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In the study of the physical properties of non-aqueous solvates considerable work has been done on the systems magnesium bromide-diethyl ether (1-3) and zinc bromide-diethyl ether (4). It is planned to extend these studies to the bromides of other elements in the same periodic group as well as to related compounds.

One of the authors (R) during a study of the three component system, water-diethyl ether-magnesium bromide, tried to determine the amount of water in a sample of ether solution by use of the drying agent Dehydrite, which is anhydrous magnesium perchlorate. It was noted that the magnesium perchlorate appeared to retain considerable ether even when heated. Since other magnesium compounds form etherates, especially the halides, it was decided to investigate this phenomenon further by means of solubility measurements of anhydrous magnesium perchlorate in diethyl ether. Willard and Smith (5) had previously determined the solubility of this compound in numerous solvents including diethyl ether at 25°. The present work was done at 0°, 15° and 25°.

Experimental

Commercial Dehydrite, prepared by G. Frederick Smith Chemical Company, was used as a starting material. Analysis of a freshly opened bottle showed about 94 to 96 per cent magnesium perchlorate by the standard pyrophosphate method. The samples used in this investigation were freshly dehydrated at 250° in flasks connected to a Cenco Hy-vac oil pump. They analyzed above 99.9 per cent pure with no trace of chlorides. The anhydrous ether was prepared by drying reagent ether over sodium, distilling and using the middle fraction. It was always kept over fresh sodium.

The apparatus for conducting the experiment was designed to hold relatively large volumes of ether (since low solubility was indicated), exclude moisture by means of mercury seals and drying tubes, permit good stirring and to allow for easy removal of the solution without contamination. Portions of the saturated solutions were removed, weighed and the magnesium perchlorate determined by analyzing for magnesium by the standard pyrophosphate method.

The first results obtained were much higher than those of Willard and Smith (5) who reported the solubility as 0.2908 grams of anhydrous magnesium perchlorate per 100 grams of diethyl ether at 25°. The solubilities ranged from 1.38 to 0.44 grams of perchlorate per 100 grams of ether, at 25°, with no apparent consistency. It seemed impossible to obtain check results for two solutions and over fifty determinations appeared to result in a lot of useless data. However, by using the same solid for a series of determinations, adding fresh ether and bringing to equilibrium for successive determinations, it was noticed that decreasing values were obtained. Not only did some of them agree fairly well with the work of Willard and Smith, but even lower values were obtained. One typical series of analyses at 25° is given in Table I to

Table I — Solubility of Magnesium Perchlorate in Diethyl Ether, Showing the Trend of Values using Same Solid For a Series of Determinations at 25°C.

Sample	gm./100 gm. Ether
# 54	0.3354
# 55	0.2010
# 56	0.1334
# 57	0.1181

show the trend. These changing values seemed to indicate that the solubility was affected by some impurity.

Since Rowley (2) had found that small amounts of water in ether increased the solubility of magnesium bromide, it was decided to find what the effect of moisture would be on the solubility of magnesium perchlorate in ether. Solutions of water in ether were made up of approximately the listed concentrations and the solubility of magnesium perchlorate in each determined by the usual method. The results are shown in Table II, and prove definitely that small quantities of water increase the solubility tremendously.

Table II — Effect of Water on the Solubility of Magnesium Perchlorate in Ether at 15° and 25°C.

Mol H_2O/1 mol Ether	gm./100 gm. Ether	
	25°	15°
0.016	0.519	0.381
0.115	1.401	

Even though great care had been exercised in handling to prevent introduction of moisture, the momentary exposure of the magnesium perchlorate to the atmosphere, when it was being placed in the flask, had been sufficient to invalidate the results. In view of the fact that water played such an important role, in the solubility, a different technique had to be adopted whereby the materials did not come in contact with the air.

The apparatus finally used consisted of two pyrex flasks of about 50 and 250 ml. capacity which were sealed together near the top by a piece of tubing, 20 cm. in length, containing a stopcock. The neck of each flask had been drawn down so that it could be sealed off when necessary.

About 150 ml. of dry ether was placed in the larger flask and fresh sodium wire run into the flask. When the sodium had ceased reacting, the stopcock was closed, a gentle suction was applied and the flask sealed off. The solid magnesium perchlorate was placed in the bottom of the smaller flask which was surrounded by an electric furnace at 250°. The outlet of this smaller flask was connected to an oil vacuum pump and after several hours the outlet tube was sealed off and the sample allowed to cool in vacuum. The tube containing the sample was then cooled to –78° with "dry-ice" and the stopcock in the connecting tube opened. With the larger flask at room temperature, the ether distilled over readily onto the sample. When approximately 50 ml. had distilled, the connecting tube to the ether flask was sealed off. This method enables one to prepare both the anhydrous ether and the anhydrous magnesium perchlorate and to bring them together without exposure to the air.

The tubes when prepared as above, were placed in a constant temperature bath and turned end over end for at least 24 hours. After allowing the solid to settle, the end of the tube was broken off and the clear solution quickly filtered through glass wool in an enclosed tube into weighing bottles and then analyzed. The results of typical analyses at 25°, 15° and 0° are given in Table III. Considering the low solubility, the limitation of small samples of solution, the difficulty of getting the solution out of the sealed tubes, and finally the pyrophosphate ignitions for such small amounts of magnesium, the agreement is good.

Table III — Solubility of Anhydrous Magnesium Perchlorate in Anhydrous Diethyl Ether. Grams/100 gm. Ether

Sample	25°	15°	0°
# 74	.0591		
# 77	.0674		
# 78	.0663		
# 80		.0588	
# 82			.0438
# 83			.0436
Mean:	.0643	.0588	.0437

Discussion

The most interesting fact discovered was the low solubility of magnesium perchlorate in diethyl ether as compared to that previously reported. Willard and Smith (5) reported the solubility as 0.2908 grams per 100 grams of ether, whereas the present investigation shows a solubility of 0.0643 grams per 100 grams of ether. In view of the fact that both the anhydrous ether and the anhydrous magnesium perchlorate are powerful dehydrating agents, it is not to be wondered that previous results were high. In the technique outlined by Willard and Smith, a transfer was made of the crystals formed from a digested solution, to other tubes in which the solubility was determined. It is possible that the contamination with even slight traces of water from the atmosphere would give high results, as shown in this study.

Such low solubility of the magnesium perchlorate makes it unsuited for study of any possible etherate formation by this method. In many cases solid solvates can be detected by changes in the slope of the solubility curves. In the present case, however, the solubilities are so small that experimental errors make it difficult to determine the true slope of the curve.

On the other hand, the large evolution of heat when ether is brought into contact with anhydrous magnesium perchlorate leads one to suspect solvate formation. The solid phases in equilibrium with the saturated ether solutions at 0° and 25° were therefore analyzed and the results given in Table IV. Due to the fact that

Table IV — Analyses of Solids in Equilibrium with Ether Solutions at Various Temperatures

Sample	Temp. °C.	$Mg(ClO_4)_2$ Percentage	Mole Ratio Ether/$Mg(ClO_4)_2$	Theoretical Requirement
# 74	25°	63.7	1.75	60.2 per cent for $Mg(ClO_4)_2 . 2Et_2O$
# 78	25°	64.7	1.65	
# 80	25°	62.8	1.79	
# 81	25°	58.4	2.15	
# 1	0°	50.2	2.99	50.2 per cent for $Mg(ClO_4)_2 . 3Et_2O$
# 2	0°	45.4	3.64	

the solids are wet with solution and that the higher etherates have relatively high vapor pressures, exact agreement is not to be expected. However, other tests confirm the existence of three etherates of magnesium perchlorate. The trietherate is in equilibrium with the solution at 0° and possibly at 25°. The dietherate is fairly stable but loses one ether molecule fairly readily at 25° and much more slowly at 0°. The monoetherate of magnesium perchlorate has a relatively low vapor pressure and is fairly stable up to 100° or above.

Summary

1. The solubility of anhydrous magnesium perchlorate in diethyl ether has been determined at 0°, 15° and 25°C. The values found are considerably lower than those reported in the literature.
2. The presence of moisture has a pronounced influence on the solubility of this compound in ether.
3. The existence of three solid etherates was established: the mono-, di-, and trietherates of magnesium perchlorate.

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