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Liquid–liquid extraction of palladium(II) in diantipyrylalkane–benzoic acid–HCl–H_2O stratifying systems

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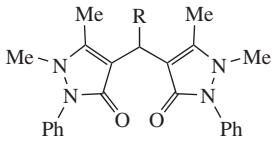
The study of palladium(II) extraction in stratifying systems containing diantipyrylmethane, butyldiantipyrylmethane, hexyldiantipyrylmethane, benzoic acid, hydrochloric acid and water has revealed that Pd^{2+} ions form the complex compound $[DAA{\cdot}H]_2(PdCl_4)$ (DAA is diantipyrylalkane) which is extracted by an anion exchange mechanism.

Liquid–liquid extraction is an efficient method for Pd recovery from aqueous solutions. The extraction of palladium(II) is performed with the use of soft bases.[1–11] However, toxic, volatile, fire-hazardous and explosive organic solvents are required for this process. Therefore, the development of extraction systems without such solvents is in high demand. The aim of this work was to study the effect of reagent structures on the extraction of Pd^{II}, the extraction mechanism and the stoichiometry of extracted compounds and to optimize extraction conditions in the diantipyrylalkane (DAA)–benzoic acid (BA)–HCl–H_2O systems.†

The results of Pd extraction from aqueous chloride solutions (total acidity, 1 M) using diantipyrylmethane (DAM), butyldiantipyrylmethane (BDAM) and hexyldiantipyrylmethane (HDAM)



DAM R = H
BDAM R = Bu
HDAM R = hexyl

† The test solution of $PdCl_2$ ($T_{Pd^{2+}/PdCl_2}$ = 1000 μg cm^{-3}) was prepared by dissolving palladium chloride in 100 ml of 0.1 M hydrochloric acid. In order to optimize extraction conditions, DAA and BA (2 mmol each) were placed in a graduated 20 ml test tube along with 50 μl of the solution of $PdCl_2$. In batch experiments, the total acidity of extraction systems was adjusted to 0.1, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 M by the addition of distilled water with a necessary amount of 11.64 M hydrochloric acid. The total volume of the extraction system was 20 ml. The DAA, BA, $PdCl_2$ and HCl used were of RG, ACS and PG grades, respectively.

Extraction systems were thermostated at 80 °C for 15 min with shaking until the complete dissolution of DAA–BA. The systems were cooled to room temperature until complete stratification; organic and aqueous phases were separated, and 5 ml of the aqueous phase was sampled for determining palladium on a Varian 710-ES ICP–AES instrument. Difference between the amount of Pd in the initial solution and water phase was used for estimating Pd^{2+} percentage extraction and distribution coefficient.

For establishing the influence of Cl^- concentration on Pd extraction, experiments were carried out analogously under the following conditions: n(DAA) = 2 mmol; n(BA) = 1 mmol; $[Pd^{2+}]$ = 1.5 mmol dm^{-3}; $[H_2SO_4]$ = = 0.5 mol dm^{-3}; 1.5 mmol dm^{-3} ⩽ $[Cl^-]$ ⩽ 15 mmol dm^{-3}. To estimate the effect of DAA concentration on Pd extraction, the experimental conditions were as follows: n(DAA) = n(BA) = 2 mmol; $[Pd^{2+}]$ = 1.5 mmol dm^{-3}; [HCl] = 1 mol dm^{-3}; 1.5 mmol dm^{-3} ⩽ [DAA] ⩽ 15 mmol dm^{-3}. To evaluate the stoichiometry of the complex compound, the average values of five parallel assays were bilogarithmically normalized and linearly approximated using MS Excel.

Table 1 Extraction properties of Pd^{2+} from 1 M hydrochloric media in DAA–BA–HCl–H_2O systems at 25 °C.

DAA–BA	$V_{org.\ phase}$/ml	Percentage extraction, PE (%)
DAM–BA	1.0	72.6
BDAM–BA	1.3	94.2
HDAM–BA	1.8	98.5

extractants show that a considerable growth of organic phase volume and percentage extraction are proportional to the molecular mass of the alkyl substituent at the central carbon atom in the DAA molecule (Table 1). The effect can be ascribed to the increase of positive inductive effect on DAA molecule with the growth of alkyl substituent molecular mass; hence, the percentage of interacting with palladium(II) and BA protonated reagent form $DAA{\cdot}H^+$ is raising.

Figure 1 shows that the highest values of Pd^{2+} percentage extraction are obtained using HDAM over the whole test range of acidity. The tendency of extraction parameters to increase with the concentration of HCl is attributed to $DAA{\cdot}H^+$ concentration magnification. The presence of peak values indicates that the raise of HCl concentration favors the formation of the insoluble compound $[DAA{\cdot}H]_2Cl_2$ detached to the organic phase formation process[13]

$$DAA{\cdot}H^+_{(A.P.)} + BA^-_{(A.P.)} = (DAA{\cdot}H)BA_{(A.P.)} \quad (1)$$

(A.P. and O.P. refer to compounds in aqueous and organic phases, respectively).

The direct dependence of organic phase volume upon DAA molecular mass was established within the whole range of HCl concentrations. The results correlate with previously reported data[13] (Figure 2). The presence of maximum values in the diagram over a range of 1.5–2.5 M HCl concentration arises from the shift of benzoic acid dissociation equilibrium: the percentage of deprotonated benzoic acid decreased with the concentration of HCl.

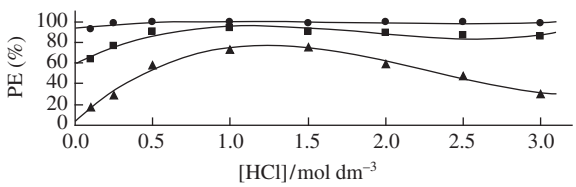


Figure 1 Effect of HCl concentration on Pd^{2+} extraction in the (▲) DAM–BA, (■) BDAM–BA and (●) HDAM–BA systems.

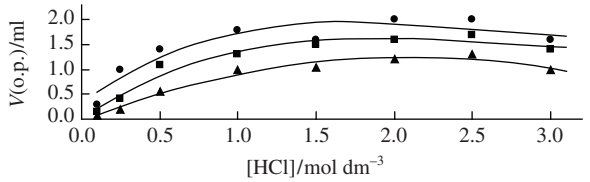


Figure 2 Effect of HCl concentration on organic phase volume in the (▲) DAM–BA, (■) BDAM–BA and (●) HDAM–BA systems.

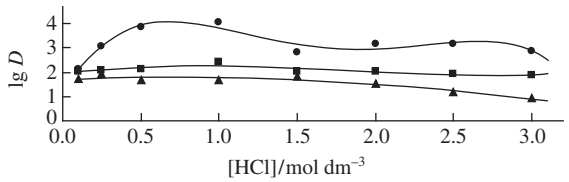


Figure 3 Logarithmic relation between the distribution coefficient of Pd^{2+} (*D*) and HCl concentration in the (▲) DAM–BA, (■) BDAM–BA and (●) HDAM–BA systems.

Figure 3 exhibits that the upper values of the distribution coefficients of palladium(II) extraction were achieved within the whole acidity range with the HDAM reagent. The dependence is consistent with published data.[12,13] Distribution coefficient peak values localization was identified within a range from 0.5 to 1.5 M HCl.

Studying the effect of Cl^- concentration on distribution coefficient revealed that the slope of linear approximated models to the *x* axis is about 4 (Figure 4). On the basis of slope measurements, a conclusion is made that the Pd : Cl ratio is 1 : 4 in extracted complex compound. Estimated ratio correlates with

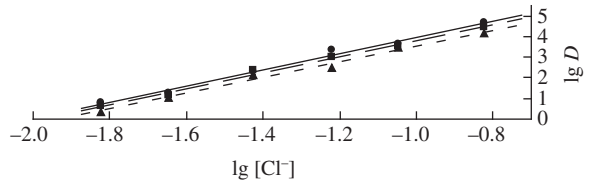


Figure 4 Logarithmic plot of a relation between Pd^{2+} distribution coefficient and Cl^- concentration in the (▲) DAM–BA, (■) BDAM–BA and (●) HDAM–BA systems.

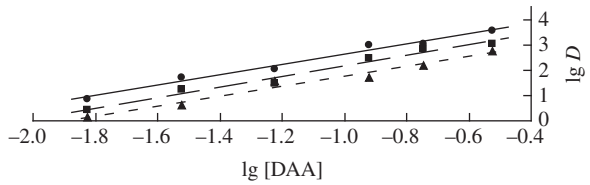


Figure 5 Logarithmic plot of a relation between Pd^{2+} distribution coefficient and DAA concentration in (▲) DAM–BA, (■) BDAM–BA and (●) HDAM–BA systems.

the published data in terms of which Pd^{2+} ions are represented by $[PdCl_4]^{2-}$ anions if the concentration of HCl in water solution rises above 0.5 M.[14]

Figure 5 shows that the slope of linear approximated models to the *x* axis is about 2. Thus, the DAA : Pd ratio is 1 : 2 in the extracted complex compound.

From the results, it was concluded that the distribution coefficient and percentage extraction tend to rise with the molecular mass of alkyl substituents in DAA molecules. Optimal conditions of palladium(II) extraction ($R \geqslant 98\%$) from aqueous chloride medium were achieved using HDAM as a reagent within a range from 0.5 to 1.5 M HCl. The stoichiometry of the extracted complex compound is Pd : DAA : Cl = 1 : 2 : 4. Thus, the structure of the extracted palladium(II) compound in DAA–BA–HCl–H_2O is $(DAA{\cdot}H^+)_2[PdCl_4^{2-}]$; the complex formation occurs by the reaction

$$2\,DAA_{(A.P.)} + 2\,H^+_{(A.P.)} + 4\,Cl^-_{(A.P.)} + Pd^{2+}_{(A.P.)} = (DAA{\cdot}H)_2[PdCl_4]_{(O.P.)} \quad (2)$$

Therefore, the complex compound is formed by an anion exchange mechanism.

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