

EXTRACTION OF NITRIC ACID BY TBP SOLUTIONS IN KEROSENE

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Received March 7th, 1984

Extraction of nitric acid from aqueous solutions to tributyl phosphate-kerosene solvents has been studied in the concentration regions $2-6 \text{ kmol m}^{-3}$ of nitric acid and $0.5-2 \text{ kmol m}^{-3}$ of tributyl phosphate. At these concentration levels, the transfer process is greatly enhanced by interfacial turbulence. This effect was taken into account by the model suggested for the mathematical description of the extraction kinetics.

Extraction by solvation plays an important role in many industrial processes of metal and acid extractions. Kinetics of nitric acid extraction by tributyl phosphate-hexane was studied by Olander and Benedict¹ in the region of moderate concentrations of HNO_3 . These authors established that the extracted species $\text{HNO}_3 \cdot \text{TBP}$ is formed by a very fast reaction occurring at the interface and that the extraction process is controlled by diffusion. It was found that in the region of higher acid concentrations the transfer process is considerably enhanced by interfacial turbulence.

The aim of this work is to study the extraction of nitric acid by tributyl phosphate-kerosene solvents in the region of high concentrations and to describe the extraction rate in the presence of interfacial turbulence.

THEORETICAL

The kinetic model will be derived on the basis of the film theory of mass transfer. In order to facilitate the description of the interfacial transport in this complex system, several simplifying assumptions have been made.

It is assumed that in the studied concentration range nitric acid is extracted only in the form of 1 : 1 solvate²⁻⁴ and that the extraction equilibrium can be described by the conditional extraction constant

$$K_{\text{cx}} = \frac{[\text{HNO}_3 \cdot \text{TBP}]_1}{[\text{NO}_3^-]_2^2 [\text{TBP}]_1} \quad (1)$$

The reaction between nitric acid and tributyl phosphate occurs instantaneously in a very thin reaction zone located at the interface. Nitric acid enters the organic phase only in the form of the complex. Extraction of the free acid to the organic phase and the extraction of tributyl phosphate to the aqueous phase is neglected. Transfer of nitric acid in the aqueous phase is treated as the transfer of a single component without taking into account the dissociation equilibrium in the diffusional film. Tributyl phosphate is further referred to as component A, nitric acid in all forms as B, and the extracted complex as E.

Assuming quasistationary transfer, when the concentrations of the reaction components change only in the diffusional films, the extraction rate can be expressed as the interfacial flux of the acid, J , which is equal to the fluxes of the individual components in the diffusional films:

$$J = k_{A1}(c_{A1} - c_{A1}^+) \quad (2)$$

$$= k_{E1}(c_{E1}^+ - c_{E1}) \quad (3)$$

$$= k_{B2}(c_{B2} - c_{B2}^+) \quad (4)$$

At the interface, the concentrations of the reaction components are practically at physical and chemical equilibrium, since the reaction is assumed to be instantaneous:

$$c_{E1}^+ = K_{ex}c_{A1}^+(c_{B2}^+)^2 \quad (5)$$

The unknown concentrations at the interface can be eliminated from Eqs (2)-(5) which leads to a cubic equation for the interfacial flux:

$$J^3 + a_2J^2 + a_1J + a_0 = 0, \quad (6)$$

where

$$a_2 = -2k_{B2}c_{B2} - k_{A1}c_{A1},$$

$$a_1 = k_{B2}^2c_{B2}^2 + 2k_{A1}k_{B2}c_{A1}c_{B2} + k_{A1}k_{B2}^2/(K_{ex}k_{E1}),$$

$$a_0 = -k_{A1}k_{B2}^2c_{A1}c_{B2}^2 + k_{A1}k_{B2}^2c_{E1}/K_{ex}.$$

The derivation of this equation does not take into account possible effect of interfacial turbulence on the extraction rate. Interfacial turbulence generally enhances mass transfer between the phases. It can be assumed that in systems with an instantaneous chemical reaction, it affects only the mass transfer coefficients and not the concentration differences between the bulk and the interface.

The effect of interfacial turbulence in systems with an instantaneous reaction was studied by Řeháková and Rod⁵, who suggested the relation for the mass transfer coefficients under condition of interfacial turbulence

$$k' = k \left(1 + \left(\frac{k^\sigma}{k} \right)^4 \right)^{1/4}, \quad (7)$$

where k represents mass transfer coefficient in the system without interfacial turbulence and k^σ an apparent value of mass transfer coefficient corresponding to the contribution of interfacial turbulence. The ratio k^σ/k is the same for all components in both phases and increases with increasing concentration gradients at the interface. It is assumed here that this ratio is proportional to the interfacial flux J ,

$$k^\sigma/k \sim J. \quad (8)$$

As the concentration differences between the bulk and the interface are not affected by the interfacial turbulence, the interfacial flux in the system in presence of interfacial turbulence can be expressed with regard to relations (2)–(4) and (7)–(8) as

$$J' = J(1 + (bJ)^4)^{1/4}, \quad (9)$$

where J is the positive root of Eq. (6) and b is a parameter characterizing interfacial turbulence in the studied system.

EXPERIMENTAL

Aqueous solutions of nitric acid were prepared from *p.a.* HNO₃. Weighed amounts of purified² commercial grade TBP were used in preparation of the extractant solutions in kerosene PL-4 (b.p. 150–260°C). Nitric acid concentrations in samples from equilibrium and from kinetic experiments were determined by titration with 0.1M-CH₃ONa using methylene red as indicator, the concentrations of uncombined TBP were calculated from the material balance.

Equilibrium data were obtained by contacting equal volumes of phases with varying nitric acid content and TBP concentrations in a thermostated bath. Aqueous phases were presaturated with TBP. After equilibrium had been reached, the acid content in the samples of separated phases was determined.

Kinetic measurements were carried out in a thermostated mass transfer cell with a flat interface⁶ at constant mixing intensity controlled by amplitude and frequency of the vibrational mixer with perforated mixing plates. The kinetic experiments were performed at three levels of the initial acid concentration and three levels of extractant concentration, with two repetitions. The progress of the extraction process was followed by taking samples of the organic phase in regular intervals and analysing them for nitric acid content. The survey of experimental conditions is given in Table I.

RESULTS

Results of the equilibrium measurements are presented by experimental points in Fig. 1. Data obtained from the three sets of experiments with different overall TBP concentrations were treated separately by the least squares method. The conditional extraction constants, evaluated from the data, are given in Table II. The calculated concentrations of the nitric acid in the organic phase are plotted in Fig. 2 as solid lines.

All kinetic data were treated simultaneously by Marquardt's optimization technique. The concentrations of the nitric acid in the aqueous and organic phases were calculated by numerical integration of differential equations

$$-V_2 \frac{dc_{B2}}{dt} = V_1 \frac{dc_{E1}}{dt} = J'A \quad (10)$$

TABLE I
Experimental conditions

Initial concentration of TBP, kmol m^{-3}	0.5	1.0	2.0
Initial concentration of HNO_3 in aq. phase, kmol m^{-3}	2.0	4.0	6.0
Volume of aq. phase, m^3	$1.00 \cdot 10^{-4}$		
Volume of org. phase, m^3	$1.00 \cdot 10^{-4}$		
Interfacial area, m^2	$2.00 \cdot 10^{-3}$		
Frequency of vibration, Hz	300		
Amplitude of vibration, mm	0.25		

TABLE II
Equilibrium and kinetic parameters

TBP concentration, kmol m^{-3}	0.5	1.0	2.0
Conditional extraction constant K_{ex} , $\text{kmol}^{-2} \text{m}^6$	0.191	0.185	0.172
Mass transfer coefficient in org. phase, m s^{-1}	$1.51 \cdot 10^{-3}$		
Mass transfer coefficient in aq. phase, m s^{-1}	$5.65 \cdot 10^{-3}$		
Parameter b , $\text{kmol}^{-1} \text{m}^2 \text{s}$	$1.6 \cdot 10^{-4}$		

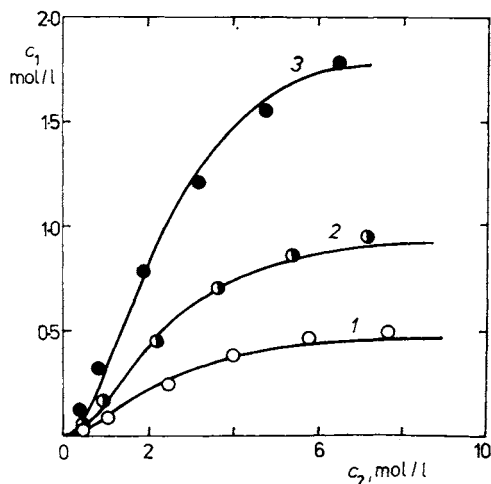


FIG. 1

Equilibrium distribution of HNO_3 in HNO_3 - H_2O /TBP-kerosene system. 1 0.5 kmol m^{-3} TBP, 2 1 kmol m^{-3} TBP, 3 2 kmol m^{-3} TBP

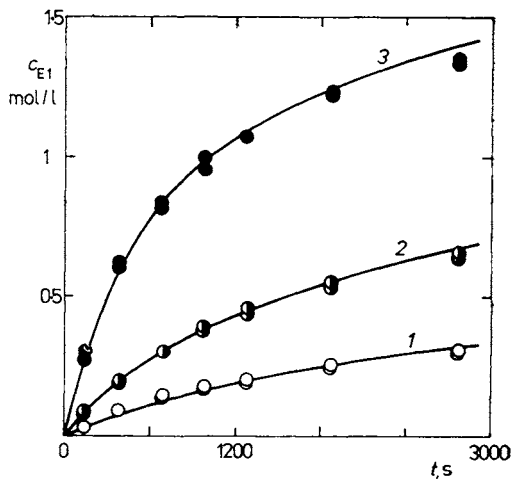


FIG. 2

Dependence of acid concentration in organic phase on the time of contact. Initial concentrations: 1 4 kmol m^{-3} HNO_3 , 0.5 kmol m^{-3} TBP; 2 4 kmol m^{-3} HNO_3 , 1.0 kmol m^{-3} TBP; 3 4 kmol m^{-3} HNO_3 , 2.0 kmol m^{-3} TBP; 4 2 kmol m^{-3} HNO_3 , 0.5 kmol m^{-3} TBP; 5 2 kmol m^{-3} HNO_3 , 1.0 kmol m^{-3} TBP

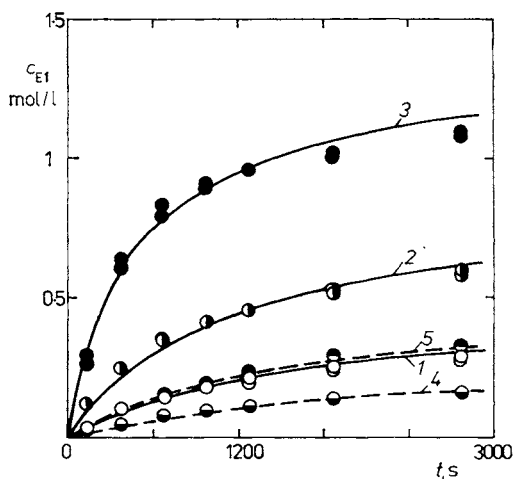


FIG. 3

Dependence of acid concentration in organic phase on the time of contact. Initial concentrations: 1 6 kmol m^{-3} HNO_3 , 0.5 kmol m^{-3} TBP; 2 6 kmol m^{-3} HNO_3 , 1.0 kmol m^{-3} TBP; 3 6 kmol m^{-3} HNO_3 , 2.0 kmol m^{-3} TBP; 4 2 kmol m^{-3} HNO_3 , 0.5 kmol m^{-3} TBP; 5 2 kmol m^{-3} HNO_3 , 1.0 kmol m^{-3} TBP

at known initial concentrations in both phases. The molar flux J was being determined by solution of Eq. (6) with the value of the extraction constant K_{ex} obtained from corresponding equilibrium data. The calculated value J was corrected for the effect of the interfacial turbulence by means of Eq. (8). It was assumed that the diffusivity ratio D_{A1}/D_{E1} is equal to one and $k_{A1} = k_{E1}$. The calculated optimum values of the parameters, *viz.* mass transfer coefficient of TBP in organic phase, mass transfer coefficient of nitric acid in the aqueous phase and the constant b in Eq. (8) are given in Table II. Figs 2 and 3 illustrate the dependence of the concentration of nitric acid in organic phase on the time of contact. The points represent the experimental data, the solid lines the calculated values.

DISCUSSION

Equilibrium data were described by the conditional extraction constant based on overall nitric acid concentrations. It has been found that a single value of this constant correlates the data well for a given overall TBP concentration in the studied range of nitric acid concentrations. The values of the extraction constant slightly decrease with increasing TBP concentration. The resulting values given in Table I are in fair agreement with the data obtained by other authors for nitric extraction systems with similar TBP-kerosene solutions²⁻⁴.

Preliminary treatment of kinetic data on the basis of the described model, without taking into account the effect of interfacial turbulence, resulted in a poor fit, especially for experiments with high TBP and high acid concentrations. The values of the mass transfer coefficients were found to be higher by factor 2–6 than the values predicted from the correlation given in ref.^{6,7} and the physical properties of the phases. This disagreement was attributed to the presence of strong interfacial turbulence in the system studied. The interfacial instabilities were observed on single stationary water phase drops during mass transfer process and confirmed by schlieren photographs of the drop surface. When the relation (9), describing the effect of the interfacial turbulence was included into the extraction rate calculation, the mean deviation between the experimental and calculated values of concentrations was decreased by factor 8. Initial extraction rate is very high in this system because of the high concentration gradients enhancing the interfacial turbulence. When the interfacial turbulence was taken into account, no significant effect of the initial concentrations on mass transfer coefficients was found and therefore all kinetic data were evaluated together. The resulting optimum values of parameters are given in Table II. The model with these parameter values enabled us to estimate the effect of the interfacial turbulence on mass transfer. In case of concentrated solutions (2 kmol m⁻³ TBP, 6 kmol m⁻³ HNO₃), initial extraction rate was enhanced approximately by factor 6, in case of dilute solutions (0.5 kmol m⁻³ TBP, 2 kmol m⁻³ HNO₃), the calculated enhancement was less than 10%.

LIST OF SYMBOLS

A	interfacial area, m^2
b	constant in Eq. (9), $kmol^{-1} m^2 s$
c	concentration, $kmol m^{-3}$
J	molar flux, $kmol m^{-2} s^{-1}$
k	mass transfer coefficient, $m s^{-1}$
k^σ	mass transfer coefficient due to interfacial turbulence, $m s^{-1}$
K_{ex}	conditional extraction constant
t	time, s
V	volume, m^3

Subscripts

A	TBP
B	nitric acid in all forms
E	HNO_3 .TBP
1	organic phase
2	aqueous phase

Superscripts

+	at the interface
'	affected by interfacial turbulence

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