in excess of 100% (see Tables 2 and 2′) are found only in solutions of $CaCl_2$, $AlCl_3$,[42,45] and $MgSO_4$.[43,45] These results are unacceptable, particularly since neither the experimental method of measuring the solubility of hydrogen nor the magnitude of the measurement error is mentioned in those papers[42,43,45].

Because of the small number of publications on the salting-out and salting-in behaviour of carbon dioxide, hydrogen sulphide, and ethylene, a discussion of the consistence and reliability of the data (Tables 2 and 2′) is not justified.

The theories of salting out and salting in of non-electrolytes discussed above differ very substantially in their treatment of the phenomenon. Hence a comparison of the theoretical K values for oxygen and hydrogen with experimental data should provide a reliable criterion of the relative success of the various theoretical treatments.

Table 3. Comparison of experimental mean values of K for oxygen at 25°C with values calculated by different theoretical equations.

Electrolyte	K_{exper}	$10^8 b$, cm	K (10)	K (19)	K (33)	K (34)
HCl	0.031	4.54	0.095	0.205	0.043	0.030
HNO_3	0.018	4.47	0.097	0.225	0.021	—
H_2SO_4	0.100	3.55	0.123	0.428	0.044	—
LiF	from 0.725 to −0.385	3.03	0.143	0.216	—	—
LiCl	from 0.112 to 0.070	3.51	0.124	0.198	—	0.109
LiBr	from 0.252 to 0.084	3.63	0.120	0.160	—	—
LiI	0.163	3.88	0.112	0.158	—	—
$LiNO_3$	from 0.196 to −0.040	3.44	0.126	0.198	—	—
$LiClO_4$	from 0.218 to 0.066	3.72	0.117	0.154	—	—
LiOH	from 0.332 to 0.091	3.87	0.112	0.237	—	—
Li_2SO_4	0.244	2.61	0.166	0.470	—	—
Li_2CO_3	0.254	2.40	0.181	—	—	—
NaF	0.284	3.34	0.130	0.254	—	0.235
NaCl	0.131	3.82	0.114	0.162	0.134	0.131
NaBr	0.119	3.94	0.110	0.173	0.125	0.126
NaI	0.120	4.19	0.104	0.185	0.118	0.097
$NaNO_3$	0.124	3.75	0.116	0.175	0.112	0.109
$NaClO_4$	0.160	4.03	0.108	0.173	—	0.091
NaOH	0.180	4.18	0.104	0.249	0.179	0.205
Na_2SO_4	0.335	2.95	0.147	0.485	0.226	0.471
Na_2CO_3	0.464	2.67	0.163	—	0.225	—
KF	0.203	3.82	0.114	0.283	—	—

It is evident from our view of the existing theories that a strict thermodynamic theory of the salting in and salting out of non-electrolytes is not available at present. Hence we cannot expect full agreement between theory and experiment. Furthermore, some of the physicochemical quantities which appear in the theoretical equations are not known with high precision, and therefore any observed discrepancy between theory and experiment cannot be ascribed wholly to inadequacies of the theory.

The salting-out coefficients for oxygen in electrolyte solutions calculated by various theoretical equations are listed in Table 3. The ionic radius b which appears in formula (10) was calculated (for a 1–1 electrolyte) by the expression

$$b = r_a + r_c,$$

where r_a and r_c are the radii of the hydrated anion and cation.

For polyvalent electrolytes the ionic radius was determined as suggested by Debye and McAuley[5] by formula (8); the hydrated ion radii for Li^+, Na^+, K^+, Rb^+, Cs^+, F^-, Cl^-, Br^-, and I^- were taken from Ref. 48, those for H^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, OH^-, NO_3^-, ClO_4^-, and SO_4^{2-} from Ref. 15. The r_1^h value for the CO_3^{2-} ion was taken from Ref. 49.

In the calculation of K by formula (19) we took V_{ne} from Ref. 50, δ_e from Refs. 8 and 12, V_e^0 from Refs. 14, 15, and 51, h_e^0 from Refs. 14, 15, 52, and 53, and ϵ_{ne} from Ref. 54.

In the calculation of K by formula (34) V_{ne}^0 was taken from Ref. 50 and $(V_e^g - V_e^0)$ from Ref. 27. The K values for hydrogen in electrolyte solutions (Table 4) were calculated with constants taken from the same sources as those for oxygen.

Table 4. Comparison of experimental mean values of K for hydrogen at 25°C with values calculated by formulae (10), (19), (22), and (32), and from Ref. 24.

Electrolyte	K_{exper}	$10^8 b$, cm	K (10)	K (19)	K (33)	K (34)
HCl	0.026	4.54	0.080	0.176	0.019	0.025
HNO_3	0.021	4.47	0.081	0.198	−0.003	—
H_2SO_4	0.076	3.55	0.103	0.270	0.020	—
LiCl	0.071	3.51	0.104	0.171	—	0.091
NaCl	0.098	3.82	0.095	0.139	0.110	0.126
$NaNO_3$	0.080	3.75	0.097	0.152	0.088	0.091
NaOH	0.141	4.18	0.087	0.196	0.155	0.248
Na_2SO_4	0.278 (15°)	2.95	0.128 (15°)	0.263	0.196 (15°)	0.394 (15°)
Na_2SO_3	0.293 (15°)	2.67	0.141 (15°)	—	0.195 (15°)	—
KCl	0.078	4.30	0.085	0.123	0.093	0.101
KNO_3	0.061	4.23	0.086	0.121	0.071	—
KOH	0.134	4.66	0.078	0.224	0.138	—
K_2CO_3	0.273 (15°)	3.01	0.125 (15°)	—	0.161 (15°)	—
$MgSO_4$	0.302 (15°)	3.88	0.097 (15°)	0.312	0.065 (15°)	—
$CaCl_2$	0.217 (15°)	3.56	0.106 (15°)	0.248	0.087 (15°)	—
$BaCl_2$	0.190	3.40	0.107	0.266	0.100	0.298
$ZnSO_4$	0.211 (15°)	5.36	0.070 (15°)	—	0.062 (15°)	—
NH_4NO_3	0.036 (15°)	3.91	0.096 (15°)	—	0.019 (15°)	—
KCl	0.132	4.30	0.101	0.152	0.117	0.121
KBr	0.120	4.42	0.098	0.154	0.108	—
KI	0.092	4.67	0.093	0.193	0.101	—
KNO_3	0.101	4.23	0.103	0.207	0.095	—
$KClO_4$	0.150	4.51	0.096	0.184	—	—
KOH	0.172	4.66	0.093	0.259	0.162	—
K_2SO_4	0.324	3.38	0.128	0.462	0.192	—
K_2CO_3	0.379	3.01	0.144	—	0.191	—
RbF	0.146	3.96	0.110	—	—	—
RbCl	0.120	4.44	0.098	0.236	—	0.109
RbBr	0.104	4.56	0.095	—	—	—
RbI	0.086	4.81	0.090	—	—	—
$RbNO_3$	0.096	4.37	0.099	—	—	—
$RbClO_4$	0.138	4.65	0.093	—	—	—
RbOH	0.168	4.80	0.090	—	—	—
Rb_2SO_4	0.290	3.48	0.125	—	—	—
CsF	0.114	4.18	0.104	—	—	—
CsCl	0.098	4.66	0.093	—	—	0.091
CsBr	0.078	4.78	0.091	—	—	—
CsI	0.062	5.03	0.086	—	—	—
$CsNO_3$	0.066	4.59	0.095	—	—	—
CsOH	0.158	5.02	0.086	—	—	—
Cs_2SO_4	0.255	3.64	0.119	—	—	—
$MgCl_2$	0.442	3.69	0.118	0.230	0.115	—
$CaCl_2$	0.397	3.56	0.122	0.249	0.117	—
$BaCl_2$	0.524	3.40	0.128	0.269	0.124	0.356

Inspection of Tables 3 and 4 shows that the agreement between calculated and experimental values of K is best when Eqn. (33) is used to calculate K. However, as we have already pointed out, this equation is merely the sum of empirical constants for the electrolyte ions and for the

non-electrolyte which allow the salting-out coefficient to be calculated to some approximation. In the case of 1–1 electrolytes this approximation is adequate both for hydrogen and for oxygen (see Tables 3 and 4). With polyvalent electrolyte solutions Eqn. (33) gives an error approaching 100% in some cases.

Eqn. (34), obtained by the "effective pressure" theory, is the next most succesful. This suggests that the electrostriction of non-electrolyte solutions produced by the addition of electrolytes can adequately account for all the phenomena involved in the salting out and salting in of non-electrolytes in solutions of electrolytes. However the range of application of this equation is limited by the lack of published values of $(V_e^g - V_e^0)$ for many electrolytes, and for the same reason the equation cannot be tested against a comprehensive range of experimental data. The agreement with experimental data is again unsatisfactory when K values are calculated by Eqn. (34) for polyvalent electrolytes.

In all cases, agreement to within 10% between theoretical and experimental values of K was considered satisfactory.

It is interesting to note from Tables 3 and 4 that the fairly complicated equation (19), proposed[12] as an improved expression of the Debye–McAuley electrostatic theory, produces K values for hydrogen and oxygen less consistent with experimental data than the simpler equation (10) of the electrostatic theory. This is because the parameters which appear in Eqn. (19) are not accurately known, published values differing by as much as 50–70%. Under these conditions even the mean of the published values, used in the calculations of K by Eqn. (19), could be seriously in error.

Table 5. Values of $V_e^h/1000$ in Eqn. (22) for different electrolytes.

Electrolyte	$V_e^h/1000$, litre mole^{-1}	Electrolyte	$V_e^h/1000$, litre mole^{-1}
LiCl	0.107	KBr	0.109
LiBr	0.097	KI	0.096
LiI	0.089	RbCl	0.096
NaF	0.148	RbBr	0.095
NaCl	0.125	RbI	0.090
NaBr	0.118	CsCl	0.094
NaI	0.110	CsBr	0.099
KF	0.135	CsI	0.093
KCl	0.112		

Eqn. (22), derived from the Frank–Conway electrostatic theory, is difficult to test against experimental data for purely mathematical reasons: the second term of Eqn. (22) depends on the concentration of the electrolyte through the concentration dependence of the radius of the co-ordination sphere $r_n = (3/4\pi n_e)^{1/3}$. Thus the salting-out coefficient given by Eqn. (22) will have different values, according to the concentration of the electrolyte. This is incompatible with the definition of the salting-out coefficient as a constant for a given non-electrolyte in a given electrolyte. But if we assume that the K value given by Eqn. (22) is dominated by the term $V_e^h/1000$, and we calculate $V_e^h/1000$ by formula (23), we arrive at K values for hydrogen and oxygen fairly close to the experimental values. However there can be no doubt that the equation should take account of the specific aspects of the salting-out behaviour of the non-electrolyte, and in this respect Eqn. (22) is practically useless. Calculated values of $V_e^h/1000$ are given in Table 5.

The values of V_e, h, and v_s^h which appear in Eqn. (23) were taken from Ref. 19. The following approximation is suggested[19] for v_s^h:

$$v_s^h = v_s + 2 \text{ ml mole}^{-1},$$

where v_s is the molar volume of the solvent. If the solvent is water $v_s^h = 20$ ml mole^{-1}.

The effect of temperature on the salting-out coefficient has been studied only for hydrogen and oxygen in KOH solutions[34,41]. Only the "effective pressure" theory gives an analytic expression for dK/dT [see Eqn. (42)]. However there are no published data on dV_e^0/dT for hydrogen and oxygen in KOH solutions, and without such data the temperature coefficient of K cannot be calculated by Eqn. (42).

We must conclude from this attempt at comparing the various theories of salting out and salting in of non-electrolytes with experiment that none of the present theories gives acceptable agreement with the experimental values for hydrogen and oxygen in all electrolytes. This conclusion is not unexpected, since none of the theories takes account of all the factors which have a bearing on salting out and salting in. However the three main theoretical approaches described in this review have laid the foundations for a generalised thermodynamic treatment of the salting out and salting in of non-electrolytes in solutions of electrolytes. Eqn. (15) is a good example of the adoption by one theory of some aspects of a different theory which approaches the theoretical interpretation of the phenomenon from an entirely different direction[3]: this equation combines the best features of the hydration theory and of the improved Debye–McAuley electrostatic theory.

VII. USE OF EXPERIMENTAL DATA ON SALTING OUT AND SALTING IN TO DETERMINE SOME PHYSICO-CHEMICAL CHARACTERISTICS OF SOLUTIONS

The activity coefficient is one of the most important characteristics of dissolved substances. The f_e values for electrolytes have been fully investigated up to quite high concentrations. On the other hand, until recently the f_{ne} values could be determined experimentally only by complex laboratory methods requiring high-precision equipment as well as being very time-consuming.

By using the salting-out coefficient of the non-electrolyte in conjunction with Eqn. (40) the f_{ne} values for the non-electrolyte at various electrolyte concentrations can readily be calculated. The use of this equation is justified because the solubility of gaseous non-electrolytes in water and in electrolyte solutions is usually small (~10^{-3} to 10^{-5} mole litre^{-1}). Since $f_{ne}^0 = 1$ Eqn. (40) can be re-written

$$\lg f_{ne} = Kc_e. \qquad (46)$$

A new electrochemical method has been developed in our laboratory[55] to measure f_{ne} and other physico-chemical properties of three-component solutions (water–electrolyte–gaseous non-electrolyte) by using salting out data for the non-electrolyte. The method is based on the measurement of the limiting diffusion currents for the electrolytic reduction or oxidation of the dissolved non-electrolyte at an electrode separated from the solution by a polyethylene, polypropylene, or Teflon-4 membrane 10–40 μm thick. We have shown[55] that the limiting diffusion current I_d for a dissolved gas on such an electrode is

proportional to the activity rather than to the concentration of the gas in solution:

$$I_d = k_i a_{ne} = k_i f_{ne} c_{ne}. \quad (47)$$

If I_d is measured at saturation of the electrolyte solution by the gaseous non-electrolyte we have

$$I_d = k_i f_{ne} s_{ne}. \quad (48)$$

Since according to Eqn. (1) $s_{ne} = s^0_{ne} - 10^{Kc_e}$, by substituting this expression into Eqn. (48) we obtain

$$f_{ne} = \frac{I_d}{k_1 (s^0_{ne} - 10^{Kc_e})}. \quad (49)$$

The coefficient k_1 in Eqn. (49) is determined by measuring I^I_d for a saturated solution of the non-electrolyte in water, for which $s_{ne} = s^0_{ne}$, so that k_1 becomes

$$k_1 = I^I_d / s^0_{ne}.$$

From measurements of I_d in non-electrolyte–water–electrolyte solutions we can determine the volume of 1 mole of hydrated electrolyte molecules V^h_e. It has been shown[56] that

$$\lg f_{ne} = -\lg (1 - c_e V^h_e). \quad (50)$$

Thus we can calculate the volume of 1 mole of hydrated molecules of the electrolyte in solution by using Eqn. (50) together with the f_{ne} value calculated by Eqn. (49).

By measuring limiting diffusion currents of non-electrolytes in water and in electrolyte solutions saturated with one of the non-electrolytes we can determine the hydration numbers of the electrolytes at different electrolyte concentrations. The method relies on the observation[55] that the I_d values of non-electrolytes at an electrode covered by a membrane are the same in water and in electrolyte solutions of different concentrations if the solvent is saturated with the non-electrolyte. This shows that the I_d value for an electrode of this type is proportional to the activity rather than to the concentration of the non-electrolyte. The activity of the non-electrolyte in the liquid phase is proportional to the partial pressure of the non-electrolyte over the saturated water or electrolyte solution of the non-electrolyte. But since both the water and the electrolyte solutions are saturated with the non-electrolyte at the same partial pressure, the activity of the non-electrolyte is constant.

The number of free water molecules per non-electrolyte molecule (n^I_w) in water saturated with the non-electrolyte is given by

$$n^I_w = \frac{c^I_w}{s^0_{ne}} = \frac{c^I_w k_1}{I^I_d}, \quad (51)$$

where c^I_w is the molar concentration of water in the solution of non-electrolyte in water. This quantity is given by

$$c^I_w = c_w - V_{ne}. \quad (52)$$

If we add electrolyte to water saturated with the non-electrolyte to a molar concentration c_e of the electrolyte the number of free water molecules per molecule of the non-electrolyte (n^{II}_w) decreases as a result of the hydration of the electrolyte and becomes

$$n^{II}_w = \frac{c^{II}_w - c^h_w}{s^{II}_{ne}} = \frac{(c^{II}_w - c^I_w) k_2}{I^{II}_d}, \quad (53)$$

where c^{II}_w is the molar concentration of water in the water–electrolyte–non-electrolyte solution, c^h_w is the number of moles of water in 1 litre of this solution taken up by the hydration shells of the dissolved electrolyte, s^{II}_{ne} is the solubility of the non-electrolyte in a solution of electrolyte of concentration c_e expressed in mole litre^{-1}. Eqn. (53) was obtained by using the expression

$$s^{II}_{ne} = \frac{I^{II}_d}{k_2}.$$

The quantity c^{II}_w in Eqn. (53) is given by

$$c^{II}_w = c_w - V_{ne} - V_e, \quad (54)$$

where V_e is the intrinsic volume of 1 mole of electrolyte.

Since $I^I_d = I^{II}_d$, we obtain from Eqns. (51) and (53)

$$c^I_w k_1 = (c^{II}_w - c^h_w) k_2, \quad (E)$$

or in other words

$$c^h_w = (c^{II}_w k_2 - c^I_w k_1)/k_2. \quad (55)$$

By using Eqn. (55) the hydration number h_e of the electrolyte at the given concentration c_e can easily be determined:

$$h_e = \frac{c^h_w}{c_e} = \frac{c^{II}_w k_2 - c^I_w k_1}{c_e k_2}. \quad (56)$$

The quantities k_1 and k_2 are calculated from the measured values of I^I_d and I^I_d in water saturated with the non-electrolyte and in the water–electrolyte–non-electrolyte solution. The required values of s^{II}_{ne} are determined from Eqn. (1) using the known salting-out coefficient of the non-electrolyte in the solution of interest.

Ruetschi and Amlie[3] suggested the use of Eqn. (2) of the hydration theory together with their Eqn. (5) to calculate the volume of a mole of hydrated electrolyte molecules (V^h_e) and the intrinsic volume of a mole of the electrolyte at infinite dilution. They inserted s^0_{ne}/s_{ne} from Eqn. (5) into Eqn. (2) and, knowing V^h_e, they calculated $\nu_e V^0_e$ for KOH. Hence they arrived at the radius r_h of the hydrated KOH molecule, and they obtained a value in good agreement with those reported by other workers. By the same procedure Ruetschi and Amlie calculated V^0_e for HCl, LiCl, NaCl, KCl, NaOH, and KOH. However Eqns. (2) and (5) of the hydration theory of salting out and salting in are only approximate, as was pointed out above, and therefore Ruetschi and Amlie's calculations must also be treated as approximate.

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