

MECHANISM OF THE SLOW EXTRACTION OF IRON(III) FROM ACID PERCHLORATE SOLUTIONS BY DI(2-ETHYLHEXYL)PHOSPHORIC ACID IN *n*-OCTANE*

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Abstract—The rate of iron(III) extraction by di(2-ethylhexyl)phosphoric acid (HDEHP, HA) in *n*-octane from acid perchlorate solutions, as $\text{FeA}_3 \cdot 3\text{HA}$, is controlled by series and parallel reactions in the introduction of the first and second anion ligands, all occurring at the interface. (In the following subscripts, 1 and 2 refer to first and second anion ligands, *m* to extractant monomer, *d* and *df* to extractant dimer, *s* to interface saturation.) The measured rate/[Fe], $r \equiv -d[\text{Fe}]/[\text{Fe}]dt$, is well fitted by the step rates (25°C)

$$\begin{aligned}r_{1m} &= 5.5 \times 10^{-4} [\Sigma\text{HA}]^{0.5} / [\text{H}^+] \\ r_{1d} &= 1.8 \times 10^{-3} [\Sigma\text{HA}] / [\text{H}^+]\end{aligned}$$

for parallel reactions introducing the first anion ligand, in series with

$$\begin{aligned}r_2 &\approx 4 \times 10^{-4} / [\text{H}^+]^2 \\ r_{2s} &= 1.5 \times 10^{-7} / [\text{H}^+] [\text{Fe}] \\ r_{2d} &= 9.0 \times 10^{-6} [\Sigma\text{HA}]^{1.5} / [\text{H}^+]^2 \\ r_{2df} &= 1.2 \times 10^{-5} [\Sigma\text{HA}]^2 / [\text{H}^+]\end{aligned}$$

for parallel reactions introducing the second anion ligand. Step $2s$ is zero order, while all the other steps are first order, with respect to the aqueous iron concentration. In extractions through a quiescent interface these step rates combine so that

$$r = (r_{1m} + r_{1d})(r_{2s} + r_{2d} + r_{2df}) / \Sigma r_i$$

and in extractions with dispersion mixing so that

$$r = (r_{1m} + r_{1d})r_2 / (r_{1m} + r_{1d} + r_2).$$

The rate decreases slightly with increasing ionic strength, increases with increasing temperature (heat of activation ≈ 10 – 15 kcal/mole) and with conditions that increase the ionization of HA, and increases sometimes markedly with addition of proton-accepting complexers that can bypass the interface steps $1m$ and $1d$ with analogous reactions homogeneous in the aqueous phase.

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INTRODUCTION

WHILE equilibration is usefully rapid in the extraction of many metal ions by di(2-ethylhexyl)phosphoric acid (HDEHP, HA), it was noted early in the development of Dapex extraction processes[1] that some metal ions, notably iron(III) and aluminum, were very slow to reach equilibrium. Kinetics studies are in progress in this laboratory to find the reasons for and mechanisms of the slow extractions. Besides its importance in the fundamental study of solvent extraction, an understanding of slow extractions should aid in safeguarding against difficulties in extraction processes and may also provide basis for devising ways to exploit the different rates in specific separations.

This report covers kinetics and mechanisms in the simplified system, HDEHP-*n*-octane-Fe(ClO₄)₃-HClO₄-NaClO₄-water, plus aqueous-soluble proton-accepting complexers in certain specified cases. The equilibria in this system have been previously reported[2]. Extraction rates were measured both with a quiescent interface (interfacial area constant) and with dispersion in a baffled mixer (interfacial area proportional to turbine speed). We first surveyed the system with mixing by dispersion, next utilized the much better definition and accuracy of the quiescent interface to determine the responses to the system variables and to evaluate the constants, and finally cross-checked key points by dispersion mixing under conditions that have been standardized for scale-up [3, 4]. The mechanism of the rate control is not identical in the two modes of mixing. At macro iron concentrations and intermediate HDEHP concentrations an interfacial saturation with partially complexed iron occurred with the quiescent interface (pertinent to extraction chromatography) but not with dispersion (pertinent to conventional solvent extraction), and the power dependence of rate on HA concentration decreased at high HA concentrations in dispersion mixing but not with quiescent interface.

Karpacheva and Ilozheva[5] reported a study of kinetics in essentially the same system, and proposed a different mechanism. However, they examined only a relatively narrow range of conditions and thus did not observe the shifting dependences of rate on the concentrations of HDEHP, aqueous acid, and iron that we report here. One major aspect of their reported results appears to be in direct contradiction to our results, but may be resolvable (see below). The rest of their results appear to be consistent with ours.

Kletenik and Navrotskaya[6, 7] studied the iron extraction kinetics in a related system. Our results appear to be consistent with theirs where comparable, and also to explain several effects noted by them.

Interfacial area in dispersions. In the quiescent-interface cells, both interfacial

1. C. A. Blake *et al.*, *USAEC Rep.* ORNL-1903 (May 13, 1955).
2. C. F. Baes, Jr. and H. T. Baker, *J. phys. Chem.* **64**, 89 (1960).
3. W. A. Rodger, V. G. Trice, Jr. and J. H. Rushton, *Chem. Engng Progr.* **52**, 515 (1956).
4. J. H. Rushton and J. Y. Oldshue, *Chem. Engng Progr.* **49**, 161 (1953).
5. S. M. Karpacheva and L. V. Ilozheva, *Radiokhimiya* **11**, 37 (1969); *transl. Sov. Radiochem.* **11**, 32 (1969).
6. Yu. B. Kletenik and V. A. Navrotskaya, *Zh. neorg. Khim.* **12**, 3114 (1967); *transl. Russ. J. inorg. Chem.* **12**, 1648 (1967).
7. V. A. Navrotskaya and Yu. B. Kletenik, *Zh. neorg. Khim.* **14**, 1900 (1969); *transl. Russ. J. inorg. Chem.* **14**, 997 (1969).

area and volume are measured directly. (We found it appropriate to define the specific interfacial area on basis of the aqueous volume $a = A/V_{Aq} = 2A/V$ at 1:1 phase ratio.) In dispersion mixing, the interfacial area varies with power input and must be measured by special techniques or estimated by correlation with such measurements. In a mixer suitably baffled to prevent swirling and vortex formation, the specific interfacial area a is proportional[8] to the cube root of the specific power input, $(P/V)^{1/3}$, where the total power input[4] is $P = N^3 D^5 K \rho / g$. N is the impeller speed, D is the impeller diameter, K is a constant for the type of impeller[4], ρ is the mean density of the two phases, and g is the gravity constant. From this

$$a = A/V_{Aq} = kN(D^5 K \rho / V)^{1/3} \quad (1)$$

where k is a proportionality constant for similar systems in geometrically similar mixers. Its relative values in different systems can be estimated from published correlations of the effects of density, kinematic viscosity, interfacial tension, and settling time[3],

$$k \propto A/V \propto (\exp \Delta\rho/\rho_{\text{cont}}) (\nu_{\text{disp}}/\nu_{\text{cont}})^{1/5} (\sigma_i^{-0.36}) (t_s^{1/6}).$$

Thus, $k/2 = 7.3$ (c.g.s. units) obtained by fitting to the specific areas A/V calculated in Ref.[8] led to k values in the range of 16–24 for the various conditions used here.

EXPERIMENTAL

Reagents

The HDEHP was obtained from several sources (Union Carbide Corporation; Virginia-Carolina Chemical Corporation; Eastman Organic Chemicals, No. 8755) and was purified by several methods. Most of the tests used Virginia-Carolina HDEHP purified by either the method of Schmitt and Blake[9] or the method of Partridge and Jensen[10]. Attempted purification by molecular distillation was not satisfactory, because of incomplete decontamination and/or degradation in distillation even at < 0.02 mm Hg. All of the HDEHP used had a neutralization equivalent between 323 and 325 (theoretical, 322).

The *n*-octane diluent was obtained from Phillips Petroleum Company (minimum purity 99 mole%) and was further purified by the usual sulfuric acid washing. All other chemicals were reagent grade and were used without further purification.

The ^{59}Fe tracer (45.1-day γ -emitter) was received as ferric chloride[11, 12] in hydrochloric acid solution. It was purified as described by Baes and Baker[2] (see also Moore and Kraus[13]), as also was the normal iron perchlorate for stock solutions.

Instrumentation

Measurements of radioactivity were made with either a Packard Tri-Carb scintillation spectro-

8. A. D. Ryon, F. L. Daley and R. S. Lowrie, *Chem. Engng Progr.* **55**, 70 (1959); more fully in *USAEC Rep.* ORNL-2951 (Sept. 15, 1960).
9. J. M. Schmitt and C. A. Blake, Jr., *USAEC Rep.* ORNL-3548 (Feb. 17, 1964).
10. J. A. Partridge and R. C. Jensen, *J. inorg. nucl. Chem.* **31**, 2587 (1969).
11. Fe-59-P, obtained from the Isotopes Division of Oak Ridge National Laboratory (no longer available).
12. Fe-59-ISA, obtained from Nuclear Science Division, A Division of International Chemical and Nuclear Corporation.
13. G. E. Moore and K. A. Kraus, *J. Am. chem. Soc.* **72**, 5792 (1950).

meter model 3002 with automatic cyclic summation and readout, or a Nuclear-Chicago Corporation automatic gamma well counting system. The pH was measured with either a Beckman expanded scale meter (No. 76004) or a Beckman research meter (No. 101900).

The apparatus (Fig. 1) used in most of the quiescent (limited) interface experiments was similar to that described by Lewis[14], except that it was not necessary to bevel the horizontal faces of the annular interface baffles nor to exclude air-space from above the liquids. In the earlier tests, both phases were sampled (separately) as previously described and illustrated[15], each sample being drawn through a flexible tube into a glass tube lying across a scintillator for counting, and then being returned to the cell. For most of the tests at 25°C this was replaced by a continuous flow sampling of the organic phase only, circulated by either a peristaltic pump or a stainless-steel bellows pump at a rate of at least one organic volume (1/2 cell volume) per min. With automatic interval timing, summation, and printout by the counter, this system could operate unattended for as long as required by the slowest extractions encountered. The pump and lines were exposed in an air-conditioned room at $25 \pm 2^\circ\text{C}$, with the cell in a water bath at $25 \pm 0.05^\circ\text{C}$. At higher temperatures the cell was immersed in water pumped from a thermostat, and sampling was intermittent.

The apparatus used for most of the dispersion tests consisted of a baffled tank mixer and two-blade (paddle) turbine, both of glass, of standardized shape as described and illustrated in Refs.[4, 8]. The mixer was 69 mm I.D., with four vertical glass strips 5 mm wide fused to the wall at equal spacing. The paddle diameter (width across both blades) was 30 mm, by 7.5 mm depth, on a 7-mm glass shaft. It was driven by an electronic-controlled 0–3000 rev/min motor[16]. The actual rev/min was measured in each test by a stroboscopic tachometer[17]. The mixer top was covered loosely with sheet plastic, and the mixer was immersed to above the liquid level in 25.5°C water pumped from a thermostat. The dispersion tests shown in Fig. 10 were run in a similar mixer with larger, rounded baffles and a larger (20 × 15 mm) paddle, at room temperature ($25 \pm 1^\circ\text{C}$), with the same motor and tachometer.

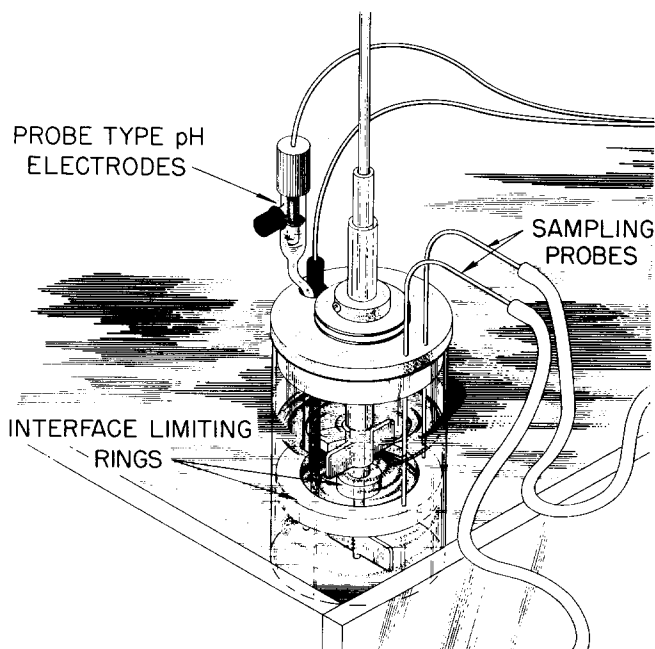


Fig. 1. Quiescent interface extraction cell (see also Fig. 1 of Ref.[15]).

14. J. B. Lewis, *Chem. Engng Sci.* **3**, 248 (1954).

15. W. J. McDowell and C. F. Coleman, *J. inorg. nucl. Chem.* **27**, 1117 (1965).

16. Cole-Parmer, *Constant Speed and Torque Control Unit Model 4425*.

17. General Radio Company, *Strobotac Type 1531-AB*.

Physical properties

Interfacial tensions were measured by the ring method. Densities were measured by means of the Hennion modification of the Sprengel-Ostwald pycnometer. Kinematic viscosities were measured by means of a Cannon-Fenske viscometer for transparent liquids.

Procedures

In a typical quiescent-interface cell experiment, the two phases were at first preequilibrated in the absence of iron and separated, and the appropriate amount of iron (carrier plus tracer) was added to the aqueous phase. This phase was then placed in the cell, the stirrer was started, and an equal volume of organic phase was carefully added through the sampling tube, avoiding agitation of the interface. The timing was started upon addition of the first portion of the organic phase. In the experiments with intermittent sampling, samples were taken at 30–60 min intervals, counted, and returned to the cell [15]. In the closed-loop flow system, automatic counting was summed over equal time intervals (usually 10 min) for the organic phase only. Except for the tests to determine the effects of temperature and ionic strength, all experiments were performed at $25 \pm 0.05^\circ\text{C}$ and ionic strength of 2.

In the dispersion experiments, equal portions of both phases were preequilibrated at the desired stirrer speed. The required amount of iron (carrier plus tracer) was then added and the timing started. The dispersions were all aqueous continuous. Samples were taken from the cell at regular intervals without interruption of mixing. The phases separated quickly (typically in 30–40 sec), and appeared clear. Both phases were counted, and good material balances indicated that there was no significant entrainment. Nevertheless, only the aqueous-phase counts were used in calculating the rates, to avoid any possibility of errors from entrainment of the higher-activity aqueous in the lower-activity organic phase.

In all the tests the iron:HDEHP ratio was kept small, and the rate was calculated over only a small fraction of the approach to equilibrium (less than 10 per cent except in a few tests with extraction coefficient $E_a^0 > 200$, and then never more than 25 per cent), so that the reverse reaction and any change of the free HDEHP concentration were both negligible.

Computations

The rates were calculated as

$$\begin{aligned} \text{rate} &= -d[\text{Fe}]/dt = d[\text{Fe}]_{\text{org}}/dt = r[\text{Fe}], \\ rt &= \ln([\text{Fe}]_{\text{init}}/[\text{Fe}]) = \ln([\text{Fe}]_{\text{init}}/([\text{Fe}]_{\text{init}} - [\text{Fe}]_{\text{org}})) \end{aligned}$$

where r is identical to the first-order rate constant when the rate is pure first order. The best value of r and its standard deviation of fitting were determined for each test by a modification of the program developed by Marquardt [18]. As the kinetics model of the extraction developed, the component rates r_i were evaluated by another modification of the same program, and results were plotted by means of the INTRIGUE [19] or the ORGRAPH [20] program.

RESULTS AND DISCUSSION

The preliminary survey tests conformed to first-order kinetics with respect to the iron concentration. The apparent first-order rate constant $k_1 = d[\text{Fe}]/[\text{Fe}]dt$ decreased in nearly linear inverse proportion to the aqueous perchloric acid concentration. It increased with increasing HA concentration, but with widely varying power dependence, about 0.3 below 0.2 M HA and nearly 1.5 above 0.5 M HA. It decreased somewhat with increasing ionic strength, and increased with increasing temperature.

Tests with quiescent interface. Results were the same in a cell with annular baffles inserted at the interface and in cells without the baffles. Most of the

18. D. W. Marquardt, *J. SIAM Appl. Math.* 11, 431 (1963).

19. D. K. Trubey and M. B. Emmett, *USAEC Rep.* ORNL-3447 (June 10, 1963).

20. N. B. Gove *et al.*, *USAEC Rep.* ORNL-4596, In preparation.

quiescent interface measurements are summarized in Figs. 2-5. These were all at 25°C and 1:1 phase ratio. Other tests confirmed that the rate is proportional to the specific interfacial area (Table 1) and gave estimates of the heat of activation

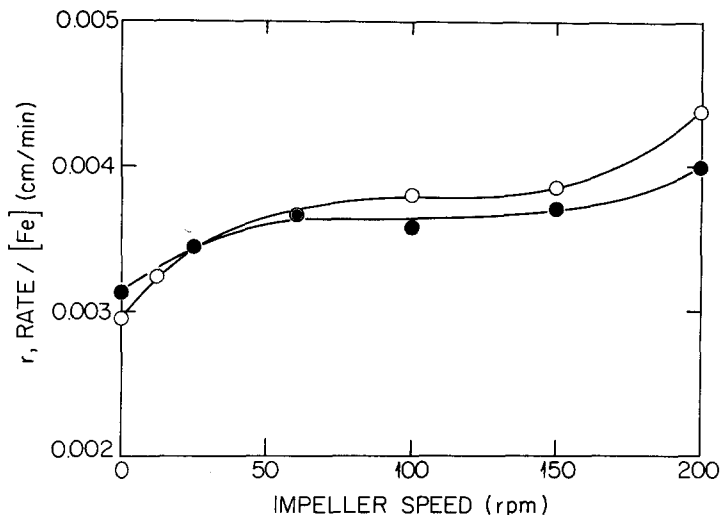


Fig. 2. Effect of stirring speed on rate of iron extraction through quiescent interface. Phases stirred independently, one phase (○—organic or ●—aqueous) at constant 60 rev/min and the other at the speed shown. 0.1M HA, 0.02M HClO₄, $I = 2$, 0.002M Fe.

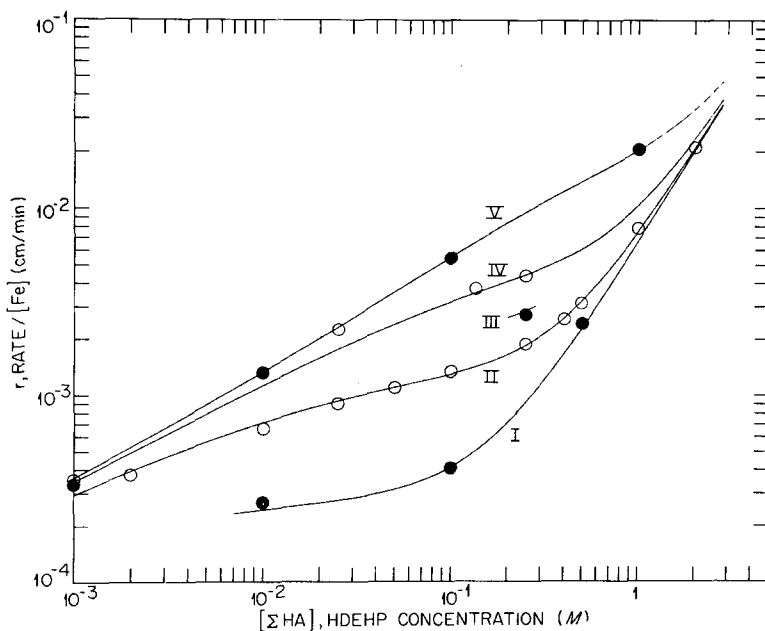


Fig. 3. Dependence of extraction rate on HDEHP concentration; effect of iron concentration—(I) 0.01, (II) 0.002, (III) 0.001, (IV) 0.0005, (V) 0.0001 initial M Fe. Quiescent interface. Aqueous acid concentration, 0.052M. Ionic strength $I = 2$. Points: experimental; curves: calculated from Equation (14).

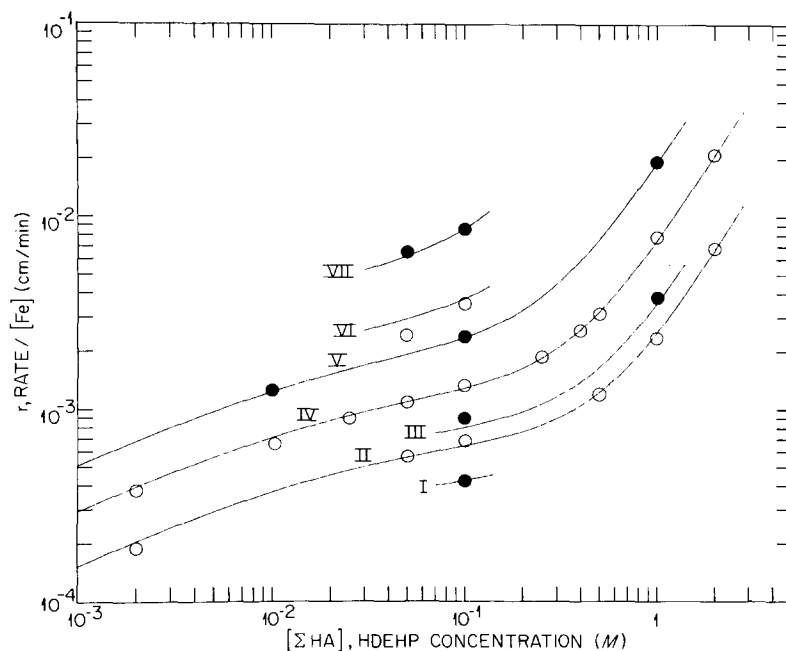


Fig. 4. Dependence of extraction rate on HDEHP concentration; effect of aqueous acid —(I) 0.15, (II) 0.1, (III) 0.081, (IV) 0.052, (V) 0.03, (VI) 0.02, (VII) 0.01 M $HClO_4$. Ionic strength $I = 2$. Initial iron concentration = 0.002M. Quiescent interface. Points: experimental; curves: calculated from Equation (14).

Table 1. Relation of iron extraction rate to specific interfacial area. 0.002M Fe, $I = 2$; 0.1M HDEHP; 25°C; 0.02M H^+ except as noted

V_A^* (cm ³)	Interfacial area		Rate $\times 10^4$	
	A (cm ²)	a (cm ² /cm ³)	ra (min ⁻¹)	r (cm/min)
125	44.7	0.358	13.0	36
	37.6	0.301	11.0	37
	17.7‡	0.142	4.8	34
	15.6‡	0.125	4.4	35
	8.3‡	0.066	2.4	36
125	37.6	0.301	2.1	6.9†
375	37.6	0.100	0.65	6.5†

* V_0 constant at 125 cm³.

‡ Area decreased from 37.6 cm² by annular baffles.

† 0.1M H^+ .

at 10–15 kcal/mole (Table 2). These observations, together with the long region of almost complete independence from stirrer speed (Fig. 2), indicate that the rate is controlled by chemical reaction at the interface, rather than by diffusion or by homogeneous reaction in either phase. The rate decreases slightly with increasing ionic strength (Table 3).

The decrease of iron extraction rate with increasing acidity, in contrast to the independence from acidity of the moderately fast extraction rates of uranium

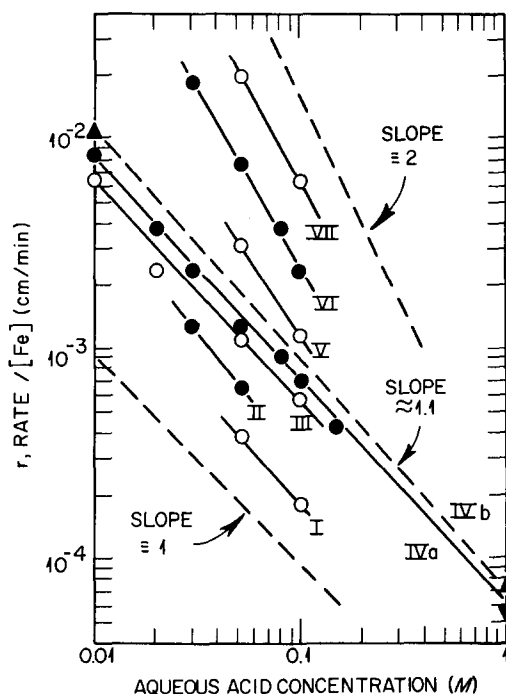


Fig. 5. Dependence of extraction rate on aqueous acid concentration. Initial iron concentration = 0.002M. Ionic strength: \blacktriangle —1; \circ — \bullet —2; \blacktriangledown —3; HDEHP concentrations: (I) 0.002, (II) 0.01, (III) 0.05, (IV) 0.1, (V) 0.5, (VI) 1, (VII) 2M. Quiescent interface.

Table 2. Effect of temperature on iron extraction rate.
0.002M Fe, $I = 2$ except as noted

[H ⁺]	0.05	0.05	1.0	1.0
[Σ HA]	0.1	1.0	0.1	1.0
$r \times 10^3$	25°	1.35	7.8	0.074*
(cm/min)	40°		18	0.093†
	45°	6.5		
	60°	19	46	1.15*
Est'd ΔH_{act}		15	10	15
(kcal/mole)				17

* $I = 1$.

†From extrapolation by Equation (14).

(VI) and europium, etc.[21], suggests that those may react readily (at the interface) with the unionized organic acid, but that iron can react only with the anions. The organic-phase concentration of the anions, A^- or HA_2^- , as sodium salts, decreases as the aqueous acidity increases[15]. (The ionization of the organic acid adsorbed at the interface at any moment is of course constrained to a corres-

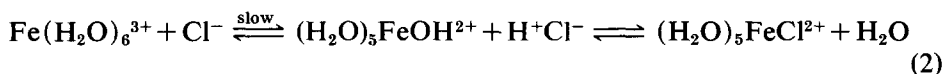
Table 3. Effect of ionic strength on iron extraction rate

I \ [H ⁺]:	$r \times 10^4$ (cm/min)			
	Quiescent interface*			Dispersion†
	0.01	0.05	1	1
0.5		30		
1	110	20	0.74	1.8
1.5		16		
2		13.5		1.5
3		10.5	0.56	
4				1.7

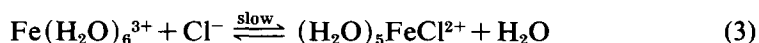
*0.1M HDEHP, 0.002M Fe.

†0.05M HDEHP, 0.0001M Fe.

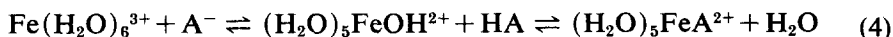
ponding equilibrium, even in the absence of an extractable cation.) Eigen [22] has shown that the formation of ferric chloride complex actually occurs by a two-step reaction



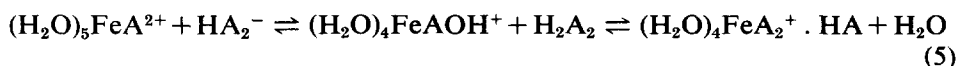
in which the rate-controlling first step is the spontaneous ionization of one of the waters of hydration to leave a ferric hydroxyl complex. The subsequent substitution of chloride for hydroxyl is fast. Although the spontaneous ionization is slow, the direct substitution of chloride for a water



is much slower still. It should be emphasized that the $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ in Equation (2) is just that formed transiently by hydrate water ionization in fortuitous proximity to a suitable anion; it has no connection with the (\sim constant) amount of the same species formed by the equilibrium, $(\text{H}_2\text{O})_6\text{Fe}^{3+} + \text{OH}^- \rightleftharpoons (\text{H}_2\text{O})_5\text{FeOH}^{2+} + \text{H}_2\text{O}$. It is reasonable to assume that an analogous slow step controls the rate of iron reaction with HA. According to the changing slopes in Figs. 3–5, at low HA concentrations this would be in the introduction of the first anion ligand by reaction with monomer ion,

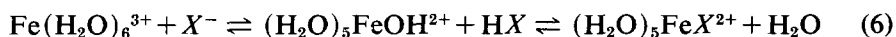


and at high HA concentrations, in the introduction of the second anion ligand by reaction with dimer ion,

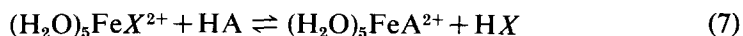


all occurring at the interface. These lead to rates proportional to $[\Sigma\text{HA}]^{0.5}/[\text{H}^+]$ and to $[\Sigma\text{HA}]^{1.5}/[\text{H}^+]^2$, respectively (see below). Presumably the dicomplexed iron can then enter the bulk organic phase, where formation of the final complex $\text{FeA}_3 \cdot 3\text{HA}$, Ref.[2], is completed without further influence on the rate of the extraction.

If these reactions are correct, the iron extraction should be faster when strontium replaces sodium as the gross cation in the aqueous phase, since more strontium than sodium is extracted by HA at a given pH, i.e. more of the extractant is ionized[15]. Table 4 shows that the extraction is significantly faster in the presence of strontium. The extraction should also be faster in the presence of chloride or other aqueous-soluble, proton-accepting complexer that can, via Reaction (2) or an equivalent, put more of the iron in a form ready for fast reaction with HA:



(homogeneous in the aqueous phase) and



(at the interface). Addition of several aqueous complexers to the perchlorate solution did indeed speed up the extraction, some by large factors (Table 5). Note that sulfate failed to speed up the extraction. If sulfate forms an outer-sphere complex, with a water between it and the iron[23, 24], that would account directly for the failure to catalyze the extraction according to Equations (6) and (7). Or, the sulfate complex might be unsuitable for Reaction (7) for steric or other reasons. It is also notable that the rate with 0.1 M HA plus 0.1 M acetate was nearly as high as that with 1 M HA plus 0.1 M acetate, consistent with the hypothesis that the slow steps starting through A^- or HA_2^- are bypassed by a faster parallel step starting through the acetate.

Equations (4) and (5) cannot account for the complete mechanism of the rate control, however, for at least three obvious reasons: First, the slope of the

Table 4. Iron extraction is faster from strontium perchlorate than from sodium perchlorate solution. 0.002M Fe, HClO_4 - NaClO_4 or HClO_4 - $\text{Sr}(\text{ClO}_4)_2$, $I = 2$; 0.1M HDEHP; 25°C

pH	$r \times 10^3$ (cm/min)	
	Medium: $\text{Sr}(\text{ClO}_4)_2$	NaClO_4^*
0.96	5.2	0.6
1.18	7.5	1.2
1.68	8.3	3.5
1.73	11	3.9

* r from NaClO_4 solutions interpolated to the pH values measured in the $\text{Sr}(\text{ClO}_4)_2$ solutions.

23. C. K. Jørgensen, *Inorganic Complexes* p. 85(f). Academic Press, New York (1963).

24. M. T. Beck, *Coordn. chem. Rev.* 3, 91 (1968).

Table 5. Acceleration of HDEHP extraction of iron(III) by proton-accepting complexers (see Equations (6) and (7)).
0.002M Fe, 2M (H, Na)ClO₄, pH 1, 25°C

Additive, 0.1M	$r \times 10^4$ (cm/min)	
	0.1M HA	1.0M HA
None	6	25
Sulfate	6	
Chloride	9	
Nitrate	30	
Ethylenediamine	35	
Phosphate	70	
Dichloroacetate	85	
Acetate	105	130
Citrate	110	

lower branch of Curve II in Fig. 3 is close to 0.3, not 0.5. Second (and more stringent), the transition in Curve II is both from lower to higher rate and from lower to higher slope, i.e. lower to higher power dependence on HA concentration. Thus, this transition in rate control must be between steps that are parallel, while transition from control by Reaction (4) to control by Reaction (5) is between steps in series. Third, the bend is too sharp for Curve II to be the sum of just two linear components, for such a curve would pass above the intersection of its asymptotes by a factor of 2 (i.e. by 0.3 log cycle), but Curve II passes within 0.13 log cycle above the intersection of its apparent asymptotes. Hence, there must be at least one more controlling step, at intermediate HA concentrations, between control by Reaction (4) and control by Reaction (5).

One simple hypothesis can reconcile all of these considerations, namely, that the intermediate controlling step is independent of HA concentration, so that the succession of slopes is $0.5 \xrightarrow{\text{series transition}} 0 \xrightarrow{\text{parallel transition}} 1.5$. Zero slope implies rate control involving a saturation with some critical species, and the most plausible saturation step proved to imply that the kinetics at HA concentrations near 0.1 M should be zero order instead of first order with respect to iron. At the time we first considered this hypothesis, the only points that had been measured in Fig. 3 were those of Curve II, at a single iron concentration, and the suggestion of a zero-order component was surprising. Nevertheless it proved to be correct, as is now obvious from the other curves in Fig. 3. The curves are displaced with changing iron concentration so that

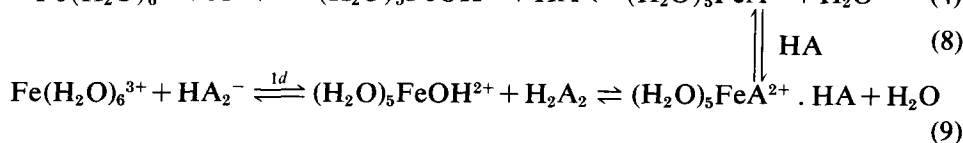
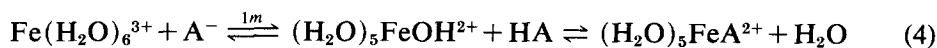
$$r = -d[\text{Fe}]/[\text{Fe}]dt = k/[\text{Fe}]$$

equivalent to $-d[\text{Fe}]/dt = k$, zero order.

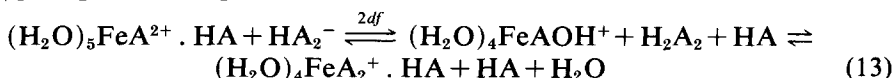
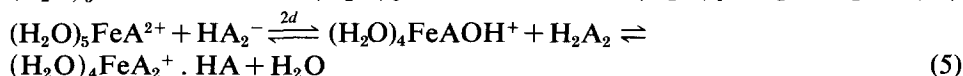
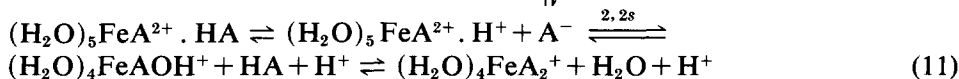
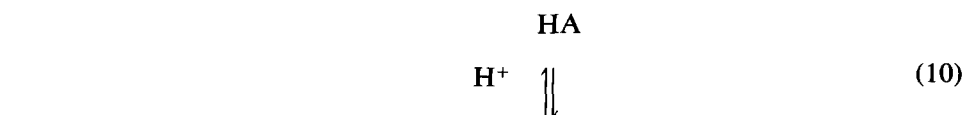
On the basis of the foregoing, the best model we have found for the extraction mechanism involves most or perhaps all of the following reactions, all at the interface. The postulated slow step of each numbered reaction is indicated by the notation "1 m ", etc. on the arrow. In these notations, "1" and "2" refer to introduction of, respectively, the first and the second anion ligand, "m" refers to extractant monomer and "d" to extractant dimer, "df" arbitrarily distinguishes

the dimer reaction in Equation (13) from that in Equation (5), and "s" refers to saturation of the interface with monocomplexed iron. With rapid equilibrium adsorption of HA_2^- and A^- at the interface —

First anion ligand



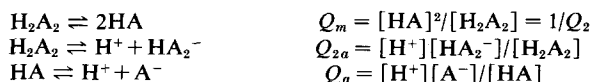
Second anion ligand



followed by rapid desorption of the dicomplexed iron into the bulk organic phase.

Here again, as in Equation (2), it should be emphasized that the $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ is just that formed transiently by hydrate water ionization fortuitously close to a suitable anion, and has no connection with $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ formed by equilibrium with OH^- .

These reactions, combined with the dimerization and ionization equilibria of HA, predict step rates that are first order with respect to aqueous-phase iron, except that Reaction (11) approaches zero order when the interface approaches saturation. (HDEHP is almost completely dimerized in *n*-octane solution.)



$$[\Sigma\text{HA}] \approx 2[\text{H}_2\text{A}_2]; [\text{Fe}] \approx [w_6\text{Fe}^{3+}]$$

$$r_i = -d[\text{Fe}]/[\text{Fe}]dt = -d \ln [\text{Fe}]/dt.$$

$$\begin{array}{l} \text{For Equation (4): } -d[\text{Fe}]/dt \propto [w_6\text{Fe}^{3+}][\text{A}^-] \\ \propto [\text{Fe}]Q_a\sqrt{Q_m[\text{H}_2\text{A}_2]}/[\text{H}^+] \\ = k_{1m}[\text{Fe}][\Sigma\text{HA}]^{0.5}/[\text{H}^+] \end{array}$$

$$r_{1m} = k_{1m}[\Sigma\text{HA}]^{0.5}/[\text{H}^+].$$

For Equation (9): $-d[\text{Fe}]/dt \propto [w_6\text{Fe}^{3+}][\text{HA}_2^-]$
 $\propto [\text{Fe}]Q_{2a}[\text{H}_2\text{A}_2]/[\text{H}^+]$
 $= k_{1d}[\text{Fe}][\Sigma\text{HA}]/[\text{H}^+]$

$$r_{1d} = k_{1d}[\Sigma\text{HA}]/[\text{H}^+].$$

For Equation (11): $-d[\text{Fe}]/dt \propto [w_5\text{FeA}^{2+} \cdot \text{H}^+ \{A^-\}]$
 Here $\{A^-\}$ is not the bulk concentration $[A^-]$, but the A^- produced in the first step of Reaction (11) and not consumed by Reaction (10), $\{A^-\} \propto 1/[\text{H}^+]$.
 Since $[w_5\text{FeA}^{2+} \cdot \text{H}^+] \propto [w_5\text{FeA}^{2+} \cdot \text{HA}]$

$$-d[\text{Fe}]/dt \propto [w_5\text{FeA}^{2+} \cdot \text{HA}]/[\text{H}^+].$$

When the interface approaches saturation, $[w_5\text{FeA}^{2+} \cdot \text{HA}] \rightarrow \text{constant}$, and

$$-d[\text{Fe}]/dt \rightarrow k_{2s}/[\text{H}^+]$$

$$r_{2s} = k_{2s}/[\text{H}^+][\text{Fe}].$$

For Equation (12): $Q_4 = [w_5\text{FeA}^{2+}][w]/[\text{Fe}][A^-]$

$$-d[\text{Fe}]/dt \propto [w_5\text{FeA}^{2+}][A^-]$$

$$\propto Q_4[\text{Fe}][A^-]^2/[w]$$

$$\propto Q_4[\text{Fe}]Q_a^2Q_m[\text{H}_2\text{A}_2]/[w][\text{H}^+]^2$$

$$= k_{2m}[\text{Fe}][\Sigma\text{HA}]/[\text{H}^+]^2$$

$$r_{2m} = k_{2m}[\Sigma\text{HA}]/[\text{H}^+]^2.$$

For Equation (5): $Q_{9,8} = [w_5\text{FeA}^{2+}][\text{HA}][w]/[\text{Fe}][\text{HA}_2^-]$

$$-d[\text{Fe}]/dt \propto [w_5\text{FeA}^{2+}][\text{HA}_2^-]$$

$$\propto Q_{9,8}[\text{Fe}][\text{HA}_2^-]^2/[\text{HA}][w]$$

$$\propto Q_{9,8}[\text{Fe}]Q_{2a}^2[\text{H}_2\text{A}_2]^2/\sqrt{Q_m[\text{H}_2\text{A}_2]}[w][\text{H}^+]^2$$

$$= k_{2d}[\text{Fe}][\Sigma\text{HA}]^{1.5}/[\text{H}^+]^2$$

$$r_{2d} = k_{2d}[\Sigma\text{HA}]^{1.5}/[\text{H}^+]^2.$$

For Equation (13): $Q_9 = [w_5\text{FeA}^{2+} \cdot \text{HA}][w]/[\text{Fe}][\text{HA}_2^-]$

$$-d[\text{Fe}]/dt \propto [w_5\text{FeA}^{2+} \cdot \text{HA}][\text{HA}_2^-]$$

$$\propto Q_9[\text{Fe}][\text{HA}_2^-]^2/[w]$$

$$\propto Q_9[\text{Fe}]Q_{2a}^2[\text{HA}_2^-]^2/[w][\text{H}^+]^2$$

$$= k_{2df}[\text{Fe}][\Sigma\text{HA}]^2/[\text{H}^+]^2$$

$$r_{2df} = k_{2df}[\Sigma\text{HA}]^2/[\text{H}^+]^2.$$

The proportionality constants k_i for these relations (i.e. the log-log intercepts at unit HA and H^+ concentrations, see Fig. 6) were evaluated by nonlinear least-squares fitting to the data of Figs. 3 and 4. The best fit was obtained by recognizing contributions, over the range of HA concentrations, from Reactions (4, 9, 11, 5, and 13), omitting Reaction (12). In this evaluation, the total extraction throughput by a set of parallel steps is simply the sum of their individual throughputs. For the steps in series, there is reciprocal interaction between the total first-ligand steps and the total second-ligand steps, because each first-step product not only is the starting reactant for the second step, but also (while it

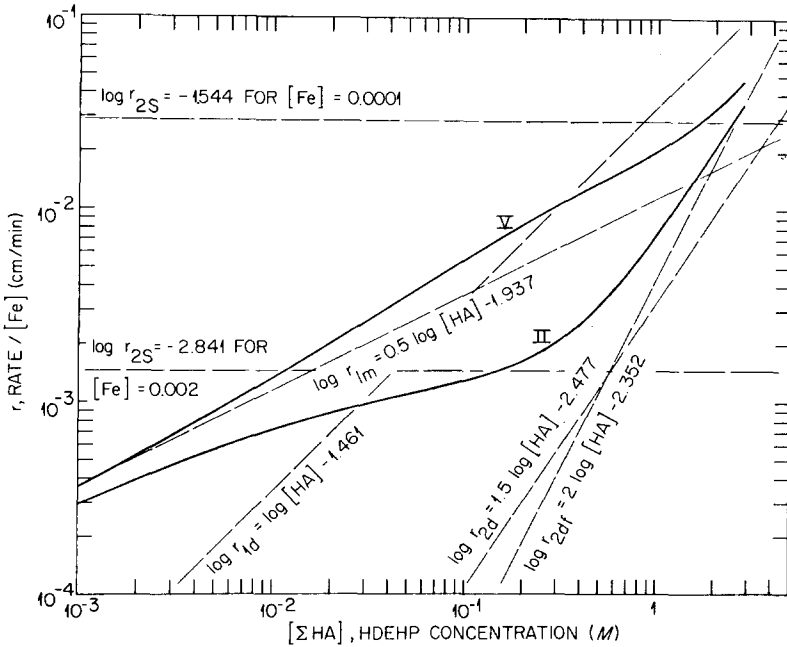


Fig. 6. Combination of parallel and series rate controlling steps. Calculated for 0.0001 and 0.002M Fe, 0.052M HClO₄, $l = 2$ (see Equation (14) and Fig. 3, curves II and V). The curves of total r vs. $[HA]$ shift with changing $[Fe]$ because the component $r_{2s} \propto [Fe]^{-1}$.

exists) blocks off some of the interface from further first-step reaction:

$$+d \ln [Fe]_{int}/dt \propto (a - a_{Fe}) \Sigma r_1$$

$$-d \ln [Fe]_{int}/dt \propto a_{Fe} \Sigma r_2.$$

Here a_{Fe} represents the area blocked off by the monocomplexed iron, and $(a - a_{Fe})$ is the specific interfacial area remaining open. At steady state transport through the interface,

$$r = +d \ln [Fe]_{int}/dt = -d \ln [Fe]_{int}/dt$$

$$a_{Fe}/(a - a_{Fe}) = \Sigma r_1/\Sigma r_2$$

so that a_{Fe} increases with increasing Σr_1 but decreases with increasing Σr_2 . The resistances to transport through the two steps are given by the reciprocals of the throughputs, the total resistance is the sum of the series resistances, $1/\Sigma r_1 + 1/\Sigma r_2$, and the total throughput is the reciprocal of the total resistance, $1/(1/\Sigma r_1 + 1/\Sigma r_2) = \Sigma r_1 \Sigma r_2 / (\Sigma r_1 + \Sigma r_2)$. Hence the total combination of the series and parallel steps is

$$\frac{-d[Fe]}{[Fe] dt} \equiv r = \frac{\Sigma r_1 \Sigma r_2}{\Sigma r_i} = \frac{(r_{1m} + r_{1d})(r_{2s} + r_{2d} + r_{2df})}{r_{1m} + r_{1d} + r_{2s} + r_{2d} + r_{2df}} \quad (14)$$

where

$$\begin{aligned}
 r_{1m} &= 5.4_7 \times 10^{-4} [\Sigma\text{HA}]^{0.5} / [\text{H}^+] \\
 r_{1d} &= 1.8_2 \times 10^{-3} [\Sigma\text{HA}] / [\text{H}^+] \\
 r_{2s} &= 1.5_2 \times 10^{-7} / [\text{H}^+] [\text{Fe}] \\
 r_{2d} &= 8.9_5 \times 10^{-6} [\Sigma\text{HA}]^{1.5} / [\text{H}^+]^2 \\
 r_{2df} &= 1.1_6 \times 10^{-5} [\Sigma\text{HA}]^2 / [\text{H}^+]^2 \\
 \sigma &= 9.5 \times 10^{-5} \text{ (standard deviation of fitting).}
 \end{aligned}$$

These separate components and their combination are illustrated in Fig. 6. The curves in Figs. 3 and 4 were calculated by Equation (14) with these constants, showing the fit to the experimental points over the wide ranges of HA, perchloric acid, and iron concentrations. At lowest HA concentrations, the rate is controlled mainly by step *1m*; it is faster than step *1d* (parallel) and slower than step *2* (series). At higher $[\Sigma\text{HA}]$ the rates through steps *1m* and *1d* increase, until the interface approaches saturation with mono-ligand complex, blocking further increases, so that step *2s* takes over the rate control. At still higher $[\Sigma\text{HA}]$ the rates through steps *2d* and *2df* become significant, and at highest $[\Sigma\text{HA}]$ they bypass step *2s* and decrease the blocking of the interface.

In anticipation of criticism that "five adjustable parameters can fit almost anything", it may be well to point out that such a criticism would be pertinent only for a function of a single variable. Here we have three independent variables, the definitions of the parameters are set by the model rather than being arbitrary, and they serve to give satisfying fit to several *different* curves. It is also worth mention that the values obtained from Curve II (Fig. 3) alone are not much different from the best values from all the data; specifically, they are $k_{1m} = 5.6_2 \times 10^{-4}$, $k_{1d} = 1.8_4 \times 10^{-3}$, $k_{2s} = 1.4_6 \times 10^{-7}$, $k_{2d} = 9.4_6 \times 10^{-6}$, and $k_{2df} = 1.1_1 \times 10^{-5}$, as compared with the values listed under Equation (14). With these the σ of fitting of all the data rises only to 11×10^{-5} from 9.5×10^{-5} .

Other hypotheses. The hydrated Fe^{3+} may be adsorbed to a significant extent at the interface, by loose association with one or more of the HA species there. This would not conflict with the model hypothesized above, and might support it by accounting for enhanced proximity and perhaps favorable orientation of the reactants in Reactions (4) and (9). However, we have not yet found a way to test this hypothesis.

Our results do not actually reject Reaction (12), above, but indicate a rather low probability that it contributes significantly to the extraction. The same is true, with decreasing probabilities, of various other increasingly complicated equations that can be written in general analogy to Reactions (4–13).

Of alternative hypotheses, we have given most consideration to those involving *equilibrium* iron hydroxyl species, particularly hydrous FeOH^{2+} and $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$. From the published hydrolysis and formation constants[25], the

varying concentrations of these species will correlate at least qualitatively with the dependences of the extraction rate on acidity, on temperature, and perhaps on ionic strength, but *not* with its dependence on iron concentration. It is possible to write separate step reactions of FeOH^{2+} and $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$ with H_2A_2 , HA, etc. that will predict rate contributions with several different power dependences on $[\text{H}^+]$ and $[\Sigma\text{HA}]$. However, we have not been able to devise a coherent model from such step reactions to account for the observed sequences of power dependences, including the region of zero order with respect to iron and low (probably zero) power dependence on $[\Sigma\text{HA}]$.

Other hypotheses we tried and rejected were those assuming the very small quantity of HDEHP distributing to the aqueous phase to be a significant reactant, including attempts to attribute the zero order region to aqueous saturation with HA.

Tests with dispersion mixing. Tests of extraction with complete dispersion in a standard-geometry mixer (Fig. 7) showed only a small shift of the observed rate ra with changing initial iron concentration, i.e. a much smaller contribution from a zero-order step in the rate control than there was with the quiescent interface. This is not surprising, as the changing interfaces of the rapidly forming and recoalescing droplets may not have time to reach saturation. The change of $\log ra$ with $\log \text{rev/min}$ from 750 to 2930 rev/min was nearly linear. Its slope was a little below the expected value of 1; hence, the subsequent comparisons were made at close to a single speed, 1000 rev/min.

The specific interfacial area a (cm^2/cm^3 aqueous) was calculated as described above, and the resulting values of r are shown in Figs. 8 and 9. This calculation also shows that the increase of ra with increasing ionic strength, Fig. 7, was due to the increase of k (Equation (1)) and hence of a at constant rev/min with increasing aqueous-phase density. The corresponding values of r (Table 3) are nearly constant.

Although the precision of the dispersion tests is noticeably poorer than that of

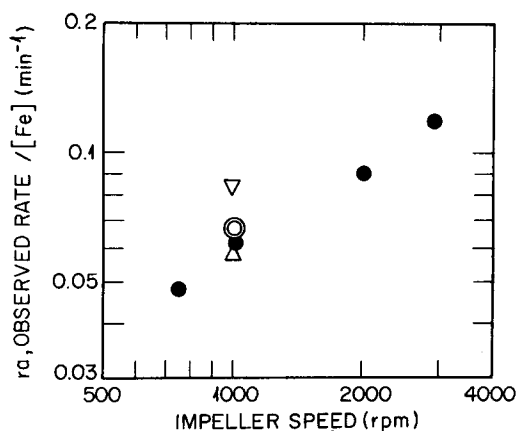


Fig. 7. Extraction rate in dispersion mixing: Effects of impeller speed, iron concentration, and ionic strength. $[\text{HA}] = 0.05$; $[\text{HClO}_4] = 1$, Δ — $I = 1$; \circ , \bullet — $I = 2$; ∇ — $I = 3$, \circ — $[\text{Fe}] = 0.0001$; \bullet — $[\text{Fe}] = 0.002$.

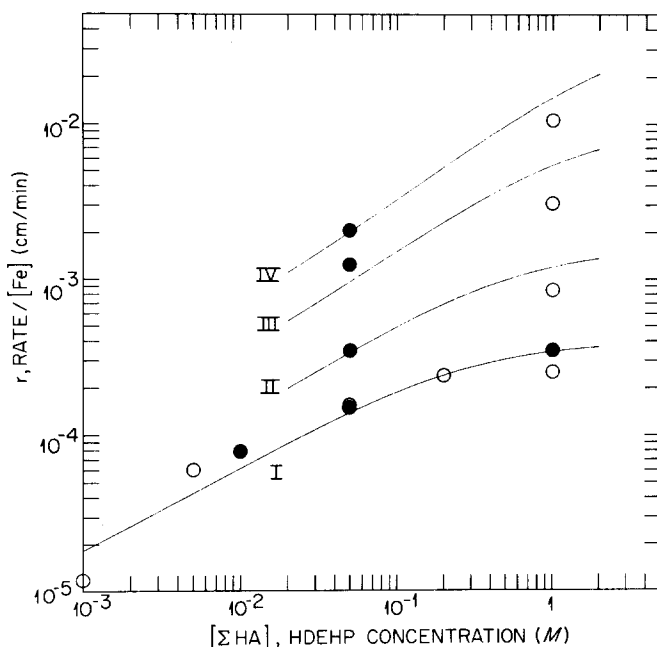


Fig. 8. Extraction rate in dispersion mixing: Dependence on HDEHP concentration. Points: $ra(\text{exptl})/a(\text{calc. cm}^2/\text{cm}^3 \text{ aq})$; $[\text{Fe}] = 0.0001$ —(○) and 0.002 —(●); $[\text{HClO}_4] = 1$ (I), 0.5 (II), 0.2 (III), and 0.1 (IV); $I = 2$. Curves: calculated from Equation (15) with r_2 taken as $4 \times 10^{-4}/[\text{H}^+]^2$.

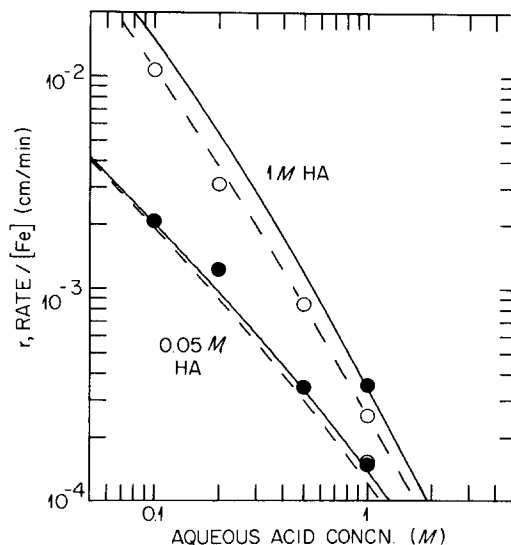


Fig. 9. Extraction rate in dispersion mixing: Dependence on aqueous acid concentration. Points: $ra(\text{exptl})/a(\text{calc. cm}^2/\text{cm}^3 \text{ aq})$; $[\text{Fe}] = 0.0001$ —(○) and 0.002 —(●); $I = 2$. Curves: calculated from Eq. 15 with r_2 taken as (solid lines) $4 \times 10^{-4}/[\text{H}^+]^2$ or (dashed lines) $2.8 \times 10^{-4}/[\text{H}^+]^{1.8}$.

the quiescent interface tests (because of inherently lower precision in sampling, plus all of the cumulative uncertainties in the estimation of the specific areas), comparison of Fig. 8 with Fig. 3 leaves no question that at least one step of the extraction path is changed by the changed mode of contact. From 0.001 to 0.01 M HA, in the region where the first-ligand steps r_{1m} and r_{1d} predominate, there is not much difference (no more than could be due to a general bias in a). Between 0.01 and 0.1 M HA there is the striking absence already noted of the behavior attributed to the second-ligand step r_{2s} , i.e. zero order with respect to $[\text{Fe}]$ and independence from $[\Sigma\text{HA}]$ at high $[\text{Fe}]$. Then above 0.1 M the dependence on $[\Sigma\text{HA}]$ does decrease, instead of increasing in this region as in Fig. 3. The log-log slope vs. $[\text{H}^+]$ (Fig. 9) increases with increasing $[\Sigma\text{HA}]$, approaching 2, and indicates that some step in introduction of the second anion ligand is becoming important.

These considerations suggest that the parallel steps r_{1m} and r_{1d} are in series with some step $r_2 \propto f([\Sigma\text{HA}])/F([\text{H}^+])$, first order with respect to iron, where $f([\Sigma\text{HA}])$ approaches $[\Sigma\text{HA}]^0$ and $F([\text{H}^+])$ approaches $[\text{H}^+]^2$. The identity and characteristics of such a step remain to be investigated. One speculation is that it may involve interface association of aqueous acid with HDEHP, related to the small but definite extraction of inorganic acid by unionized HDEHP acting as a neutral phosphoryl compound[26]. Meanwhile, the arbitrary use of $r_2 = k_2/[\text{H}^+]^2$ as an empirical function gives a usefully close fit to the dispersion-extraction rates. The combination corresponding to Equation (14) is

$$r = (r_{1m} + r_{1d})r_2 / (r_{1m} + r_{1d} + r_2). \quad (15)$$

The solid curves in Figs. 9 and 8 are plotted according to Equation (15) with $r_2 = 4 \times 10^{-4}/[\text{H}^+]^2$. (Still better apparent fit at the higher $[\Sigma\text{HA}]$ can be obtained by adjusting the exponent and coefficient, as illustrated by the dashed curves in Fig. 9 plotted for $r_2 = 2.8 \times 10^{-4}/[\text{H}^+]^{1.8}$, but this much manipulation is hardly justified.)

Comparison with previously published results. As noted above, there appears to be one important contradiction between this work and that of Karpacheva and Ilozheva[5]. They state the observed extraction rate to be independent of mixer speeds above 800 rev/min and hence independent of interfacial area, whereas we found the observed rate proportional to rev/min and hence proportional to the specific interfacial area. Unfortunately, they gave no information on their tests at any speed besides 1500 rev/min nor on the size and geometry of their mixing equipment. We duplicated their stated solution conditions for their only test at 25°C (test No. 2 of Fig. 5–Table 3–Fig. 6 in Ref.[5]) in a baffled mixer generally similar to that used for our tests in Figs. 7–9. Figure 10 (circles) shows the observed extraction rate (their K''' or K_1 , our ra) increasing in direct proportion to impeller speed from 900 to 2900 rev/min. We then repeated tests with the same impeller and in the same size and shape of mixer vessel, but without baffles. This produced marked swirling and a deep vortex. The observed rate leveled

26. A. N. Zelikman and V. M. Nerezov, *Zh. neorg. Khim.* **12**, 768 (1967); *transl. Russ. J. inorg. Chem.* **12**, 402 (1967).

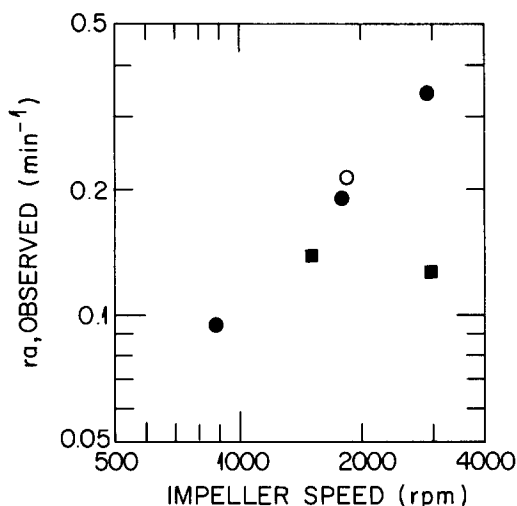


Fig. 10. Extraction rate in dispersion mixing: Comparison of fully turbulent and swirling mixing. $[HA] = 0.048$, $[HClO_4] = 0.5$, $I = 1$.

Baffled mixer, fully turbulent { \circ —0.0004M Fe
 \bullet —0.0035M Fe
 Unbaffled mixer, swirling \blacksquare —0.0035M Fe.

off, approximately constant (Fig. 10, squares). Thus, we can speculate that Karpacheva and Ilozheva may have used an insufficiently turbulent mixing system, so that their observed extraction rate leveled off because the power input and interfacial area leveled off instead of increasing with increasing rev/min. Of course we cannot know how our impeller speeds relate to theirs without knowing the size of their equipment; if it were much larger than ours, their 800 and 1500 rev/min could correspond to higher speeds than our 900–2900 rev/min. However, this seems unlikely since their K''' is not higher than the range of ra we found.

In other respects there appears to be at least qualitative agreement, in that the power dependence on HA concentration is about 0.5 and on aqueous acid concentration appreciably above 1, and that the heat of activation is too high to be consistent with diffusion control of the rate.

Kletenik and Navrotskaya studied the kinetics of iron(III) extraction by di-isoamyl phosphoric acid (HDIAP) in benzene from several acid solutions, using both quiescent interface[6] and dispersion mixing[7], and concluded that the rate is controlled by a chemical reaction at the interface. As in our HDEHP extractions from perchlorate, but to a smaller extent, the HDIAP iron extraction rate from hydrochloric acid decreased with increasing iron concentration. Also, the rate from hydrochloric acid (although not from perchloric acid) increased on shift from quiescent interface to dispersion mixing. They demonstrated catalysis by hydrochloric acid and several water-soluble monoalkyl phosphoric acids added to $HClO_4$, HNO_3 , and H_2SO_4 solutions. They expressed surprise that H_2SO_4 solutions showed slower extraction than did HNO_3 solutions, instead of faster extraction as with HCl solutions. However, this as well as the

catalysis is in line with the relative effectiveness of the catalysts shown in Table 5 and explained by Equations (6) and (7).

CONCLUSIONS

The rate of extraction of iron(III) by HDEHP is controlled by series and parallel steps, at the interface, in the introduction of the first and second anion ligands in the formation of $\text{FeA}_3 \cdot 3\text{HA}$. The quantitative contribution of each step to the net rate is given (on log-log coordinates) by a linear equation with theoretical slope, and empirical intercept at unit $[\text{HA}]$ and $[\text{H}^+]$.

A step zero-order with respect to $[\text{Fe}]_A$, involving saturation of the interface with a mono- A^- intermediate complex, is important with the quiescent and hence aged interface, but not in dispersion mixing.

Extraction is accelerated by proton-accepting complexers that can bypass some of the interface steps with analogous reactions homogeneous in the aqueous phase.

Acknowledgement—It is a pleasure to acknowledge the excellent technical assistance of J. E. Thompson.