EXTRACTION OF CA(II) FROM PHOSPHORIC ACID BY D2EHPA

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ABSTRACT

A study was conducted on the stoichiometry of the complex formed by the extraction of calcium by di-2-ethyl hexyl phosphoric acid (D2EHPA) from phosphoric acid solutions. The experimental results were numerically analyzed by non-linear regression. It was found that calcium is extracted in the form of the complex ion $CaH_2PO_4^-$ which reacts with one molecule of D2EHPA. The value of the equilibrium constant of the reaction was also calculated.

Keywords: Cationic extractant, D2EHPA, Phosphoric acid, Extraction of Ca^{++}

INTRODUCTION

The commercial application of cationic agents for the solvent extraction of metal ions has advanced greatly in recent years. Information obtained on the mechanism of extraction is important for commercial application as well as data concerning distribution of metal ions between the aqueous and organic phases.

There is only one industrial process, based on cationic extractants, that is currently used for the purification of wet-process phosphoric acid (1-3). In this process the organic phase is a mixture of dinonyl naphthalene sulphonic acid (DNNSA) and di-2-ethyl hexyl phosphoric acid (D2EHPA) dissolved in kerosene.

The system Fe(III)-H_3PO_4-D2EHPA has been investigated extensively by several researchers (4-7). It was found (7) that Fe(III) forms two complexes in the organic phase with D2EHPA, namely, FeR_3 and $FeHPO_4R$, where R is the D2EHPA radical.

The system Al(III)-H_3PO_4-D2EHPA has also been studied (7). The experimental results indicated the formation of the complex $AlR_3.HR$ in the organic phase.

The literature lacks fundamental studies on the extraction of other metal ion impurities from phosphoric acid by D2EHPA.

The aim of this work is to study the distribution of calcium in the system Ca-H_3PO_4-D2EHPA and to formulate the reaction between Ca and D2EHPA.

EXPERIMENTAL

The acid used was an extra-pure reagent produced by Germed. The source of calcium ions was AR calcium carbonate produced by BDH. D2EHPA was purchased from BDH. It was purified by the manufacturer using the method of partridge (8). The purity of D2EHPA was checked in this work by potentiometric titration and was found to contain 99.2% D2EHPA. Since there was no evidence on the presence of M2EHPA, the balance 0.8% was assumed to be water and 2-ethylhexanol. The diluent was de-aromatized kerosene containing less than 2% aromatics obtained from Alexandria Petroleum Company.

Extraction experiments were carried out as follows. Equal volumes of the organic phase and the aqueous phase containing calcium ions (25 cm^3) each where pipetted into a 100 cm^3 glass bottle. The bottle was shaken for 30 minutes at 25°C, then allowed to stand until phase separation was complete. The equilibrium calcium concentration in the aqueous phase was determined by titration with EDTA (9), and the equilibrium calcium concentration on the organic phase was calculated by material balance. No significant change in the volumes of both phases was observed.

RESULTS AND DISCUSSION

The extraction of calcium by D2EHPA from phosphoric acid solutions was first studied at a constant concentration of 0.5 M phosphoric acid. The extraction

of calcium increases with the increase in the D2EHPA concentration as shown in Figure (1). Figure (2) depicts the distribution of calcium between the aqueous phase and the organic phase. It is noted that concentration of calcium in the organic phase increases with the increase of the initial calcium concentration in the aqueous phase. Therefore, it can be concluded from Figures (1) and (2), that within the range of experimental conditions investigated, the organic phase is far from being loaded with calcium.

The effect of the phosphoric acid concentration is shown in Figure (3). It was found that the extraction of calcium decreases with the increase in the concentration of phosphoric acid. These results are in agreement with other studies on different systems. (10,11)

In the general case, when only one complex is formed the following equation may take place:
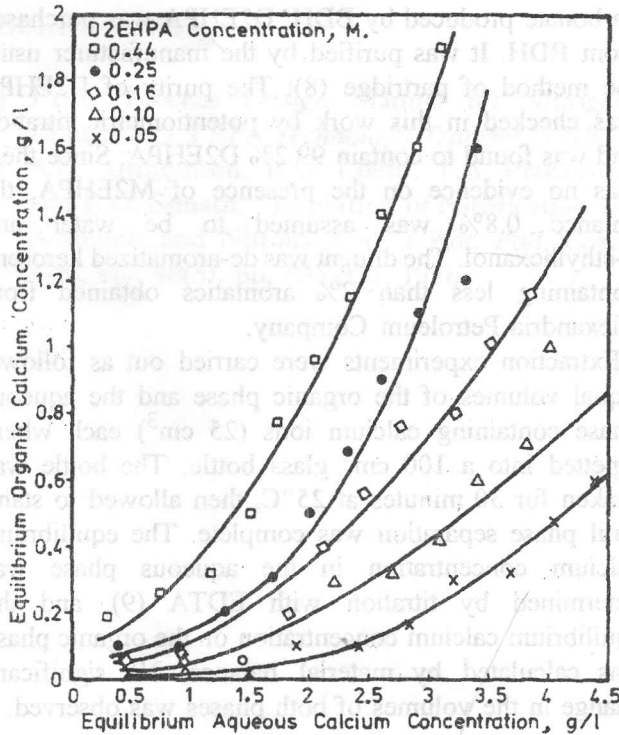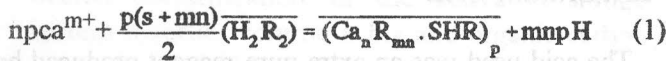
$$npca^{m+} + \frac{p(s+mn)}{2}\overline{(H_2R_2)} = \overline{(Ca_nR_{mn}.SHR)_p} + mnpH \quad (1)$$

where the overbar denotes species in the organic phase. The equilibrium constant of this reaction, K, is given

by:

$$K = \frac{[\overline{(Ca_nR_mn.SHR)_p}][H^+]^{mnp}}{[Ca^{m+}]^{np}[\overline{H_2R_2}]^{\frac{p(s-mn)}{2}}} \quad (2)$$
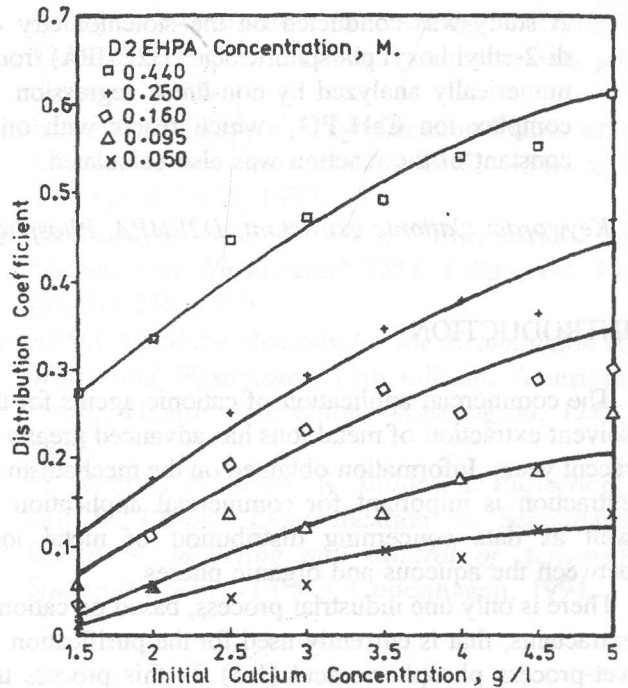
Figure 2. The effect of the initial calcium concentration on the distribution coefficient (Acid concentration=0.5M).

the above equation contains two unknown equilibrium concentrations, namely the equilibrium extractant concentration and the complex concentration. These may be substituted with formulae that contain only measurable concentrations as follows :

$$[H_2R_2] = [H_2R_2]_{total} - \frac{[\overline{Ca}](m+\frac{S}{n})}{2} \quad (3)$$

$$[\overline{(CaR_{mn}.SHR)_p}] = \frac{1}{pn}[\overline{Ca}] \quad (4)$$

where $[\overline{H_2R_2}]_{Total}$ is the total (i.e. the initial) concentration of the extractant .

Figure 1. The effect of D2EHPA concentration on the distribution of calcium (acid concentration =0.5M).
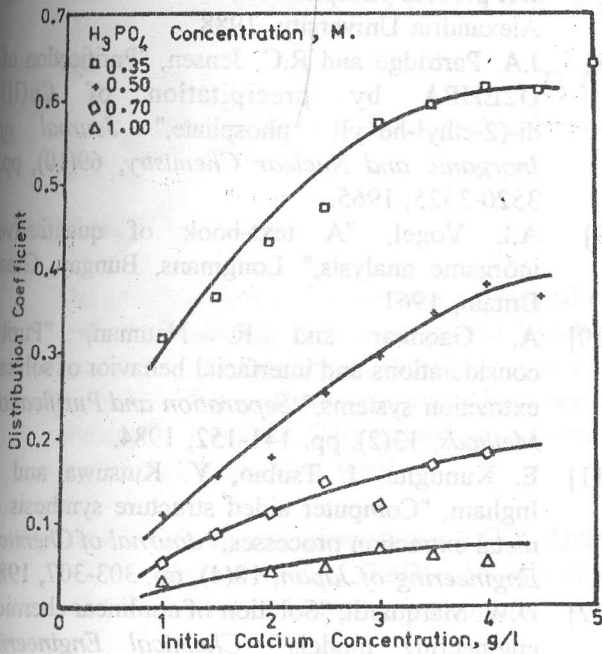
Figure 3. Effect of the initial calcium concentration on the distribution coefficient at different H_3PO_4 concentrations (D2EHPA concentration =0.25M).

Substituting equations (3) and (4) into equation (2) gives

$$K = \frac{[\overline{Ca}][H^+]^{mnp}}{pn[Ca^{m+}]^{np}([\overline{H_2R_2}]_{total} - \frac{1}{2}(m + \frac{S}{n})[\overline{Ca}])^{m(s+mn)/2}}$$

upon rearrangement

$$[\overline{Ca}] = \frac{[Kpn[Ca]^{np}\overline{([H_2R_2]}_{Total} - (\frac{1}{2}(m + \frac{S}{n})[\overline{Ca}]]^{p(s+mn)}}{[H]^{mnp}}$$

(5)

The method of nonlinear regression was used to find the equilibrium constant K and the unknown formation coefficients in the reaction model of equation (5). A computer program "ANREE" based on Marquardt algorithm (12), was used to apply nonlinear regression.

The values of the parameters determined by nonlinear regression are as follows :

K=0.00775 , n=1.000 , m=1.003 ,

s=0.337 , p=1.000 ;

and the sum of squared deviations = 0.01395 .

These values suggest the formation of the complex, $\overline{CaH_2PO_4.R}$ i.e. the calcium is extracted in the form $CaH_2PO_4^+$. The value of 0.337 for s indicates that part of the complex is solvated with one molecule of D2EHPA to give $\overline{CaH_2PO_4.R.HR}$.

The results of the numerical analysis are illustrated graphically in Figure (4) by plotting the experimental versus the calculated values of the calcium concentration in the organic phase. This Figure shows that the modal fits the experimental data properly .
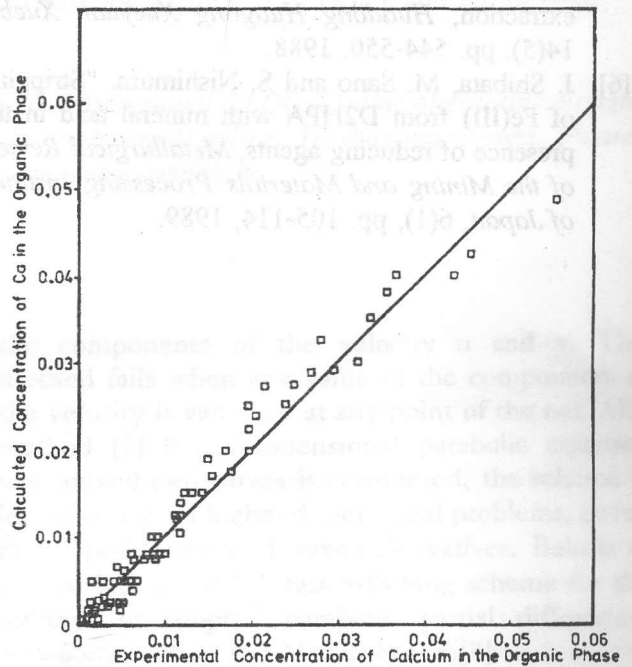

Figure 4. Experimental V_s. Calculated values of extracted calcium.

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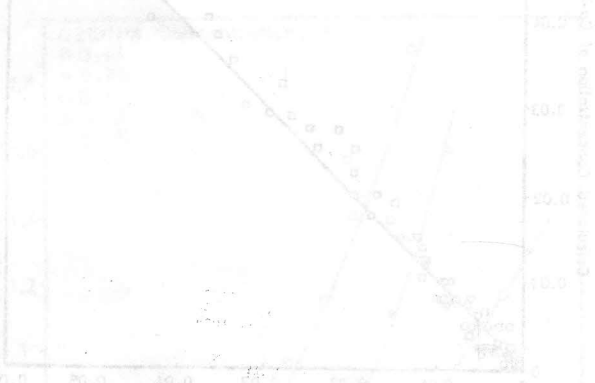
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