Part I

PHASE EQUILIBRIA

MOLECULAR TRANSPORT

THERMODYNAMICS

Water Content of Bis(2-Chloroethyl) Ether in Equilibrium at 25° C. with Aqueous Mineral Acid Solutions

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SOLVENT extraction provides a suitable method for separating metals in the form of their halide complex ions (*4*). Although many separation schemes utilizing this technique have been worked out, knowledge of the physical chemistry involved is slight. Before the significance of the observed extraction curves can be elucidated and a quantitative theoretical interpretation attempted, data are needed on several parameters, including the solubilities of each of the constituents in both of the solvent phases under the conditions of the experiments. The present results are concerned with the solubility of water in bis(2-chlorethyl) ether, a solvent which has been used extensively for extraction studies of the halides complexes of trivalent elements (*4*).

EXPERIMENTAL

In the experiments, 10 ml. of bis(2-chloroethyl) ethyl, purified by triple distillation, were equilibrated with 10 ml. of aqueous acid solution by mechanical shaking at 25° ± 1° C. After equilibration, 2-ml. aliquots were removed from the ethereal phase, 1 ml. of methanol diluent of known water concentration was added, and the resulting solution quickly titrated with standardized Harleco Karl Fischer reagent for the water content (*3*). Calculations of concentrations were not corrected for solvent volume changes because large volume changes in the aqueous or ethereal phases—i.e., greater than 10%—were observed only in the case of $HClO_4$ concentrations greater than $8.0M$. Under these conditions, not only does the volume of the ethereal phase markedly increase, but ether also dissolves in the aqueous phase, as evidenced by the separation of an ethereal phase when the aqueous phase is diluted with water.

RESULTS AND DISCUSSION

The experimental results are summarized in Figure 1. The equilibrium molar concentrations of water in the ethereal phase (solid lines) and the equilibrium molar concentrations of electrolyte in the ethereal phase (dashed lines) (*7*) are plotted against the equilibrium molar concentrations of the several electrolytes in the aqueous phase. For the sake of clarity, many of the experimental points are not shown because they cluster and superimpose. Sulfuric acid is very insoluble in the ether. The solubility of water in the ether as a function of temperature was measured and the results are given in Table I.

Since the chemical potential of water must be the same in both phases, the water concentration in the ethereal phase should depend on the activity of the water in the aqueous phase. A comparison of the solubility of water in

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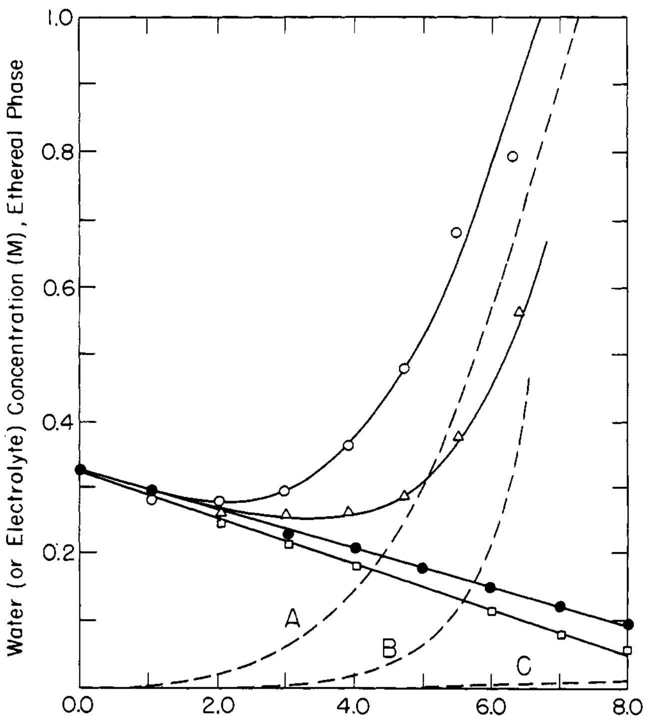

Figure 1. Solubility of water in bis(2-chloroethyl ether at 25° C. in presence of various electrolytes

○ Solubility of H_2O in the presence of HNO_3
△ Solubility of H_2O in the presence of $HClO_4$
● Solubility of H_2O in the presence of HCl, LiCl, or HBr
□ Solubility of H_2O in the presence of H_2SO_4
A Solubility of HNO_3(7)
B Solubility of $HClO_4$ (7)
C Solubility of HCl or HBr (7)

the ethereal phase with the activity of water in the aqueous phase, as given by Robinson and Stokes or calculated from molal osmotic coefficients (*5*), shows such to be the case for HCl, LiCl, H_2SO_4, and HBr. As the concentration of electrolyte in the aqueous phase increases, both the concentration of water in the ethereal phase and the activity of water in the aqueous phase decrease. Additional assumptions are necessary, however, before these concentrations can be quantitatively related.

$HClO_4$ and HNO_3 behave differently than LiCl, HCl, HBr, or H_2SO_4 (see Figure 1). This behavior is not due to oxidation of the Karl Fischer reagent by these oxidants because the Fischer titration of methanolic HNO_3 and $HClO_4$ solutions of known water content gave correct results within experimental error (approximately 3%), and the direct Fischer titration is a standard method for determining the water content of concentrated HNO_3 (*3*, p. 245). Although the activity of water in solutions of $HClO_4$ decreases more or less linearly with increasing electrolyte concentration, the solubility of water in the ethereal phase in equilibrium with aqueous solutions of this electrolyte starts to decrease as in the cases of LiCl, HCl, or HBr; but by 2.0*M* $HClO_4$, deviation is apparent, and by 4.0*M* $HClO_4$, the solubility has started to increase. The effect is more marked in the case of HNO_3. These effects cannot be attributed to the water activity for the activity of water in $HClO_4$ solutions shows no hint of a parallel variation, and they cannot be attributed to large oxy-anions for H_2SO_4 solutions fail to exhibit them. The relative acid strengths in the organic solvent may, however, provide an explanation. HCl and HBr are relatively weak acids in the ether (*2*). The extractability of the mineral acids in the present experiments

$$HNO_3 > HClO_4 \gg HBr, HCl, H_2SO_4$$

agrees with the predictions of Diamond and Tuck (*1*) based on considerations of acid strength, molecular size, and solvation. They point out that $HClO_4$, and especially HNO_3, extract in basic organic solvents better than hydrohalic acids and that H_2SO_4 does not extract at all. HNO_3 forms a hydrogen-bonded complex with diethyl ether

$$HNO_3 + (C_2H_5)_2O \rightleftarrows (C_2H_5)_2O \cdot HNO_3 \qquad (1)$$

Table I. Variation of the Solubility of Water in Bis(2-Chloroethyl) Ether with Temperature

	Equilibrium Concentration of Water in Ether	
Temp., ° C.	Moles water/liter ethereal phase	Weight, %
0.0	0.18	0.27 ± 0.02
25	0.32	0.45 ± 0.03
55	0.50	0.73 ± 0.01

The solubility of water in the ethereal phase in the presence of $HClO_4$ and HNO_3 parallels the solubilities of these acids in the ethereal phase based on data (dashed curves in Figure 1) of Rudzitis (*7*). The order of solubility of the acids in the ether is $HNO_3 > HClO_4 > HBr > HCl > H_2SO_4$ (*6*). Apparently the acids go into the ethereal phase accompanied by a certain amount of water. The number of water molecules thus transported may be estimated from the relation

$$\text{Solvation number} = [(S_w)_{HClO_4 \text{ or } HNO_3} - (S_w)_{HCl}]/S_a \qquad (2)$$

where $(S_w)_{HClO_4 \text{ or } HNO_3}$ is the solubility of water in the ethereal phase in the presence of $HClO_4$ or HNO_3, $(S_w)_{HCl}$ in the presence of HCl, and S_a is the solubility of $HClO_4$ or HNO_3 in the ethereal phase at the same acid concentrations. The value thus obtained range from 1.7 to 1.0 molecules of water per molecule of HNO_3 over the range 2.0 to 7.0*M* HNO_3 and 4.2 to 1.3 molecules of water per molecule of $HClO_4$ over the range 4.0 to 7.0*M* $HClO_4$. These values, while variable, are nevertheless in semi-quantitative agreement with the conclusion of Tuck and Diamond (*9*) that HNO_3 extracts with one water into organic solvents and $HClO_4$ with four.

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