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The Extraction of Water and Nitric Acid by Mixtures of Trilaurylamine and Octanol in Alifatic Hydrocarbons

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Mixtures of trilaurylamine and octanol are found to extract nitric acid and water nearly independently of each other. Preliminary emf-titrations on such mixtures indicate interaction between the two components probably by formation of mixed aggregates since the amine-nitric acid complex has been found to form large aggregates. The results may thus be due to the possibility that the components in the aggregates form nearly ideal mixtures.

Some years ago Sillén *et al.*[1] found that micelles containing an acid such as lauric acid and its potassium salt or a base such as dodecylamine and its acid form have an apparent pK_a independent of the total concentration, which means that they can be treated as ideal mixtures of the two components. Recently, the components in a nonaqueous micelle-forming system have been found to behave in a similar way. The system under consideration is the extraction of nitric acid and water into mixtures of trilaurylamine ($(C_{12}H_{25})_3N$), TLA, and octanol dissolved in octane or dodecane.

A preliminary report of the work described below was given at the Seventh International Conference on Coordination Chemistry (7 ICCC).[2]

THE EXTRACTION OF NITRIC ACID

In Fig. 1 the number of moles of nitric acid extracted per mole of TLA ($Z_{HNO_3,TLA}$) is plotted against the equilibrium molarity of nitric acid in the aqueous phase, C_{HNO_3}, for 0.10 M TLA alone or together with three different concentrations of octanol in octane. From Fig. 1 it is seen that the extraction of nitric acid is enhanced in the presence of alcohol. This indicates that not only the amine but also the alcohol extracts nitric acid, probably by formation of complexes with the acid. This is further illustrated in Fig. 2 where the number of moles of nitric acid extracted per mole of alcohol ($Z_{HNO_3,alc}$) is plotted against C_{HNO_3} for two concentrations of octanol in dodecane and four in octane.

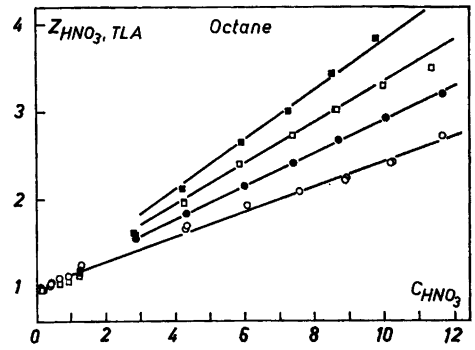

Fig. 1. $Z_{HNO_3, TLA}$ plotted against C_{HNO_3} for 0.101 M TLA and three different concentrations of octanol in octane. ○ 0.101 M TLA; ● 0.101 M TLA + 0.100 M octanol; □ 0.101 M TLA + 0.200 M octanol; ■ 0.101 M TLA + 0.301 M octanol.

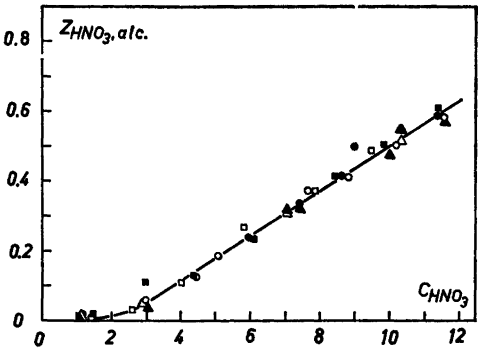

Fig. 2. $Z_{HNO_3, alc}$ plotted against C_{HNO_3} for two concentrations of octanol in dodecane and four in octane. △ 0.150 M octanol in dodecane; ▲ 0.450 M octanol in dodecane; ○ 0.300 M octanol in octane; ● 0.600 M octanol in octane; □ 0.628 M octanol in octane; ■ 0.900 M octanol in octane.

We shall now assume that *amine and alcohol extract nitric acid independently of each other*. With the aid of the curve in Fig. 2 the amount of nitric acid extracted by the alcohol in an amine-alcohol mixture at a certain C_{HNO_3} can then be computed from

$$[HNO_3]_{alc} = Z_{HNO_3, alc}[n\text{-}C_8H_{17}OH] \quad (1)$$

This amount is subtracted from the total concentration of nitric acid in the organic phase and a corrected value for the amount extracted per amine, $Z'_{HNO_3, TLA}$ can be computed from

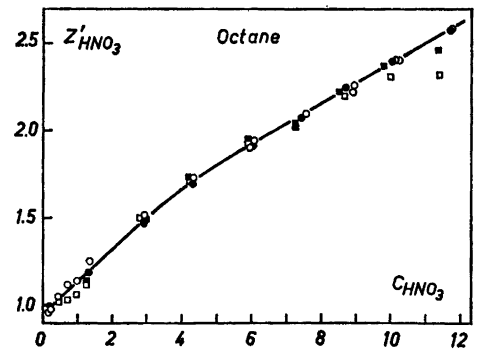

Fig. 3. $Z'_{HNO_3, TLA}$ plotted against C_{HNO_3} for 0.101 M TLA and three different concentrations of octanol in octane (*cf.* Fig. 1). ○ 0.101 M TLA; ● 0.101 M TLA + 0.100 M octanol; □ 0.101 M TLA + 0.200 M octanol; ■ 0.101 M TLA + 0.301 M octanol.

$$Z'_{HNO_3,\,TLA}=([HNO_3]_{org}-[HNO_3]_{alc})/[TLA] \quad (2)$$

In Fig. 3 $Z'_{HNO_3,\,TLA}$ is plotted against C_{HNO_3} for the data in Fig. 1. From Fig. 3 it is seen that practically all data fall on a single curve. This indicates that the above assumption is a useful one and that the amount of nitric acid extracted by the amine-alcohol mixtures can be predicted with reasonable accuracy from knowledge of the amounts extracted by the two components.

THE EXTRACTION OF WATER

We want now to investigate if the water is also extracted independently by the two components. In Fig. 4 the equilibrium molarity of water in the

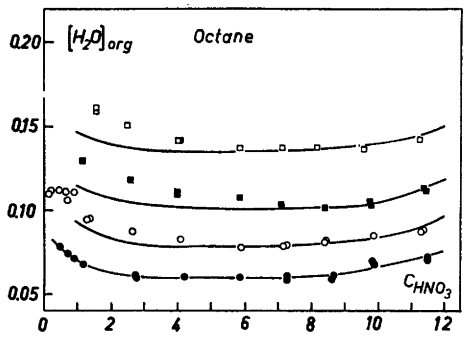

Fig. 4. $[H_2O]_{org}$ plotted against C_{HNO_3} for 0.205 M TLA and three different concentrations of octanol in octane. ● 0.205 M TLA; ○ 0.205 M TLA + 0.200 M octanol; ■ 0.205 M TLA + 0.401 M octanol; □ 0.205 M TLA + 0.609 M octanol.

organic phase is plotted against C_{HNO_3} for 0.2 M TLA and three concentrations of octanol in octane. Nearly parallel curves are obtained indicating that the amount of water due to the alcohol does not vary with C_{HNO_3}. Experiments with various concentrations of octanol in octane and dodecane indicate that the amount of water extracted is practically independent of C_{HNO_3}, although a slight increase was observed for the highest octanol concentrations studied. Disregarding this variation, the average for the number of moles of water extracted per mole of octanol, ($Z_{H_2O,alc}$) at each octanol concentration has been evaluated and in Fig. 5 this average is plotted against the total concentration

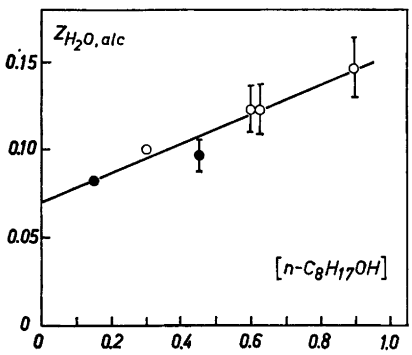

Fig. 5. The average value of $Z_{H_2O,alc}$ for each octanol concentration plotted against the total concentration of octanol, [n-$C_8H_{17}OH$], for two concentrations in dodecane and four in octane. ○ octane; ● dodecane. The spread in each average is also indicated.

of alcohol, [n-$C_8H_{17}OH$]. A spread, principally due to the fact that $Z_{H_2O,alc}$ increases slightly with increasing C_{HNO_3}, is indicated. A straight line has been fitted to the data. With the aid of this line, the water extracted by the alcohol at a certain concentration of octanol has been estimated and added to the amount of water extracted by the octanol-free amine. In this manner the curves in Fig. 4 were obtained. From Fig. 4 it is seen that the predicted values agree well with the experimental values, with the exception of the range, $C_{HNO_3} < 4$ M, where the mixtures seem to extract more water than predicted from the behavior of the two components.

DISCUSSION

It has been found that both nitric acid and water are extracted by amine and alcohol practically independently of each other.

It is known that the amine-nitric acid complex forms large aggregates of the 1:1 composition.[3] It remains to investigate the role played by the alcohol. In Fig. 6 $Z_{HNO_3,TLA}$ is plotted against $-\log [H^+] \cdot [NO_3^-]$ for 0.1 M TLA in octane alone and together with either 0.1 M or 0.3 M octanol. The results in Fig. 6 were obtained by two-phase emf-titrations with the ionic medium

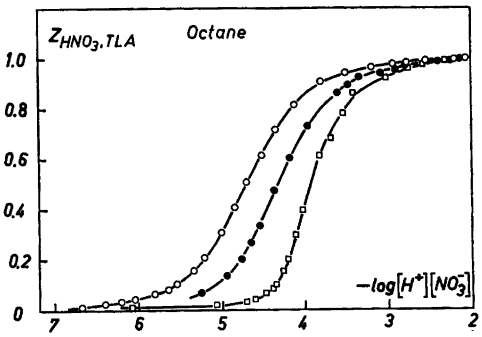

Fig. 6. $Z_{HNO_3,TLA}$ plotted against $-\log[H^+] \cdot [NO_3^-]$ for 0.1 M TLA and two concentrations of octanol in octane. The ionic medium in the aqueous phase was 1.00 M (Na^+, H^+)NO_3^-; t = 25°C. □ 0.100 M TLA; ● 0.101 M TLA + 0.100 M octanol; ○ 0.101 M TLA + 0.301 M octanol.

1 M (Na^+, H^+)NO_3^- in the aqueous phase. This technique has recently been discussed elsewhere.[4] Emf-titrations on the alcohol alone dissolved in octane showed that no acid is extracted by octanol in the range of acidity covered in Fig. 6; higher nitric acid activities are required (*cf.* Fig. 2). From Fig. 6 it is seen that the curves $Z_{HNO_3,TLA}$ ($-\log[H^+] \cdot [NO_3^-]$) are displaced towards lower values for $[H^+] \cdot [NO_3^-]$ with increasing concentration of alcohol. The large displacements indicate that the alcohol must interact with the amine, probably by participating in the formation of the aggregates. When a sufficient body of experimental data has been assembled it is hoped that the nature of these mixed aggregates can be elucidated. The experience that the amine and the alcohol extract nitric acid and water practically independently of each other may be due to the possibility that the components of the micelles form nearly ideal mixtures.

A detailed account of this work is published elsewhere.[5]

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REFERENCES

1. Seim, J., Sillén, L. G. and Ulfvarson, U. *Acta Chem. Scand.* **10** (1956) 683.
2. *Proc. 7th Intern. Conf. Coordination Chem.* Stockholm and Uppsala, Sweden, June 25–29, 1962; Högfeldt, E., Bolander, B. and Fredlund, F. *Paper 7 M 4*, p. 371.
3. Högfeldt, E. and Fredlund, F. *Acta Chem. Scand.* **18** (1964) 543,
4. Högfeldt, E. and Fredlund, F. *Trans. Roy. Inst. Technol. Stockholm.* No. 226 (1964).
5. Högfeldt, E. and Bolander, B. *Trans. Roy. Inst. Technol. Stockholm.* No. 224 (1964).

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