

Thus it appears that the luminescence of liquid solutions, at any rate of this type, can be quantitatively accounted for by the existence of absorbing and re-emitting centres consisting of one molecule of the solute associated with a definite number of solvent molecules.

Further experiments are in progress using the same solute in different solvents with the object of discovering whether any simple relations exist between the size of the centre and the physical properties (*e.g.*, dielectric constant) of the solvent.

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*The Behaviour of Electrolytes in Mixed Solvents. Part II.—The Effect of Lithium Chloride on the Activities of Water and Alcohol in Mixed Solutions.*

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In the interaction between ions and solvent molecules, two types of physical effects have been recognised. The first, solvation, may be ascribed, in the absence of definite chemical compound formation between the ions and the solvent, to the attraction exerted by the electric field of the ions on the polarisable molecules of the solvent. Since the elements of a polarisable medium tend to move into those regions where the electric field is greatest, the molecules of water in aqueous salt solutions will tend to congregate round the ions and will be held by quite considerable forces. In the presence of a second substance, having a lower dielectric constant than water, this gives rise to the second or salting-out effect. Since water molecules are attracted by the ions more strongly than those of the other substance, the latter may be displaced or salted-out from the vicinity of the ions and their activity in the solution consequently increased.

This effect has been extensively studied in dilute aqueous solutions\* either by means of solubility measurements with sparingly soluble non-electrolytes

\* *E.g.*, Setschenow, 'Ann. Chim. Phys.,' vol. 25, p. 226 (1892); Rothmund, 'Z. phys. Chem.,' vol. 33, p. 401 (1900); Glasstone and Pound, 'J. Chem. Soc.,' vol. 127, p. 2660 (1925); Glasstone, Dimond and Jones, *ibid.*, vol. 129, p. 2935 (1926).

or by experiments on the distribution of the non-electrolyte between the aqueous solution and an immiscible solvent in which the electrolyte is not soluble.

The object of the present investigation was to determine the effect of a salt on the activities of both components of a mixed solvent, when the proportion of each component was varied from 0 to 100 per cent. It was hoped that such an investigation would give information as to the relative importance of solvation and salting-out, over the whole range of composition. The substances chosen were water and alcohol, with lithium chloride, one of the few salts which are soluble to a considerable extent in both of these liquids, as the electrolyte.

### *Experimental.*

*Method of Experiment.*—The partial vapour pressures of alcohol and water in the solutions were determined by the air-bubbling method. This method, which has been extensively used by Perman\* for the determination of the vapour pressures of many aqueous solutions and by Foote and Scholes† and Dobson‡ for the determination of the partial pressures of water and ethyl alcohol in mixtures of the two, is probably more accurate than the distillation method of Zawidski§ and is certainly more convenient for determining comparatively small changes produced by a third component.

The method depends on the fact that, if air is bubbled through a solution under conditions such that equilibrium is reached, the quantity of each volatile component present in the vapour is proportional to its partial vapour pressure in the solution. Thus if a volume  $v$  of dry air be passed through the solution of water and ethyl alcohol at constant pressure  $P$  and temperature  $T$ , and if  $w_1$  be the weight of water removed as vapour and  $w_2$  the weight of alcohol removed as vapour, the volume of the water in the saturated vapour is

$$v_1 = w_1 \cdot 22400 (273 + T) \cdot 760 / M_1 \cdot 273 \cdot P \quad \text{c.c.}$$

and the volume of alcohol

$$v_2 = w_2 \cdot 22400 (273 + T) \cdot 760 / M_2 \cdot 273 \cdot P \quad \text{c.c.}$$

where  $M_1$  and  $M_2$  are the molecular weights of water and alcohol. The total volume of the saturated air at temperature  $T$  and pressure  $P$  is therefore

\* 'Proc. Roy. Soc.,' A, vol. 72, p. 72 (1903); 'Trans. Faraday Soc.,' vol. 23, p. 95 (1927).

† 'J. Amer. Chem. Soc.,' vol. 33, p. 1317 (1911).

‡ 'J. Amer. Chem. Soc.,' vol. 127, p. 2871 (1925).

§ 'Z. Phys. Chem.,' vol. 35, p. 129 (1900).



$V + v_1 + v_2$  and if the ideal gas laws are obeyed, according to Dalton's law of partial pressures, the partial pressures of water and alcohol in the vapour are :

$$p_1 = v_1/(V + v_1 + v_2) \cdot P,$$

$$p_2 = v_2/(V + v_1 + v_2) \cdot P.$$

Errors may arise in this calculation for the following reasons—(1) The actual pressure in the bubblers where saturation takes place may be slightly different from the measured atmospheric pressure. In our apparatus the difference was never greater than 1–2 mm. of mercury and was neglected. (2) Water and alcohol dissolve appreciable quantities of air. At 25° the solubility of air is 16.7 c.c. (reduced to N.T.P.) in water\* and 110 c.c. in absolute alcohol† per litre. In solutions of lithium chloride the solubilities‡ are probably lower, for it has been shown by Geffken§ among others that the solubility of a gas decreases with increasing salt concentration. Since our solutions were made up in air and a preliminary air bubbling was always carried out, they were certainly saturated with air before the bubbling of the measured volume commenced. (3) The saturated vapours may deviate from the ideal gas laws. According to Dobson (*loc. cit.*) at 25° the deviation of saturated water vapour is about 0.03 per cent. and that of alcohol vapour 0.1 per cent. Perman† also considers that the agreement between the results of the air-bubbling method and distillation methods indicates that the ideal gas law holds with considerable accuracy. (4) The presence of dissolved air affects the molar fractions of the other constituents of the solutions and therefore their partial pressures. In alcohol, the solubility of air corresponds to a total concentration of about 0.005 m., which cannot affect the molar fractions of the other constituents to a significant extent. In other solutions its solubility is smaller.

*Preparation of Materials.*—Absolute alcohol was prepared as described by Butler and Robertson in the first paper of this series. Lithium chloride was prepared from a Kahlbaum preparation, the chlorine content of which corresponded fairly accurately to  $\text{LiCl} \cdot \text{H}_2\text{O}$ . It was dissolved in alcohol and filtered to remove any other alkali chlorides present. The greater part of the alcohol in the solution was evaporated at 50° under reduced pressure. The anhydrous lithium chloride which separated on cooling was quickly filtered at the pump and transferred to a flask. It was dried in the manner described

\* Seidell, "Solubilities of organic and inorganic substances," p. 19 (1919).

† 'Trans. Faraday Soc.' vol. 24, p. 330 (1928).

‡ Comey, "Dictionary of solubilities," p. 2 (1896).

§ 'Z. Phys. Chem.,' vol. 49, p. 257 (1904).

by Pearce and Hart,\* by heating to  $170^{\circ}$  in a stream of pure dry hydrogen chloride followed by gentle heating in a stream of dry hydrogen until the last traces of hydrochloric acid had been removed. The hydrogen chloride was generated by dropping A.R. sulphuric acid into A.R. hydrochloric acid and was dried by bubbling it through sulphuric acid and then passing it over phosphorus pentoxide in a long inclined tube. The lithium chloride prepared in this way was kept in a vacuum desiccator over phosphorus pentoxide. Its chlorine content as determined by analysis was 83.58 per cent. ( $\text{LiCl}$ ,  $\text{Cl} = 83.61$  per cent).

*Apparatus.*—The apparatus (fig. 1) consisted of three parts having as their functions (a) the measurement of the volume of air used, (b) the complete

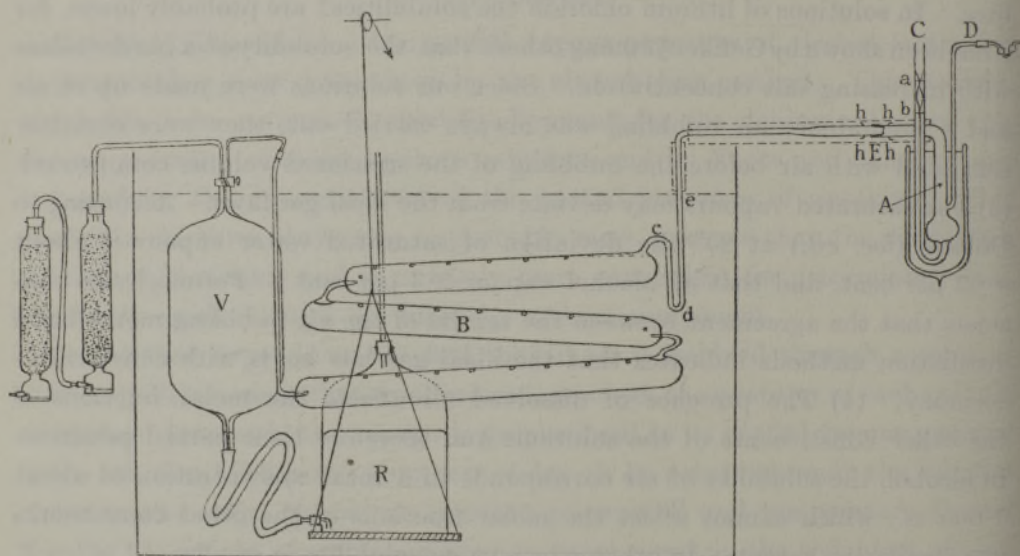


FIG. 1.—Arrangement of Apparatus.

saturation of the air with the vapour of the solution, (c) the determination of the weights of alcohol and water respectively, carried by the measured volume of air.

The measuring vessel *V* was a glass bulb fitted with a capillary two-way tap at the top, by means of which it could be put into connection either with the calcium chloride towers through which air entered or with the bubbler *B*. At its bottom end was a capillary through which connection was made by means of a length of heavy pressure tubing with the mercury reservoir *R*. The capacity of the bulb between the mark on the lower capillary and the upper

\* 'J. Amer. Chem. Soc.,' vol. 44, p. 2411 (1922).



tap was determined by weighing the volume of mercury contained between these points. At  $12^{\circ}$  it contained 10,496.6 gms. of mercury and, taking the density of mercury at this temperature to be 13.5658 gms. per cubic centimeter,\* the volume of the vessel is 773.3 c.c. This is the volume of air used in an experiment.

The bubbler B consisted of three inclined tubes fused together, each fitted with a jet to produce a stream of small bubbles of air. Owing to the small inclination of the tubes the bubbles travelled slowly and took from 10 to 15 seconds to pass through the bubbler. Complete saturation of the air was obtained, for the results were found to be reproducible and independent of the rate of passage of air within the range employed. The purpose of the bend *cde*, which did not contain liquid, was to give any spray, which might have been carried over mechanically, an opportunity of settling out. At the point *e* the air is saturated with the vapour of the solution at the temperature of the thermostat. Beyond *e*, the exit tube was kept at a higher temperature than the thermostat by electrically heated mats in order to prevent condensation on the sides of the tube. The capacity of the bubbler was about 200 c.c., so that the small amounts of material removed by evaporation caused no appreciable change in the composition of the solutions.

The total weight of alcohol and water present as vapour in the measured volume of air was 0.1 to 0.2 grams and the determination of their relative proportions presented great difficulty. It was not considered feasible to increase the volume of air so as to permit the collection of a larger quantity of liquid, as this would have greatly increased the time required to carry out each experiment and restricted the range of solutions the partial pressures of which we intended to determine. Among other methods, we tried the combustion of the vapour with red-hot copper oxide and at the surface of a platinum catalyst and the collection of the water vapour and carbon dioxide in suitable absorption tubes. In neither case could we get sufficiently reproducible results, apparently owing to the adsorption of some of the material on the oxidising surfaces. The vapours were next condensed by passing through a tube surrounded by carbon dioxide, and an attempt was made to determine the composition of a thin film of liquid by means of the dipping refractometer with an auxiliary prism. While this was fairly satisfactory in the case of solutions containing a small proportion of alcohol, in the more concentrated solutions the instrument failed to give consistent results, probably owing to the rapid evaporation of the alcohol.

\* Landolt-Börnstein Tabellen, 5th ed., p. 77.

In the method finally adopted the collecting tube was fitted with a viscosimeter, by means of which the composition of the small quantity of liquid collected could be determined with sufficient accuracy. From the exit tube of the bubbler the vapour passed into the collecting tube A, which was connected to the former by a tightly fitted ground glass joint without grease of any kind. The two parts of the apparatus were firmly wired together round the glass hooks *h*. The tube A was surrounded by carbon dioxide snow in a Dewar flask, and the condensed vapour collected at its foot. Preliminary experiments in which the air passed through weighed adsorption tubes after leaving A, showed that if the rate of passage of air was sufficiently slow, condensation was complete. In subsequent experiments a small sulphuric acid bubbler was attached to the exit of A to prevent the entry of moisture. The thermostat had plate-glass sides and was electrically controlled. The temperature remained constant to  $\pm 0.01^\circ$ .

*Procedure.*—Each solution was made up by weight from absolute alcohol, distilled water and lithium chloride. The bubbler was filled with the solution to be examined, as quickly as possible from a tap funnel, placed in position in the thermostat and attached to the air vessel, which was full of dry air. The heating mats were attached, and a stream of air passed for 10 minutes to ensure that the apparatus contained as much air and vapour in the same state as at the end of the experiment. The tube A was carefully wiped and weighed after standing in the balance case for half-an-hour. It was closed at C (fig. 1) by a piece of rubber tubing fitted with a glass rod, and a small calcium chloride tube was attached at D, so that when carbon dioxide snow was placed round the tube, dry air was sucked in. The preliminary air bubbling was stopped and the tube A attached to the bubbler. The Dewar vessel was slipped into position and filled with carbon dioxide snow. The calcium chloride tube at D was replaced by a small sulphuric acid pulsometer and the heating mats extended to the bend in tube A.

The vessel V was refilled with dry air, and with its tap in full connection with the calcium chloride towers the level of the mercury was adjusted to an etched line on the capillary at the bottom of V. The tap was now closed and the mercury reservoir raised somewhat. When the air pressure in V had become steady, the tap was opened cautiously and air began to pass through the bubbler. The rate of bubbling was adjusted until one bubble passed through the pulsometer every 2 seconds. The reason for this slow rate of bubbling was not so much to secure complete saturation of the air, for this is attained much more quickly, but to give the vapour ample time to condense in



A. At the completion of the bubbling mercury just reached the bore of the tap.

The tube A was then disconnected, removed from the Dewar flask, and, after being stoppered at E, allowed to stand for 5 minutes to come to room temperature. It was then closed at all openings and carefully wiped. After standing in the balance case for half-an-hour, the stoppers were removed with as little handling as possible, and the tube weighed.

The tube was then tightly stoppered at E and placed in the thermostat. The liquid was sucked up the fine capillary through a calcium chloride tube attached at C, until the meniscus was above *a* and allowed to flow back. The time taken for the meniscus to move from *a* to *b* was measured with a stop-watch at least 10 times. The viscosimeter had previously been calibrated with solutions containing known percentages of alcohol. The capillary ends in a very flat bulb to reduce to a minimum the variation of the time of flow with the volume of liquid. The time of flow was found to be independent of the quantity of liquid over the range of quantities actually collected.

This method of analysis is quick, the liquid is practically unexposed to the atmosphere and there is very little opportunity for the absorption of moisture and the accuracy, except in the vicinity of the maximum of the viscosity-composition curve, exceeds 0.1 per cent. Two experiments were carried out with each solution.

In solutions containing only 2 and 5 mols. per cent. of water it was desired to find the percentage change in the vapour pressure of water, caused by the presence of the salt, with considerable accuracy and a different method of analysis was employed. The total weight of liquid carried over by the volume *V* of air was determined as above. In order to find the percentage of water, another experiment was carried out, in which 9 to 10 litres of air\* were bubbled through the solution by means of an aspirator attached to the collecting tube through a calcium chloride tube (*l*) and by this means 1 to 2 grams of liquid was obtained. The composition of this liquid was determined by means of a Zeiss Industrial Interferometer, which had previously been calibrated with solutions containing known proportions of water. The accuracy with which the composition can be determined in this way is at least 0.01 per cent.

Similar determinations were made with solutions containing 6.4 mols. per cent. alcohol as, owing to the flatness of the viscosity curve in the corresponding region, the accuracy of the viscosity method with these solutions is somewhat low.

\* The time taken was about 24 hours.

*Experimental Data.*—The calibration of the viscosimeter is given in Table I, which gives the mean times of flow of at least two samples of each solution.

Table I.—Calibration of Viscosimeter. Times of Flow of Water-Alcohol Solutions.

Weight per cent. $C_2H_5OH$ .	Time of flow (secs.).	Weight per cent. $C_2H_5OH$ .	Time of flow (secs.).
100	129.8	86	176.8
99	134.8	85	179.4
98	139.5	84	182.1
97	142.5	82	187.8
96	146.1	80	193.4
95	149.4	78	198.8
94	153.0	74	208.4
93	156.2	72	213.3
92	159.4	70	217.6
91	162.8	68	221.5
90	165.9	66	225.6
89	168.7	64	229.5
88	171.4	62	232.6
87	174.0	60	235.4

Table IIa gives in full the experimental figures for 70 per cent. alcohol.  $N_A$  is the composition of the solvent, expressed as molecules per cent. ethyl alcohol;  $m$ , the molar concentration of lithium chloride (mols. in 1000 grams of solvent),  $w$  the total weight of water and alcohol collected in the passage of the measured volume of air,  $D$  the weight percentage of alcohol in the liquid collected,  $P$  the atmospheric pressure during the experiment and  $p_w$ ,  $p_a$  the calculated partial pressures of water and alcohol in millimetres of mercury.

Table IIa.

$N_A$ .	$m$ .	$w$ .	$D$ per cent. $C_2H_5OH$ .	$P$ .	$p_w$ .	$p_a$ .	Mean values.	
							$p_w$ .	$p_a$ .
70	0	gm. 0.1009	89.60	mm. 754	mm. 12.94	mm. 43.60	12.95	43.62
	0	0.1010	89.60	754	12.96	43.63		
	0.5	0.1006	90.73	742	11.50	44.04	11.47	44.06
	0.5	0.1007	90.80	744	11.43	44.08		
	1.0	0.0991	91.65	748	10.24	43.90	10.19	43.92
	1.0	0.0991	91.73	742	10.14	43.93		
	4.0	0.1317*	95.00	727	4.18	31.03	4.19	31.13
	4.0	0.1324*	95.00	741	4.20	31.23		

\* Volume of air 2V in these experiments.



Table IIb.—Mean Values of Partial Vapour Pressures of Water and Alcohol.

$N_a$	$m$	$p_w$	$p_a$	$N_a$	$m$	$p_w$	$p_a$
100	0	0	58.98	70	0	12.95	43.62
	0.5	0	57.21		0.5	11.47	44.06
	1.0	0	54.27		1.0	10.19	43.92
	4.0	0	26.72		4.0	4.19	31.13
98	0	1.141	57.24	50	0	17.24	36.65
	0.5	0.908	55.98		0.5	15.78	37.77
	1.0	0.788	53.78		1.0	14.53	38.13
	4.0	0.277	26.96		4.0	7.65	33.17
95	0	2.286	56.03	25	0	19.48	29.08
	0.5	1.816	54.73		0.5	18.84	30.19
	1.0	1.636	52.69		1.0	18.18	30.90
	4.0	0.580	27.44		4.0	12.70	32.08
90	0	5.381	52.42	6.4	0	21.94	12.29
	0.5	4.547	52.26		0.5	21.65	13.08
	1.0	3.852	50.72		1.0	21.07	13.87
	4.0	1.062	28.21		4.0	16.66	18.01
80	0	9.81	48.04	0	0	23.77	—
	0.5	8.49	47.91		0.5	23.45	—
	1.0	7.33	47.00		1.0	23.05	—
	4.0	2.534	29.65		4.0	19.21	—

The mean values of the partial vapour pressures for the whole series are given in Table IIb. The duplicate determinations rarely differed from each other by more than 5 parts in 1000. Table IIc gives a comparison of our results in water-alcohol solutions containing no lithium chloride (S. and B.), and those obtained from Dobson's data (D.) by graphical interpolation. The agreement is excellent in some cases, but generally our values are somewhat lower.

Table IIc.—Comparison of Observed Vapour Pressures with those obtained from Dobson's Data.

$N_A$	$p_a$		$p_w$	
	D.	S. and B.	D.	S. and B.
0	—	—	23.75	23.77
6.4	12.7	12.29	22.4	21.94
25	29.4	29.08	19.8	19.48
50	37.0	36.65	17.2	17.24
70	44.2	43.62	13.0	12.95
100	59.01	58.99	—	—

The effect of lithium chloride on the partial pressures of water and alcohol in the various solvents is shown in figs. 2 and 3. It can be seen that, while

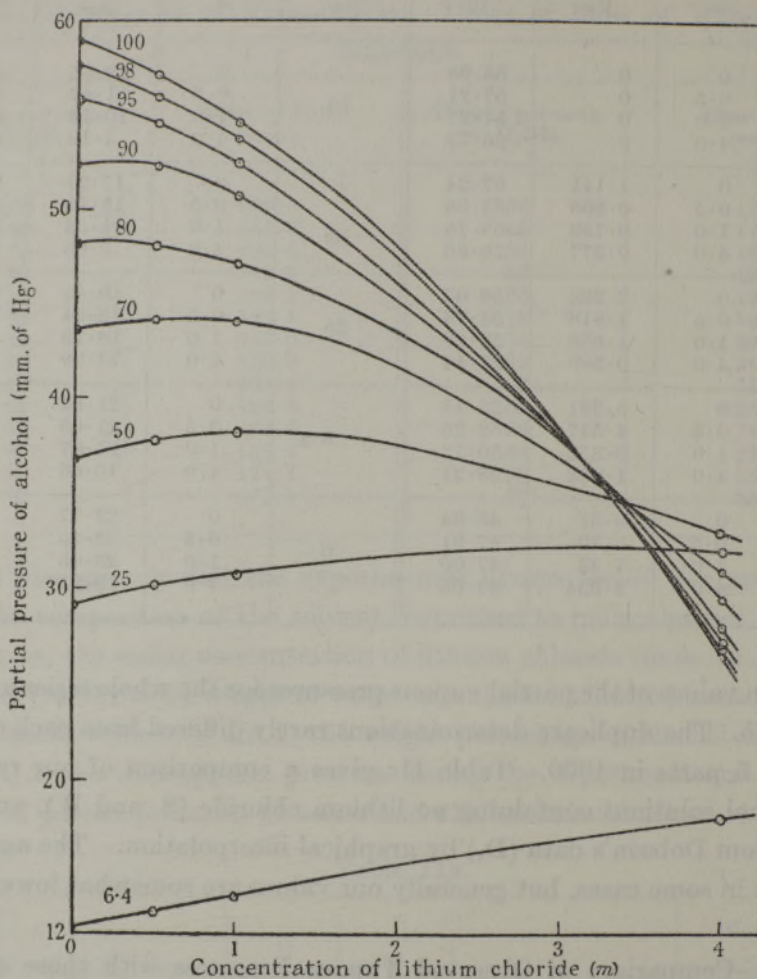


FIG. 2.—Partial Pressures of Alcohol in Water-Alcohol-Lithium Chloride Solutions. (The figures give the molar percentage of alcohol in the solvent.)

increasing concentration of lithium chloride causes a decrease in the partial pressure of water in all solutions, its effect on the alcohol varies with the composition of the solvent. In solutions containing a large proportion of alcohol, its partial pressure falls steadily as the lithium chloride concentration increases, and in the solution containing 6.4 mols. per cent. alcohol it rises steadily, while in intermediate solutions it first rises and then falls.



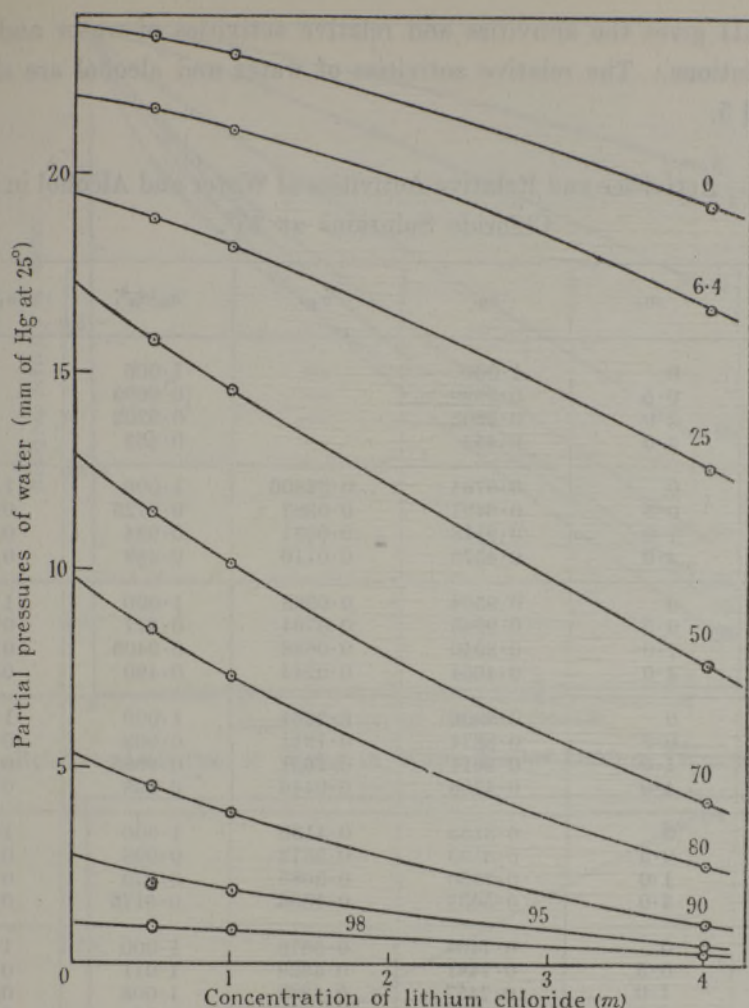


FIG. 3.—Partial Pressures of Water in Water-Alcohol-Lithium Chloride Solutions. (The figures give the molar percentage of alcohol in the solvent.)

*Activities and Relative Activities of Water and Alcohol.*—Assuming that the vapour obeys the ideal gas law, the activity of alcohol in a solution is given by

$$\alpha_a = p_a/p_a^0,$$

where  $p_a$  is the partial pressure of alcohol over the solution and  $p_a^0$  vapour pressure of pure alcohol at the same temperature. Similarly the activity of water is  $\alpha_w = p_w/p_w^0$ . In order to state concisely the effect of lithium chloride on activities in the solutions, we shall call  $\alpha_a/\alpha_a^0$ , where  $\alpha_a^0$  is the activity of alcohol in a given mixture of alcohol and water and  $\alpha_a$  its activity in the same solvent containing lithium chloride, the *relative activity* of alcohol in this solution. Similarly  $\alpha_w/\alpha_w^0$  is the relative activity of water in a solution.

Table III gives the activities and relative activities of water and alcohol in the solutions. The relative activities of water and alcohol are shown in figs. 4 and 5.

Table III.—Activities and Relative Activities of Water and Alcohol in Lithium Chloride Solutions at 25°.

$N_A$	$m$	$a_a$	$a_w$	$a_a/a_a^0$	$a_w/a_w^0$
100	0	1.000	—	1.000	—
	0.5	0.9699	—	0.9699	—
	1.0	0.9202	—	0.9202	—
	4.0	0.453	—	0.453	—
98	0	0.9764	0.04806	1.000	1.000
	0.5	0.9497	0.0383	0.9725	0.795
	1.0	0.9118	0.0331	0.934	0.690
	4.0	0.4573	0.0116	0.468	0.2425
95	0	0.9504	0.0962	1.000	1.000
	0.5	0.9286	0.0764	0.977	0.794
	1.0	0.8940	0.0688	0.9405	0.7155
	4.0	0.4654	0.0244	0.490	0.254
90	0	0.8900	0.2264	1.000	1.000
	0.5	0.8874	0.1914	0.998	0.845
	1.0	0.8611	0.1621	0.9685	0.716
	4.0	0.4786	0.0446	0.538	0.197
80	0	0.8155	0.4130	1.000	1.000
	0.5	0.8133	0.3573	0.998	0.865
	1.0	0.7980	0.3085	0.979	0.747
	4.0	0.5033	0.1066	0.6175	0.258
70	0	0.7404	0.5575	1.000	1.000
	0.5	0.7481	0.4829	1.011	0.866
	1.0	0.7457	0.4282	1.008	0.768
	4.0	0.5286	0.1763	0.714	0.315
50	0	0.6223	0.7253	1.000	1.000
	0.5	0.6410	0.6639	1.030	0.915
	1.0	0.6473	0.6114	1.040	0.843
	4.0	0.5631	0.3219	0.902	0.444
25	0	0.4938	0.8195	1.000	1.000
	0.5	0.5126	0.7928	1.038	0.967
	1.0	0.5247	0.7649	1.063	0.933
	4.0	0.5446	0.5344	1.132	0.652
6.4	0	0.2083	0.9230	1.000	1.000
	0.5	0.2217	0.9110	1.064	0.987
	1.0	0.2352	0.8864	1.129	0.960
	4.0	0.3054	0.7010	1.465	0.760
0	0	—	1.000	—	1.000
	0.5	—	0.9865	—	0.9865
	1.0	—	0.9696	—	0.9695
	4.0	—	0.8081	—	0.808



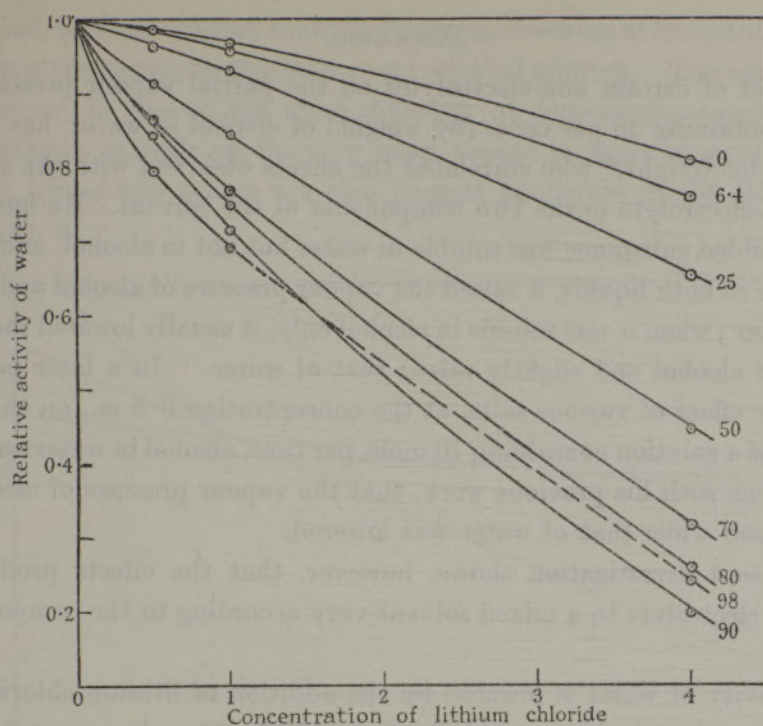


FIG. 4.—Relative Activities of Water in Water-Alcohol-Lithium Chloride Solutions.

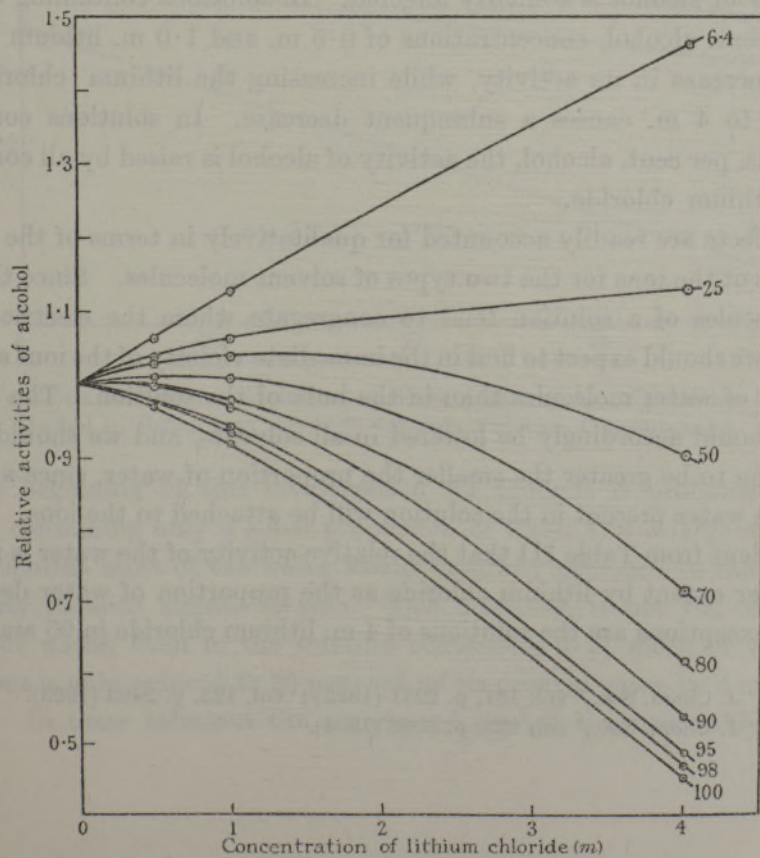


FIG. 5.—Relative Activities of Alcohol in Water-Alcohol-Lithium Chloride Solutions.

*Discussion.*

The effect of certain non-electrolytes on the partial vapour pressures of a solution containing 38 per cent. (by weight) of alcohol in water, has been investigated by Wright,\* who correlated the effects observed with the solubility of the non-electrolyte in the two components of the solvent. He found that, when the added substance was soluble in water but not in alcohol, and when it was soluble in both liquids, it raised the vapour pressure of alcohol and lowered that of water; when it was soluble in alcohol only, it usually lowered the vapour pressure of alcohol and slightly raised that of water. In a later paper† he studied the effect of various salts, at the concentration 0.5 m., on the partial pressures of a solution containing 10 mols. per cent. alcohol in water and found, in agreement with his previous work, that the vapour pressure of alcohol was always raised while that of water was lowered.

The present investigation shows, however, that the effects produced by adding an electrolyte to a mixed solvent vary according to the composition of the latter.

The activity of water is lowered by the addition of lithium chloride in all solutions, and in solutions containing from 100 to 80 mols. per cent. alcohol the activity of alcohol is similarly affected. In solutions containing 50 to 70 mols. per cent. alcohol, concentrations of 0.5 m. and 1.0 m. lithium chloride cause an increase in its activity, while increasing the lithium chloride concentration to 4 m. causes a subsequent decrease. In solutions containing 0 to 25 mols. per cent. alcohol, the activity of alcohol is raised by all concentrations of lithium chloride.

These effects are readily accounted for qualitatively in terms of the relative attractions of the ions for the two types of solvent molecules. Since the more polar molecules of a solution tend to congregate where the electric field is strongest, we should expect to find in the immediate vicinity of the ions a greater proportion of water molecules than in the bulk of the solution. The activity of water should accordingly be lowered in all solvents, and we should expect the lowering to be greater the smaller the proportion of water, since a greater part of the water present in the solution will be attached to the ions.

It is evident from Table III that the relative activity of the water is reduced to a greater extent by lithium chloride as the proportion of water decreases. The only exceptions are the solutions of 4 m. lithium chloride in 95 and 98 per

\* 'J. Chem. Soc.,' vol. 121, p. 2251 (1922); vol. 123, p. 2493 (1923).

† 'J. Chem. Soc.,' vol. 125, p. 2068 (1924).



cent. alcohol, in which we find that the fractional lowering of the water pressure is less than in the corresponding 90 per cent. alcohol solution. This abnormality may, however, be due to the great difficulty of determining accurately the effect of lithium chloride on the very small vapour pressure of water in these solutions. These two points are also present anomalies in the relationship shown in fig. 6.

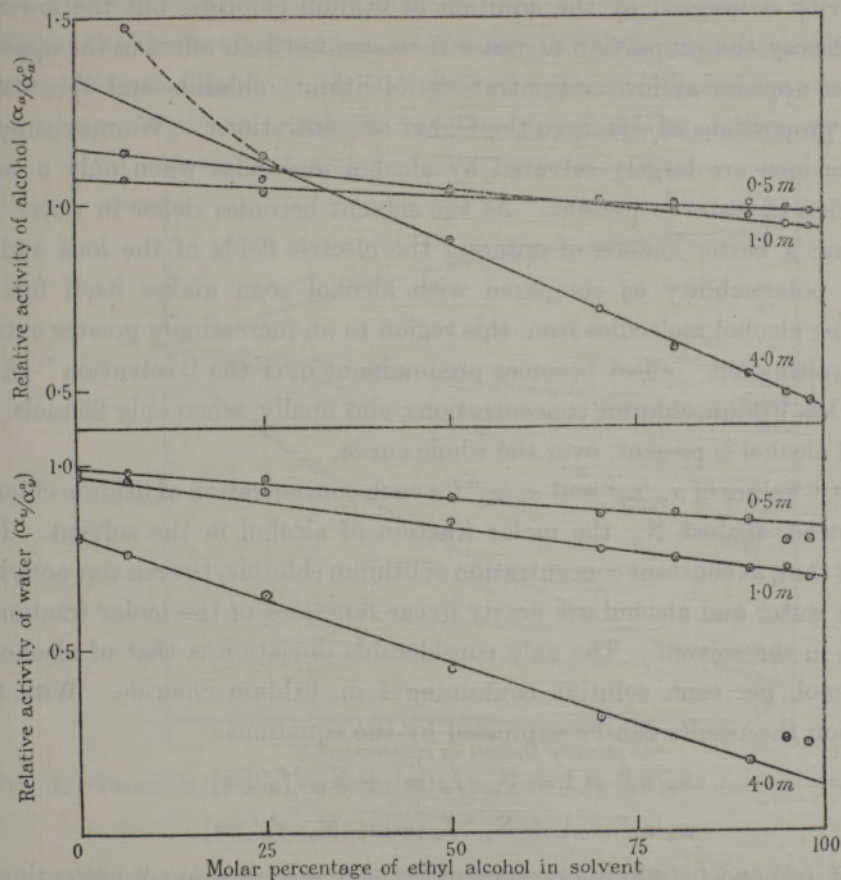


FIG. 6.—Variation of Relative Activities of Alcohol and Water with Molar Fraction of Alcohol in Solvent at constant Lithium Chloride Concentration.

At the beginning of this investigation we thought it probable that, in solutions containing only a small proportion of water and a large amount of lithium chloride most of the water would be firmly attached to the ions and its activity reduced almost to zero. This, however, is not the case. The activity of water, even in the solution containing 0.17 mols. of water per 1000 grams is only reduced to 25 per cent. of its original value by 4 m. lithium chloride. In these solutions the activity of alcohol is considerably lowered

by lithium chloride and the ions are probably largely solvated by alcohol molecules. It appears, therefore, that when only a small proportion of water molecules is present, the large excess of alcohol molecules partially compensates for the superior attraction of the ions for water molecules and prevents them being completely taken up by the ions. The behaviour of alcohol (fig. 5 and Table IV) is also in accordance with this conception. In alcohol-rich solutions its activity is lowered by the addition of lithium chloride, but the lowering diminishes as the proportion of water increases until an effect in the opposite direction appears at low concentrations of lithium chloride and spreads, in greater proportions of water, to the higher concentrations. We may suppose that the ions are largely solvated by alcohol molecules when only a small proportion of water is present. As the solvent becomes richer in water, the latter has a better chance of entering the electric fields of the ions and its greater polarisability as compared with alcohol soon makes itself felt by excluding alcohol molecules from this region to an increasingly greater extent. This "salting out" effect becomes predominant over the "solvation" effect, first at low lithium chloride concentrations, and finally, when only 25 mols. per cent. of alcohol is present, over the whole curve.

In fig. 6 values of  $\alpha_w/\alpha_w^0$  and  $\alpha_a/\alpha_a^0$  for each concentration of lithium chloride are plotted against  $N_a$ , the molar fraction of alcohol in the solvent. It is evident that, at constant concentration of lithium chloride, the relative activities of both water and alcohol are nearly linear functions of the molar fraction of alcohol in the solvent. The only considerable deviation is that of alcohol in a 6.4 mol. per cent. solution containing 4 m. lithium chloride. With this exception the results can be expressed by the equations:

$$\alpha_a/\alpha_a^0 = 1 + N_a \cdot f_a(m) + N_w \cdot f_a'(m) \quad (1)$$

$$\alpha_w/\alpha_w^0 = 1 + N_w \cdot f_w(m) + N_a \cdot f_w'(m) \quad (2)$$

where  $f_a(m)$  and  $f_w(m)$  are functions of the salt concentration, representing its effect on pure water and pure alcohol respectively, and  $f_a'(m)$  and  $f_w'(m)$  are also functions of the salt concentration, which represent the changes in the relative activities of alcohol and water produced by the addition of water and alcohol, respectively.

The values of these functions for the three concentrations of lithium chloride employed are given in Table V. Thus, in the presence of 0.1 lithium chloride the equations become:

$$\alpha_a/\alpha_a^0 = 1 - 0.0007 N_a + 0.0015 N_w$$

$$\alpha_w/\alpha_w^0 = 1 - 0.0003 N_w - 0.0031 N_a.$$



Table V.

	0.5 <i>m</i> .	1.0 <i>m</i> .	4.0 <i>m</i> .
$f_a(m)$ .....	-0.0003	-0.0007	-0.0055
$f'_a(m)$ .....	+0.00075	+0.0015	+0.0034
$f_w(m)$ .....	-0.0001	-0.0003	-0.0019
$f'_w(m)$ .....	-0.0017	-0.0031	-0.0088

Within the limits of agreement of the data with the above equations, the effects of lithium chloride on the activities of water and alcohol are completely summed up in fig. 7, in which the functions  $f_a(m)$ ,  $f'_a(m)$ ,  $f_w(m)$  and  $f'_w(m)$

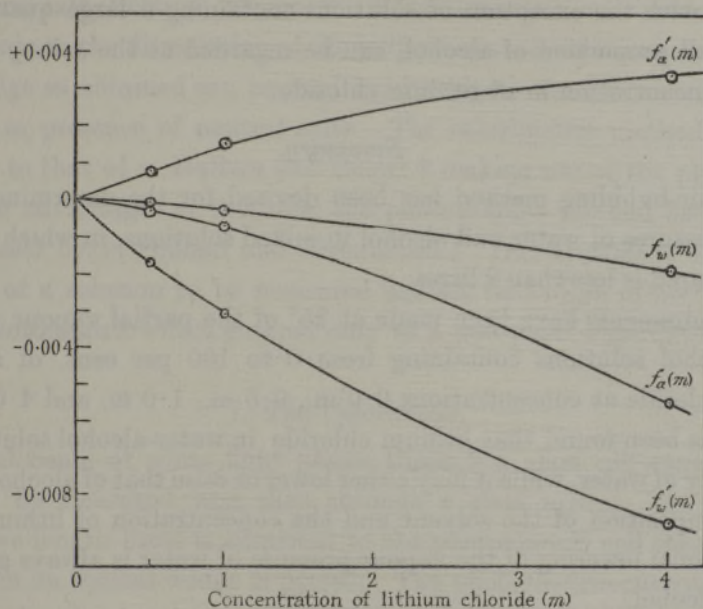


FIG. 7.—Variation of the Functions  $f_a(m)$ ,  $f'_a(m)$ ,  $f_w(m)$  and  $f'_w(m)$  with Salt Concentration.

are plotted against the salt concentrations. Thus, the curves of  $f_a(m)$  and  $f'_a(m)$  represent the effect of the salt on the relative activities of alcohol in 100 per cent. alcohol and 100 per cent. water respectively, and the curve of the relative activity of alcohol in a mixed solvent lies between these curves, its position being determined by the molar fractions of alcohol and water in the solvent according to the simple mixture rule.  $f_w(m)$  and  $f'_w(m)$  similarly represent the effect of the salt on the relative activities of water in 100 per cent. water and 100 per cent. alcohol, and the same rule applies to mixed solvents.

According to (1) the relative activity of alcohol, which is usually taken as

a measure of the salting-out effect, is a function of the molar fractions of alcohol and water in the solution. Measurements of the salting-out effect have hitherto been made exclusively in dilute aqueous solutions, in which the molar fraction of water remains nearly 1, and the part played by the molar fractions of the non-electrolyte has escaped notice. We have seen that the behaviour of alcohol can be represented by two terms, the first of which,  $N_a \cdot f_a(m)$ , is due to the solvation of the ions by alcohol, and the second,  $N_w \cdot f'_a(m)$ , to the salting-out or displacement of alcohol molecules round the ions by water molecules. This second term can be taken as a measure of the true salting-out effect, and  $f'_a(m)$ , which has nearly the same value in all mixtures, with the exception of solutions containing a large quantity of salt and a small proportion of alcohol, can be regarded as the *salting-out constant* for the concentration  $m$  of lithium chloride.

### *Summary.*

1. An air-bubbling method has been devised for the determination of the partial pressures of water and alcohol in mixed solutions, in which the volume of air required is less than 2 litres.
2. Measurements have been made at 25° of the partial vapour pressures of water-alcohol solutions containing from 0 to 100 per cent. of alcohol and lithium chloride at concentrations 0.0 m., 0.5 m., 1.0 m. and 4.0 m.
3. It has been found that lithium chloride in water-alcohol solutions lowers the activity of water, while it may either lower or raise that of alcohol, according to the composition of the solvent and the concentration of lithium chloride. The fractional lowering of the vapour pressure of water is always greater than that of alcohol.
4. An approximately linear relationship has been established between the relative activities of both water and alcohol and the molar fraction of alcohol in the solvent, at constant lithium chloride concentration.
5. It is possible to distinguish approximately the effects of the solvation of ions by alcohol molecules and the salting-out of alcohol by the interaction of the ions and water.

We wish to express our indebtedness to Imperial Chemical Industries, Ltd., for a grant which enabled us to purchase the dipping refractometer and to the Moray Research Fund of the University of Edinburgh for a grant for the purchase of the interferometer. One of us (J.A.V.B.) has also to acknowledge a Carnegie Teaching Fellowship, held during part of the period occupied by the research.

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