The Salting-out of Non-electrolytes. Part III. The Inert Gases and Sulphur Hexafluoride.*

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The salting-out of helium, krypton, and sulphur hexafluoride has been studied, electrolytes varying over a wide range of ionic size being used. Neon, argon, xenon, oxygen, *n*-butane, and benzene have also been investigated in solutions of electrolytes of special interest. Neither purely electrostatic theories of the effect nor the " internal pressure " theory of McDevit and Long is generally valid. Comparison of solutes of approximately the same size, *e.g.*, sulphur hexafluoride and benzene, suggests that the polarisability of the solute molecule is at least as important as solute volume in determining the salting-out effect especially with large ions. For the smaller ions there is a good correlation between salting-out and the entropy change in solution of the non-electrolyte in pure water at 4°.

IT has been shown that certain electrolytes give salting-out coefficients for the paraffin gases and other non-polar solutes which are approximately linear functions of the coefficients for sodium chloride (Parts I and II *). The slopes of these lines were not in general in agreement with the values predicted from purely electrostatic theories of the effect. McDevit and Long (*J. Amer. Chem. Soc.*, 1952, **74**, 1773), using benzene as solute, reached essentially similar conclusions as to the salting-out order of electrolytes, and suggested that the effect might be related to the volume change which occurs when liquid electrolyte is dissolved in water, or to the closely related " effective pressure " of the electrolyte derived from compressibility measurements.

The present investigation has been mainly concerned with the salting-out of helium, krypton, and sulphur hexafluoride, but work on neon, argon, and xenon showed that a more extended study of these gases would not affect the general conclusions reached. Sulphur hexafluoride provides an example of an inert solute of somewhat different type from those already studied. Additional data for benzene, *n*-butane, and oxygen have also been obtained.

The method of comparison previously used (Part I) has been retained, and k_x for a given salt has been plotted against k_{NaCl} at 25°. The fact that k_x is an additive function has, however, been used to give results for cations as chlorides and for anions as sodium salts. It is found that, while a number of ions give, for all the non-polar solutes so far studied, reasonably linear relation (Fig. 1), yet the remaining ions do not. In some cases (Fig. 2) the inert gases and sulphur hexafluoride show approximately normal behaviour but other solutes deviate beyond experimental error in the direction of greater salting-in. With the ions NMe_4^+ and NEt_4^+, even helium, krypton, and sulphur hexafluoride show appreciable deviations from linear behaviour, while *n*-butane and benzene are highly salted-in (Fig. 3). For salts of this type, giving a very large expansion on solution, the salting-out coefficients referred to unit volume of solution (k_v) and to unit weight of water (k_w) differ appreciably, so that although k_w indicates slight salting-in for helium and krypton, k_v would indicate salting-out of the same magnitude as for ammonium chloride. Since k_w appears to be more closely related to theoretically significant concentration units (mole-fraction) it has been retained in the present paper.

The slopes of the lines for the inert gases and sulphur hexafluoride are compared in Table 1 with those predicted (*a*) from electrostatic theories of the type suggested by Debye and McAulay (*Physikal. Z.*, 1925, **26**, 22) and (*b*) from McDevit and Long's internal-pressure theory. Although the observed slopes for the substituted ammonium salts are of necessity very approximate, they must certainly be regarded as positive, and the internal-pressure theory fails when tested in these cases on the most inert solutes available. Neither

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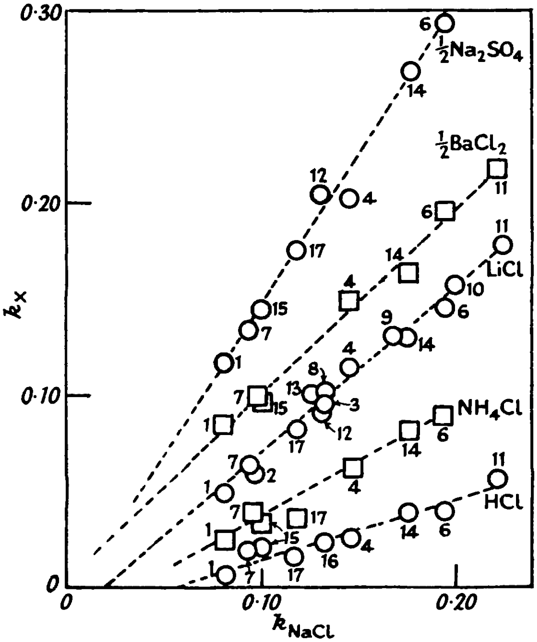
* Parts I and II, *J.*, 1952, 3814, 3819.

FIG. 1.



Key to all Figures.

1. He
2. Ne
3. A
4. Kr
5. Xe
6. SF_6
7. H_2
8. CH_4
9. C_2H_6
10. C_3H_8
11. C_4H_{10}
12. C_2H_4
13. N_2
14. C_6H_6
15. C_2H_2
16. O_2
17. N_2O

1—13. This series, Parts I, II, III. Additional data for 7, 12, 13 from Seidell ("Solubilities of Inorganic and Organic Substances," van Nostrand, N.Y.).
14. McDevit and Long (*loc. cit.*) and this paper.
15, 17. Seidell (*op. cit.*).
16. Seidell (*op. cit.*) and this paper.

FIG. 2.

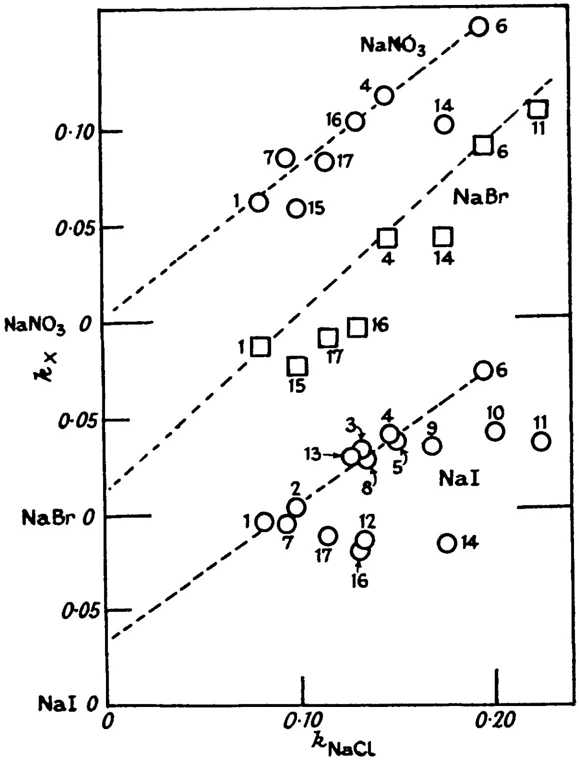
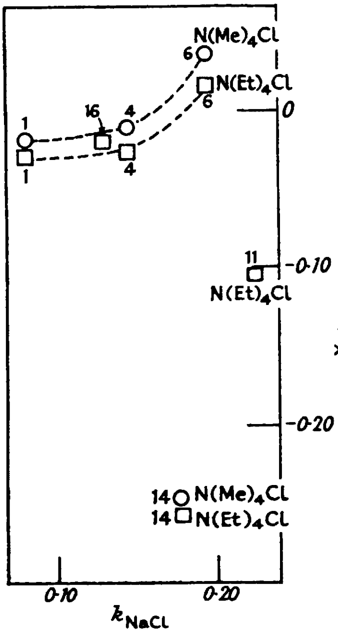


FIG. 3.



theory can, in fact, be regarded as satisfactory, although, apart from the cases mentioned, McDevit and Long's theory does reproduce better the order in which electrolytes salt out.

The most striking feature of these comparisons is the increasing deviation from inert-gas behaviour of benzene with increase in ionic size. It is clear from comparison with sulphur hexafluoride, which is probably of the same order of size as benzene, that no theory which utilises molecular volume as the only or the main solute parameter controlling salt effects can be qualitatively satisfactory, even if allowance is made, as suggested by McDevit and Long, for the finite size of solute molecules and ions. Thus neither purely electrostatic theories, which have been shown to involve solute volume as the main solute characteristic for non-polar molecules (Cohn and Edsall, " Proteins, Amino Acids and Peptides," Reinhold, N.Y.), nor the internal-pressure theory using molecular volume as the only solute parameter, is *generally* valid.

It has been suggested by several workers that van der Waals forces between ions and neutral molecules may be in part responsible for the specific effects observed in this field, and it is noteworthy that benzene and sulphur hexafluoride differ rather considerably in polarisability for substances of nearly the same molecular volume. It is therefore of interest to determine whether differences in polarisability would account empirically for the deviations from linear behaviour noted above. If, for example, we assume that the difference between k_{NaI} for the two solutes ($\Delta k = 0{\cdot}104$) is due entirely to difference in polarisability ($\Delta p_g = 6{\cdot}3 \times 10^{-24}$), a correction for salting-in, varying directly with polarisability, can be applied to all the solutes investigated. A similar, though much

FIG. 4.

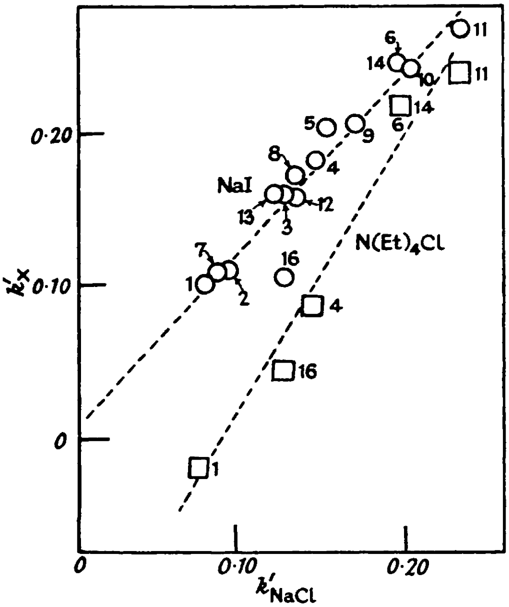


FIG. 5.

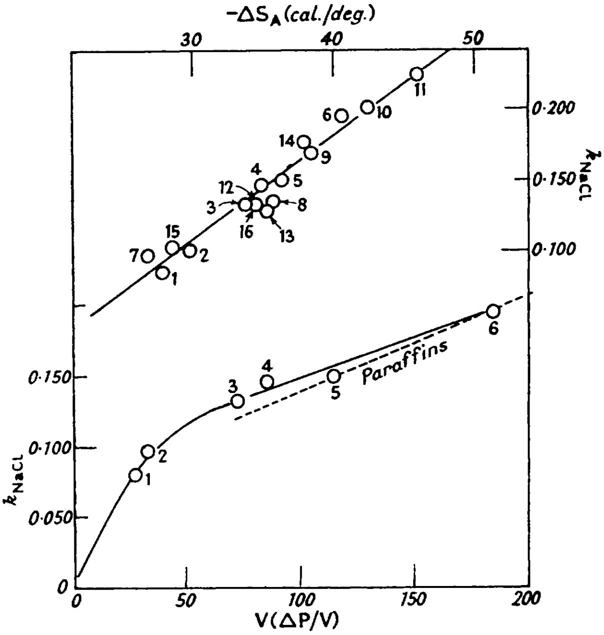


TABLE 1.

Electrolyte	Slope obs.	Slope calc. *a*	Slope calc. *b*	Electrolyte	Slope obs.	Slope calc. *a*	Slope calc. *b*	Electrolyte	Slope obs.	Slope calc. *a*	Slope calc. *b*
HCl ...	0·33	—	0·21	$\frac{1}{2}$BaCl$_2$...	0·96	1·2	1·19	NaI	0·70	0·95	0·64
LiCl ...	0·87	1·14	0·74	NMe$_4$Cl	0·4	0·75	−1·1	NaNO$_3$	0·77	—	0·74
KCl ...	0·83	0·90	0·81	NEt$_4$Cl	0·4	0·7	negative	$\frac{1}{2}$Na$_2$SO$_4$	1·50	1·28	1·58
NH$_4$Cl...	0·58	0·87	0·36	NaBr ...	0·91	0·98	0·83				

smaller, correction is necessary for sodium chloride and the corrected coefficients, k'_x, are plotted in Fig. 4. It is evident that the correction is quantitatively sufficient to account for the deviations of the paraffin series and ethylene. For the substituted ammonium salts the correction is nearly three times that for sodium iodide and the resulting plot for tetraethylammonium chloride (Fig. 4) is again reasonably linear, although we have as yet much fewer data than for the iodide. The position of oxygen, which is salted-in by iodide ions relative to chloride, is little changed when the correction is applied, and it is likely that in this case at least there is a specific interaction. In view of the chemical nature of the particles concerned, however, this is not surprising. With tetraethylammonium chloride, on the other hand, there is no such effect and oxygen shows approximately inert-gas behaviour.

Although these results suggest that polarisability is a factor of major importance in controlling salt effects, there are indications that the problem cannot be dealt with as simply as we have outlined. Thus the true order of salting-out, apart from that due to van der Waals forces, estimated from the slopes of the corrected lines would be $I > Br > Cl$ and $NMe_4 = NEt_4 > Na$, which appears unlikely. In addition, the correction leaves the line for tetraethylammonium chloride with a large negative intercept, and in view of the low polarisability of helium, no reasonable correction will remove this.

It is possible, however, that salt effects may be indirectly related to polarisability. The very marked expansion on dissolution of the substituted ammonium salts may be considered to be equivalent to a fall in " structural temperature " (Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515), in the sense that the solvent must assume a more open structure. Since the heat of solution is related to the polarisability of the solute (Eley, *Discuss. Faraday Soc.*, 1953, **15**, 150), greater salting-in would be found than would be expected if van der Waals forces were alone responsible, and the salting-in correction may be related to polarisability in a more complex manner than that considered above. A study of the effect of temperature on the salting-out coefficients for benzene and sulphur hexafluoride may enable this tentative suggestion to be tested. We may expect a structural effect to be modified by change in temperature to a greater extent than the van der Waals effect.

Although molecular volume cannot now be regarded as the only solute parameter of importance, an approximate relation between v_c and k_x may be sought in cases where the salting-in correction is likely to be small, *i.e.*, for the electrolytes of Fig. 1. The function $v_c(\Delta p/v)$ was used in Part II (*loc. cit.*) to detect such a relation in the paraffin series, and the results for the inert gases (Fig. 5) now show that the connection is unlikely to be strictly linear. The positions of helium and neon indicate an undoubted curvature towards the origin, although for larger molecules there is approximate linearity. In these respects the curve resembles those obtained by plotting ΔH°_{277} and ΔS°_{277} for the solutes in pure water against polarisability and molecular volume respectively (Morrison and Johnstone, *J.*, 1954, 3441). There is a good correlation between ΔS°_{277} and k_{NaCl} (Fig. 5) for all the non-polar solutes; that involving ΔH°_{277} is less satisfactory. The other electrolytes of this group will give similar relations, and these suggest that the problem of the primary salting-out effect requires more knowledge of the structure of the solvent round the inert molecule and how it is affected by the presence of ions than is at present available.

EXPERIMENTAL

The solubility technique has been described (Morrison and Billett, *J.*, 1952, 3819), and the inert gases were the purest obtainable from the British Oxygen Co. Ltd. Sulphur hexafluoride (at least 99% pure) was supplied by Imperial Chemical Industries Limited. As was predicted (Morrison and Johnstone, *loc. cit.*) the solubility of this gas, though slightly higher than that of carbon tetrafluoride, is very low, and the salting-out coefficients are therefore somewhat less accurate than for the more soluble gases. Errors of up to about $\pm 0{\cdot}010$ in k_x would not, however, affect the conclusions reached at the present stage of the investigation, and this margin is certainly not exceeded. Solubilities are recorded in Table 3 for a short temperature range, and from these a value for ΔS°_{277} of 40·8 cal. per degree (for transfer of gas at 1 atm. to a hypothetical solution at unit mole-fraction) was calculated.

The salting-out of benzene was determined in a few cases by measuring the solubility of air saturated with benzene vapour at 25° in an apparatus similar to that used for other gases. From the known vapour pressure of benzene and the solubility of air at 1 atm., the solubility of benzene can be obtained. This method is being developed for measuring the solubilities of volatile liquids for which analytical methods are difficult and, although air is a suitable carrier gas for benzene (making a contribution to the solubility of the mixture of only about 15 c.c. in 500 c.c.), in other cases one of the more sparingly soluble gases, such as carbon tetrafluoride, would be more satisfactory. Although the solubility of benzene by this method (1·64 g. per l. at 25°) is slightly less than that recorded by McDevit and Long (*loc. cit.*; 1·77 g. per l.) the salting-out coefficients for KCl, KI, and NMe_4I were in good agreement with the results of these workers. A determination using NEt_4Br left no doubt that very marked salting-in occurs with salts of this type.

In most cases concentrations of the electrolytes were approximately N, and were controlled by volumetric and density methods. For NMe_4I, however, the low solubility limits the concentration to about 0·25N at 25°.

Previous values of k_x for helium and argon at high salt concentrations by Akerlof (*J. Amer. Chem. Soc.*, 1935, **57**, 1196) are generally in poor agreement with our results, especially for argon (*e.g.*, $k_{NaCl} = 0{\cdot}058$ compared with our value of 0·133), but the results of Eucken and Herzberg (*Z. physikal. Chem.*, 1950, **195**, 1) on argon and xenon agree well ($k_{NaCl} = 0{\cdot}139$ for argon and 0·150 for xenon at 20°).

Results are recorded in Table 2 for a sufficient number of salts in the cases of helium, krypton, and sulphur hexafluoride to enable the additivity rule to be directly applied. In certain other cases the conversion from potassium to sodium salts was carried out by using the linear relation between k_{KCl} and k_{NaCl} which appears to apply generally to a sufficient degree of accuracy.

TABLE 2. *Salting-out coefficients,* $k = (\log s_0/s)/c$, *at* 25°. *Concentrations per* 1000 *g. of water.*

	k		
Electrolyte	He	Kr	SF_6
NaCl	0·081	0·146	0·195
LiCl	0·050	0·116	0·145
HCl	0·008	0·028	0·040
KCl	0·068	0·124	0·165
NH_4Cl	0·027	0·065	0·090
$\frac{1}{2}BaCl_2$	0·086	0·151	0·195
$\frac{1}{2}Na_2SO_4$	0·118	0·203	0·295
KI	0·083	0·120	0·145
KBr	—	0·120	0·160
NaBr	0·087	—	—
KNO_3	—	0·093	0·120
HNO_3	−0·013	−0·003	—
NMe_4I	−0·001	−0·016	0·010
NEt_4Br	−0·024	−0·032	0·010

	k		
Electrolyte	Ne	Ar	Xe
NaCl	0·097	0·133	0·149
LiCl	0·059	0·096	—
KI	0·080	0·108	0·113

	k		
	C_6H_6	n-C_4H_{10}	O_2
KCl	0·145 (0·148)	—	—
KI	0·049 (0·042)	—	—
KBr	—	0·174	—
NMe_4I ...	−0·333 (−0·336)	—	—
NEt_4Br	−0·295	−0·122	−0·046

Values in parentheses have been calculated from the data given by McDevit and Long (*loc. cit.*).

TABLE 3. *Solubility of sulphur hexafluoride* (*c.c. at N.T.P. per* 1000 *g. of water at a gas pressure of* 1 *atm.*)

t	10·9°	12·5°	14·2°	19·6°	25·0°	27·8°	29·6°
s_0	7·9	7·4	7·0	6·2	5·4	5·2	5·1

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