equation (6) was found to be sensibly constant and equal to 3.2 ± 0.3. At a pH of 3.05 equation (6) was also found to be satisfied although a slightly greater value of K of 4.5 ± 0.5 was found. This difference may be partly due to experimental errors in the measurement of the distribution and of the pH of the aqueous solution (a small error in the measurement of aH^+ has a large effect on K since the value of K depends on aH^{+2}) and to the fact that the activity coefficient of the zinc ions has not been taken into account (equation 6a). Experiments 9 and 10 in Table I show that in 1 M sodium nitrate the value of K was only slightly less than in the absence of this salt. The observed variation of K in the experiment in 1 N sodium chloride is either accidental or the result of the tendency of chloride to form a complex ion with zinc.

Summary

A simple quantitative expression for the extractability of a metal in the form of its dithizonate from water by an organic solvent has been derived. Experiments carried out with zinc showed that the theoretical expression is valid under widely varying experimental conditions.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE UNIVERSITY OF IOWA]

Physical Studies of Non-aqueous Solvates. IV. The Solubility of Zinc Bromide in Diethyl Ether[1]

BY H. H. ROWLEY AND ROBERT B. ANDERSON

Recent investigations in this Laboratory[1a] of the diethyl etherates of zinc bromide through vapor pressure measurements, indicated the existence of a dietherate at low temperatures. At about +5° this dietherate decomposes to form a monoetherate which exists up to about +20°. Above +20° the non-solvated zinc bromide appeared to be the stable form of the solid in contact with ether solution and vapor. These results differed markedly from those of Raynaud,[2] who claimed a monoetherate of zinc bromide existing at +100°.

The present study was undertaken to clear up the incongruities in the results of Raynaud and those found in this Laboratory and to ascertain more precisely the transition points by solubility determinations over the temperature range −20 to +35°.

Experimental

Apparatus and Materials.—The anhydrous zinc bromide and the diethyl ether were prepared as previously described.[1a]

The solubility cells were large test-tubes which were closed with rubber stoppers carrying two glass tubes for removing the saturated liquid. Agitation in the solution was provided by a solenoid stirring device suitable for use in constricted spaces.[3] The various temperatures −20 to +35° were maintained to less than ±0.3° by using a thermostat (water-bath), various freezing mixtures and acetone cooled by the addition of dry-ice.

Procedure.—In the handling of materials and apparatus, great care was taken at all times to exclude atmospheric moisture. The solutions of zinc bromide were prepared in a dry atmosphere chamber by adding ether to the anhydrous zinc bromide. The solutions were stirred for varying periods of time, depending upon the temperature of the determination, and then allowed to settle. Below +15°, the stable system required shorter periods for settling out due to the lower viscosity of these less concentrated solutions and the crystalline character of the solid compared to the "amorphous" solid above +20°. The conversion of the "amorphous" solid to the crystalline (solvated) phase was effected readily only by cooling the mixture to about −78°. It was then warmed to about one degree above the required temperature, stirred, and then permitted to approach equilibrium for a period of about eighteen hours, at the required temperature.

After settling, the clear supernatant liquid was forced by dry air into tared glass-stoppered Erlenmeyer flasks. The flasks were weighed immediately, and the samples dissolved in water and analyzed for bromine content by a modification of the Volhard method as revised by Caldwell.[4] A few samples also were analyzed for zinc and the results calculated as zinc bromide checked the bromine analyses very closely.

The wet solids in contact with the saturated solutions at the various temperatures were analyzed. The instability of the etherates in air at room temperature prevented complete removal of the adhering solution but they were drained as thoroughly as possible before analysis by pressing on filter paper pads at the equilibrium temperature.

Results.—Solubility data for the system zinc bromide–diethyl ether are gathered in Table I.

(1) Original manuscript received July 22, 1940.

(1a) Rowley and Olson, THIS JOURNAL, **61**, 1949 (1939).

(2) Raynaud, *Bull. soc. chim.*, **39**, 195 (1926).

(3) Rowley and Anderson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 397 (1939).

(4) Caldwell, *ibid.*, **7**, 38 (1935).

The second column gives the grams of zinc bromide dissolved in one hundred grams of diethyl ether when the solution is saturated at the various temperatures. In the fourth column is the average composition of the "wet" solid in equilibrium with the solution over the temperature range indicated, while in the fifth column is the probable solid actually in equilibrium.

TABLE I

SOLUBILITY DATA FOR THE SYSTEM ZINC BROMIDE–DIETHYL ETHER

Temp., °C.	Solubility, g. $ZnBr_2$/100 g. Et_2O	Diff. heat of soln., ΔH, kcal./mole	Compn. of solid equil. phase: Wt. % $ZnBr_2$, "Wet" Solid	Probable solid
−20	47.7 ±0.2			
		10.54		
−15.8	67.2 ±0.3			
		7.37		$ZnBr_2 \cdot 2(C_2H_5)_2O$
−10	92.3 ±0.5		59.0 ±1.0	
		4.33		60.3 (theor.)
− 5	107.7 ±0.2			
		6.22		
0	133.3 ±0.5			
+ 5	178.3 ±0.6			
		2.92		$ZnBr_2 \cdot (C_2H_5)_2O$
+10	195.7 ±0.6		73.4 ±0.2	
		4.18		75.3 (theor.)
+15	222.6 ±0.2			
0[a]	208.8 ±0.3			
+20	231.8 ±0.3			
		0.62		
+25	236.0 ±0.3		93.1 ±0.3	$ZnBr_2$
		0.57		100 (theor.)
+35	243.5 ±0.7			

[a] Supercooled from +25°.

Discussion of Results

The system zinc bromide–diethyl ether is characterized by its sluggishness and solvation of the non-etherated zinc bromide is accomplished only with difficulty.[1a] Solutions saturated at room temperature and supercooled to 0° did not readily solvate. The viscosity of the saturated solution at 25° is considerable, and as the temperature of this very concentrated solution is lowered the viscosity increases. At a temperature somewhat above that of an acetone–dry-ice-bath (−78°) an apparent solid solution is formed and from this solid or exceedingly viscous solution, either at this temperature or upon warming, the zinc bromide etherate crystallizes.

That solid etherates of zinc bromide do exist is shown by two definite breaks in the graph obtained when the solubility is plotted against the temperature. According to the van't Hoff equation, for an "ideal solution" a linear relationship exists between the logarithm of the solubility and the reciprocal of the absolute temperature provided that there is no change in the composition of the equilibrium phase and that the differential heat of solution at saturation remains constant over the temperature range. Since the solutions involved are so concentrated, we would hardly expect them to follow an "ideal" law. However, changes in the solid phase in equilibrium with the solution are usually accompanied by abrupt changes in the value of the differential heat of solution and hence in the slope of the line. When log S is plotted against $1/T$ as in Fig. 1, we see that there are definite breaks at +4° (B) and +16–17° (C). The average values of the calculated differential heats of solution (heat absorbed by the system) as listed in column 3 of Table I are markedly different over the three temperature ranges −20 to +4°, +4 to +17° and +17 to +35°, indicating at least three distinct solid phases.

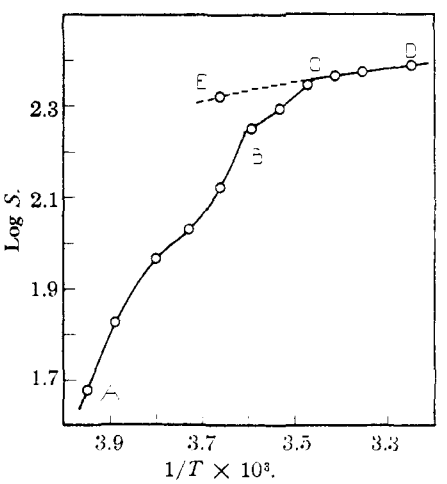

Fig. 1.—S expressed in grams $ZnBr_2$/100 grams Et_2O.

From Fig. 1 a third break, less definite than the other two, may be observed in the vicinity of −10°. This would suggest the existence of a fourth solid phase below this temperature since "if any 'break' or discontinuous change in the direction of the curve occurs, it is a sign that the solid phase has undergone alteration."[5] However, the analyses of the "wet" solids in contact with the saturated solutions indicate only three solid phases. From −20 to 0° the average analysis is 59.0 ± 1.0% zinc bromide, which corresponds quite closely to the composition of the solid zinc bromide dietherate plus adhering solution over this entire range. Also the physical

(5) Findlay, "The Phase Rule and its Applications," 8th ed., Longmans, Green and Co., New York, N. Y., 1938, pp. 171–173.

appearance of the solid equilibrium phase over this lower range remained the same but differed markedly in crystal form from that observed above +4°. Above +17° the equilibrium solid did not possess visible crystalline properties but was very finely divided with "amorphous" characteristics.

As to the cause of this possible break in the solubility curve at −10° we have no explanation. The values reported in Table I for this temperature range are the averages of over forty analyses which checked within the limits stated. When solubilities are plotted against temperature, the same type of curve as that shown in Fig. 1 is obtained and a break may be observed at −10°. However, an "S" shaped *continuous* curve can also be drawn through these same points. As is well known, the form of the solubility curve may vary in the most diverse manner[5] and for solutions in non-aqueous solvents such peculiar curves are not unusual. Inasmuch as the solutions are quite concentrated and show a tendency to separate into two partially miscible layers,[1a] and since no marked change in the equilibrium solid phase was noted, we believe the solubility curve is continuous from −20 to +4° and that no real break occurs at −10°.

The solids all contained some adhering solution that could not be removed without destroying the compound being analyzed and since the solutions were quite concentrated, it was impossible to tell exactly the true composition of the solid. Nevertheless, more thorough removal of the adhering solutions brought the analyses of the "wet" solids still closer to the probable solid phases previously suggested.[1a]

On this assumption, the section of the curve AB in Fig. 1 is the solubility curve for $ZnBr_2 \cdot 2(C_2H_5)_2O$. At +4° the diethérate loses one molecule of ether and the solubility of $ZnBr_2 \cdot (C_2H_5)_2O$ is shown by BC. Above +16–17° the unsolvated zinc bromide is the stable phase in equilibrium with the solution and its solubility is given by CD. As mentioned previously, it is possible to obtain metastable solutions with unsolvated zinc bromide as the equilibrium phase. Such a metastable system is indicated by EC. These results are consistent with those previously found in this Laboratory from vapor pressure measurements[1a] and contradict those of Raynaud[2] who claimed a monoetherate of zinc bromide at +100° and a solubility of 46% by weight at +25°.

Summary

1. Solubility determinations of zinc bromide in diethyl ether were made over the temperature range −20 to +35°.

2. The existence of two etherates of zinc bromide has been further substantiated and their transition points determined more precisely: probably zinc bromide monoetherate, $ZnBr_2 \cdot (C_2H_5)_2O$ stable below +16–17°, and zinc bromide diethérate, $ZnBr_2 \cdot 2(C_2H_5)_2O$ which decomposes above +4°.

3. The differential heats of solution at saturation were calculated over the entire temperature range studied averaging 3.5 kcal./mole for the monoetherate and 0.60 kcal./mole for the unsolvated zinc bromide. The diethérate gave a value of 6.2 kcal./mole at 0° falling to 4.3 kcal./mole at about −8° and rising to 10.5 kcal./mole at −20°.

4. The results are consistent with those obtained by Rowley and Olson and with them contradict the findings of Raynaud.

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