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SOME ASPECTS OF MASS TRANSFER INTO SINGLE DROPS IN VANADIUM (IV)/DI - 2 ETHYL HEXYL PHOSPHATE SYSTEM

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A kinetic study using the single drop technique was made of the vanadium (IV)/di-2 ethyl hexylphosphate (D2EHPA) system. Drops of the extractant in *n*-hexane diluent were made to rise through a continuum of vanadium (IV) in acid sulphate medium. The experimental data on mass transfer were tested against theoretically predicted mass transfer model equations for both stagnant and oscillating drops. The results showed that at the operating conditions, the data conformed more closely but not exactly with that of the stagnant drop model, a situation that would tend to lower the rate of mass transfer.

Key words: Single drops, Vanadium(IV)Di system, Mass transfer model.

Introduction

Several experimental techniques have been used in the investigation of the rate of metal extraction in liquid-liquid systems. Among others are the stirred tank [1], the stirred constant interfacial cell of the Lewis type [2], the static constant interfacial cell of the Hahn type [3] and the single drop [4,5]. Each method has its merits, shortcomings and limitations. Of the various methods, the single drop has been widely used by many authors [4-6]. The basic principle is to produce drops of one phase at the tip of a hypodermic needle or glass capillary and make the drop rise or fall through a vertical column filled with the other phase. The method has the advantage of simplicity and the capacity to yield information on the magnitude of the interfacial area for mass transfer. Moreover, it can be used to simulate a column contractor.

The hydrodynamics of the single drop is however, very complicated. Any attempt to treat single drops as moving spheres for the purpose of internal mass transfer has inherent short- comings because liquid drops, depending on their size differ remarkably from solid spheres in being capable of deformation, oscillation and even fragmentation. Three aspects have been identified in a log-log plot of the terminal velocity of a rising drop against the drop diameter [7]. First there exists small drops which lack internal circulation and tend to behave like rigid spheres. In second case, the drops are bigger, with internal circulation to enhance mass transfer and in third case where drops have become so large that the flow pattern becomes a combination of eddy flow an circulation. In effect, mass transfer is not favoured, not only by small drops alone, but by very large drops as well that tend to drag a wake when moving.

The aim of this study is to generate mass transfer data with the single crop experimental technique and use the results to test the model equations for systems controlled by internal mass transfer.

Experimental

pH was measured with "Orion Research pH-meter, model 701A. The concentration of vanadium (IV) was determined spectrophotometrically by the peroxide method [8], any organic phase vanadium being initially stripped into the aqueous phase with 2M sulphuric acid. Vanadium (IV) sulphate (BDH) was assayed with standard potassium permanganated (KMnO$_4$) before use. Di-2 ethyl hexyl phosphate (BDH) was purifie by the method described by Sato [9]. The diluent, n-hexane was used as supplied. The aqueous phase (0.1 M VO^{2+}) was kept at 0.5 M sodium sulphate in order to keep the ionic strength reasonably constant. The organic phase was 0.5M D2EHPA in *n*-hexane. Temperature was maintained constant at 28+0.5°, this value being within the range of temperature recommended for the extraction of vanadium (IV) from its ore [10].

The apparatus and experimental procedure for the single drop technique have been fully described elsewhere [4-6]. In this work single drops of di-2 ethyl hexyl phosphate were released from the tip of a hypodermic needle (33 gauge size) and using pressure from oxygen-free nitrogen, the drops were made to rise through a continuous phase of VO^{2+} in four pyrex tube jacked columns of heights 37.5, 71.0, 132 and 163.5 cm; and internal diameter of 24 mm. The four columns were used one at a time for a set of kinetic experiments during which the time it took for a drop to move through each column was measured. The amount of vanadium extracted per unit area per unit time was then calculated.

Results and Discussion

The data from only two experimental runs are given in the Table 1. Others are not tabulated to save space.

If the overall rate of mass transfer was controlled by internal mass transfer of the extractant molecules to the reaction site, Miller [11] has shown that the fractional change in the extractant concentration with time could be theoretically predicted from the Newman [12] equation for stagnant drops;

which for a short contact time (t < 40s) can be expressed as:

$$\frac{\overline{Ct}}{Co} = 3.38D.\frac{\sqrt{t}}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

For oscillating drops Miller [11] also showed that the equation of Kronig and Brink [13] can, for a short contact time (t < 25 s) be expressed as:

$$\frac{\overline{Ct}}{Co} = 4.65D.\frac{\sqrt{t}}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where $\frac{Ct}{Co}$ is the fraction of the extractant used in the organic phase at any time (t)

D = diffusion coefficient of the extractant, and

a = radius of the moving drop

Thus by plotting $\frac{Ct}{Co}$ against $\frac{\sqrt{t}}{a}$, the experimental data could be compared with the theoretical predictions.

The value of D was estimated to be 3.58×10^{-6} cm^2S^{-1} by the use of Wilke-Chang [14] correlation, having calculated the molar volume of D2EHPA to be 829.5 cm^3 mol^{-1} using the method of incremental atomic volume of Le Bas [15]. The value of D obtained compared favourably with $5 \times 10^{-6} cm^2S^{-1}$ reported by Peirera *et al*. [16] for D2EHPA in water where the extractant is known to monomerize unlike in n-hexane where it is expected to be dimeric [17]. The quantity of extractant used up was calculated from the amount of vanadium loaded into the organic phase by using a mole ratio of vanadium: D2EHPA of 1:2 as previously established [6].

The two straight lines in the figure represent theoretical predictions for oscillating and stagnant drops. Most of the experimental points are noticed to be close to the stagnant drop model but many of them actually fall below this line. It appears that under the experimental condition, the overall rate of mass transfer was slower than diffusion and hence the extraction mechanism could not have been limited by diffusion alone.

Miller [11] made similar plots for the overall rate of mass transfer for the extraction of copper with LIX64N from alkaline leach and found that the experimental data clustered around the lines for both stagnant and oscillating drop models depending on the experimental conditions; thus suggesting that the system was mainly mass transfer controlled. When he made similar plots for copper extraction with LIX64N from an acid medium which has been shown to be controlled by chemical kinetics [18], his experimental data fell below the predicted lines. It appears therefore that the mechanism of vanadium extraction by D2EHPA in the system under investigation is neither controlled alone by mass transfer nor chemical kinetics. It might be a case of mass transfer with simultaneous chemical reaction.

TABLE 1. KINETIC DATA FOR TESTING MASS TRANSFER MODEL.

Drop rise time t(s)	Radius of drop a(cm)	Vanadium Conc. in the organic phase (VO^{2+}) Mdm^{-3}	t/a ($S_{1/2}$ cm^{-1})	Ct/Co
3.0	0.09	0.0492	19.25	0.1688
3.0	0.09	0.0368	19.25	0.1472*
7.0	0.11	0.0561	24.05	0.2244
7.0	0.085	0.0492	31.13	0.1968*
12.0	0.08	0.0683	43.30	0.2732
11.0	0.085	0.0578	39.02	0.2312*
14.0	0.085	0.0759	44.02	0.3036
14.0	0.09	0.0633	41.57	0.2532*

* Data in the row belong to second experimental run..

Conclusion

Mass transfer mechanism in the solvent extraction of Vanadium (IV) from the acid sulphate aqueous phase into rising drops of di-2 ethyl hexyl phosphate in *n*-hexane does not appear to be controlled by internal mass transfer as the experimental data did not quite fit the theoretical models. Complete interpretation of the data would appear to require a model that considers the influence of diffusion and chemical kinetics.

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