BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (6), 1799—1801 (1979)

Solvent Extraction Equilibria of Acids. VII. The Co-extraction of Water with Strong Mineral Acids by Trioctylphosphine Oxide

Masaru NIITSU,* Nobuhiko IRITANI, and Tatsuya SEKINE†

Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02

†*Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162*

(Received October 27, 1978)

The extraction of water from a 1 mol dm^{-3} sodium perchlorate solution with trioctylphosphine oxide (TOPO) in four organic solvents and the co-extraction of water with hydrochloric, hydrobromic, hydroiodic, perchloric, nitric, and thiocyanic acids from 1 mol dm^{-3} of the acid solution by TOPO in hexane have been studied at 25 °C. The extraction constants of water in the absence of any of the acids, $K'_{H_2O}=[TOPO\cdot H_2O]_{org}[TOPO]_{org}^{-1}$, were determined to be $10^{0.40}$, $10^{0.00}$, $10^{-0.12}$, and $10^{-0.36}$ in benzene, hexane, carbon tetrachloride, and chloroform respectively. A discrepancy from the 1: 1 molar ratio of TOPO and water in the extract was observed in the higher-TOPO-concentration region in the hexane system. The co-extraction of water with the acids disolvated by TOPO was greater in the order of $HCl \simeq HBr > HI > HClO_4$, and it was much poorer with the monosolvated acids, nitric and thiocyanic acid. The equilibria for these co-extractions of water with the acids are complicated.

The co-extraction of water with various acids by oxygen-containing solvents has been studied with ethers, ketones, alcohols, and tributyl phosphate.[1,2] The extraction of acids and the co-extraction of water with the acids into various organic diluents containing trioctylphosphine oxide (TOPO) have also been studied, and the equilibria have been considered from several standpoints.[3-8]

After a series on the extraction equilibria of several acids with TOPO,[9-14] the present authors have studied the co-extraction of water with some of these acids. The present paper will describe the experimental results and will discuss the equilibria of these co-extractions.

Experimental

All of the experiments were carried out in a thermostatted room at 25 °C in a manner essentially similar to that described previously.[9-14] A portion of a 1 mol dm^{-3} aqueous electrolyte solution and the same volume of an organic solution were placed in a stoppered glass tube, and the contents were vigorously agitated and centrifuged. The concentration of water in the organic phase was determined by the Karl Fischer method.

Statistical

In the present paper, HX and E denote an acid and TOPO, and the subscript "org" denotes chemical species in the organic phase.

In the absence of any acid, the extraction equilibrium of water with TOPO may be written by the following equations, on the basis of the results to be presented later:

$$E(org) + H_2O \rightleftarrows E\cdot H_2O(org) \quad (1)$$

$$K'_{H_2O} = [E\cdot H_2O]_{org}[E]_{org}^{-1} \quad (2)$$

The concentration of water in the organic phase is written as

$$[H_2O]_{org,total} = [H_2O]_{org,blank} + [H_2O]_{org,E} \quad (3)$$

where $[H_2O]_{org,blank}$ and $[H_2O]_{org,E}$ are the concentrations of free water in the diluent and of bound water with TOPO respectively.

In the presence of an acid, the concentration of water in the organic phase may be written as

$$[H_2O]_{org,total} = [H_2O]_{org,blank} + [H_2O]_{org,E} + [H_2O]_{org,HX} \quad (4)$$

where $[H_2O]_{org,HX}$ is the concentration of the water co-extracted with the acid. Since the extraction of the acids in the absence of TOPO is negligible, the concentration of the extractant may be written as

$$[E]_{org,total} - a[H^+]_{org} = [E]_{org} + [E\cdot H_2O]_{org} \quad (5)$$

where $[H^+]_{org}$ is the concentration of the acid in the organic phase and where a is the mole of TOPO combined with one mole of the acid. As has been described previously,[9,10,13] the value for this a is two for hydrochloric, hydrobromic, hydroiodic, and perchloric acid, while it is one for nitric and thiocyanic acid.

The concentration of the acid-free TOPO, that is, TOPO combined with no acid, can be calculated by means of Eq. 5, and the amount of water combined with the acid-free TOPO, $[H_2O]_{org,E}$, can be calculated from the calibration curves, log $[H_2O]_{org,E}$ *vs.* log $[E]_{org,total}$. Finally, the concentration of the water co-extracted with the acid can be calculated by introducing this calculated value of $[H_2O]_{org,E}$ and the experimentally obtained value of $[H_2O]_{org,blank}$ into Eq. 4.

Results

The concentrations of water in the organic solvents containing no TOPO and being equilibrated with an aqueous 1 mol dm^{-3} sodium perchlorate solution are listed in Table 1. The amounts of water in the organic phases containing TOPO and being equilibrated with this aqueous solution (thus, no extraction of any acid

TABLE 1. THE VALUES OF THE EXTRACTION CONSTANT IN Eq. 2 AND THOSE OF THE WATER CONCENTRATION DISSOLVED BY THE DILUENT AT EQUILIBRIUM

	log $[H_2O]_{org,blank}$	log K'_{H_2O}
Benzene	−1.45	0.40
Hexane	−2.39	0.00
Carbon tetrachloride	−2.02	−0.12
Chloroform	−1.14	−0.36

Org. phase: diluent containing TOPO. Aq. phase: 1 mol dm^{-3} sodium perchlorate solution.

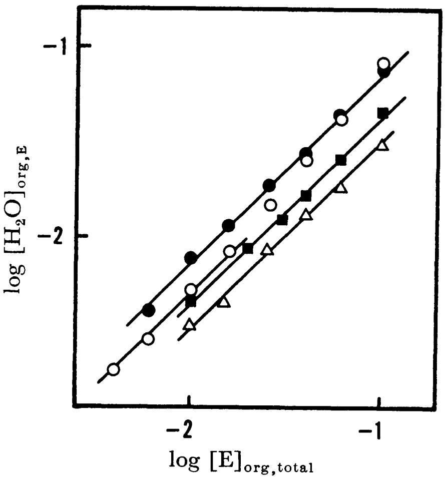

Fig. 1. Variation of water content of the organic phase with total TOPO concentration in benzene (●), hexane (○), carbon tetrachloride (■), or chloroform (△), after correction for the dissolved water by the diluent. The straight lines are slope of +1. The aqueous phase was 1 mol dm^{-3} sodium perchlorate solution.

was expected) were also determined; the $[H_2O]_{org,E}$ values were calculated by means of Eq. 3. Figure 1 shows these calculated values as a function of the total TOPO concentration in the organic phase. The values of K'_{H_2O} were calculated from these data by using Eq. 2; they are listed in Table 1. (For the calculation of the value in the hexane system, only those data which fitted with the straight line of a slope one were employed).

The co-extraction of water with mineral acids by TOPO was studied only when the diluent was hexane. The concentration of the co-extracted water with the acid by TOPO was calculated by means of Eq. 4.

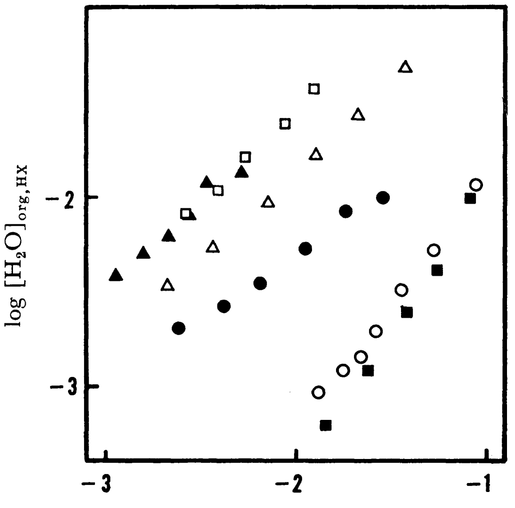

Fig. 2. Co-extracted water with hydrochloric (▲), hydrobromic (□), hydroiodic (△), perchloric (●), nitric (○), or thiocyanic (■) acid-TOPO complex in the hexane phase containing various amount of TOPO, where the aqueous phase for thiocyanic acid system was 0.9 mol dm^{-3} hydrochloric acid and 0.1 mol dm^{-3} sodium thiocyanate, and that for others was 1 mol dm^{-3} only the acid.

Figure 2 shows the values as a function of the concentration of the extracted acid in the organic phase. In these experiments, the aqueous phase was a solution of the acid at 1 mol dm^{-3} except in the thiocyanic acid system; in this case, the aqueous phase contained 0.9 mol dm^{-3} of hydrochloric acid and 0.1 mol dm^{-3} of sodium thiocyanate, and the calculation was made by assuming that the extraction of the hydrochloric acid was negligible compared to that of the thiocyanic acid (*cf.* Refs. 10 and 13).

It is anticipated that the error in the water co-extracted with hydrochloric acid is greater than that co-extracted with the other acids, because its extraction with TOPO was poor, and so much smaller amounts of co-extracted water had to be determined.

Another series of experiments on the co-extraction of water were also made by keeping the TOPO concentration at 0.04 mol dm^{-3}, while changing the hydrogen-ion concentration in the 1 mol dm^{-3} $(H,Na)ClO_4$ or 1 mol dm^{-3} $(H,Na)NO_3$ ionic media. The log $[H_2O]_{org,HX}$ *vs.* log $[H^+]_{org}$ plots obtained from these data were found to overlap approximately with those shown in Fig. 2.

Discussion

The above results may be summarized as follows.

i) TOPO in benzene, carbon tetrachloride, and chloroform, and that in hexane at its low concentrations (below 0.02 mol dm^{-3}), extract water from a 1 mol dm^{-3} sodium perchlorate solution as a 1 : 1 species, TOPO·H_2O. The mole fractions of the TOPO·H_2O species relative to the total TOPO are 0.72, 0.50, 0.43, and 0.30 in benzene, hexane, carbon tetrachloride, and chloroform respectively. Thus, the TOPO is not completely hydrated. In hexane, a discrepancy from the 1 : 1 mole ratio in the extract was observed when the TOPO concentration was higher.

ii) The amount of water co-extracted into hexane with the three hydrohalogenic acids was proportional to the amount of acid extracted. One mole of hydrochloric and hydrobromic acid in hexane which is combined with two moles of TOPO[10,13] co-extracted approximately three moles of water, but one mole of hydroiodic acid which is also combined with two moles of TOPO[13] co-extracted only approximately 1.3 moles of water.

iii) One mole of perchloric acid which is combined with two moles of TOPO in hexane[9] co-extracts less than one mole of water, and the amounts of water co-extracted per mole of the acid decrease with an increase in the acid concentration.

iv) The co-extractions of water with nitric and with thiocyanic acid, each of which is combined with one mole of TOPO in hexane,[9,13] are approximately the same as each other, and much less than with the other acids; only about one-tenth mole of water is co-extracted with one mole of each of the acids, but the mole ratio of water and acid slightly increases with an increase in the acid concentration.

The extraction of water in the absence of acid in the present work is similar to that in the previous reports;[3–5] moreover, the present results when the solvent is hexane are similar to those when the solvent was cyclohexane or isooctane in the previous reports.

Attempts were made to find species other than $TOPO \cdot H_2O$ in the hexane system in the higher TOPO concentrations by statistical treatments of the data, but they were not successful. Thus, the present authors can not conclude whether the discrepancy from unity of the slope of the plot in Fig. 1 is due to the formation of higher aggregates such as $(TOPO)_b(H_2O)_c$ (where b/c is lower than unity) or is due to changes in the chemical activities of the solutes. The same kind of discrepancy found in the previous work was explained in terms of the formation of a species, $(TOPO)_3(H_2O)_4$.[15]

It is noticeable that, although a 1:1 species of TOPO and water is formed in the organic phase, still a certain fraction of TOPO, sometimes more than a half of the total TOPO, is in the unhydrous state. Although the salt in the aqueous phase may affect the extraction of water, this can not be explained by the decrease in the water activity because the water activity in a 1 mol dm^{-3} sodium perchlorate solution is about 0.96; thus, the change is not serious.[16]

As may be seen from Fig. 2, the co-extraction of water was proportional to the extraction of the acid when it was a hydrogen halogenide. However, the slope of the $\log [H_2O]_{org,HX}$ *vs.* $\log [H^+]_{org}$ plot was somewhat lower than unity when the acid was perchloric acid and higher than unity when the acid was nitric or thiocyanic acid (in the latter cases, the slopes were about 1.5). It is difficult to give an explanation of these values of the slope of the $\log [H_2O]_{org,HX}$ *vs.* $\log [H^+]_{org}$ plot or of the observation that the molar ratio of the extracted acid and the co-extracted water is quite different when the acid is different. Furthermore, these results can not explain why certain monoprotonic acids are extracted with two molecules of TOPO in the organic phase.

As was previously reported,[9,10,13] only perchloric and the three hydrohalogenic acids among the monoprotonic inorganic acids we have studied were disolvated with TOPO in hexane. One of the explanations for this disolvation to one proton may be that the proton in the extract is in the oxonium-ion form; two of the hydrogens are combined with the phosphoryl oxygen of TOPO, and the last hydrogen is combined with the anion. However, this does not explain the finding that the average composition of the extract was $(TOPO)_2(HClO_4)(H_2O)_d$, where d is a number decreased by an increase in the acid concentration in the organic phase and always lower than unity. Moreover, for the three extracted hydrohalogenic acid species, whose average compositions were $(TOPO)_2(HX)(H_2O)_e$, where e was about 1.3 for hydroiodic acid and about 3 for the other two acids, we should consider that a certain proportion of co-extracted water was in a form other than the oxonium-ion form.

Diamond and his coworkers studied the co-extraction of water with hydrochloric, hydrobromic, perchloric, perrhenic, and tetrachloroauric acid by TOPO in various solvents and reported a tendency similar to that shown by the present results.[3-6] Since less than one mole of water was co-extracted with one mole of the perchloric, perrhenic, and tetrachloroauric acid which were disolvated with TOPO, they concluded that the proton combined with the TOPO molecules was not a oxonium-ion, but was unhydrous, and that the anion which was assumed to combine with the proton as an ion pair was responsible for the co-extraction of water.

However, when the water is assumed to be co-extracted only by an "ion-paired" anion, the very poor co-extraction of water with nitric and thiocyanic acid can not be explained; a nitrate ion should interact with water molecules more strongly than a perchlorate ion.

It is noticeable that the two monoprotonic acids which co-extracted water only poorly were monosolvated by TOPO in the organic phase, while the other monoprotonic acids, which co-extracted greater amounts of water than nitric and thiocyanic acid, were disolvated. It is also marked that these monosolvated acids were weaker acids than the disolvated ones. These facts seem to lead us to other kinds of explanations. For example, none of the anions of the monosolvated acids are in the form of an ion pair in the organic phase; they all interact with the proton more strongly, and thus are less available for the water molecules than the ion-paired anion, and/or each of the two phosphoryl oxygens of TOPO in the disolvated acid species interact with the proton less strongly than that in the monosolvated acid species, thus becoming more available for hydration. However, since spectroscopic measurements have not been made, no final conclusion can be reached on the basis of only the results in the present study.

References

1) Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, New York (1969).

2) T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry," Marcel Dekker, New York (1977).

3) T. J. Conocchioli, M. I. Tocher, and R. M. Diamond, *J. Phys. Chem.*, **69**, 1106 (1965).

4) J. J. Bucher, M. Zirin, R. C. Laugen, and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **33**, 3869 (1971).

5) J. J. Bucher and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **34**, 3531 (1972).

6) J. A. Labinger, B. A. Sudbury, and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **37**, 221 (1975).

7) M. Senegacnik, C. Klofutar, S. Paljk, and L. Smrekar, *J. Inorg. Nucl. Chem.*, **32**, 1659 (1970).

8) A. I. Mikhailichenko, *Radiokhimiya*, **12**, 594 (1970).

9) M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **37**, 1054 (1975).

10) M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **38**, 1053 (1976).

11) M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **38**, 1057 (1976).

12) T. Sekine, Y. Zeniya, and M. Niitsu, *Bull. Chem. Soc. Jpn.*, **49**, 2629 (1976).

13) M. Niitsu and T. Sekine, *Bull. Chem. Soc. Jpn.*, **50**, 1015 (1977).

14) M. Niitsu and T. Sekine, *Bull. Chem. Soc. Jpn.*, **51**, 705 (1978).

15) M. A. Lodhi, P. R. Danesi, and G. Scibona, *J. Inorg. Nucl. Chem.*, **33**, 1889 (1971).

16) Y. Hasegawa, *Bull. Chem. Soc. Jpn.*, **42**, 1429 (1969).