730. *The Salting-out of Non-electrolytes. Part II.* The Effect of Variation in Non-electrolyte.*

By T. J. MORRISON and F. BILLETT.

The salting-out of a number of gases and aromatic liquids has been compared with the requirements of theory, molecular volume and total polarisation being used as variable characteristics of the solute molecules. For gases, part of the salting-out appears to be independent of these variables, and the remainder varies in an approximately linear manner for a group of gases. Ethylene and the aromatic hydrocarbons do not lie on the same line. The invariant portions of the effect give values for the primary hydration of the salts which are of the correct order of magnitude, but place the salts in the inverse order to that generally accepted.

CURRENT theories of the salting-out effect require a knowledge of the effect of the solute molecule on the dielectric constant of the solvent to predict the approximate magnitude of the effect (Bebye, *Z. phys. Chem.*, 1927, **130**, 56; Butler, *J. Phys. Chem.*, 1929, **33**, 1015). The deduction used by Butler, and extended by Bockris, Bowler-Reed, and Kitchener (*Trans. Faraday Soc.*, 1951, **47**, 184), suggests, however, that the effect should depend to a large extent on the molecular volume of a non-polar molecule.

Butler's equation may be written :

$$k = Kv_c(p_b/v_b - p_c/v_c) = Kv_c(\Delta p/v)$$

where k has already been defined, and p and v are total polarisation and molecular volume of a solute (c) and solvent (b) respectively; K is a constant containing temperature, ionic radii, and dielectric constant of solvent and should be independent of the solute.

The substances used in the present investigation have small values of p_c/v_c compared with those for water, and the salting-out should therefore be determined largely by v_c. Some difficulty arises in assigning values of molecular volume, but in the absence of data on partial molar volumes it is thought that a satisfactory test can be applied by using molecular volumes measured under comparative conditions, such as parachors, it being assumed that the actual volumes in solution are approximately proportional to these.

The results are shown graphically in Fig. 1 (25°) and Fig. 2 (71·7°) for three salts. Values of $v_c(\Delta p/v)$ were calculated from recorded values of parachors and total polarisations except in the case of ethylbenzene, where a value for p_c was obtained from the additive nature of total polarisation. No essential difference in the nature of the curves is found if values for k are plotted against the actual parachors. For the saturated hydrocarbons with sodium and lithium chlorides there appears to be a reasonably linear relation between salting-out and the polarisation factor, and the results for hydrogen and nitrogen fall fairly near this line. If the relation is a linear one, however, an appreciable amount of salting-out appears to be independent of the properties of the solute gas. It was considered at first that this might be ascribed to primary hydration of the salt. The approximate intercepts (I) and the number of molecules of water corresponding to this salting-out are given in Table I. The order of magnitude of the calculated hydration is in agreement with the values collected by Bockris (*Quart. Reviews*, 1949, **3**, 173), although the effect for sodium chloride is somewhat greater than for lithium chloride.

TABLE 1.

NaCl				LiCl			
At 25°		At 71·7°		At 25°		At 71·7°	
I	H_2O	I	H_2O	I	H_2O	I	H_2O
0·07	8	0·055	7	0·05	6	0·035	4

The results for potassium iodide do not appear to be in agreement with the above view.

---

* Part I, preceding paper.

If the lines are regarded as approximately linear, the intercept at 25° (excluding H_2) indicates a higher primary hydration than for lithium chloride, which is unlikely. The results at higher temperature, however, show a distinct curvature for the paraffin series and the curve might pass through the origin. The solution of the problem of the precise nature of the variation of *k* with molecular volume seems to require in the first place data on non-polar substances which are salted-out to an even smaller extent than those used in the present work, and it is hoped that work on the inert gases will provide this. The points for the aromatic series, although approximately linear, involve too great an extrapolation, but it is noteworthy that, the parachor being used as a measure of molecular volume, they fall on a different line from the aliphatic series. Ethylene also lies consistently off the aliphatic line. It therefore appears that Butler's simple treatment of the effect does not include a sufficient number of variables to predict the behaviour of even relatively simple molecules. The treatment by Bockris and his co-workers, which may be regarded as introducing a salting-in term in Butler's equation, suggests that any salting-in occurring in these systems will be greatest for C_4H_{10}–KI, the combination of the largest ions and the most polarisable molecule, and least for H_2–LiCl. It is therefore possible that the anomalous behaviour of potassium iodide is due, in part at least, to the dispersion effect used in the above theory. The structural effect mentioned in Part I may also be in part responsible for the rather complex behaviour described.

FIG. 1.

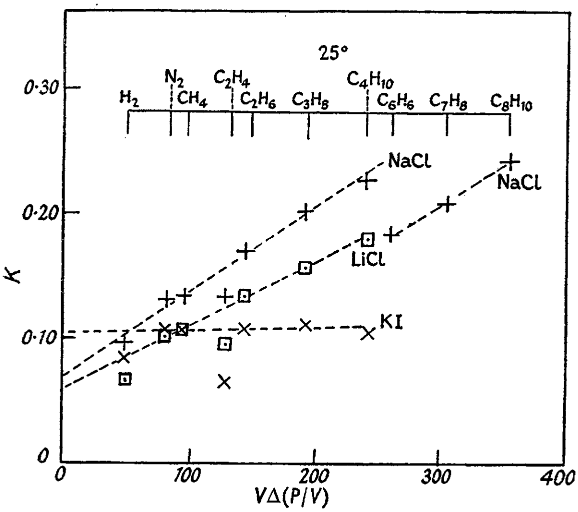


FIG. 2.

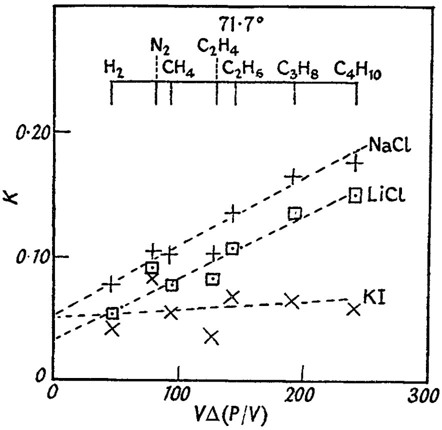
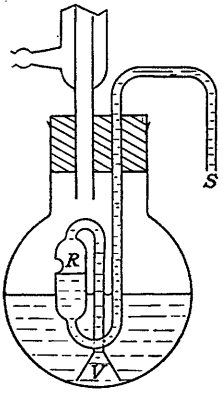
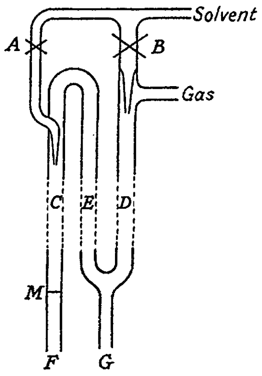


FIG. 3.



S, Siphon to solubility apparatus.
R, Constant-level reservoir.
V, Vapour pump.

FIG. 4.



EXPERIMENTAL (Parts I and II)

(i) *Gas Solubilities.*—An improved method of preparing solvents has been devised in place of that described (*J.*, 1948, 2033). This is based on the vapour-pump principle (Fig. 3) and ensures constant level, freedom from bumping, and more rapid removal of dissolved gases. Considerable use has also been made of the modification mentioned in the previous paper in which the gas measuring tube is separated from the absorption tube. In Fig. 4, *C*, *E*, and *D* are respectively a spiral with absorption tube, a gas burette, and a levelling tube (which also has a short spiral to ensure saturation). Readings are taken with liquid in *C* at the mark *M*. *F* leads to the graduated cylinder and *G* is used when filling with gas. This type of apparatus has the great advantage that gases with such diverse solubilities as nitrogen and carbon dioxide can be studied. The possibility of error due to the thin film of liquid in the absorption tube of the previous apparatus is also removed, and the absorption tube can more easily be filled with solvent at the end of a run so that the tube is always kept wet, an essential point if the apparatus is to be used for many determinations. The substitution of rubber tubing and clips for greased taps at *A* and *B* also contributes to the useful life of a tube.

The paraffin hydrocarbons were prepared from Grignard reagents. A sample of *n*-butane, stated to be over 99% pure, was kindly supplied by the Anglo-Iranian Oil Company, and gave the same results as gas prepared from Grignard reagents. Ethylene was prepared from ethanol and phosphoric acid, hydrogen from pure zinc and hydrochloric acid (giving the same results as a sample of electrolytic hydrogen). Nitrogen from a cylinder and from ammonium nitrite gave the same results within experimental error. Carbon dioxide was prepared from marble and hydrochloric acid, the usual precautions being taken with regard to freedom from air. Oxygen from a cylinder gave the same results as that from potassium permanganate (Table 2).

TABLE 2. *Solubilities of gases (in c.c. at N.T.P.) per* 1000 *g. of water at a total gas pressure of* 1 *atm.* (s_0).

Temp.	s_0	Temp.	s_0	Temp.	s_0	Temp.	s_0	Temp.	s_0
Hydrogen		Methane		Ethane		Propane		*n*-Butane	
12·3°	19·23	11·9°	39·90	12·3°	53·46	12·3°	50·70	10·9°	43·85
16·1	18·71	14·7	37·41	12·6	52·60	15·5	45·39	14·1	38·28
17·3	18·54	20·5	32·96	16·4	47·53	21·5	37·07	20·0	30·83
23·0	17·86	25·2	30·06	17·6	46·13	22·8	35·65	25·0	25·88
25·0	17·70	35·0	25·35	24·6	38·55	25·5	32·58	30·1	22·18
33·2	16·98	41·0	23·82	30·5	33·73	26·0	32·21	35·0	19·41
45·0	16·37	46·8	22·44	32·5	32·36	31·5	28·25	40·1	16·98
47·3	16·29	51·8	21·38	35·3	30·83	40·3	22·86	45·0	15·14
54·4	16·18	62·3	19·86	40·9	28·25	49·0	19·50	49·9	13·77
60·3	16·07	71·5	19·10	49·1	25·23	59·0	16·94	58·0	11·99
65·5	16·14	75·2	18·84	62·4	21·88	64·5	16·03	65·4	10·86
71·7	16·14			69·5	20·80	74·1	14·55	66·0	10·72
				71·4	20·46			70·8	10·16
				72·4	20·46			76·1	9·71

Ethylene		Nitrogen		Oxygen		Carbon dioxide			
13·8°	140·9	12·5°	18·37	12·7°	36·39	13·3°	1059	42·5°	502·0
17·1	128·8	15·5	17·22	13·5	35·56	14·9	1010	46·4	465·0
20·5	118·0	20·3	15·89	17·3	32·58	17·6	927	48·4	455·0
21·1	115·1	25·5	14·76	21·5	30·13	19·8	873	51·1	425·6
25·0	107·2	30·0	13·77	30·0	26·49	25·8	744·7	54·3	404·6
30·3	95·5	35·6	12·74	39·4	23·33	29·8	662·2	63·1	349·1
35·2	87·3	41·6	11·97	49·3	21·09	30·3	660·0	68·2	327·3
40·0	81·1	46·4	11·53	58·5	19·77	33·2	615·2	72·4	306·9
44·6	75·2	51·0	11·25	65·3	19·05	34·3	606·7	74·7	300·6
49·0	70·5	55·5	11·07	72·5	18·32	34·6	599·8		
54·9	65·5	63·8	10·72	74·9	18·20				
60·2	62·2	72·5	10·54						
65·0	59·2								
72·9	56·1								

In all cases determinations with water as solvent were made at about ten points in the range 12—75°. In the case of salt solutions the aim was to obtain data at temperatures of 12·6°, 30·0°, 49·4°, and 71·7°, corresponding to values of $1/T$ of 0·0035, 0·0033, 0·0031, and 0·0029. In many cases, however, runs at intermediate temperatures confirmed the general tendency of the salting-out results.

The solutions were prepared from "AnalaR" material wherever possible and were controlled during runs by volumetric methods and density determinations. Small corrections were made in several cases to allow for the fact that the concentrations varied from the desired value of 1 g.-equiv. per 1000 g. of water. In several cases it was shown that the Setschenow equation applied with sufficient accuracy for this correction. In the cases of the multivalent ions Ba^{2+} and La^{3+}, experiments showed that the concentration effect was approximately normal, and that no very different conclusions would be reached by working at unit ionic strength. In the case of hydrogen chloride (with *n*-butane), the concentration effect does not appear to be normal, and further work is proposed on this point. Salting-out values are shown in Table 3.

TABLE 3. *Salting-out constants*, $k = (\log s_0/s)/c$.

Gas :	*n*-Butane							Propane		
Salt :	NaCl	LiCl	KI	KCl	HCl	$\frac{1}{2}BaCl_2$	$\frac{1}{3}LaCl_3$	NaCl	LiCl	KI
$1/T$										
0·0035	0·243	0·198	0·109	0·200	0·080	0·250	0·182	0·216	0·175	0·121
0·0033	0·217	0·171	0·098	0·182	0·049	0·210	0·154	0·194	0·152	0·103
0·0031	0·194	0·155	0·080	0·164	0·031	0·180	0·154	0·178	0·138	0·085
0·0029	0·176	0·150	0·059	0·144	0·028	0·165	0·140	0·165	0·138	0·067

Gas :	Ethane			Methane			Hydrogen			
Salt :	NaCl	LiCl	KI	NaCl	LiCl	KI	NaCl	LiCl	KI	$\frac{1}{3}LaCl_3$
$1/T$										
0·0035	0·184	0·155	0·125	0·153	0·130	0·130	0·097	0·064	0·088	0·079
0·0033	0·162	0·124	0·101	0·127	0·097	0·097	0·092	0·065	0·081	0·078
0·0031	0·145	0·110	0·080	0·111	0·082	0·071	0·082	0·061	0·066	0·076
0·0029	0·135	0·107	0·065	0·102	0·077	0·054	0·066	0·054	0·043	0·075

Gas :	Nitrogen			Ethylene			
Salt :	NaCl	LiCl	KI	NaCl	LiCl	KI	$\frac{1}{3}LaCl_3$
$1/T$							
0·0035	0·154	0·125	0·134	0·140	0·104	0·070	0·112
0·0033	0·121	0·095	0·100	0·127	0·089	0·061	0·100
0·0031	0·106	0·084	0·086	0·114	0·082	0·050	0·105
0·0029	0·106	0·092	0·084	0·101	0·083	0·036	0·095

Liquid :	Benzene		Toluene		Ethylbenzene	
	c	*k*	*c*	*k*	*c*	*k*
At 25° in NaCl soln.	0·491	0·195	0·506	0·225	0·508	0·234
	0·755	0·186	0·767	0·213	0·985	0·250
	1·021	0·177	1·002	0·203		
	2·015	0·173	2·022	0·194		

(ii) *Liquid Solubilities.*—The aromatic hydrocarbons were redistilled samples from the purest obtainable material. After an excess of liquid had been shaken with about 1 l. of water at 25°±0·1° for about a week, a known volume of saturated solution was made slightly alkaline, and a stream of pure air passed through to drive off the hydrocarbon. After passage through a silica tube packed with cupric oxide and heated to redness, the water was removed by concentrated sulphuric acid and calcium chloride, and the carbon dioxide absorbed and weighed in soda-asbestos. The precautions usual in organic combustions were taken. The results are the mean of a large number of determinations which varied by about 0·5% for benzene and toluene. Because of the low solubility of ethylbenzene, the error was about 1% in water and about 2% in salt solutions. The solubilities of benzene, toluene, and ethylbenzene were found to be respectively 0·0220, 0·00582, and 0·00155 g.-mol. per 1000 g. of water. Previous measurements (Seidell, "Solubilities of Inorganic and Organic Substances," van Nostrand, N.Y.) give 0·0231 for benzene and 0·00527 for toluene (in the same units). Salting-out was determined over a range of salt concentration (Table 3).

Thanks are offered to the Hallett Trustees for the award of a scholarship to one of us (F. B.).

TECHNICAL COLLEGE, BRIGHTON. [*Received, April* 30*th*, 1952.]