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# A NEW METHOD ON THE DETERMINATION OF HEAT CHANGE IN SOLVENT EXTRACTION OF METALS. THE EXTRACTION OF ZINC(II) FROM HYDROCHLORIC ACID SOLUTIONS BY TRIOCTYLMETHYLAMMONIUM CHLORIDE

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To measure directly the heat change associated with the extraction of zinc(II) from hydrochloric acid solutions by trioctylmethylammonium chloride (TOMAC) in benzene has been succeeded by using twin type isoperibol calorimeter. It is proved that the heat change depends on the concentration of acid in aqueous phase.

Most argument on the thermodynamics in solvent extraction has been based on the thermodynamic value estimated by the use of van't Hoff plot.[1)] Little attention has been given to measure directly the heat change associated with metal extraction. Lately we have delved into detecting the heat change using an isoperibol calorimeter. This paper is concerned with the results obtained for the extraction of zinc(II) from hydrochloric acid solutions by trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in benzene whose equilibrium is expressed as

$$ZnCl_4^{2-}(aq) + 2R_3R'NCl(org) \rightleftharpoons (R_3R'N)_2ZnCl_4(org) + 2Cl^-(aq) \qquad (1)$$

TOMAC (>99 %, Koei Chemical Co., Ltd.) used without further purification was diluted with benzene. Aqueous zinc chloride solution was prepared by dissolving zinc chloride in hydrochloric acid of selected concentration. The change in temperature during the complete extraction of zinc was measured at 25 °C using twin type isoperibol calorimeter TIC-22I (Tokyo Riko Co., Ltd.) equipped with integrator: Mixed solutions of 0.05 mol $dm^{-3}$ TOMAC in benzene (70 $cm^3$) and hydrochloric acid (15 $cm^3$) were introduced into sample reaction vessel, while the same volumes of benzene and hydrochloric acid solution into reference reaction vessel. Zinc chloride solution (4 $cm^3$ each) containing hydrochloric acid was placed in both vessels in separate from the mixed solutions. At a quasi-adiabatic state the extraction of zinc was carried out by contacting zinc chloride solution with mixed solutions. Under the condition described above, it was confirmed that the heat arising from the dilution of zinc chloride and from a slight difference in the concentration of acid between the aqueous solutions of zinc chloride and hydrochloric acid was compensated experimentally. Moreover preliminary experiments affirmed that large endotherm due to the vaporization of water interfered the measurements, when no hydrochloric acid solution was in the vessels.

The observed heat change $\Delta q_{obs}$ rises linearly with increasing the reacted zinc concentration ($[Zn]_{react}$) at a constant acid concentration, as shown in Fig.1 exhibiting representative result at $[HCl]_{init\ aq}$ = 2 mol $dm^{-3}$. The straight line

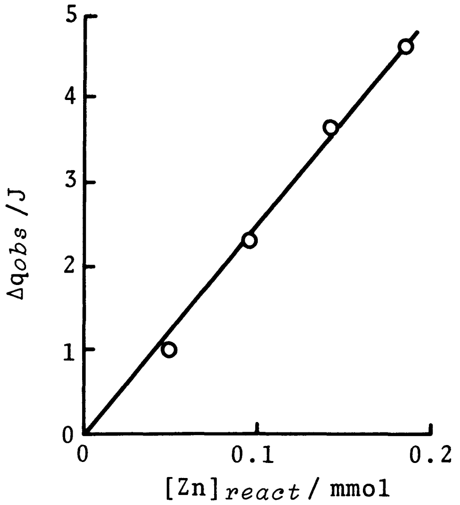

Fig. A plot of $\Delta q_{obs}$ vs. $[Zn]_{react}$. [TOMAC] = 0.05 mol dm$^{-3}$, $[HCl]_{init\ aq}$ = 2 mol dm$^{-3}$

Table 1 Calorimetric data for the extraction of zinc(II)* from hydrochloric acid solutions by 0.05 mol dm$^{-3}$ TOMAC in benzene

| $[HCl]_{init\ aq}$ mol dm$^{-3}$ | $\Delta q_{obs}$ mJ | $\Delta Q$ kJ mol$^{-1}$ |
|---|---|---|
| 0.1 | -381 | -1.99 |
| 0.2 | 120 | 0.59 |
| 0.5 | 639 | 3.34 |
| 0.7 | 1160 | 6.17 |
| 1 | 2290 | 11.3 |
| 2 | 4600 | 24.9 |
| 3 | 4750 | 24.3 |
| 5 | 3670 | 19.1 |
| 7 | 1780 | 9.41 |

* Reacted Zn(II) concn. is about 0.2 mmol.

intercepts at the origin of coordinate within the limits of experimental error. On the other hand, apparent molar heat change for zinc $\Delta Q$ (defined as $\Delta q_{obs}/[Zn]_{react}$) depends on the concentration of acid in aqueous phase (Table 1): The heat change associated with zinc extraction at $[HCl]_{init\ aq}$ = 0.1 mol dm$^{-3}$ is endothermic, while that at $[HCl]_{init\ aq}$ > 0.2 mol dm$^{-3}$ is exothermic in accordance with the results estimated from the temperature-dependence on distribution coefficient for zinc.$^{1)}$

As the analytical signal in this system is composed of the total heat change caused by some simultaneous reactions in addition to the reaction (1), the observed heat change includes the heat change produced by some incidental reactions which are attributed to the existence of a few aqueous chloro complexes of zinc(II) different from the species $ZnCl_4^{2-}$. This suggests that a linear relationship between the heat change and the reacted zinc concentration should be held at a constant hydrochloric acid concentration in aqueous phase, although the apparent molar heat change varies with hydrochloric acid concentration. The obtained results (Fig.1 and Table 1) satisfy this expectation, confirming that the present method can be applied to measure the total heat change associated with metal extraction. As the apparent molar heat change shows a maximum endotherm at $[HCl]_{init\ aq}$ of 2-3 mol dm$^{-3}$ where the distribution isotherm of zinc exhibits a maximum,$^{2)}$ it appears that the observed heat change is governed by the heat change of the reactions in which the species $ZnCl_2$ participates in aqueous phase. Considering the items mentioned above, numerical estimation of the heat of reaction in Eqn.(1) is now in progress, on the basis of the data given in Table 1.

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References

1) E.g., T.Sato, T.Nakamura and T.Fujimatsu, Bull.Chem.Soc.Jpn.,54,2656(1981).
2) T.Sato and S.Murakami, Anal.Chim.Acta,82,217(1976).

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