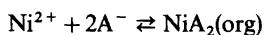


Solvent Extraction Chemistry of Dialkyldithiophosphates. V. Formation and Partition of Nickel Bis(dimethyldithiophosphate) Species in the System Toluene – 1 M Na(DMDTP, ClO₄)

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The extraction of nickel from an aqueous 1 M perchlorate solution into toluene with dimethyldithiophosphate (A^-) as a chelating reagent was studied. It was found that nickel is extracted as the complex $Ni[S_2P(OCH_3)_2]_2$ according to the equilibrium



and no evidence could be found for formation of the nickel complexes NiA^+ or NiA_2 in the aqueous phase. The activity coefficient changes in the ionic medium 1 M Na(DMDTP, ClO₄) could be described according to the Harned rule. No oligomerization of the extracted nickel complex was noted for high metal concentrations ($\leq 1 \text{ g l}^{-1}$) in the organic phase. By an indirect method the protolysis constant of dimethyldithiophosphoric acid was estimated to $pK_a = -0.33$.

The use of dialkyldithiophosphoric acids (HD(R)DTP) as extractants for nickel has gained interest for analytical^{1,2} as well as industrial^{3,4} applications. These reagents are, however, less promising for the latter use due to their instability against oxidation and hydrolysis.^{5,6} On the other hand, the high distribution ratios obtained for nickel even in strongly acidic solutions makes HD(R)DTP quite unique in the metal extraction field. For a high distribution ratio (D) to occur with a chelating extractant, the partition constant of the neutral metal chelate complex (λ_2 in the actual case of a divalent metal ion) must be high, but in the acidic region a high value of the complex formation constant for this complex (β_2) might also be needed. It has been argued that the high D -values

obtained for HD(R)DTP are due to strong complexation.⁷ On the contrary, one must regard the complex formation with D(R)DTP, at least for zinc, as being rather weak ($\log \beta_2 = 2.27$).⁸ When one takes into account the pseudohalogenide character of D(R)DTP anions, a still weaker complex with nickel would be expected. The formation of some Ni-D(R)DTP complexes has been studied in ethanolic medium,⁹ but the results – apart from a questionable evaluation – are not conclusive with regard to the complexation in a purely aqueous medium. It has been reported that nickel dialkyldithiophosphates are stable in organic solvents, but that 80% are decomposed in the presence of only 20% H₂O in ethanol.¹⁰ A quantitative evaluation of the complex formation is not available, however. The present investigation was carried out in order to answer this question.

Some preliminary distribution experiments with dibutyldithiophosphoric acid in heptane showed that very high distribution ratios ($\log D_{Ni} > 3$) are obtained with this reagent. However, the kinetics of extraction were rather slow and back extraction experiments did not yield the same results as extraction experiments even for contact times on the order of one hour. To facilitate the experimental procedure it was then decided to use the dimethyl ester (HDMDTP) as reagent. With toluene as the organic solvent, distribution ratios of a reasonable order of magnitude were obtained ($\log D_{Ni}$ in the range -2 to $+1$), and the extraction was fast (equilibrium reached within 30 min). Since it was necessary to use high ligand concentrations, the comparatively small molar volume of DMDTP⁻ means that DMDTP⁻ would probably have less

influence on the ionic medium than a higher ester. On the other hand, the complex formation should not be influenced appreciably by the use of a shorter alkyl chain.

EXPERIMENTAL

Chemicals. ^{63}Ni was purchased from Amersham Radiochemical Center. Dimethyl dithiophosphoric acid was synthesized as reported previously.¹¹ A stock solution of about 1 M NaDMDTP was prepared by neutralization of the acid with NaOH and the ionic strength was adjusted to 1 M with NaClO_4 . All other chemicals were of reagent grade and were used without further purification.

Distribution experiments were carried out in 10 ml test tubes sealed with polyethylene stoppers. Varying amounts of 1 M ligand stock solution, 1 M NaClO_4 and ^{63}Ni in 1 M NaClO_4 were pipetted into each test tube to make up an aqueous volume of about 5 ml; the volume of the organic phase (toluene) added was kept constant = 5 ml. The total hydrogen ion concentration was 0.02 M by the addition of 1 M HClO_4 ; this was necessary in order to prevent precipitation of nickel sulfide with the H_2S formed by the hydrolysis of the reagent. (The decomposition of DMDTP in the neutral stock solution was hardly significant, less than 1%, after 1 week of storage under nitrogen atmosphere and in the dark at 0 °C in a refrigerator.) After equilibration of the phases for 1 h in a Griffin shaking machine at 25 ± 1 °C, the test tubes were centrifuged and samples were withdrawn from both phases and analyzed for ^{63}Ni and total ligand concentration in the aqueous phase.

Analytical procedures. The total content of ligand in the aqueous phase was determined iodometrically by oxidation of DMDTP with excess iodine in an alkaline medium followed by backtitration of I_2 with thiosulfate in ≈ 0.1 M H_2SO_4 . This procedure has been described by Bode and Arns-wald.⁵ In the actual case the direct titration of DMDTP^- with I_2 in an acidic medium gave less reproducible results, especially for low ligand concentrations. The concentrations in the organic phase were always very small; no study of the distribution of the ligand acid ($\log k_d$ about -1) was attempted by this method, since any presence of reducing impurities would have influenced the results heavily.

The determination of ^{63}Ni was performed by liquid scintillation spectrometry using a Packard Tri-Carb 2425. Aqueous samples (1 ml) were diluted in the polyethylene counting vials with 4 ml distilled H_2O before addition of 5 ml INSTA-GEL (Packard Instrument Co.). Organic samples (1 ml)

were diluted with 4 ml of toluene instead of water. From separate experiments it was ascertained that quenching was not affected by changing the amounts of ligand, acid or metal ion along the full investigated concentration range for either phase.

Since the counting efficiency was not equal for both phases, corrections had to be made. It was found, however, that even small amounts of water (≈ 0.1 ml) in the organic samples (from the use of an aqueous ^{63}Ni standard solution) affected the results significantly. Therefore another procedure of internal calibration was employed for each set of samples where the distribution of ^{63}Ni varied considerably. Let \bar{R} and R denote the net counting rates per ml of the organic and aqueous phases, respectively. When the counting efficiencies of the organic and aqueous phases are denoted $\bar{\psi}$ and ψ respectively, the distribution ratio is given by eqn. (1).

$$D = \bar{R}\bar{\psi}/R\psi \quad (1)$$

The ratio $\psi/\bar{\psi} = \eta$ may be called the counting correction factor. Since ψ and $\bar{\psi}$ have both been shown to be constants, η should also be a constant and depend primarily on extraneous factors such as instrumental settings and sample treatment. For each series of measurements, where these factors are the same, the activity balance is given by the equation

$$[\text{Total initially added activity } (A_0)] = [\text{Total activity in the aqueous phase}] + [\text{Total activity in the organic phase}]$$

i.e. eqn. (2), where V and \bar{V} are the volumes of the

$$A_0 = VR\psi^{-1} + \bar{V}\bar{R}\bar{\psi}^{-1} \quad (2)$$

aqueous and organic phases respectively. Eqn. (2) can be rearranged as eqn. (3).

$$R = A_0 V^{-1} \psi - (\bar{V}/V) \eta \bar{R} \quad (3)$$

Thus a plot of R vs. \bar{R} should give a straight line with slope $-(\bar{V}/V)\eta$, when \bar{V}/V is kept constant. Alternatively, a plot of RV vs. $\bar{V}\bar{R}$ would give a straight line with slope $-\eta$, when V and/or \bar{V} are not kept constant. Fig. 1 shows a plot for a case of constant \bar{V}/V . (Least squares analysis of these data gave $\eta = 0.681 \pm 0.005$.) Of course, this method can only be used when A_0 is the same for each experimental series and ψ and $\bar{\psi}$ do not change significantly. Its merit lies primarily in the fact that more data can be used for the evaluation of η and it is applicable when — as in the present case — the addition of standard activity solutions influences the counting efficiency.

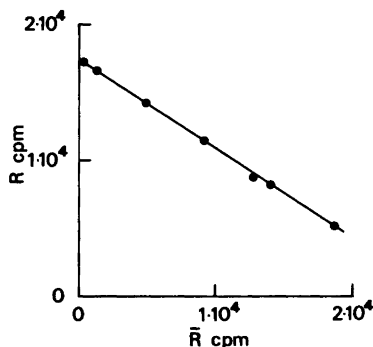


Fig. 1. Example of a plot for evaluation of the counting correction factor η .

RESULTS AND DISCUSSION

A plot of $\log D_{\text{Ni}}$ vs. pA ($= -\log [A]$, where $A = \text{DMDTP}^-$) is shown in Fig. 2. It is evident that the distribution curve is a straight line for $pA > 0$. A linear regression on these data yields a slope of -2.02 ± 0.005 ($\pm \sigma$). It has been well-established in earlier work^{4,12} that nickel is extracted by D(R)DTP as the complex NiA_2 , i.e. without the

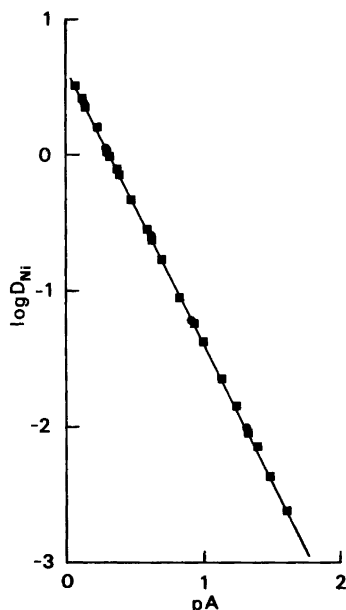
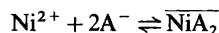


Fig. 2. Extraction of nickel with dimethyl dithiophosphate into toluene as a function of free ligand concentration. The round dots denote back extraction experiments.

formation of selfadducts of the type $\text{NiA}_2(\text{HA})_x$. The constant slope of about -2 might therefore be taken as a proof of very weak complexing between nickel and D(R)DTP. However, this conclusion is obscured by the fact that aqueous phase activity coefficients cannot be assumed to be constant when the ionic medium changes from 1 M NaClO_4 to 1 M NaDMDTP . For high pA values the extraction of Ni should be well-described by the simple heterogeneous equilibrium



with the equilibrium quotient $= \lambda_2 \beta_2$ referring to 1 M NaClO_4 as the ionic medium. In order to evaluate $\log \lambda_2 \beta_2$, Harned's rule^{13,14} was used for extrapolation to zero concentration of DMDTP^- , eqn. (4), where α is a constant and c_A the analytical

$$\log D_{\text{Ni}} + 2pA = \log \lambda_2 \beta_2 + \alpha c_A \quad (4)$$

concentration of DMDTP^- in the aqueous phase. Linear regression analysis using eqn. (4) gave $\log \lambda_2 \beta_2 = 0.612 \pm 0.004$ and $\alpha = 0.038 \pm 0.01$. In these calculations it has been assumed that the concentrations of the complexes NiA^+ and NiA_2 in the aqueous phase are negligible. Nevertheless it would be of interest to obtain a rough estimate of the largest value of β_2 , which might be hidden by experimental errors. The maximum deviations in $\log D_{\text{Ni}}$ from eqn. (4) is ≈ 0.025 . When complexes are present in the aqueous phase the distribution curve is given by eqn. (5).

$$\log D_{\text{Ni}} = \log \lambda_2 \beta_2 [A]^2 - \log(1 + \beta_1 [A] + \beta_2 [A]^2) + \alpha c_A \quad (5)$$

If the second term on the right hand side of this equation is larger than -0.025 , it follows that $\beta_1 [A] + \beta_2 [A]^2 < 0.06$. For $[A] = 1$ M and with the assumption that $\beta_1 \ll \beta_2$ one obtains $\beta_2 < 0.06$, or, say, $\log \beta_2 < -1$. The order of magnitude for $\log \lambda_2 \beta_2$ should not change due to variations in ionic medium, and thus $\log \lambda_2$ probably is > 2 . This value is not extremely high considering the molar volume of the complex (about 250 cm^3 , or somewhat less than the double molar volume of the ligand acid¹⁶).

As mentioned above, the distribution experiments were performed in an acidic solution (0.02 M HClO_4). This might have provided an erroneous interpretation of the extraction data, if it were not

for the fact that HD(R)DTP are fairly strong acids with pK_a around or below zero.¹⁵ In order to study the influence of acidity, distribution experiments were carried out with varying initial concentrations of $HClO_4$ at constant ionic strength = 1. Let c_H denote the analytical concentration of hydrogen ions in the aqueous phase; c_H was not found to be significantly different from the initial H^+ concentration. The mass balances for A^- and H^+ in the aqueous phase is given by eqns. (6) and (7),

$$c_A = k_a^{-1}h[A] + [A] \quad (6)$$

$$c_H = k_a^{-1}h[A] + h \quad (7)$$

respectively, where h is the free hydrogen ion concentration. $[A]$ is calculated according to eqn. (4) from the experimental values of c_A and D_{Ni} , and h is given by eqns. (6) and (7). According to eqn. (6) a plot of $c_A/[A]$ should give a straight line of slope k_a^{-1} and an ordinate intercept = 1. This is found to be the case, see Fig. 3. A least squares analysis of data gave $k_a = 2.1 \pm 0.3$ M and the intercept = 1.001 ± 0.005 . Thus the obtained estimation of pK_a ($= -0.33 \pm 0.05$) is in agreement with the low acid formation constant value determined earlier for the dibutyl ester ($pK_a = -0.24$) in the system 1 M (Na,H)ClO₄.¹⁵ A shorter alkyl chain is expected to give a higher value of k_a .¹⁶ However, it should be noted that the calculated value of k_a in this case refers to an ionic medium of about 0.4 M NaDMDTP + 0.6 NaClO₄. Subsequently eqn. (6) was tested for calculation of $[A]$ to be used in eqn. (4), but the deviation from the use of 0.02 M acid was hardly significant.

Some neutral metal chelates have been shown to be oligomerized, at least in anhydrous solvent systems and in the solid state, *e.g.*, nickel acetyl-

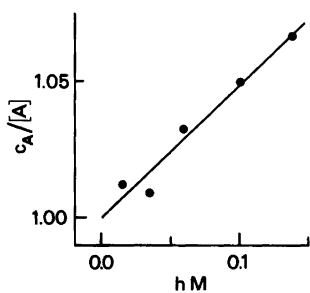


Fig. 3. $c_A/[A]$ as a function of free hydrogen concentration.

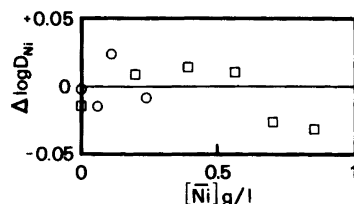


Fig. 4. Deviations of experimental $\log D_{Ni}$ from those calculated with eqn. (4) as a function of metal concentration in the organic phase. Total ligand concentration was 0.55 M (○) and 0.35 M (□). The equilibrium concentrations of ligand in the aqueous phase were corrected for the amounts bounded as NiA_2 in the organic phase.

acetate,¹⁷ zinc acetylacetonate¹⁸ (trimers) and copper (II) methylethylglyoximate¹⁹ (dimer). Any such oligomerization of NiA_2 in the organic phase is ruled out at tracer ($\approx 10^{-5} - 10^{-6}$ M) concentrations of nickel; otherwise D_{Ni} should have been more strongly dependent on $[A]$ than was actually found. However, in some cases – notably the Cu(II)-methylglyoxime/ $CHCl_3$ system referred to above – the oligomerization could not be observed until much higher metal concentrations. Therefore a series of distribution experiments were carried out with initial nickel concentrations up to as high as 0.05 M at different total ligand concentrations. The experimental $\log D_{Ni}$ values were then compared with those calculated according to eqn. (4). The deviations $\Delta \log D_{Ni} = \log D_{Ni}(\text{exp.}) - \log D_{Ni}(\text{calc.})$ did not show any significant trend within the investigated range of metal concentrations, *cf.* Fig. 4. Thus oligomerization could definitely be ruled out.

The final conclusion must be that nickel is strongly extracted from acidic solutions by HD(R)-DTP not because of the formation of strong complexes in the aqueous phase, but because of the large values of the partition constant of the neutral complexes. This also holds true for extraction of zinc with dibutylthiophosphoric acid.⁸ A direct comparison with the oxygenated analogues to HD(R)DTP (dialkylphosphoric acids) is not possible because of the fact that the latter ligands are dimerized in free form as well as when bounded to metals in extractable complexes. All that can be said in this respect is that the sulfur analogues are expected to give higher λ_2 values because of the slightly polar P(S)S group.

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