[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NORTHWESTERN UNIVERSITY]

# Physical Studies of Non-Aqueous Solvates. I. The Solubility of Magnesium Bromide in Ethyl Ether[1]

BY H. H. ROWLEY

The figures on the solubility of magnesium bromide in ethyl ether as given in the "International Critical Tables"[2] are based on the work of Menschutkin.[3] Recently, Evans and Rowley[4] studying the vapor pressures of the ethyl etherates of magnesium bromide demonstrated the existence of a trietherate, stable below +12–13°, that was unknown to Menschutkin. In view of this fact, it was decided to repeat the work of Menschutkin over a temperature range from −20 to +30° and see if the solubility curve also gave indications of a change of phase. At the same time, the preparation of magnesium bromide in ethyl ether solution was studied.

## Experimental

**Method of Preparation.**—The magnesium bromide was prepared according to Zelinsky[5] by treating pure magnesium turnings in ethyl ether with liquid bromine and agitating until the solution was colorless, cooling the flask when necessary to avoid too violent a reaction. As was previously known,[3-5] when the concentration of magnesium bromide reached a value of about 3.5%, an oily, immiscible liquid separated out and, as the reaction proceeded, increased in amount. This immiscible layer was often brown in color, but when properly prepared was almost colorless. When precipitated from a solution of magnesium bromide, saturated at a higher temperature, by cooling, this oily liquid was absolutely colorless. When pure, it crystallized under ether at about +22–23° but was capable of being supercooled 20 to 30° for several hours. However, agitation or seeding with a crystal of magnesium bromide etherate caused it to solidify into a white crystalline mass, which melted under ether above +23° re-forming the heavy layer.

The magnesium turnings were of reagent quality used in the preparation of Grignard reagents. The bromine was taken from a freshly opened bottle of C. P. grade, transferred to a dropping bottle and kept in a desiccator over phosphorus pentoxide. The ethyl ether was kept over calcium chloride for several days, filtered onto freshly cut sodium and kept in a subdued light for at least three or four days. It was then filtered onto fresh sodium and if no reaction occurred was distilled and kept over sodium in subdued light. The first and last fractions of the distillate were discarded and the freshly distilled middle portion used in less than a week. In this way the amount of degradation products present was kept at a minimum.

**Determination of Solubility.**—The samples were prepared in 150–250-cc. Erlenmeyer flasks as described above and either used directly or recrystallized, depending upon the purity as shown by the first analysis. The flasks, protected with calcium chloride tubes throughout the preparation and analysis, were immersed in a thermostat at the proper temperature held to less than 0.1°. For the determination at 0°, the melting point of ice was used, while at −10 and −20° an acetone-bath cooled with solid carbon dioxide was maintained at the proper temperature with the aid of an iron–constantan thermo element. In most cases, whenever feasible, the solutions were saturated a few degrees above the bath temperature in order that the equilibrium might be reached from supersaturation rather than unsaturation. After placing the samples in the bath, the flasks were agitated at intervals for at least an hour to ensure equilibrium. When the solid phase was crystalline, the oily immiscible layer was first solidified in ice and then melted before placing in the thermostat. After the immiscible layer had once been solidified and then remelted, the amount of supercooling, so characteristic of this substance, was greatly decreased and crystallization occurred rather quickly at temperatures where the crystal phase was stable.

After the solution had come to equilibrium, the flask was removed from the bath and a sample of the clear solution quickly poured into a tared flask and weighed. The weighed solution was then poured into water acidified with dilute nitric acid, the ether removed by evaporation and boiling, and the total bromide concentration determined as silver bromide. All of the solubility measurements were determined by this method and reported in grams of magnesium bromide dissolved in 100 g. of ethyl ether. In a series of experiments, a second sample was weighed in a tared crucible, the ether removed by evaporation on a steam-bath and the residue treated with concentrated sulfuric acid which was later removed by heating on a hot-plate and finally the magnesium sulfate was heated to redness and weighed as such. The determination of magnesium by this method was well suited to the conditions, since the concentrated sulfuric acid destroyed all the organic matter which might interfere with other methods. The disadvantage, aside from the hygroscopic character of anhydrous magnesium sulfate, was that considerable loss of ether from the open crucible occurred before weighing which would lead to higher results than by the bromide method. This was consistently shown in the determinations but, even so, the agreement was quite good.

The results of the analyses are shown in Table I and Fig. 1. The solubility of magnesium bromide at each temperature is the average of at least two individual samples taken from separate preparations. The more important

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[1] Presented before the Inorganic Division of the American Chemical Society at Kansas City, Mo., April, 1936.

[2] "International Critical Tables," New York, Vol. IV, 1928, p. 203.

[3] B. N. Menschutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

[4] W. V. Evans and H. H. Rowley, THIS JOURNAL, **52**, 3523 (1930).

[5] N. Zelinsky, *Chem. Zentr.*, **74**, II, 277 (1903).

TABLE I

SOLUBILITY OF $MgBr_2$ IN ETHYL ETHER

| Temp., °C. | Solubility, g. $MgBr_2$/100 g. $Et_2O$ | Temp., °C. | Solubility, g. $MgBr_2$/100 g. $Et_2O$ |
|---|---|---|---|
| Equilibrium Phase: | Crystalline | | |
| −20 | 0.27 | +13.0 | 1.47 |
| −10 | .40 | +15.0 | 1.76 |
| 0 | .70 | +16.5 | 1.99 |
| +3.0 | .84 | +18.0 | 2.14 |
| +7.8 | 1.05 | +20.0 | 2.52 |
| +10.1 | 1.19 | | |
| Equilibrium Phase: | Immiscible Liquid | | |
| 0 | 2.16 | +24.9 | 3.20 |
| +13.1 | 2.62 | +27.5 | 3.33 |
| +20.0 | 2.95 | +32.0 | 3.63 |

points such as at 0, +16 and +25° were checked by analysis of five or more samples. During the course of the investigation, well over 150 separate preparations were made. The accuracy of the points is ±0.05 g. of magnesium bromide per 100 g. of ether.

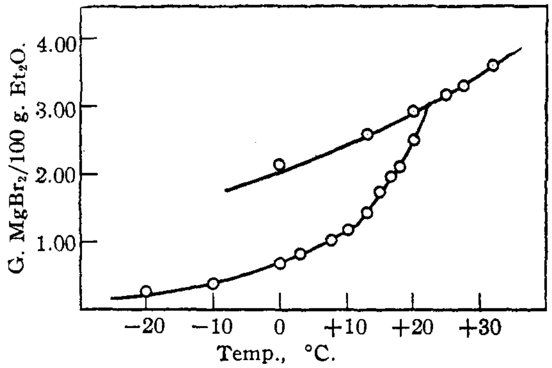

Fig. 1.—Solubility of $MgBr_2$ in ethyl ether.

### Factors Influencing Purity

It was found during the investigation that high and inconsistent results were frequently encountered. The possibility of impure reagents was eliminated inasmuch as inconsistent results were often obtained using identically the same materials in successive runs. Since moisture was known to decompose the etherates,[4,6] this was one of the first factors to be investigated.

**Effect of Moisture during the Preparation.**—Dry, freshly distilled ether was mixed with a known quantity of water and this moist ether was then used in preparing the magnesium bromide solutions in the usual manner. The reaction of bromine on the magnesium was always immediate with moist ether, whereas dry ether required a minute or more before a reaction was visible. With wet ether there appeared to be a gas given off even when the solution was cold. The results of a series of analyses at +24.9° are given in Table II. Small amounts of moisture in the ether during the preparation do not appear to affect the apparent solubility.

**Effect of Moisture after the Preparation.**—The magnesium bromide was prepared in the usual manner using dry ether. The immiscible layer was crystallized by cooling and the original solution decanted. Ether with a known moisture content was added, the crystals melted and the solution saturated at +24.9°. The amount of magnesium bromide in solution was determined both by the magnesium sulfate and the silver bromide methods. The results of the series are given in Table III and show that the presence of moisture, after the solutions are prepared, definitely raises the apparent solubility of the magnesium bromide.

TABLE II

EFFECT OF MOISTURE DURING PREPARATION

ANALYSIS AT +24.9°

| Sample no. | Mols. $H_2O$/liter $Et_2O$ | Solubility, g. $MgBr_2$/100 g. $Et_2O$ | Remarks |
|---|---|---|---|
| 55 | 0.0001 | 3.34 | Prepd. in daylight |
| 58 | .0005 | 3.36 | Prepd. in daylight |
| 60 | .01 | 3.36 | Prepd. in daylight |
| 73 | .01 | 3.20 | Prepd. in semi-darkness |

TABLE III

EFFECT OF MOISTURE AFTER THE PREPARATION

ANALYSIS AT +24.9°

| Sample | Moles $H_2O$/liter $Et_2O$ | $MgBr_2$/100 g. $Et_2O$ Mg analysis | Br analysis |
|---|---|---|---|
| 75 | 0.001 | 3.43 | 3.42 |
| 74 | .005 | 3.51 | 3.45 |
| 71 | .01 | 3.59 | 3.52 |
| 59 | .02 | 3.68 | 3.57 |

To overcome this source of error, the apparatus and reagents were carefully dried and the reaction flasks fitted with calcium chloride tubes. During the preparation and recrystallization, the flasks were never opened except in an atmosphere of air dried by calcium chloride and concentrated sulfuric acid.

**Effect of Light during the Preparation.**—The fact that the solubility of the magnesium bromide could be lowered to a constant value by careful recrystallization from fresh ether, indicated that the apparent high solubilities frequently obtained were due to certain conditions existing during the preparation. There seemed to be good indications that ether, not freshly distilled, caused high results but frequently freshly distilled ether also gave somewhat high values not traceable to moisture. In practically all these cases, when the sample was poured into water and the ether boiled off, there was a more or less strong odor of some organic compound or compounds, frequently lachrymatory in nature, that was difficult to boil out of solution. This organic material caused the silver bromide precipitate to be oily and to stick to the side of the beaker. That the high results were not due exclusively to inclusion of this organic material in the silver bromide, is shown by parallel magnesium determinations which also were high. Since the magnesium sample was evaporated to dryness (residue dark when organic matter is present, white when not) then treated with concentrated sulfuric acid and heated to redness, all the organic matter including the combined ether was destroyed.

Believing that this organic matter might be formed by the action of bromine on ethyl ether in the presence of light, a series of runs was made to test this. The room was partially darkened and the sample exposed to strong light

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(6) B. N. Menschutkin, *Chem. Zentr.*, **77**, I, 646 (1906).

for definite intervals during the preparations. A 200-watt daylight gas-filled lamp set in a 30-cm. silver reflector was used as a light source and the sample flask held 15 cm. from the bulb. It was noticed that, during the exposure to a strong light, a gas was given off even though the solution was below room temperature.

During several runs when the concentration of bromine was rather high and the reaction was vigorous, the two-layer system would appear normal after the free bromine color had disappeared but almost immediately the heavy immiscible layer would begin to darken. In ten or fifteen minutes it would be a deep purple and the upper ether layer would acquire a light purple color. On further standing for an hour or so, this would fade to a green and finally the immiscible layer would become clear yellow and the ether layer colorless. During these color changes, the liberation of a gas frequently was observed. In all such cases, the analyses were very high and showed the presence of a large amount of high-boiling organic material. The results of the experiments with light are shown in Table IV. When the strong light was not in use, the samples were not in total darkness but were not exposed to any direct daylight.

TABLE IV

EFFECT OF LIGHT DURING THE PREPARATION ANALYSIS AT +24.9°

| Sample | Exposure to strong light | G. $MgBr_2$/100 g. $Et_2O$ | | Remarks |
|---|---|---|---|---|
| | | Mg analysis | Br analysis | |
| 62 | None | 3.38 | 3.34 | Reaction violent; no color changes |
| 63 | None | 3.41 | 3.29 | |
| 65 | None | 3.37 | 3.23 | |
| 66 | None | 3.28 | 3.18 | |
| 71 | None | 3.34 | 3.30 | |
| 74 | None | 3.34 | 3.30 | |
| 64 | 1 min. | 3.22 | 3.20 | |
| 67 | 1 min. | 3.36 | 3.34 | |
| 70 | 1 min. | 3.32 | 3.29 | |
| 69 | 2 min. | 3.53 | 3.51 | Reaction violent; color changes |
| 76 | 3 min. | 3.42 | 3.43 | Slight color changes. |
| 77 | 3 min. | 3.29 | 3.24 | Less $Br_2$ concn. than No. 76 |
| 61 | 15–20 min. | 3.59 | 3.61 | Color changes |

A few rough experiments were performed to determine whether ethyl ether did react with liquid bromine to a certain extent in the presence of light. Ether that had been distilled about six days previously and kept over sodium in semi-darkness was used. In total darkness 50 cc. of this ether and 1.8 g. of bromine still showed a strong bromine color after five days. However, exposure of this sample to a strong light caused the color to disappear in less than two hours. Another 75-cc. portion took up about 0.9 g. of bromine in a few hours in daylight giving a colorless solution and another gram of bromine more slowly on exposure to the 200-watt lamp. When colorless, this sample reacted vigorously with magnesium giving a homogeneous solution. Analysis of this solution showed a concentration of 0.0125 mole of magnesium and 0.0135 mole of bromine per 100 g. of solution. There was considerable organic material in both samples.

## Discussion

Examination of Fig. 1 shows two discontinuities in the solubility curve of magnesium bromide, one at about +22.5° the other, less distinct, at about 12°. If it is assumed that the heat of solution remains constant over this temperature range, a plot of the logarithm of the solubility against the inverse absolute temperature should give a straight line as long as the phase in equilibrium with the solution does not change. Plotting in this manner, in Fig. 2, straight lines are obtained and show very distinctly a change of crystal phase between +11 and +12°. The solid phase in equilibrium with the ether solution along the line AB is magnesium bromide triethyl etherate.[4]

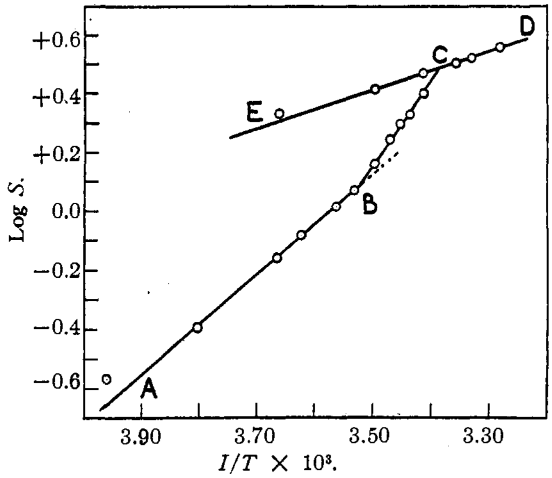

Fig. 2.—Solubility of $MgBr_2$ in ethyl ether.

At approximately +12° (B) the trietherate decomposes to form magnesium bromide diethyl etherate which is the solid phase in equilibrium along BC. The dietherate, which in the absence of excess ether exists to +28°,[3,4] reacts with excess ether at +22.6° (C) and forms an immiscible liquid layer which is the phase in equilibrium along CD. As noted previously, this liquid can be greatly supercooled and the solubility in the metastable state below +22.6° follows along CE.

Though Menschutkin[3] made only a few measurements below +10°, when his data are plotted in the same manner as Fig. 2, a break is also obtained at about +12°. The transition temperature of magnesium bromide triethyl etherate at +12 ± 0.5° as determined from the solubility data agrees very well with the value of +13 ± 0.5° found by Evans and Rowley[4] from vapor pressure measurements. Likewise, the change to a liquid phase of the diethyl etherate of magnesium bromide under ether, as determined in this work, checks Menschutkin's value to within a few tenths of a degree.

From the slope of the lines AB and BC (Fig. 2), the heat of solution of one mole of the crystal phase in an almost saturated ethyl ether solution can be calculated. Thus, the average differential heat of solution is −4.03 kcal. for magnesium bromide triethyl etherate over the temperature range −20 to +10°, while the average differential heat of solution is −6.47 kcal. for the diethyl etherate from +12 to +22°.

The determination at 0° when the immiscible layer is in equilibrium with the solution is known to be somewhat high. It was frequently difficult to obtain absolutely pure samples without recrystallizing the magnesium bromide and since there is little supercooling in a sample that has once been crystallized, the metastable points below +22.6° had to be obtained with fresh samples. Quite a number of samples had to be prepared before the points at +13 and +20° were obtained. Even so, all the values obtained were considerably lower than those found by Menschutkin and reported in the "International Critical Tables"[2] amounting to an average difference of 0.1 g. $MgBr_2$/100 g. $Et_2O$ for the trietherate; 0.2–0.3 g. $MgBr_2$/100 g. $Et_2O$ for the dietherate; and 0.4–0.5 g. $MgBr_2$/100 g. $Et_2O$ for the immiscible layer. Experimental values taken from the smooth curve and compared to the literature values are given in Table V.

TABLE V

SOLUBILITY OF $MgBr_2$ IN ETHYL ETHER

| Temp., °C. | G. $MgBr_2$/100 g. $Et_2O$ | Moles % $MgBr_2$ | |
|---|---|---|---|
| | | Experimental | "I. C. T." |
| Solid Phase: $MgBr_2 \cdot 3(C_2H_5)_2O$ | | | |
| —20 | 0.22 | 0.09 | .. |
| −10 | .40 | .16 | 0.24 (−8°) |
| 0 | .70 | .28 | .32 |
| +10 | 1.18 | .47 | .52 |
| Solid Phase: $MgBr_2 \cdot 2(C_2H_5)_2O$ | | | |
| +14 | 1.58 | 0.65 | 0.67 |
| +16 | 1.84 | .74 | .79 |
| +18 | 2.14 | .85 | .94 |
| +20 | 2.50 | .99 | 1.10 |
| +22 | 2.91 | 1.16 | 1.32 |
| Immiscible Liquid Phase | | | |
| 0(m) | 2.04 | 0.82 | 0.94 |
| +10(m) | 2.47 | 0.98 | 1.14 |
| +20(m) | 2.95 | 1.17 | 1.36 |
| +30 | 3.49 | 1.38 | 1.56 |

The effect of moisture on the purity of the sample shows, in Table II, that the presence of a slight amount of moisture during the preparation does not materially affect the result. This might be expected since the free bromine would probably combine with the water to give hydrobromic acid which would react immediately with the magnesium, forming magnesium bromide and free hydrogen.

However, the presence of traces of moisture after the magnesium bromide is prepared affects the apparent solubility as shown in Table III. It is well known that water will displace completely the ethyl ether from etherates.[4,6] Possibly small amounts of water would displace only part of the solvated ether, giving rise to mixed solvates. These mixed solvates might be expected to be somewhat soluble in ether and in turn have little effect on the solubility of unchanged magnesium bromide etherate so that the net result would be an increase of magnesium and bromide in the solution. The analysis of magnesium by magnesium sulfate and of bromide by silver bromide would not distinguish between these two compounds in solution. In all cases when moist ether was used to crystallize the magnesium bromide, there appeared to be a white solid mixed with the immiscible layer. Menschutkin[6] claimed that small amounts of water give $Mg(OH)Br \cdot MgBr_2 \cdot 2(C_2H_5)_2O$ which is practically insoluble in ethyl ether. Possibly this compound is more soluble than he thought.

## Summary

1. The solubility of magnesium bromide in ethyl ether was measured from −20 to +30°.

2. Two discontinuities in the solubility curve were found: one at +12 ± 0.5° where $MgBr_2 \cdot 3(C_2H_5)_2O$ decomposes to form $MgBr_2 \cdot 2(C_2H_5)_2O$; the other at +22.5 ± 0.5° where $MgBr_2 \cdot 2(C_2H_5)_2O$ melts under ether to form an immiscible liquid layer.

3. The average differential heat of solution for $MgBr_2 \cdot 3(C_2H_5)_2O$ over the temperature range −20 to +10° was calculated to be −4.03 kcal. The average differential heat of solution for $MgBr_2 \cdot 2(C_2H_5)_2O$ from +12 to +22° was calculated to be −6.47 kcal.

4. The values of the solubility of magnesium bromide were found to be consistently lower than those reported in the "International Critical Tables."

5. The purity of the magnesium bromide prepared in ethyl ether solutions was studied and it was found that traces of moisture during the prepa-

ration had little effect on the solubility values, whereas the presence of very small amounts of water after the preparation was complete caused an increase in the apparent solubility.

6. The effect of light during the preparation was studied and the conclusion reached that bromine reacted to a certain extent with recently distilled ethyl ether in the presence of light giving rise to side reactions and impurities.

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# A Study of Some Reactions between Dry Inorganic Salts. III*

BY E. B. THOMAS WITH LYMAN J. WOOD

In two previous papers[1,2] the authors have reported results obtained from a study of a few of the possible reactions occurring between the dry alkali halides in the fused state. The remaining 42 of the 60 possible reactions have now been studied and some of the previously reported reactions have been studied in greater detail. Also 12 new salt pairs having a common ion have been examined in order to determine in which cases solid solutions can be formed. These solid solubility relationships as well as the course of the reactions mentioned above have been determined by the method of x-ray crystal analysis.

The general plan of the work was very similar to that followed in the previous work. The material to be examined was melted and held in the molten condition for a short time, after which it was quenched and quickly placed in a desiccator to avoid the possible absorption of water. The mixture was then ground to a fine powder (approximately 200-mesh) and placed in a small, thin-walled glass tube of 0.6–0.7 mm. inside diameter, in which container it was exposed to the x-ray beam. The molybdenum $K_\alpha$ doublet, filtered through zirconia, was used for all exposures, the scattered rays being photographed according to the well-known powder method of Debye, Scherrer and Hull.

Those mixtures which showed a tendency to absorb water were handled in a "Dry Box" to which rubber sleeves were attached, or were ground in a mortar on a hot-plate from which the small tubes were filled. The chloride, bromide and iodide of lithium and the fluorides of rubidium and cesium were found to be extremely hygroscopic, and the fluoride of potassium moderately so.

## Results

In order to supplement the table of miscibilities previously published,[2] all the binary mixtures of salts having a common ion, in which the percentage deviation from the mean cube edge is less than 10, have been examined in order to determine in which cases solid solutions are formed. The results obtained are shown in Table I. As is to be seen, no solid solutions have been observed in any case in which the per cent. deviation from the mean cube edge is greater than 8.20.

In Table II are assembled the results for the 42 new reactions not reported in the previous papers. These results were found to be in excellent agreement with the former findings. In each case the reaction goes to completion in such a direction that the average cube edge of the stable pair is less than that of the reciprocal pair. In each case the stable pair has the cation of smaller atomic weight united with the anion of smaller atomic weight, and the cation of larger atomic weight united with the anion of larger atomic weight. In each case the sum of the heats of formation of the stable pair is greater than that of the reciprocal pair. With the exception of the lithium salts one member of the stable pair always has the highest melting point of the four compounds involved.

It should be mentioned that the value for the cube edge of sodium bromide used in this paper is a little larger than the previously used value of 5.940 Å. which is listed by Wyckoff[3] as the favored value. A survey of the literature showed that Davey[4] reported a value of 5.936 Å. for the cube edge of sodium bromide, that Wyckoff[5] reported a value of 5.95 Å., while Ewald's "Structurbericht" lists the value of 5.962 Å. A very careful com-

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(*) Read at the Kansas City Meeting of the American Chemical Society.

[1] E. B. Thomas and Lyman J. Wood, THIS JOURNAL, **56**, 92 (1934).

[2] E. B. Thomas with Lyman J. Wood, *ibid.*, **57**, 822 (1935).

[3] Wyckoff, "The Structure of Crystals," Second edition, The Chemical Catalog Co., New York, 1931.

[4] W. P. Davey, *Phys. Rev.*, **21**, 143 (1923).

[5] R. W. G. Wyckoff, *J. Wash. Acad. Sci.*, **11**, 429 (1921).