XLI.—*The Equilibrium between Ethyl Alcohol and the Alkali and Alkaline-earth Salts. Part I.*

By DAVID GLYNWYN ROBERT BONNELL and WILLIAM JACOB JONES.

THE first investigator in this field was Graham (*Phil. Mag.*, 1828, **4**, 265, 331), who prepared the ethyl alcoholate of calcium chloride. His work was repeated by Einbrodt (*Annalen*, 1848, **65**, 115), by Chodnew (*Bull. Acad. St. Petersburg*, 1865, **8**, 150), by Heindl (*Monatsh.*, 1881, **2**, 200), and by Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1010). The calcium bromide tri-alcoholate (Roques, *J. Pharm.*, 1895, **1**, 301), the hexa-alcoholates of magnesium chloride (Simon, *J. pr. Chem.*, 1879, **20**, 371), bromide and iodide (Menschutkin, *Bull. St. Petersburg Polytec. Inst.*, 1906, **3**, 12), the tetra-alcoholates of lithium chloride (Simon, *loc. cit.*) and bromide (Turner and Bissett, J., 1914, **105**, 1783) have all been described. Solubility determinations over ranges of temperatures have been carried out as follows : lithium chloride (Turner and Bissett, J., 1913, **103**, 1904), sodium and potassium iodides (Tyrer, J., 1910, **97**, 621) and calcium chloride (Menschutkin, *loc. cit.*).

The purpose of the present series of investigations was to determine the following : (1) The solubility over a wide range of temperature. (2) The composition of the various solid phases. (3) The transition temperatures. In the present paper are described the conditions of equilibrium between ethyl alcohol and the following salts : lithium bromide, sodium bromide, calcium bromide, barium bromide, and barium iodide.

EXPERIMENTAL.

For obvious reasons great attention was directed to the purity of the substances used, and especially to their freedom from traces of water, since, owing to the far greater affinity of salts for this than for alcohol, the composition of the solid phase is particularly influenced by its presence.

The alcohol was purified by Lapworth's method (J., 1910, **97**, 24).

The densities, without correction of the weighings to vacuum, of the two specimens that were used in the present work were $d_{4^\circ}^{25^\circ}$ 0·78494 and 0·78496. Great care was exercised both during the purification and preservation and in subsequent work to exclude atmospheric moisture.

The salts were purified by recrystallisation from water and then dehydrated by Turner and Bissett's method (P., 1913, **29**, 233) (Found by the gravimetric silver halide method: LiBr 99·81, NaBr 99·93, $CaBr_2$ 99·90, $BaBr_2$ 99·89, BaI_2 99·87%).

The graduated vessels, weights and thermometers had been carefully standardised. In the solubility determinations above 20° ordinary thermostats, which kept constant within 0·02°, were used. At 15° and at 10°, the temperature was maintained constant within 0·04° by a regulated inflow of cold water and by continuous and vigorous stirring. For 0°, a bath of washed, finely powdered ice was used. In each determination the anhydrous salt and alcohol were put together in a clean, dry, glass-stoppered flask, which thereafter was kept in the thermostat, and as far as possible in the dark. A tightly fitting, thick paper cap was tied over the stopper. The mixtures were shaken by hand at intervals over a long period, and a portion of the solution was then withdrawn for analysis after the solid had settled completely. Thereafter the mixtures were again shaken and the procedure described was repeated until two consecutive analyses agreed within the experimental error. By operating in this manner saturation was ensured and incursion of atmospheric moisture was better precluded than if an internal stirring arrangement had been used. In some of the experiments, the equilibrium point was approached by first preparing a saturated solution at a temperature at which the solubility was greater than at the temperature under investigation, then placing it in the thermostat at the latter temperature, and, after keeping it therein for some time with frequent shaking, analysing the liquid phase. In all cases, the solubility so found was identical with that found by the procedure previously described. There can therefore be no doubt that in our experiments the systems were truly in equilibrium when the solubility determinations were made.

For the determination of the composition of the solid phase a small quantity was scooped out, quickly dried between filter-paper, and analysed. For such solid phases as were stable only at temperatures much above the ordinary, the procedure was modified as follows. Some of the salt was suspended by means of a basket of metal gauze in a saturated solution in a stoppered flask, which was immersed in the thermostat. When equilibrium had been attained, the basket was drawn up into the vapour space above the solution and was there allowed to drain. When draining was complete, the solid in the basket was withdrawn and analysed.

The transition temperatures obtained by the solubility determinations were confirmed by the dilatometric method.

Results.

	Solubility in gram of salt per gram of alcohol, of				
Temp.	sodium bromide.	barium bromide.	barium iodide.	calcium bromide.	lithium bromide.
0°	0·02445	0·05880	0·7775	0·4670	0·3261
10	0·02379	0·05067	0·7735	0·4801	0·3602
15	0·02343	0·04590	—	0·5051	—*
20	0·02322	0·04130	0·7700	0·5350	—*
25	0·02314	—	—	0·5395	0·7210
30	0·02292	0·03322	0·7660	0·5552	0·7251
40	0·02276	0·02433	0·7620	0·6011	0·7303
50	0·02259	0·01837	0·7585	0·6564	0·7752
60	0·02312	0·01479	0·7550	0·7602	0·8284
70	0·02345	0·01253	0·7510	0·9381	0·8913
75	—	—	—	1·0220	0·9412
80	—	—	—	1·0310	0·9910
85	—	—	—	1·0610	—

* Retroflex region (see later table).

All the above values were determined directly.

Throughout in the cases of sodium bromide, barium bromide, and barium iodide the solid phases were respectively NaBr, $BaBr_2$, and BaI_2.

In the case of calcium bromide, below 17·0° the solid phase is $CaBr_2,4C_2H_5{\cdot}OH$, between 17·0° and 73·9° $CaBr_2,3C_2H_5{\cdot}OH$, and above 73·9° $CaBr_2,C_2H_5{\cdot}OH$ ($CaBr_2,4C_2H_5{\cdot}OH$: ethyl alcohol found, 48·6; calc., 48·0%. $CaBr_2,3C_2H_5{\cdot}OH$: ethyl alcohol found, 42·4; calc., 40·9%. $CaBr_2,C_2H_5{\cdot}OH$: ethyl alcohol found, 20·5; calc., 18·7%). The form of the solubility curves exhibits a close parallelism to those of calcium chloride in water and in methyl alcohol.

When lithium bromide and alcohol were brought together, great heat was developed and a solution of a slightly brown tint was obtained. At 25° and 30° the solution was very viscous, and consequently took a long time to settle sufficiently to allow of measurements being taken. In the temperature range 13·2° to 23·8° there is a retroflex region, the solid phase being $LiBr,4C_2H_5{\cdot}OH$ (ethyl alcohol found, 69·2; calc., 67·9%). The congruent melting point of the tetra-alcoholate was 23·8°, and the solid phase in contact with the saturated solution at the higher temperatures has the composition LiBr. The eutectic point for the anhydrous salt and the alcoholate is 13·2°. The alcoholate crystallises in flat plates which are highly deliquescent in the atmosphere, and, owing to the hygroscopicity of the salt, it was impracticable to determine its affinity for alcohol. Greater detail regarding the eutectic region is given in the following table :

Retroflex Region of the Solubility of Lithium Bromide in Ethyl Alcohol.

	Solubility in gram of lithium bromide per gram of ethyl alcohol with solid phases.		
Temp.	LiBr.	$LiBr,4C_2H_5\cdot OH$.	$LiBr,4C_2H_5\cdot OH$.
13·2°	0·700	0·700	0·700
15·0	0·702	0·687*	0·381
16·0	0·704	0·675*	0·390
20·0	0·708	0·606*	0·420
23·0	0·712	0·530*	0·460
23·8	0·713	0·472	0·472

The asterisked values were obtained by thermal analysis, the remaining values being obtained either by direct determinations of solubility or from a graph.

When the barium iodide was brought into contact with the alcohol great heat was developed, and in a short time the solution acquired an orange tint due to the presence of traces of free iodine. A fresh solution was made in a black flask, but even in this the colour again developed and it was found impossible to obtain colourless solutions.

UNIVERSITY COLLEGE, CARDIFF. [*Received, November 28th, 1925.*]