# The Solubility of Magnesium Bromide in Di-n-Butyl Ether

John A. Ricketts and Paul Brown, DePauw University

Rowley (1) has extensively investigated the solubility of magnesium bromide in diethyl ether, $Et_2O$, and has found that magnesium bromide forms a solid mono-, di-, and tri-etherate with transition temperatures of 12° C. (tri-etherate to di-etherate) and 22.6° C. (di-etherate to mono-etherate). This investigation measures the solubility of magnesium bromide in di-n-butyl ether, $Bu_2O$, in the temperature range of 5° C. to 56° C. and also determines the chemical nature of the solid phase in equilibrium with the saturated solution of magnesium bromide in $Bu_2O$.

## Experimental

Solubility measurements were taken at approximately 5° C. intervals. Any of the fixed temperature points that were used were controlled to $\pm$ 0.02°C. Excess solid was added to 50 ml. of pure $Bu_2O$ contained in a 100 ml. round-bottomed flask. All $Bu_2O$ used in the experiments was purified by fractional distillation from sodium on to sodium and only the fraction which distilled in the temperature range 141-2° C. was used. The refractive index of the $Bu_2O$ was measured as 1.3990 at 20° C. (lit. 1.3992). The vapor phase chromatogram of the liquid contained only a single peak. The flask was mounted in the constant temperature bath and the closed system stirred mechanically for a period of time ranging from 4 to 12 hours. Samples of the liquid phase were withdrawn, weighed, and analyzed, one sample for magnesium ion using EDTA with Erichrome Black T as indicator and another sample from the same flask for bromide ion by the Vohlhard method. In withdrawing the liquid samples the tip of the pipet was covered with filter cloth so as to exclude any solid material; in addition the temperature of the pipet was slightly warmer than the temperature of the solution in order to prevent any precipitation of dissolved magnesium bromide during the transferring process. The validity of any determination was checked through the ratio of the weight of magnesium ion per gram of solution to the weight of bromide ion per gram of solution. The theoretical ratio is 0.1521; these ratios that deviated from the expected value by greater than three per cent were discarded.

Solubility measurements using anhydrous magnesium bromide (purity 99.9 per cent) as the initial solid phase gave irreproducible results even though the ratio of magnesium ion to bromide ion was acceptable. Suspecting that the stable solid phase was a di-n-butyl etherate of magnesium bromide, the solid starting material was synthesized as follows. Initially $MgBr_2.3Et_2O$ was prepared according the procedure described by Rowley (2). Excess c. p. magnesium turnings suspended in c. p. anhydrous $Et_2O$ were reacted with chorine-free liquid bromine. The reaction was carried out under anhydrous conditions at the temperature of melting ice under a nitrogen atmosphere. The liquid layers were then separated from the excess magnesium. Solid $MgBr_2.3Et_2O$ separated

from the liquid when it was cooled with an ice-salt mixture. The solid tri-etherate was washed several times with $Bu_2O$ and suspended in $Bu_2O$. Distillation of the mixture at a temperature below 75° C. removed all of the $Et_2O$. The solid phase was then washed with $Bu_2O$ until the liquid layer remained water clear. Samples of the solid were freed from excess $Bu_2O$ by suction filtration over an atmosphere of nitrogen, weighed, and analyzed for magnesium bromide. If the formula for the solid were $MgBr_2.Bu_2O$, the predicted percentage by weight of magnesium bromide is 58.48. Experimental percentages ranged between 53 and 60 per cent. Because the solid hydrolyzes rapidly in air and because the sample may not have been completely freed of physically adsorbed $Bu_2O$ by the filtration process, the experimental results are thought to be precise enough to establish the formula for the solid phase as $MgBr_2.Bu_2O$. All the reported solubility measurements used the $MgBr_2.Bu_2O$ as the starting solid material.

**Results and Discussion**

Figure 1 summarizes the solubility data for magnesium bromide in $Bu_2O$. It has been constructed using data from three separate runs with

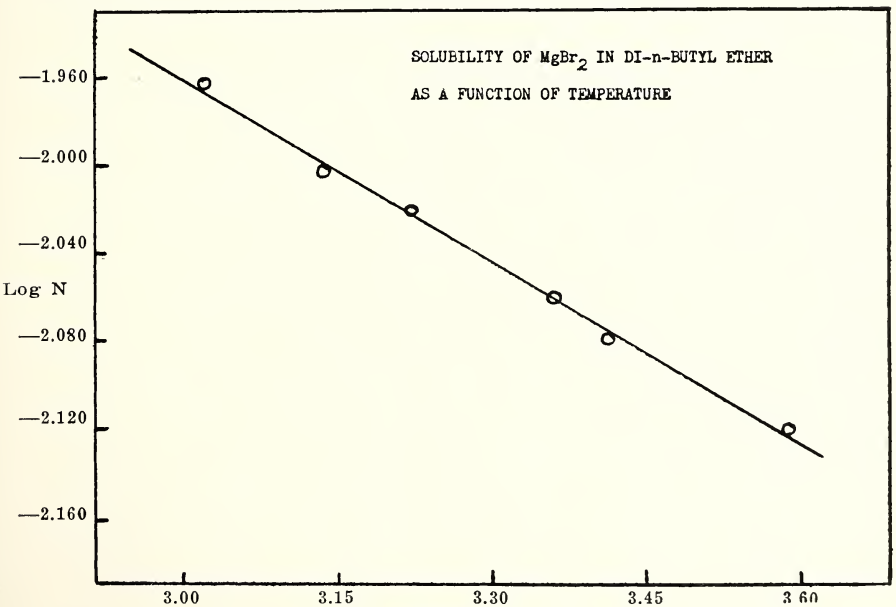


Figure 1

different preparations of $MgBr_2.Bu_2O$ as the solid phase. Treatment of the entire set of data, 22 separate determinations, by the method of least squares indicates that the equation which best represents the solubility of magnesium bromide in $Bu_2O$ in the temperature range of 5.70° C. to 59.90° C. is

$$\log N = -\frac{283.7}{T} - 1.109 \qquad (1)$$

where N represents the solubility of magnesium bromide in terms of its mole fraction in the solution and T the absolute temperature. From equation 1 the differential heat of solution of $MgBr_2.Bu_2O$ in $Bu_2O$ is calculated to be 1.30 $\pm$ 0.02 kcal. $mole^{-1}$. The curve, since no discontinuities occur, also indicates that in the temperature range studied the stable solid phase is $MgBr_2.Bu_2O$.

## Literature Cited

1. ROWLEY, H. H. 1936. Physical Studies of Non-Aqueous Solvates. I. The Solubility of Magnesium Bromide in Ethyl Ether. J. Am. Chem. Soc. **58**:1337.
2. ROWLEY, H. H., and W. V. EVANS. 1930. The Etherates of Magnesium Bromide. J. Am. Chem. Soc. **52**:3533.