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DETERMINATION OF THE HEAT CHANGE IN THE EXTRACTION OF DIVALENT COPPER, ZINC AND CADMIUM FROM HYDROCHLORIC ACID SOLUTIONS BY TRIOCTYLMETHYLAMMONIUM CHLORIDE IN VARIOUS ORGANIC SOLVENTS

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ABSTRACT

In the extraction of divalent Cu, Zn and Cd from HCl solutions by trioctylmethylammonium chloride in various organic solvents, the heat change associated with the uptake of metal has been examined by using a twin type isoperibol calorimeter. As a result, it is found that the heat change detected is interpreted as the summation over the change in enthalpies for the relevant steps to the extraction, taking the change in enthalpy obtained from the temperature-dependence of the distribution coefficient into account, and that the distribution of metal between aqueous and organic phases can be explained by assuming a regular solution.

INTRODUCTION

In previous papers (1), dependency of the distribution coefficient and the change in enthalpy estimated from the distribution data by the use of van't Hoff plot on solubility parameter of diluent has been investigated for the extraction of divalent metals from HCl solutions by trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in various diluents. With regard to application of titration-calorimetry to solvent extraction, there are only a few papers. This work is, therefore, undertaken by calorimetry to elecidate further the diluent effect in the extraction of Cu(II), Zn(II) and Cd(II) from HCl solutions by TOMAC.

EXPERIMENTAL

Reagents The high purity TOMAC (> 99 %, Koei Chemical Co., Ltd.) was used without further purification and diluted with the various organic solvents such as C_6H_6, C_6H_5Cl, *o*-$C_6H_4Cl_2$, $C_6H_5CH_3$, *m*-$C_6H_4(CH_3)_2$, $C_6H_5NO_2$, CCl_4 and *1,2*-$C_2H_4Cl_2$. The concentration of TOMAC was determined by Volhard's method. Aqueous solutions of divalent metals were prepared by dissolving their chlorides ($CuCl_2 \cdot 2H_2O$, $ZnCl_2$ and $CdCl_2 \cdot 2.5H_2O$) at 0.1, 0.05 and 0.05 M, respectively, in HCl of the selected concentration. Other chemicals used were of analytical reagent grade.

Extraction and Analytical Procedures The distribution coefficient was obtained as described previously (2). The concentration of metal in aqueous solution was determined by EDTA titration using XO for Cu and Zn and Cu-PAN for Cd as indicator (3,4).

Calorimetric Measurement The heat change associated with the complete extraction of metal was measured at 25 °C using twin type isoperibol calorimeter, TIC-22I (Tokyo Riko Co., Ltd.), designated to have high sensitive thermistors (0.067 °C/mV) and a very rapid response, and equipped with integrator (7).

RESULTS AND DISCUSSION

In the extraction of Zn(II) of 0.0125-0.05 M from HCl solutions with 0.05 M TOMAC in benzene, it is found that the observed heat change varies with the concentration of acid in aqueous phase in spite of almost the same amount of Zn extracted into organic phase: The heat change is endothermic at 0.1 M HCl, while exothermic at above 2 M HCl. In the latter concentration range of HCl, the heat change increases exothermally with increasing aqueous [HCl] to a maximum which occurs at 2-3 M HCl, and then falls again. This phenomenon is more clarified by the plot of the apparent molar heat change (the value of the change in heat obtained with regard to the concentration of zinc reacted, ΔQ) against initial aqueous [HCl]. Similar trend is also observed in the case of other diluents used. In the extraction from mixed solutions of 0.01 M HCl and LiCl with 0.05 M TOMAC in benzene, ΔQ increases exothermally with increasing aqueous [Cl]. Its behaviour follows closely the heat change for the extraction from HCl solutions in the absence of LiCl, although no maximum is given in the range of [Cl] up to 4 M. It is thus noticed that up to 2 M HCl the increase in ΔQ depends on the aqueous [Cl], suggesting that the distribution of the species $ZnCl_j^{(2-j)+}$ in aqueous phase affects the heat change associated with Zn(II) extraction. At higher [HCl] above 2 M, the decrease in ΔQ arises from the formation of the species such as $R_3R'NCl \cdot HCl$ (5) in organic phase. This is proved by the fact that the molar ratios $[HCl]_{org}/[R_3R'NCl]_{org}$ at 0.5, 1, 2, 3, 5 and 7 M in equilibrated organic phase are found to be 0.038, 0.080, 0.16, 0.28, 0.69 and 1.6, respectively.

Change in enthalpy for stepwise formation of the species $ZnCl^+$, $ZnCl_2$ and $ZnCl_3^-$ in aqueous phase at $\mu = 3.0$ ((Na,H)Cl + $NaClO_4$) has been estimated to 5.44, 37.1 and 0 kJ M^{-1}, respectively, at 25 °C (7). Taking into consideration of these results and stability constants for $ZnCl_j^{(2-j)+}$ in aqueous phase (4,8,9) it is evident that the apparent molar heat change varies with aqueous [Cl]. Accordingly the hypothetical steps which contain the reactions in aqueous phase should be considered for the theoretical estimation of ΔQ associated with Zn(II) extraction by TOMAC in various diluents. These hypothetical steps provide the relation

$$\Delta Q = -(1/n_t)\sum_{j=0}^{3} n_j\ h_j - Y \qquad (1)$$

where $Y = f_d + \text{const}$ in the term f_d depending on the kind of diluent, Δn_j and n_t are initial concentration of the species $ZnCl_j^{(2-j)+}$ and total [Zn] in aqueous phase, respectively, and Δh_j refers to the change in enthalpy for the respective steps, $ZnCl_j^{(2-j)+}(aq) + (4-j)\ Cl^-(aq) \rightarrow ZnCl_4^{2-}(aq)$. Here it is noticed that Y corresponds to the change in enthalpy estimated by using van't Hoff equation.

Eq.(1) is applied to the estimation of the total heat change associated with Zn(II) extraction with 0.05 M TOMAC in benzene, putting -3.4 kJ M^{-1} obtained from the distribution data into Y. Linear least squares yield the values of Δh_0, Δh_1, Δh_2 and Δh_3 to be 6.67 ± 1.74, 4.26 ± 3.24, -37.2 ± 18.4 and -111.7 ± 26.1, respectively, in which the degree of formation of the species $ZnCl_j^{(2-j)+}$ is calculated using the overall stability constants (4). Calculated heat change fits to the experimental one. From Δh_j's value obtained, the change in enthalpy for stepwise formation of the species $ZnCl_j^{(2-j)+}$ is calculated to be 2.42 ($ZnCl^+$), 41.5 ($ZnCl_2$), 74.8 ($ZnCl_3^-$) and -111.7 kJ M^{-1} ($ZnCl_4^{2-}$), respectively. Magnitude of the change in enthalpy for the stepwise formation of the species $ZnCl^+$ and $ZnCl_2$ agrees with those at $\mu = 3$, supporting that the heat change detected is considered as the sum of the change in enthalpy over the respective steps and that the variation in ΔQ is accounted for the change in the distribution of the species $ZnCl_j^{(2-j)+}$ in aqueous phase as a function of aqueous [Cl].

The difference between ΔQ at 0.5 and 1 M HCl, which is 13.5 kJ M^{-1} for 1,2-$C_2H_4Cl_2$, is more than twice as large as that for *m*-$C_6H_4(CH_3)_2$ which gives the smallest one of all. One of the reason for this gap is considered as due to the difference trend in increase of the amount of HCl extracted into organic phase with increasing initial aqueous [HCl]. However, since the present evidence is not enough to take into account of such effect, the values of Y for respective diluents are estimated as $-\Delta h_4$ in the step, $R_3R'NCl \cdot nHCl(org) \rightarrow R_3R'NCl(org) + nHCl(aq)$, of invariance independent of aqueous [HCl] throughout the present treatment for the data. Parameter Y is evaluated to be -1.26 ($C_6H_5CH_3$), -0.69 (m-$C_6H_4(CH_3)_2$), -10.0 (C_6H_5Cl), -15.8 (o-$C_6H_4Cl_2$), -36.4 ($C_6H_5NO_2$), 41.1 ($1,2$-$C_2H_4Cl_2$) and 0.01 kJ M^{-1} (CCl_4), respectively, by the use of Δh_j's values estimated for benzene.

By assuming a regular solution, the parameter Y is related with the solubility parameter:

$$\begin{aligned}(Y - Y_s)/(\delta_d - \delta_s) &= (f_d - f_s)/(\delta_d - \delta_s)\\ &= (V_c\phi'_d{}^2 - 2V_e\phi_d{}^2)(\delta_d + \delta_s) + 2(2V_e\phi_d{}^2\delta_e - V_c\phi'_d{}^2\delta_c) \qquad (2)\end{aligned}$$

where V, δ and ϕ (ϕ') denote molar volume, solubility parameter and volume fraction, respectively, subscripts c, e, d and s stand for the complexes formed in the organic phase, extractant, diluent and the diluent chosen as standard, respectively. The plots of $(Y - Y_s)/(\delta_d - \delta_s)$ *vs.* $(\delta_d + \delta_s)$using $C_6H_5NO_2$ as standard reveal a linear relationship, indicating that the Eq.(2) is satisfied for the extraction of Zn(II) from HCl solutions by TOMAC in various diluents (except $1,2$-$C_2H_4Cl_2$). Similarly the linear relation is also maintained in the extraction systems of Cu(II) and Cd(II) by TOMAC, although the Y is replaced by the ΔQ.

In comparison of the result obtained by means of the temperature-dependence of the distribution coefficient with that by calorimetry, it is concluded that the Y correlates with the solubility parameter of diluent, supporting that the regular solution thoery accounts for the diluent effect on the extraction of Cu(II), Zn(II) and Cd(II) from HCl solutions by TOMAC.

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