Salting-out of Alkanols by Inorganic Electrolytes

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The free energies, entropies and enthalpies associated with the salting-out of alkanols (mainly butanol) by eight inorganic electrolytes have been determined at 20°C. The results are discussed in terms of the scaled particle theory (in the case of 1 : 1 electrolytes) and the thermodynamic theory of McDevit and Long. It is concluded that alternative approaches to the treatment of salting-out would be desirable. A simple, semi-empirical method for the calculation of salting coefficients is proposed. It is based on the effect which the electrolyte has on the surface tension of the solvent (water) and is found to be relatively successful for many systems.

In a previous paper [1] we described the salting-in of n-alkanols in aqueous solution by symmetrical tetra-n-alkylammonium bromides. The present work is concerned with the salting-out of alkanols (mainly butanol) by several inorganic electrolytes. Standard free energies, entropies and enthalpies of transfer of the solutes, at high dilution, from water to solutions of the electrolytes at various concentrations have been determined.

Various kinds of theoretical approach have been made to explain salting-out. In the electrostatic treatments the salt effect is supposed to arise from the change in the electrical energy of a salt solution resulting from changes in the relative permittivity of the solvent caused by the presence of the non-electrolyte. Apart from the theoretical shortcomings of these treatments, the various molecular parameters required to test the theories are not usually readily available. McDevit and Long [2] introduced a thermodynamic theory which has proved moderately successful. Free energy changes accompanying salting-out can frequently be predicted to within a factor of two or three of the experimental values. We have applied this theory to our present results with similar levels of success.

The scaled particle theory has recently been applied to salt effects [3] and it has been found to be more satisfactory than the McDevit–Long theory in most of the rather limited number of cases for which it has been tested. We have found the theory to give satisfactory results for some of the present systems. In particular the enthalpies of transfer of alcohols from water to solutions of NaCl are predicted quite closely.

We have devised a simple, semi-empirical method for the calculation of salting coefficients, which is based on the effect the electrolyte has on the surface tension of the water. It appears to be usually considerably more successful than the McDevit–Long theory (to which it bears some resemblance) and easier to apply than the scaled particle theory.

EXPERIMENTAL

Distribution ratios of the alcohols between water and salt solutions were determined by allowing the solute to attain equilibrium between the aqueous phases via n-dodecane, as described elsewhere.[1] The enthalpies of transfer of the solute from water to the electrolyte solutions were determined calorimetrically.[1]

MATERIALS

The n-dodecane (Koch–Light) was $>99.5 \%$ pure (estimated by g.l.c.) and was passed through chromatographic alumina immediately before use. The samples of butan-1-ol and hexan-1-ol were Fluka *puriss* grade, and pentan-1-ol was a Fluka *purum* sample. After distillation all had an estimated purity $>99 \%$. Water was twice distilled using all glass apparatus.

The salts used were AnalaR grade except RbCl and NaH_2PO_4 which were G.P.R. grade. In the case of NaCl, RbCl and Na_2CO_3, the salts were dried at $120°C$ and allowed to cool in a desiccator; then standard solutions were prepared by weight. Solutions of $MgCl_2$ and $CaCl_2$ were made up approximately and then standardised using silver nitrate, with dichloro-fluorescein as indicator. Sodium sulphate solutions were standardised using standard barium chloride solution, the end point being detected conductometrically. Concentrations of solutions of NaH_2PO_4 were determined gravimetrically by precipitation as $MgNH_4PO_4 \cdot 6H_2O$. Ammonium bromide solutions were standardised using the Volhard method.

RESULTS

As discussed elsewhere,[1] the standard free energy change accompanying the transfer of one mole of solute at constant mole fraction (at high dilution) from water to salt solution is given by

$$\Delta\mu^{\ominus}(x) = RT \ln(x_w/x_s) = 2.303\ RT \log f, \qquad (1)$$

where x_w and x_s are mole fractions of the solute in water and in salt solution respectively, at distribution equilibrium, and f is an activity coefficient of the solute in the salt solution. The results obtained for the salting-out of butanol are given in fig. 1 as plots of $\log f$ against the salt molality, m_s. In all cases except that for NaH_2PO_4, $\log f$ is a linear function of m_s. The slope is denoted $k(x)$ and referred to as the salting coefficient. For NaH_2PO_4, $k(x)$ is taken as the initial slope i.e. $(\mathrm{d}\log f/\mathrm{d}m_s)_{m_s=0}$.
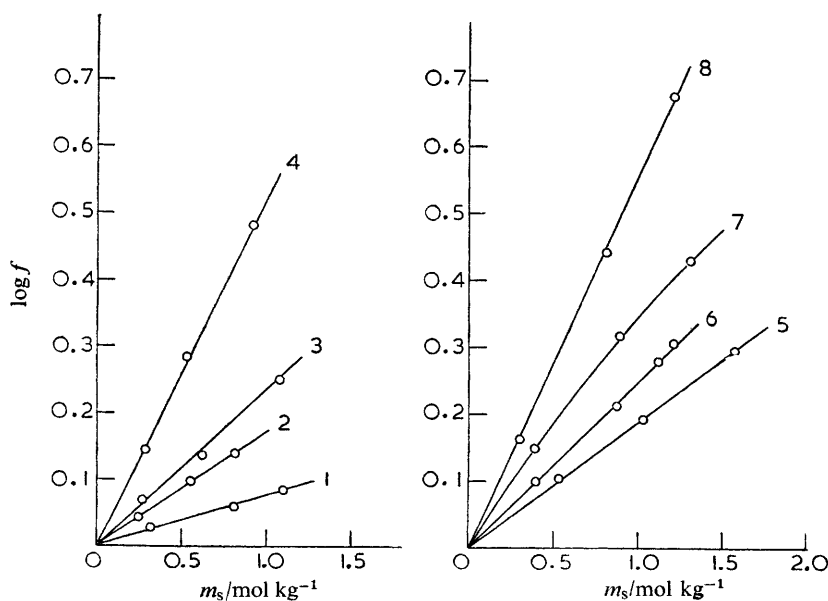

FIG. 1.—Variation of $\log f$ with salt molality m_s, for salting-out of butanol at $20°C$. 1, NH_4Br; 2, RbCl; 3, $MgCl_2$; 4, Na_2SO_4; 5, NaCl; 6, $CaCl_2$; 7, NaH_2PO_4; 8, Na_2CO_3.

SALTING-OUT OF ALKANOLS

The enthalpies of transfer, $\Delta H^\ominus$ have been obtained as the difference between the enthalpy of solution of the solute in water $\Delta H^\ominus_w$ at high dilution, and in salt solution, $\Delta H^\ominus_s$ also at high dilution. Values obtained for $\Delta H^\ominus_w$ at 20°C for butanol, pentanol and hexanol are 10.25 ± 0.06, 9.74 ± 0.05, and 7.93 ± 0.20 kJ mol^{-1} respectively. Enthalpies of solution in salt solutions are listed in table 1, where the errors shown represent the maximum experimental scatter obtained in the five or six determinations made of each value of $\Delta H^\ominus_s$. Within the experimental errors, $\Delta H^\ominus$ is a linear function

TABLE 1.—ENTHALPY OF SOLUTION OF ALCOHOLS, AT HIGH DILUTION IN SALT SOLUTIONS, MOLALITY m_s, AT 20°C

| solute	salt	m_s/mol kg^{-1}	$-\Delta H^\ominus_s$/kJ mol^{-1}
butanol	NaCl	0.06	10.16 ± 0.10
		0.15	10.05 ± 0.10
		0.55	9.44 ± 0.10
		0.81	8.96 ± 0.10
		1.07	8.40 ± 0.07
		1.57	7.72 ± 0.07
pentanol		0.67	8.53 ± 0.05
		1.16	7.45 ± 0.10
		1.76	6.24 ± 0.05
hexanol		0.53	6.96 ± 0.05
		1.03	5.84 ± 0.15
butanol	RbCl	0.81	9.01 ± 0.06
		1.25	8.31 ± 0.03
	NH$_4$Br	1.12	8.94 ± 0.10
		1.62	8.38 ± 0.10
	CaCl$_2$	0.06	10.15 ± 0.05
		0.16	10.02 ± 0.08
		0.24	9.99 ± 0.05
		0.45	9.43 ± 0.06
		0.61	9.04 ± 0.03
		1.03	7.83 ± 0.10
		1.12	7.75 ± 0.04
		1.29	7.39 ± 0.04
		1.54	6.79 ± 0.01
		1.55	6.60 ± 0.02
		1.83	5.77 ± 0.10
		2.27	4.62 ± 0.04
	MgCl$_2$	0.42	9.56 ± 0.10
		0.61	9.23 ± 0.02
		1.01	8.58 ± 0.12
butanol	MgCl$_2$	1.23	8.14 ± 0.06
		1.24	8.16 ± 0.02
		1.79	7.25 ± 0.02
		2.22	6.22 ± 0.10
	Na$_2$CO$_3$	0.23	9.27 ± 0.15
		0.53	8.38 ± 0.15
		0.91	7.06 ± 0.06
	Na$_2$SO$_4$	0.28	9.11 ± 0.10
		0.63	7.76 ± 0.07
		0.92	6.57 ± 0.05
	NaH$_2$PO$_4$	0.38	9.05 ± 0.05
		0.84	7.64 ± 0.02
		1.31	6.52 ± 0.10

of m_s, certainly up to concentrations of 1 mol kg^{-1} salt. Values of $\Delta\mu^{\ominus}(x)$, $\Delta H^{\ominus}$ and the entropy of transfer at constant mole fraction, $\Delta S^{\ominus}(x)$ are shown in table 2 for the transfer from water to 1 mol kg^{-1} salt solutions at 20°C.

TABLE 2.—STANDARD THERMODYNAMIC PARAMETERS OF TRANSFER OF ALCOHOLS FROM WATER TO 1 mol kg^{-1} SALT SOLUTIONS AT 20°C

solute	salt	$\Delta\mu^{\ominus}(x)/$ kJ mol^{-1}	$\Delta H^{\ominus}/$ kJ mol^{-1}	$\Delta S^{\ominus}(x)/$ J mol^{-1} K^{-1}
butanol	NaCl	1.07	1.57	1.71
	RbCl	0.95	1.55	2.05
	NH$_4$Br	0.42	1.15	2.49
	NaH$_2$PO$_4$	2.13	2.90	2.63
	CaCl$_2$	1.39	2.20	2.76
	MgCl$_2$	1.32	1.66	1.16
	Na$_2$CO$_3$	3.13	3.55	1.43
	Na$_2$SO$_4$	2.92	4.00	3.69
pentanol	NaCl	1.18	1.87	2.35
hexanol	NaCl	1.29	1.95	2.25

DISCUSSION

Assuming that salting-out results from additive contributions from the different ions in solution,[4] the orders in increasing effectiveness for salting-out of butanol are

$$\tfrac{1}{2}Mg^{2+} < \tfrac{1}{2}Ca^{2+} < Rb^+ < Na^+,$$

and

$$Cl^- < \tfrac{1}{2}SO_4^{2-} < \tfrac{1}{2}CO_3^{2-} < H_2PO_4^-.$$
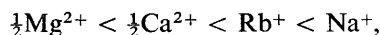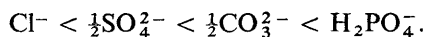
For all the electrolytes studied, $\Delta\mu^{\ominus}(x)$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}(x)$ are positive. Values of $\Delta\mu^{\ominus}(x)$ are similar in magnitude to $\Delta H^{\ominus}$ the latter always being greater than $T\Delta S^{\ominus}(x)$; $\Delta\mu^{\ominus}(x)$ is an approximately linear function of $\Delta H^{\ominus}$. The situation can be contrasted with that prevailing for the salt effects caused by the symmetrical tetraalkylammonium bromides (R$_4$NBr),[1] where $\Delta\mu^{\ominus}(x)$ (which is negative) is small compared to both $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}(x)$ (which are positive). It was possible to advance a plausible explanation of the salting-in caused by R$_4$NBr, based on the changes in water structure supposed to occur in the vicinity of the solute and the cation. No such simple explanation appears possible in the case of the inorganic ions. Stern and Hermann [5] studied the salting-out of ethyl acetate by several inorganic electrolytes and in most cases obtained negative values for the entropy of transfer. They suggest that this can be explained, at least in part, by the simple hydration theory i.e. by supposing that the electrolyte removes water from its solvent role and thus produces an " unmixing " effect on the solute. If such an effect is given, it certainly is not predominant in the present systems.

We now consider the application of some existing theories to our data and suggest a new approach to the calculation of salting coefficients.

SCALED PARTICLE THEORY (SPT)

This theory has been applied recently to salt effects on non-polar solutes,[3,6] as well as on alcohols.[7] The equations given by Masterton and Lee [3] were formulated for 1 : 1 electrolytes and we have applied them to the present systems containing such electrolytes. The parameters used for the electrolytes in testing the theory, are listed in table 3; σ_3 and σ_4 are the diameters of the cation and anion respectively, α_3 and α_4 are the cation and anion polarisabilities, and ϕ_0 is the apparent molal volume of the

electrolyte at infinite dilution in water. Values of the energy parameter, ε_2/k and diameter, σ_2 for water (85.3 K and 2.75 Å) were taken from Pierotti.[8] Values of ε_1/k and σ_1 for the alcohols were calculated using the empirical equations proposed by Stiel and Thodos [1] for organic materials, i.e.

$$\varepsilon_1/k = 65.3 \, T_c Z_c^{18/5} \tag{2}$$

$$\sigma_1 = 0.812 (T_c/P_c)^{1/3} Z_c^{-13/15}. \tag{3}$$

Z_c is the critical compressibility factor $P_c V_c/RT_c$ where T_c, P_c, and V_c are the critical temperature (K), critical pressure (atm.), and critical volume (cm^3 mol^{-1}). The critical constants for butanol and pentanol were taken from Reid and Sherwood,[10] but values for hexanol were not available. However, it was found that ε_1/k and σ_1 are almost linear functions of the alcohol chain length and the values for hexanol were determined by extrapolation from the lower homologues.

TABLE 3.—PARAMETERS USED IN THE APPLICATION OF SCALED PARTICLE THEORY

electrolytes

	σ_3/Å	σ_4/Å	$10^{24}\alpha_3$/cm^3	$10^{24}\alpha_4$/cm^3	ϕ_0/cm^3 mol^{-3}
NaCl	2.02 [a]	3.64 [a]	0.21 [d]	3.02 [d]	15.98 [c]
RbCl	2.92 [a]	3.64 [a]	1.81 [d]	3.02 [d]	31.94 [c]
NH$_4$Br	2.86 [b]	3.96 [a]	1.43 [e]	4.17 [d]	42.60 [c]

alkanols

	(ε_1/k)/K	σ_1/Å	$10^{24}\alpha_1$/cm^3
butanol	284	6.15	8.81 [f]
pentanol	298	6.52	10.66 [f]
hexanol	333	6.84	12.55 [f]

[a] T. C. Waddington, *Trans. Faraday Soc.*, 1966, **62**, 1482 ; [b] W. L. Masterton, D. Bolocofsky and T. P. Lee, *J. Phys. Chem.*, 1971, **75**, 2809 ; [c] ref. (11) ; [d] B. E. Conway, *Electrochemical Data* (Elsevier, New York, 1952) ; [e] *Landolt-Bornstein, Zahlenwerke und Functionen aus Physik, Chemie, Astronomie, Geophysik, Technik*. Vol. 1 (Springer, Berlin, 1950) Part I, p. 404 ; [f] obtained by adding bond refractions given by N. E. Hill, W. E. Vaughn, A. H. Price and M. Davies, *Dielectric Properties and Behaviour* (Van Nostrand-Reinhold, New York, 1969).

TABLE 4.—CALCULATED AND EXPERIMENTAL VALUES OF $k(x)$

		NaCl	RbCl	NH$_4$Br	MgCl$_2$	CaCl$_2$	Na$_2$SO$_4$	Na$_2$CO$_3$
butanol	(i)	0.19	0.17	0.07	0.24	0.25	0.52	0.56
	(ii)	0.25	0.03	0.08	—	—	—	—
	(iii)	0.45	0.39	−0.07	0.90	1.23	1.41	1.67

pentanol+NaCl	(i)	0.21			hexanol+NaCl	(i)		0.23
	(ii)	0.26				(ii)		0.27
	(iii)	0.53				(iii)		0.62

(i) experimental value ; (ii) from SPT ; (iii) from MLT.

Values of $k(x)$ obtained from SPT are compared with the experimental values in table 4. Apart from the result for RbCl the agreement is quite satisfactory. A further test of the theory can be made by examination of the temperature variation of $k(x)$ i.e. by calculating the enthalpies of transfer.

It has been assumed that the only parameter to vary significantly with temperature is ϕ_0. This does not appear unreasonable, but in any event temperature coefficients of the other parameters are not available. We have calculated the temperature variation of $k(x)$ for the salting-out of butanol, pentanol, and hexanol by NaCl in the temperature range 5 to 40°C. Values of ϕ_0 were taken from the compilation of Millero,[11] and $\Delta H^\ominus$ for 20°C has been obtained graphically with the aid of the expression

$$\mathrm{d}k(x)/\mathrm{d}T = -\Delta H^\ominus/2.303\ RT^2. \qquad (4)$$

The calculated values of $\Delta H^\ominus$ for the alkanols butanol to hexanol are 2.0, 2.0 and 2.1 kJ mol^{-1}, compared to the corresponding experimental values of 1.57, 1.87 and 1.95 kJ mol^{-1}. We consider the agreement to be satisfactory.

THEORY OF MCDEVIT AND LONG (MLT)

This thermodynamic theory of salt effect was considered the most generally satisfactory until the advent of SPT. It is supposed that salting-out results from the electrostriction of the solvent caused by addition of electrolyte. The expression for $k(x)$ given by the theory is

$$k(x) - (0.016 - 10^{-3}\overline{V}_s^\circ/2.3) = \lim_{c_s \to 0} \frac{\overline{V}_i^\circ}{2.3RT}\frac{\mathrm{d}P_e}{\mathrm{d}c_s} = \frac{\overline{V}_i^\circ(V_s - \overline{V}_s^\circ)}{2.3RT\beta_0}. \qquad (5)$$

$\overline{V}_s^\circ$ is the partial molal volume of the electrolyte at infinite dilution (which is equal to the apparent molal volume, ϕ_0 at infinite dilution) and V_s is the (hypothetical) liquid molar volume of the pure salt at temperature T. $\overline{V}_i^\circ$ is the partial molal volume of the solute at infinite dilution, and is often taken as the molar volume of the pure solute, since the two volumes are frequently similar in magnitude. β_0 is the compressibility of water and c_s is the molarity of the salt solution.

The quantity V_s cannot be known with certainty and it is better to obtain $k(x)$ using " effective pressures ", P_e (see later), of the electrolyte solutions where these are known. Values of $k(x)$ calculated from MLT are included in table 4. Molar volumes V_m of pure liquids were used for $\overline{V}_i^\circ$; it is known that for butanol for example the two quantities differ by only 8 %. For NaCl, Na$_2$SO$_4$ and Na$_2$CO$_3$ values of $\mathrm{d}P_e/\mathrm{d}c_s$ were available. In the case of the other electrolytes V_s has been equated to the molar volume of the crystalline salt. We have found that for many electrolytes, where $\mathrm{d}P_e/\mathrm{d}c_s$ is known, V_s obtained from the effective pressure is close to the molar volume in the crystal. Values of $k(x)$ obtained from (5) relate to 1 mol dm^{-3} salt whereas the experimental values are for 1 mol kg^{-1} salt. The two coefficients should not differ by more than about 3 % on this account and the corrections have not therefore been made.

The theoretical values of $k(x)$ are larger than the experimental values by a factor of between 2 and 5. A similar situation is reported by McDevit and Long for the salting-out of benzene, which has a molar volume very close to that of butanol, and for the salts studied in common (NaCl, Na$_2$SO$_4$, RbCl) the experimental $k(x)$ values are close for the two solutes. It appears therefore that the polarity of the butanol does not have a very large effect on the salting-out. We note that, although the absolute values of $k(x)$ from MLT are in error, the order of the salt effects on butanol is correctly predicted.

We have calculated the salting coefficients for butanol with NaCl using eqn (5), over the temperature range 5 to 40°C, allowing for the variation with temperature of $\overline{V}_i^\circ$ (taken as V_m),[12] β_0,[13] and $\overline{V}_s^\circ$.[11] The value of $\Delta H^\ominus$ at 20°C obtained by the use

of eqn (4) is 5.5 kJ mol^{-1} as compared to the experimental value of 1.57 kJ mol^{-1}. The agreement (or lack of it) between experiment and theory is thus of the same order as for the free energies of transfer. It is far less satisfactory than that obtained using SPT.

APPROACH RELATING SALTING COEFFICIENTS TO THE EFFECT OF ELECTROLYTE ON SURFACE TENSION OF WATER

As seen, MLT gives poor absolute agreement with experiment, and although, for the cases tested, SPT is much more satisfactory there will frequently be difficulty in selecting unambiguous values of the Lennard–Jones parameters for the solutes. There is therefore scope for new approaches, theoretical or empirical, which will be useful in a predictive sense. We describe below a simple, relatively successful semi-empirical method for the calculation of salting coefficients.

The approach is similar to that in MLT. In the latter, the free energy of transfer, $\Delta\mu^{\ominus}(c)$ of the solute, at constant molarity, from water to salt solution is calculated as the difference in the work of forming a volume $\bar{V}_i^{\circ}$ in water and in salt solution. This difference is equated with $P_e\bar{V}_i^{\circ}$ where P_e is the " effective pressure " [14] of the salt solution. P_e can be regarded as the amount by which the internal pressure of the salt solution exceeds that of pure water.[15] In this formulation however the work of forming cavities of total volume $\bar{V}_i^{\circ}$ is independent of the state of dispersion of the volume. In other words it is implied that the work is done against a *constant* internal pressure, irrespective of the size of individual cavities formed.

We have calculated the work of forming one mole of cavities, each of volume $\bar{V}_i^{\circ}/N_A$, in terms of the surface area of the cavities. Thus

$$\Delta\mu^{\ominus}(c) = N_A\Omega\Delta\gamma, \qquad (6)$$

where Ω is the surface area of a molecular cavity and $\Delta\gamma = \gamma - \gamma_0$, γ and γ_0 being the surface tension of the salt solution and water respectively. It follows that [see eqn (1)] at $T = 293$ K

$$k(c) = \Delta\mu^{\ominus}(c)/2.3\,RT = 1.07\times10^{-3}\Omega\Delta\gamma, \qquad (7)$$

where Ω and $\Delta\gamma$ are expressed in Å^2 and mN m^{-1} respectively. The approach is only crude in that (*a*) it is assumed that the surface tension of a cavity wall is equal to the macroscopic value, and (*b*) as in MLT, no account is taken of the different interactions between the solute and its surroundings in water and in salt solution. Assumption (*a*) may not be too serious since it is a *difference* in surface tension which is used, and any errors involved may therefore largely cancel. It will be noted that the formulation is in terms of the solute transfer at constant molarity rather than constant mole fraction, since the quantity $\Delta\mu^{\ominus}(x)$ contains a contribution from the change in total volume available to the solute on transfer from water to salt solution, whereas $\Delta\mu^{\ominus}(c)$ does not. However, the difference between $k(c)$ and $k(x)$ (= $0.016 - 10^{-3}\,\phi_0/2.3$) [16] is usually small for inorganic electrolytes.

The theory is tested initially using results from the literature for the salting-out of benzene [2] and of butane [17]; $k(c)$ is plotted against $\Delta\gamma$ [18] in fig. 2; $k(c)$ is a reasonably linear function of $\Delta\gamma$, the lines passing through the origin. For benzene, for which most data are available, the points for NH$_4$Cl and LiCl fall below the line and those for NaOH and Na$_2$SO$_4$ (not shown) are above the line $\Delta\gamma$ is for 1 mol kg^{-1} salt.

These deviations may arise from the lack of consideration of the interactions between the solute and solvent species. It is possible that a rough allowance for this effect could be made by using interfacial tensions between the pure solute and water, or salt solution, rather than simply using surface tensions. However, the relevant

data are not available but it is intended to determine the necessary interfacial tensions to test this proposition.

The values of Ω for benzene and butane calculated from the slopes of the lines in fig. 2 are 104 and 135 $Å^2$ respectively. Assuming pure liquid benzene to consist of close-packed spherical molecules, the surface area of benzene is 110 $Å^2$ molecule^{-1}, in close agreement with value obtained from $k(c)$. An estimate of the value of Ω for butane can be obtained by supposing the molecule to be a square prism. Assuming the width of the chain to be 4.7 Å and the resolved C—C distance along the chain to be 1.26 Å, Ω is given as 139 $Å^2$, again in excellent agreement with the value calculated from $k(c)$.
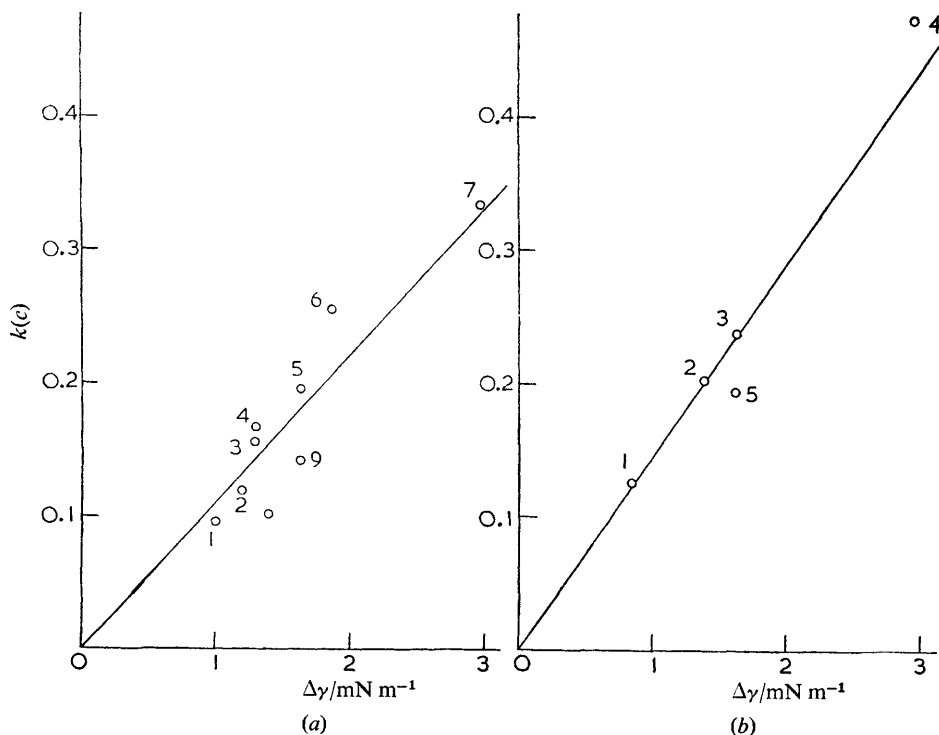

FIG. 2.—Variation of $k(c)$ with $\Delta\gamma$. (a) Salting-out of benzene by 1, NaI; 2, NaNO$_3$; 3, NaBr; 4, KCl; 5, NaCl; 6, NaOH; 7, BaCl$_2$; 8, NH$_4$Cl; 9, LiCl. (b) Salting-out of butane by 1 KI; 2, KCl; 3, NaCl; 4, BaCl$_2$; 5, LiCl.

We have further tested the theory using data for the salting-out of a large number of benzene derivatives,[1, 17] and naphthalene and biphenyl,[19] by NaCl in the following way. For simplicity we have made the approximation that all the solutes are spherical molecules which are close-packed in their pure condensed state. It is then readily shown that

$$k(c) = 9.7 \times 10^{-3} \, V_m^{\frac{2}{3}}(V_m \text{ in cm}^3 \text{ mol}^{-1}). \tag{8}$$

Values of $k(c)$ obtained from eqn (8) are compared with experimental results in table 5. The success of (8) for these systems is apparent. The largest difference between experiment and theory is only about 20 % and for the non-polar solutes the agreement is to within 10 %.

We now consider the application to salt effects on the n-alkanols. The particular rôle of the —OH moiety in salt effects is likely to be unusual since there is the possibility that this group enters into the water structure through H-bonding. We have therefore applied the theory indirectly. Consider first the salting-out by NaCl. For butanol, pentanol and hexanol respectively, the area of the alkyl chain exposed to water (calculated as for butane) is approximately 120, 140 and 160 Å². Using eqn (7), values of $k(c)$ for the alkyl chains are 0.21, 0.25 and 0.28 respectively. The value of $k(c)$ for the —OH in each of the alkanols can now be determined as the difference between $k(c)$ determined experimentally for the whole molecule and the calculated $k(c)$ for the chain. Thus $k(c)$ for the —OH in butanol, pentanol and hexanol is found to be −0.02, −0.05 and −0.07 respectively. The mean value of −0.05 is close to that (−0.03) calculated by Wilcox and Schrier [7] from experimental data using only the assumption that $k(c)$ is made up from the additive contributions from the constituent groups of the solute. It thus appears that the theory based on surface tension increments produced by the electrolytes is successful for the salting-out of alkanols by NaCl.

TABLE 5.—EXPERIMENTAL VALUES OF $k(c)$ AND VALUES CALCULATED USING EQN (8) FOR THE SALTING-OUT OF AROMATIC COMPOUNDS BY NaCl

solute	$k(c)$ expt.	$k(c)$ eqn (8)	solute	$k(c)$ expt.	$k(c)$ eqn (8)
benzene	0.20	0.19	phenol	0.17	0.19
toluene	0.23	0.22	o-toluic acid	0.23	0.24
ethylbenzene	0.24	0.24	o-nitrobenzoic acid	0.18	0.22
aniline	0.16	0.20	2-hydroxybenzoic acid	0.20	0.20
benzoic acid	0.18	0.20	naphthalene	0.26	0.24
phthalic acid	0.18	0.21	biphenyl	0.28	0.31

It is not yet possible to test the theory for the salting-out of butanol by the other electrolytes used in this study since experimental values of $k(c)$ for the —OH are not available. Nonetheless it seems likely that those electrolytes which give anomalous results for benzene will do the same for the alkanols. As for benzene however, we believe it may be possible to take approximate account of these effects by using appropriate interfacial tensions rather than surface tensions.

Finally we note the situation with regard to the application of the surface tension approach to salting-in caused by R_4NBr salts. These electrolytes adsorb strongly at both the macroscopic oil/water and air/water interface, with consequent lowering of surface tension. Hence salting-in is predicted by the model. However, quantitative agreement is very poor, the model predicting a much greater salting-in than is observed. This is perhaps not surprising when it is realised that, for example Bu_4NBr has a partial molal volume in water (~ 300 cm³ mol⁻¹) of the order of 3 times that of butanol (~ 90 cm³ mol⁻¹). Thus to suppose that the " adsorption " of the cations at the cavity surface is similar to that at a macroscopic plane surface is clearly unrealistic. It would appear that the present model should be most applicable to large solutes (i.e. cavities) and small ions.

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