Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Equilibria, Kinetics, and Modeling of Extraction of Citric Acid from Aqueous Solutions with Alamine 336 in 1-Octanol

K. N. Prasanna Rani[a]; T. Prathap Kumar[b]; J. S. N. Murthy[c]; T. Sankarshana[c]; B. Vishwanadham[b]
[a] Lipid Science & Technology Division, Indian Institute of Chemical Technology, Hyderabad, India [b] Chemical Engineering Sciences, Indian Institute of Chemical Technology, Hyderabad, India [c] University College of Technology, Osmania University, Hyderabad, India

To cite this Article Rani, K. N. Prasanna , Kumar, T. Prathap , Murthy, J. S. N. , Sankarshana, T. and Vishwanadham, B.(2010) 'Equilibria, Kinetics, and Modeling of Extraction of Citric Acid from Aqueous Solutions with Alamine 336 in 1-Octanol', Separation Science and Technology, 45: 5, 654 — 662
To link to this Article: DOI: 10.1080/01496390903566804
URL: http://dx.doi.org/10.1080/01496390903566804

Separation Science and Technology, 45: 654–662, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903566804

Equilibria, Kinetics, and Modeling of Extraction of Citric Acid from Aqueous Solutions with Alamine 336 in 1-Octanol

K. N. Prasanna Rani,[1] T. Prathap Kumar,[2] J. S. N. Murthy,[3] T. Sankarshana,[3] and B. Vishwanadham[2]

[1]*Lipid Science & Technology Division, Indian Institute of Chemical Technology, Hyderabad, India*
[2]*Chemical Engineering Sciences, Indian Institute of Chemical Technology, Hyderabad, India*
[3]*University College of Technology, Osmania University, Hyderabad, India*

Experimental equilibrium and kinetic data on the extraction of citric acid from aqueous solutions using Alamine 336 in 1-octanol have been determined. The distribution coefficient has increased from 0.029 to 71.727 with increase of Alamine 336 concentration from 0 to 30% (v/v). The chemical equilibria was interpreted as a result of consecutive formation of acid-amine species with 1:1 stoichiometry and the equilibrium complexation constant, K_{E1}, has been estimated as 20.186 $m^3\,kmol^{-1}$. The mass-transfer coefficients of citric acid, Alamine 336, and 1:1 acid-alamine complex in 1-octanol were calculated from acetic acid mass-transfer coefficient, which was determined by measuring its fluxes of simple diffusion from kerosene to water. Based on the Hatta number and the criterion given by Doraiswamy and Sharma, the reaction regime has been found to be instantaneous reaction regime occurring at the interface on the organic phase side. An extraction model comprising 1:1 equilibrium complextion constant, K_{E1}, and complex mass-transfer coefficient, k_{BA} ($3.79 \times 10^{-6}\,m\,s^{-1}$), has been developed, and it explained the present system satisfactorily.

Keywords 1-octanol; alamine 336; citric acid; extraction equilibria; extraction model; kinetics

INTRODUCTION

Citric acid is the most commonly used acid in the food and pharmaceutical industry because of its high solubility, palatability, strong chelating power, and low toxicity, and the global production of citric acid has reached 1.4 million tonnes per annum by 2004 (1). The food industry is the largest consumer of citric acid, using almost 70% of the total production, followed by about 12% by the pharmaceutical industry and 18% for other applications. There is an annual growth of 3.5 – 4.0% in demand/consumption rate of citric acid (2). Although citric acid can be obtained by chemical synthesis, it is produced commercially almost exclusively by fermentation with *Aspergillus niger* because of the much lower cost. The recovery of organic acids such as citric acid, lactic acid, levulinic acid etc. from aqueous solutions is an industrially important separation process, especially because of their low concentration in the fermentation broths (< 10%). The industrial method of recovery of the acid involves the precipitation of citric acid as calcium citrate by adding hydrated lime, and treatment with sulphuric acid for citric acid separation. However, this method of recovery is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste (3).

The physical extraction with conventional solvents is not an efficient method for the recovery of these acids because of very low distribution coefficients (K_D). Therefore, reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids (4,5). Reactive extraction represents a joint between the chemical phenomena (the reaction between the solute and extractant) and physical phenomena (diffusion and solubilization of the compound resulted from the chemical reaction). Organic bases such as tertiary amines offer advantages over other extractants, on the grounds of lower cost and generally higher equilibrium distribution coefficients (K_D). However, amines of very high molecular weight are less effective as extractants compared with intermediate molecular weight amines because of their greater hydrocarbon-like character (6). Alamine 336 (a straight chain tertiary amine containing C_8-C_{10} alkyl groups) diluted with a suitable solvent yields a good combination of high K_D, low solubility in water and good regenerability. Many factors have an important influence on the extraction characteristics—the nature of the acid extracted, the concentration of the acid and the extractant, and the type of the diluent used (7,8).

Juang and Huang (9) studied the rate of extraction of citric acid from aqueous solutions with tri-*n*-octylamine

---

Received 28 July 2009; accepted 12 September 2009.

Address correspondence to B. Vishwanadham, Indian Institute of Chemical Technology, Chemical Engineering Sciences, Hyderabad 500 607, India. E-mail: vishvanadham@iict.res.in

dissolved in xylene using a stirred membrane-based cell. They found that under the conditions studied, both extraction and stripping were mainly controlled by chemical reaction occurring at the interface on the organic phase side. The intrinsic rate constants for the formation and dissociation of the acid complex were determined and a possible reaction mechanism was proposed. Nikhade et al. (10) have carried out the equilibrium and kinetic studies for the extraction of citric acid with Alamine 336 in Methyl isobutyl ketone, and found that the reaction was kinetic controlled and first order in both Alamine 336 and citric acid. Y. S. Jun et al. (11) studied the kinetics for the extraction of succinic acid from aqueous solution with 1-octanol solutions of tri-*n*-octylamine (TOA) using a stirred cell with a microporous hydrophobic membrane. They found that the overall extraction process was controlled by the chemical reaction at or near the interface on the organic phase side.

Kyuchoukov et al. (12) investigated simultaneously the influence of active and inert diluents on the extraction of lactic acid by tri-*n*-octylamine (TOA) and the tri-*iso*-octylamine (TIOA). Uslu (13) has conducted equilibrium studies and determined physical mass-transfer coefficient of propionic acid for Alamine 336 in toluene system. Bayazit et al. (14) have also investigated the reactive extraction of citric acid by Amberlite LA-2 or Tridodecylamine (TDA) dissolved in different solvents and determined 1-octanol as the most effective solvent.

The back extraction/re-extraction of citric acid from Alamine 336-octanol phase is also an important step in the overall process for separation of acids from fermentation broths. There are different processes for the re-extraction of acids from extractant-solvent phase (15–19). Of all these re-extraction methods, the gas-antisolvent-induced method proposed by McMorris and Husson (19) appears to be suitable for citric acid recovery from Alamine 336-octanol phase because this process does not require any toxic material like TMA and also the energy requirement is low compared to other processes.

The design of an amine extraction process requires

(1) equilibrium and
(2) kinetic data and mass-transfer parameters for the acid-amine (solvent) system used.

Considerable information on the equilibrium of several acid-amine systems is available in the literature. However, only limited information pertaining to kinetics is available (10,20). Most of the authors have used empirical rate equations for finding the kinetics of extraction. The present work aimed at the experimental determination of equilibrium and kinetic data on the extraction of citric acid from aqueous solutions using Alamine 336 in 1-octanol diluent.

THEORETICAL

In reactive extraction, the solute reacts with the amine in the organic phase and the resulting acid-amine complexes are supposed to be stabilized due to the hydrogen bonding with the diluent (10,21,22). Because of their hydrophobic nature, the complex formation enhances the extraction of solute from aqueous to organic phase.

The extraction involves the partitioning of the solute A available in the aqueous phase to the organic phase.

$$A_{aq} \rightarrow A_{org}$$

The solute A present in the organic phase combines with the organic reactant (amine), B, and forms complex.

$$A + \gamma B \Leftrightarrow Complex$$

The extraction of citric acid with amine can be described by the set of reactions involving the formation of complexes with n acid molecules and one amine molecule.

$$(H_3A)_{aq} + (B_0)_{org} \overset{K_{11}}{\longleftrightarrow} (BH_3A)_{org} \tag{1}$$

where H_3A and B_0 represent, respectively, the citric acid and the amine.

$$(H_3A)_{aq} + (BH_3A)_{org} \overset{K_{21}}{\longleftrightarrow} B(H_3A)_{2,org} \tag{2}$$

$$(H_3A)_{aq} + B(H_3A)_{n-1,org} \overset{K_{n1}}{\longleftrightarrow} B(H_3A)_{n,org} \tag{3}$$

Then the equilibrium complexation constant, K_{En}, is

$$K_{En} = \frac{[(BH_3A)_n]_{org}}{[B_0]_{org}[H_3A]^n_{aq}} \tag{4}$$

For 1:1 complex, the Eq. (4) becomes,

$$K_{E1} = \frac{[(BH_3A)]_{org}}{[B_0]_{org}[H_3A]^*_{aq}} \tag{5}$$

The extent to which the organic phase (Alamine 336 + 1-octanol) can be loaded with citric acid is expressed as the loading ratio. The loading of the extractant, z, is defined as the total concentration of acid in the organic phase divided by the total concentration of amine in the organic phase (10,21,22).

$$z = \frac{[H_3A]_{org}}{[B_0]} \tag{6}$$

The value of z depends on the extractability of the acid (the strength of the acid-base interaction) and its aqueous concentration, and is independent of the amine content in an inert diluent (23).

By substituting z from Eq. (6) in Eq. (5), we get,

$$\frac{z}{1-z} = K_{E1} C^*_{Aaq} \tag{7}$$

Determination of Individual Mass-Transfer Coefficients, k_A, K_B and k_{BA} in 1-Octanol Phase

The mass-transfer coefficients are required to determine the reaction regime. The water/acetic acid/kerosene system can be used as a reference system for determining the mass-transfer coefficients in 1-octanol phase. Since acetic acid has a sufficiently small value of distribution coefficient in a water/kerosene system, the resistance of the aqueous diffusion film can be neglected. So the organic diffusion film resistance on the organic side can be determined by the overall mass-transfer coefficient of acetic acid in water/kerosene system (24–26).

When acetic acid is transferred from the organic phase (kerosene) to the aqueous phase (water), the mass-transfer rate is defined by (24–26),

$$-\left(\frac{V_o}{S}\right)\left(\frac{dC_o}{dt}\right) = K_o(C_o - mC_w) = k_o(C_o - C_{oi}) = k_w(C_{wi} - C_w) \tag{8}$$

where

$$m = \frac{C^*_o}{C^*_w} \tag{9}$$

and

$$\frac{1}{K_o} = \frac{m}{k_w} + \frac{1}{k_o} \tag{10}$$

Because of a low value of m, the terms mC_w and $\frac{m}{k_w}$ are negligible compared to C_o and $\frac{1}{k_o}$. Hence the simplified relations are obtained as:

$$\ln\left(\frac{C^0_o}{C_o}\right) = \left(\frac{S}{V_o}\right) K_o t \tag{11}$$

and

$$\frac{1}{K_o} = \frac{1}{k_o} \Rightarrow K_o = k_o \tag{12}$$

So the value of K_o or k_o can be obtained from the slope of plot of $\ln\left(\frac{C^0_o}{C_o}\right)$ vs. $\left(\frac{S}{V_o}\right)t$.

And, the mass-transfer coefficient on the organic side, k_o, for various systems can be determined by using the following relationship as reported by earlier investigators (9,11,24,27–29):

$$k_o \propto D_j^{\frac{2}{3}} \gamma^{-\frac{1}{6}} \tag{13}$$

where D_j and γ are diffusivity of the solute and kinematic viscosity of the solvent respectively.

Thus the mass-transfer coefficients for citric acid, Alamine 336, and 1:1 acid-amine complex in 1-octanol can be obtained by using the above relationship.

Extraction Model

When the reaction is occurring at the interface on the organic phase side, the extraction model can be formulated on the basis of Whitman's two-film theory of mass-transfer at the interface (30). In the present system, Alamine 336 extracts citric acid from the aqueous solution by forming a complex of citric acid and Alamine 336 with an interfacial reaction at the interface between the aqueous and organic phases.

At the quasi-steady state, the reaction rates are equal for all the components because of equimolar 1:1 complex formation, and then

$$R_A a = R_B a = R_{BA} a \tag{14}$$

The ratio of the mass-transfer coefficients in organic phase is given by

$$\beta = \frac{k_B}{k_{BA}} \tag{15}$$

Since the extraction equilibrium prevails at the interface, the constant K_{E1} is expressed as,

$$K_{E1} = \frac{C_{BAi}}{C_{Ai} C_{Bi}} \tag{16}$$

From the Eqs. (14–16), we get

$$R_A^2 + pR_A + q = 0 \tag{17}$$

where

$$p = k_{Aaq} C_{Aaq} + k_B C_B + \frac{k_{Aaq}\beta}{K_{E1}} \tag{18}$$

$$q = -\left[k_{Aaq} C_{Aaq} k_B C_B - \frac{k_{BA} C_B}{K_{E1}} (k_{Aaq}\beta)\right] \tag{19}$$

So the solution for Eq. (17) is

$$R_A = \left[-\left(\frac{p}{2}\right) + \left(\frac{p^2}{4} - q\right)^{1/2}\right] \tag{20}$$

Then the rate of disappearance of citric acid in the aqueous phase is given by

$$-\frac{dC_A}{dt} = R_A a = a\left[-\left(\frac{p}{2}\right) + \left(\frac{p^2}{4} - q\right)^{1/2}\right] \tag{21}$$

MATERIALS AND METHODS

Materials

Citric acid monohydrate (99.5%) and 1-Octanol (99%) were supplied by S. D. Fine-Chem Ltd. (Mumbai, India) and Loba Chemie (Mumbai, India) respectively. Alamine 336 (Henkel Co., USA), a C_8–C_{10} saturated straight-chain tertiary amine mixture, is a pale yellow liquid practically insoluble in water (<5 ppm), with an average molecular weight, $M = 392\,g\,mol^{-1}$, and a density of $810\,kg\,m^{-3}$ at 20°C. Acetic acid (99.9%) and kerosene were supplied by Merck India Ltd. (Mumbai, India) and S. D. Fine-Chem Ltd. (Mumbai, India) respectively. Sodium hydroxide used was of reagent grade. All the chemicals were used without further purification. Double-distilled water was used for all the experiments.

Equilibrium Data

The physical and chemical equilibrium experiments were carried out at room temperature (30°C). For the physical equilibrium, the aqueous solution of citric acid (25 mL) and an equal volume of 1-octanol (organic phase) were contacted on a temperature-controlled shaker bath for 12 h, and the two phases were allowed to settle for 2 h. The aqueous phase was titrated with NaOH using phenolphthalein as indicator to determine the concentration of citric acid. The corresponding acid concentration in the organic phase was calculated by mass balance. The initial concentration of citric acid was varied from 0.05 to $0.50\,kmol\ m^{-3}$. This comparatively low concentration range was used because the acid concentrations are not expected to be high in the practical case of acid recovery from fermentation broths (4). The same procedure was used for determining chemical equilibrium isotherms for 10% ($0.2066\,kmol\,m^{-3}$), 20% ($0.4132\,kmol\,m^{-3}$) and 30% ($0.6198\,kmol\,m^{-3}$) Alamine 336 (v/v) in 1-octanol.

Kinetic Data

A stirred cell with constant interfacial area was used for kinetics measurement. The cell is a cylindrical glass vessel of 0.064 m diameter and 0.1 m height, with a flat bottom and a stirrer with two paddle impellers of four blades each (21). The speed of agitation of the stirrer was maintained through a controlled variable speed drive. This was equipped with digital display and was supplied by Remi Motors Ltd. (Mumbai, India). The stirred cell apparatus was provided with an arrangement at the bottom for the removal of the aqueous samples with the help of a syringe without interrupting the stirring. First, 100 mL of aqueous solution of citric acid was taken in the cell. The position of the four-blade paddle impellers was adjusted to 5 mm below and 5 mm above the interface. Then 100 mL of the organic phase was added without disturbing the interface, and the stirring of the mixture was started immediately at a specific speed of agitation. The aqueous layer samples were taken at different intervals of time. Using acid-base titration with NaOH and phenolphthalein as indicator, citric acid concentration in the aqueous phase was determined. The concentration of acid in the organic phase was determined by mass balance. Some experiments (approximately 40%) were repeated to check the reproducibility and the results were found to be reproducible within ±3%. The reaction between citric acid and Alamine 336 is reversible particularly under conditions of high loading in the organic phase and initial rates measurement was considered for evaluation of the kinetics to avoid problems due to reversibility (31). The initial rate ($kmol\,m^{-3}\,s^{-1}$) was obtained from the slope of the citric acid concentration in aqueous phase (C_{Aaq}) vs. time plot at time, $t = 0$. This value was then divided by interfacial area, i.e., the cross-sectional area of the stirred cell, $0.003242\,m^2$, and multiplied by volume of aqueous phase to yield the specific rate of extraction, R_A ($kmol\,m^{-2}\,s^{-1}$).

$$R_A = -\frac{V_{aq}}{S}\frac{dC_{Aaq}}{dt}\bigg|_{t=0} \tag{22}$$

RESULTS AND DISCUSSION

Extraction Equilibria

The physical equilibrium and the chemical equilibrium isotherms, with 10%, 20%, and 30% Alamine 336 (v/v) in 1-octanol, for the distribution of citric acid between water and organic phase (in 1:1 volume ratio) within the range of 0.05–$0.5\,kmol\,m^{-3}$ initial citric acid concentrations were determined at 30°C and are shown in Fig. 1. It can be inferred from Fig. 1 that the distribution of citric acid

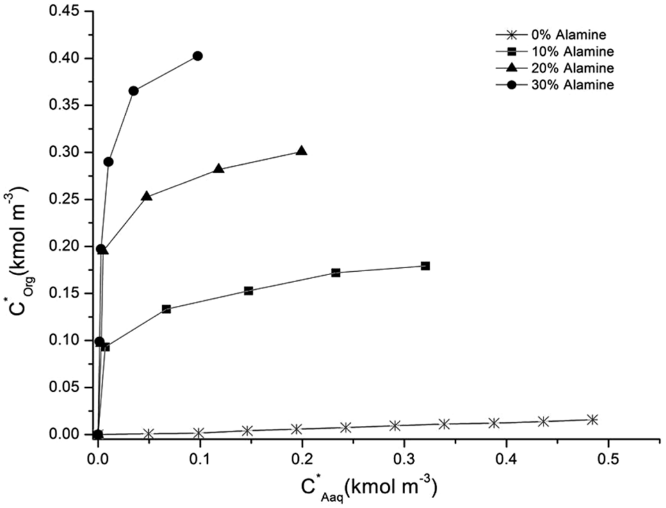

FIG. 1. Equilibrium isotherms for reactive extraction of citric acid with various concentrations of Alamine 336 in 1-Octanol at 30°C.

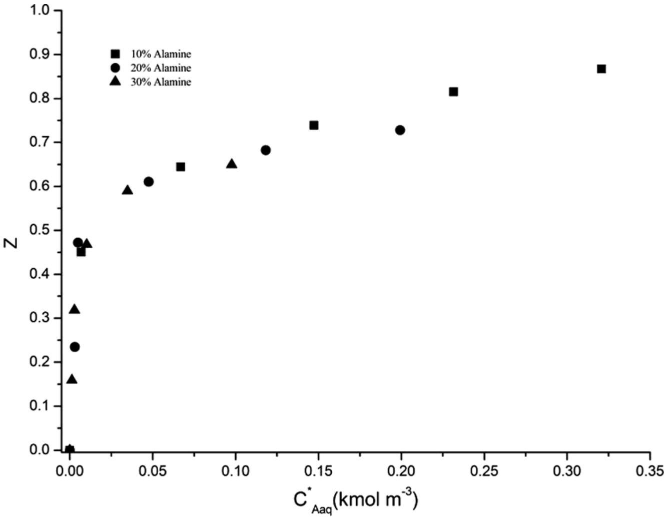

FIG. 2. Loading of Alamine 336 with citric acid.

increased with the increase of concentration of Alamine 336 in 1-octanol.

Distribution Coefficient, K_D

From Fig. 1, the effect of Alamine 336 in 1-octanol on the extraction is evident. The amount of acid extracted from aqueous solutions at any initial acid concentration increased with increasing amine concentration. The values of the distribution coefficient, K_D, at 0.2 kmol m^{-3} initial acid concentration, for 0%, 10%, 20% and 30% Alamine 336 (v/v) in 1-octanol are given in Table 1 and it increased significantly from 0.029 to 71.727.

This data can be used for in situ recovery of the product using Alamine 336 in 1-octanol from the fermentation broth without adding units for pH adjustment. It has been observed that the distribution coefficients are high when aqueous citric acid concentrations are below 0.1 kmol m^{-3}, i.e., 2% by weight, and this acid concentrations are also much less than the acid concentrations observed by earlier investigators, i.e., <5%, for good microbial activity in fermentation broths (5,32).

TABLE 1
Distribution coefficient, K_D, for reactive extraction of citric acid from aqueous solutions with different concentrations of Alamine 336 in 1-Octanol at 0.2 kmol m^{-3} initial citric acid concentration

% alamine (v/v)	K_D
0	0.029
10	1.992
20	39.650
30	71.727

Loading and Equilibrium Complexation Constant, K_{E1}

The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase, *z*. The equilibrium concentration of citric acid in aqueous phase for 10%, 20% and 30% (v/v) Alamine 336 in 1-octanol was plotted against loading of amine, *z*, in Fig. 2, and it is observed that the loading ratio is more or less same for all concentrations of Alamine 336. It happens only when the same type of complex forms at different concentrations of Alamine 336. Since there is a decrease in loading with increasing Alamine 336 concentration, it is clear that complexes involving only one amine are formed (33).

The 1:1 complex is formed if the organic phase is not highly concentrated, i.e., at very low loading ratios, and the Eq. (7) has to be satisfied. So to confirm the formation of 1:1 complex, the values of $\frac{z}{1-z}$ were plotted against C^*_{Aaq} for 10% (v/v) Alamine 336 in Fig. 3, and it has given a straight line with a slope of 20.186. Hence it is concluded that citric acid is forming a 1:1 complex with Alamine 336 for low concentrations of citric acid in the organic phase while extracting citric acid from aqueous solutions with a complexation constant, K_{E1}, of 20.186 m^3 kmol^{-1}. The same type of complex has been observed by earlier workers also (10). This is the case when the organic phase is not overloaded and moles of acid per mole of Alamine 336 in the organic phase are less than unity (8).

Extraction Kinetics for Determination of Reaction Regime

Individual Mass-Transfer Coefficients, k_A, k_B, k_{BA} in 1-Octanol Phase

The plot of $\ln\left(\frac{C_o^0}{C_o}\right)$ vs. $\left(\frac{S}{V_o}\right)t$ for acetic acid in water/kerosene system is shown in Fig. 4, and the acetic acid

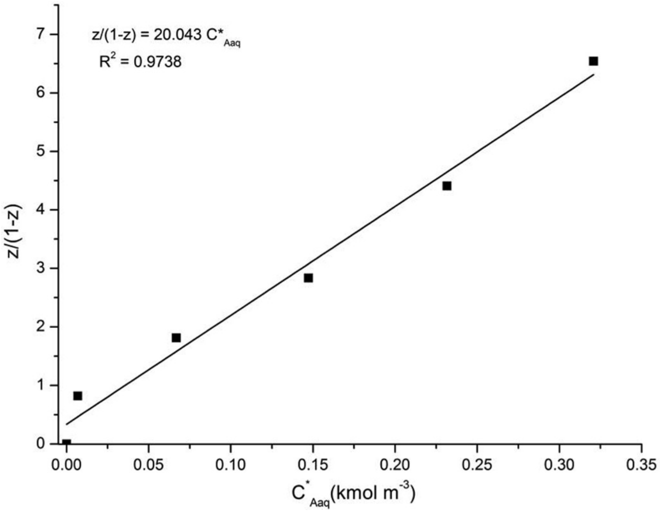

FIG. 3. Estimation of 1:1 citric acid-Alamine complex Equilibrium complexation constant for 10% (0.2066 kmol m^{-3}) Alamine 336.

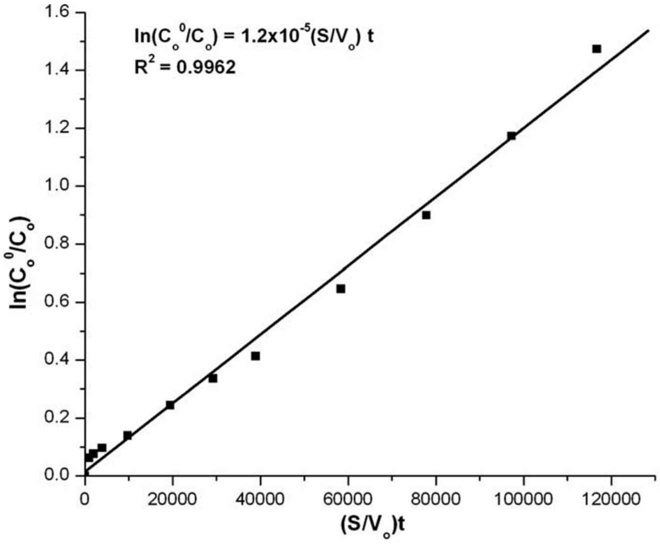

FIG. 4. Determination of overall mass-transfer coefficient for acetic acid in kerosene/water. $[C_o^0] = 0.133\,\text{kmol}\,\text{m}^{-3}$, Speed of agitation = 1 rev s^{-1}.

mass-transfer coefficient in kerosene, k_o, is found to be $1.2 \times 10^{-5}\,\text{m}\,\text{s}^{-1}$. The diffusivities of acetic acid in kerosene, and citric acid, Alamine 336, and 1:1 citric acid-alamine complex in 1-octanol are estimated by the Minhas-Hayduk method (24, 34). The kinematic viscosities of kerosene and 1-octanol at 303 K are 1.52×10^{-6} and $7.36 \times 10^{-6}\,\text{m}^2\,\text{s}^{-1}$, respectively. The molar volumes of kerosene, 1-octanol, citric acid, Alamine 336, and 1:1 citric acid-alamine complex are 259.9, 190.82, 202.4, 622.5, and $792.7\,\text{cm}^3\,\text{mol}^{-1}$ respectively, calculated by structural contributions (34). The parachors for kerosene, 1-octanol, Alamine 336 and 1:1 citric acid-alamine complex are 146.3, 365.5, 1679.6 and $2177.2\,\text{cm}^3\,\text{g}^{1/4}\,\text{s}^{-1/2}$, respectively, calculated by the Tyn and Calus method (34). The calculated diffusion coefficients and individual mass-transfer coefficients are given in Table 2.

Effect of Speed of Agitation on R_A

This is required to confirm the reaction regime. The speed of agitation was varied in the range of 0.8 to 1.4 rev s^{-1} so that the liquid–liquid interface was flat and the interfacial area for extraction was equal to the geometric cross-sectional area of the interface in the stirred cell. The concentration profiles of the aqueous phase citric acid at $0.2\,\text{kmol}\,\text{m}^{-3}$ initial citric acid concentration and $0.21\,\text{kmol}\,\text{m}^{-3}$ (10% v/v) Alamine 336 in 1-octanol at different speeds of agitation are plotted in Fig. 5. From Fig. 5, the specific rates of extraction, R_A, as given in Eq. (22), were determined. The plot of the specific rates of extraction, R_A vs. speed of agitation is depicted in Fig. 6, which shows that there is no increase in the specific rate of extraction, R_A, with increase in the speed of agitation. This shows that the specific rate of extraction is independent of mixing.

Order of Reaction w.r.t Citric Acid Concentration

In order to find the order of reaction w.r.t citric acid, the R_As have been determined by varying initial citric acid concentration from 0.1 to $0.25\,\text{kmol}\,\text{m}^{-3}$ at $0.21\,\text{kmol}\,\text{m}^{-3}$ (10% v/v) Alamine 336 in 1-octanol and 1 rev s^{-1} speed of agitation. The rates of extraction, $R_A a$, are plotted in Fig. 7, and the order of rate of extraction w.r.t citric acid, m, is found to be 1 by regression analysis.

Order of Reaction w.r.t Alamine 336 Concentration

In order to find the order of reaction w.r.t Alamine 336, the R_As have been determined for varied Alamine 336 concentrations from 5 to 20% (v/v) in 1-octanol at 0.2 kmol m^{-3} initial citric acid concentration and 1 rev s^{-1} speed of agitation. The rates of extraction, $R_A a$, are plotted in Fig. 8, and the order of reaction w.r.t Alamine 336, n, is found to be 1 by regression analysis.

Rate Constant, K_2

The second order rate constant, K_2, was obtained from Fig. 9 by regression analysis, and is found to be $3.8 \times 10^{-3}\,\text{m}^3\,\text{kmol}^{-1}\,\text{sec}^{-1}$.

Criteria for the Reaction Regime

The Hatta number, M_H, $\frac{\left(\frac{2}{m+1} D_A K_{mn} [A^*]^{m-1} [B_o]^n\right)^{1/2}}{k_L}$, which becomes $\frac{(D_A K_2 [B_o])^{1/2}}{k_L}$ for $m = 1$ and $n = 1$, is found to be

TABLE 2
Diffusion and mass-transfer coefficients at 303 K

System (solute/medium)	Diffusion coefficient (m^2 s^{-1})	Mass-transfer coefficient (m s^{-1})*
Acetic acid/kerosene	3.899×10^{-10}	1.2×10^{-5}
Citric acid/1-octanol	2.239×10^{-10}	6.373×10^{-6}
Alamine 336/1-octanol	1.145×10^{-10}	4.075×10^{-6}
1:1 Acid-alamine complex/1-octanol	1.027×10^{-10}	3.79×10^{-6}

*At 1 rev s^{-1}.

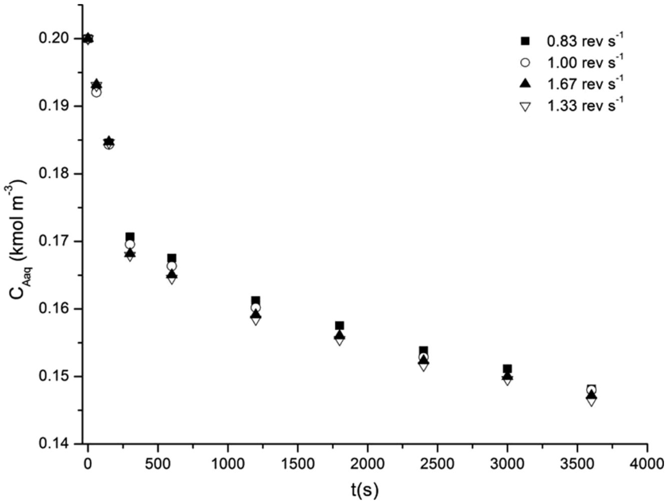

FIG. 5. Concentration profiles of C_{Aaq} at different speeds of agitation. Initial citric acid concentration = 0.2 kmol m^{-3}, Alamine concentration = 10% (0.2066 kmol m^{-3}).

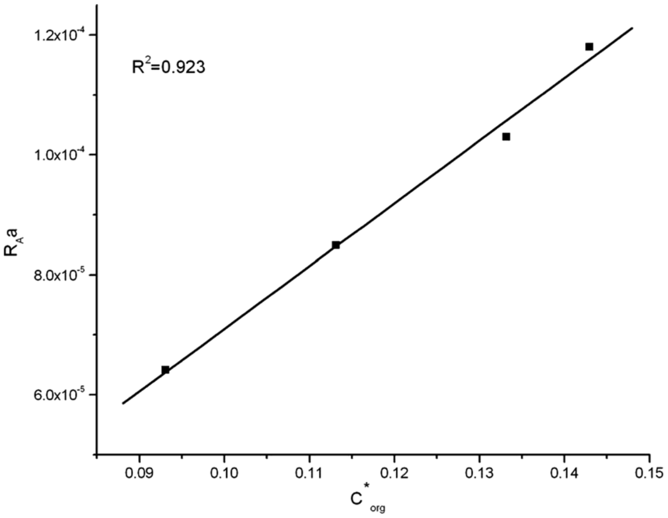

FIG. 7. Determination of order of reaction w.r.t citric acid concentration, *m*.

varying from 4.65 to 9.3 for the studied range of Alamine 336 concentrations at 1 rev s^{-1} speed of agitation, and this shows that the reaction is fast or instantaneous that is taking place in the organic film (35). To differentiate between the instantaneous reaction and the fast reaction occurring in the organic film, the value of $\frac{[B_o]}{Z[A^*]}\sqrt{\frac{D_B}{D_A}}$, as given by Doraiswamy and Sharma (36), was calculated and is found to be varying from 0.66 to 2.61 for the studied concentration ranges of citric acid and Alamine 336, and this value is less than the Hatta number. This confirms that the reaction is instantaneous reaction occurring at a reaction plane in the organic film. Since the specific rate of extraction is independent of speed of agitation and also the available Alamine 336 concentration for reaction is high, it can be deduced that the reaction plane is formed at the interface itself and the reaction is taking place at the interface in the organic phase (35).

Applying Extraction Model

Since citric acid is highly soluble in aqueous phase and Alamine 336 is also highly soluble in 1-octanol phase, it is assumed that the resistances for citric acid transfer in the aqueous film and Alamine 336 transfer in organic film are negligible. For the initial part of the extraction, i.e., at $t = 0$, $C_{BA} = 0$ and Eqs. (20) and (21) become,

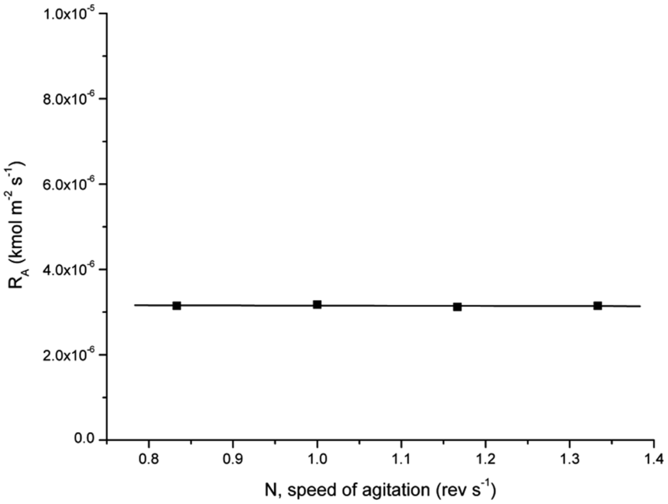

FIG. 6. Effect of speed of agitation on specific rate of extraction. Initial citric acid concentration = 0.2 kmol m^{-3}, Alamine concentration = 10% (0.2066 kmol m^{-3}).

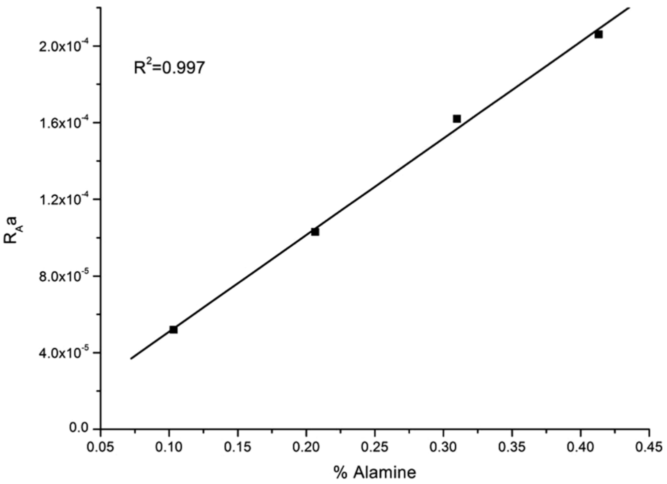

FIG. 8. Determination of order of reaction w.r.t Alamine 336 concentration, *n*.

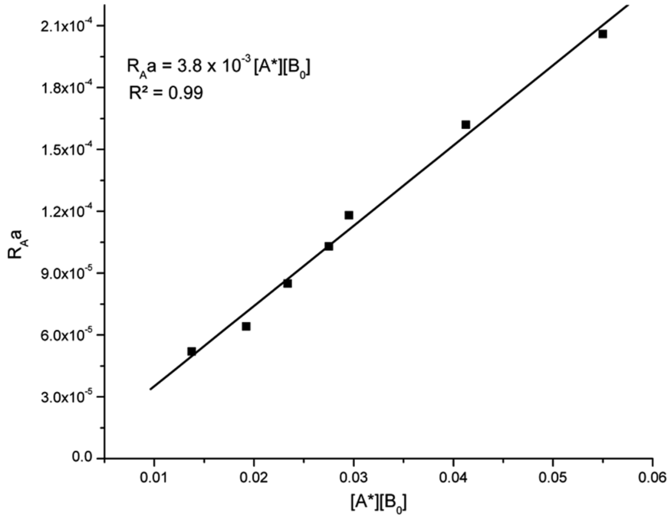

FIG. 9. Determination of second order reaction rate constant, K_2.

$$R_A = K_{E1} k_{BA} C^0_{Aaq} C^0_B \tag{23}$$

and

$$-\frac{dC_A}{dt} = R_A a = a\left[K_{E1} k_{BA} C^0_{Aaq} C^0_B\right] \tag{24}$$

The theoretical values of R_A were calculated using the Eq. (23), and are plotted against experimental values in Fig. 10. It can be concluded from Fig. 10 that the developed model explains the present system of extraction of citric acid from aqueous solutions using Alamine 336 in 1-octanol satisfactorily with a deviation of ±5%.

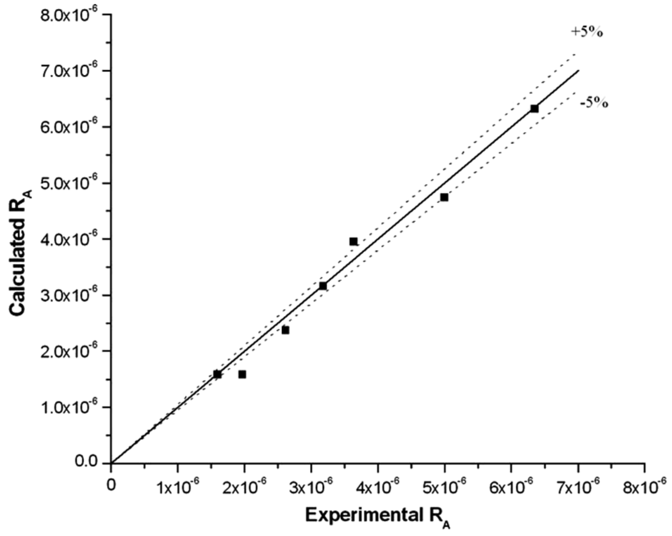

FIG. 10. Comparison of experimental R_A and calculated R_A by Eq. (23).

CONCLUSIONS

The physical and chemical equilibria for the extraction of citric acid by Alamine 336 in 1-octanol have been determined, and the extraction equilibrium isotherms showed that the distribution coefficient, K_D, at 0.2 kmol m^{-3} initial citric acid concentration, increased from 0.029 to 71.727 with the increase of Alamine 336 concentration in 1-octanol from 0 to 30% (v/v). The loading of Alamine 336 with citric acid, z, was proportional to Alamine 336 concentration in 1-octanol. The chemical equilibria was interpreted as a result of consecutive formation of acid-amine species with 1:1 stoichiometry and the equilibrium complexation constant, K_{E1}, has been estimated as 20.186 m^3 kmol^{-1}.

The mass-transfer coefficients of citric acid, Alamine 336 and 1:1 acid-alamine complex in 1-octanol were calculated from the mass-transfer coefficient of acetic acid, which was first determined by measuring its fluxes of simple diffusion from kerosene to water. The kinetic analysis was done based on the initial rates, and the specific rate of extraction, R_A, was constant for different speeds of agitation in the range of 0.8 to 1.4 rev s^{-1}. Based on the Hatta number, the criterion given by Doraiswamy and Sharma, the effect of speed of agitation and high Alamine 336 concentration, the reaction regime was found to be instantaneous occurring at the interface on the organic phase side. An extraction model comprising K_{E1} and k_{BA} parameters has been developed for the initial part of the extraction and it explained the present mass-transfer with chemical reaction system satisfactorily within ±5% error. This extraction model could be effectively utilized for designing an extraction process to recover citric acid using Alamine 336 in 1-octanol from fermentation broths.

ACKNOWLEDGEMENTS

The authors are grateful to Dr JS Yadav (Director) and Dr RBN Prasad (Head, Lipid Science & Technology), Indian Institute of Chemical Technology, Hyderabad, India, for their valuable support.

NOMENCLATURE

S	Cross-sectional area of the stirred cell (m^2)
a	Interfacial area per unit volume (m^{-1})
C	Acid concentration (kmol m^{-3})
K_D, m	Distribution coefficient (–)
K_2	Second-order reaction rate constant (m^3 kmol^{-1} s^{-1})
K_{E1}	(1:1) Citric acid-alamine equilibrium complexation constant (m^3 kmol^{-1})
K	Overall mass-transfer coefficient (m s^{-1})
k	Individual mass-transfer coefficient (m s^{-1})
Z	Stoichiometric coefficient

Superscripts

*	Equilibrium

0	Initial

Subscripts

A	Citric acid
B	Alamine 336 in organic phase
BA	Acid-amine complex in organic phase
aq, w	Aqueous phase
org, o	Organic phase
i	Interface

REFERENCES

1. Soccol, C.R.; Vandenberghe, L.P.S.; Rodrigues, C.; Pandey, A. (2006) Citric acid Production. *Food Tech. Biotechnol.*, 44: 141.
2. Vandenberghe, L.P.S.; Soccol, C.R.; Pandey, A.; Lebeault, J.M. (2000) Solid-state fermentation for the synthesis of citric acid by Aspergillus niger. *Bioresource Technol.*, 74: 175.
3. Shreve, R.N.; Brink, J.A. (1977) *Chemical Process Industries*, 4th Ed.; McGraw-Hill: New York, USA.
4. Wardell, J.M.; King, C.J. (1978) Solvent equilibria for extraction of carboxylic acids from water. *J. Chem. Eng. Data*, 23: 144.
5. Wennersten, R. (1983) Extraction of carboxylic acid from fermentation broth using solution of tertiary amine. *J. Chem. Tech. Biotechnol.*, 33 (B): 85.
6. Ricker, N.L.; Pittman, E.F.; King, C.J. (1980) Solvent extraction with amines for recovery of acetic acid from dilute aqueous industrial streams. *J. Sep. Proc. Technol.*, 1: 23.
7. Inci, I. (2002) Extraction of aqueous solution of gluconic acid with organic solutions of Alamine 336. *Chem. Biochem. Eng. Q.*, 16: 185.
8. Tamada, J.A.; Kertes, A.S.; King, C.J. (1990) Extraction of carboxylic acids with amine extractants. 1. Equilibrium and law of mass action modeling. *Ind. Eng. Chem. Res.*, 29: 1319.
9. Juang, R.S.; Huang, T.H. (1995) Kinetic studies on the extraction of citric acid from aqueous solutions with tri-n-octylamine. *J. Chem. Eng. Jpn.*, 28: 274.
10. Nikhade, B.P.; Moulijn, J.A.; Pangarkar, V.G. (2004) Extraction of citric acid from aqueous solutions with Alamine 336: Equilibrium and kinetics. *J. Chem. Tech. Biotechnol.*, 79: 1155.
11. Jun, Y.S.; Huh, Y.S.; Hong, W.H.; Hong, Y.K. (2005) Kinetics of extraction of succinic acid with tri-n-octylamine in 1-octanol solution. *Biotechnol. Prog.*, 21: 1673.
12. Kyuchoukov, G.; Labbaci, A.; Albet, J.; Molinier, J. (2006) Simultaneous Influence of active and "Inert" diluents on the extraction of lactic acid by means of Tri-*n*-octylamine (TOA) and Tri-*iso*-octylamine (TIOA). *Ind. Eng. Chem. Res.*, 45: 503.
13. Uslu, H. (2006) Linear solvation energy relationship (LSER) Modeling and kinetic studies on propionic acid reactive extraction using alamine 336 in a toluene solution. *Ind. Eng. Chem. Res.*, 45: 5788.
14. Bayazit, S.S.; Uslu, H.; Inci, I. (2009) Comparative equilibrium studies for citric acid by amberlite LA-2 or tridodecylamine. *J. Chem. Eng. Data*, 54: 1991.
15. Yabannavar, V.M.; Wang, D.I.C. (1991) Extractive fermentation for Lactic acid production. *Biotechnol. Bioeng.*, 37: 1095.
16. Jung, M.; Schierbaum, B.; Vogel, H. (2000) Extraction of carboxylic acid from aqueous solutions with the extractant system alcohol/tri-n-alkylamines. *Chem. Eng. Technol.*, 23: 70.
17. Poole, L.J.; King, C.J. (1991) Regeneration of carboxylic acid-amine extracts by back-extraction with an aqueous solution of a volatile amine. *Ind. Eng. Chem. Res.*, 30: 923.
18. Tamada, J.A.; King, C.J. (1990) Extraction of carboxylic acids with amine extractants. 3. Effect of temperature, water co-extraction and process consideration. *Ind. Eng. Chem. Res.*, 29: 1333.
19. McMorris, J.; Husson, S.M. (2001) Gas antisolvent-induced regeneration of lactic acid-laden extractants. *Sep. Sci. Technol.*, 36: 1129.
20. Poposka, F.A.; Nikolovski, K.; Tomovska, R. (1998) Kinetics, Mechanism and mathematical modeling of citric acid with isodecanol/n-paraffins solutions of trioctylamine. *Chem. Eng. Sci.*, 53: 3227.
21. Wasewar, K.L.; Heesink, A.B.M.; Versteeg, G.F.; Pangarkar, V.G. (2002) Equilibria and kinetics for reactive extraction of lactic acid using Alamine 336 in decanol. *J. Chem. Tech. Biotechnol.*, 77: 1068.
22. Gaidhani, H.K.; Wasewar, K.L.; Pangarkar, V.G. (2002) Intensification of enzymatic hydrolysis of penicillin G: Part 1. Equilibria and kinetics of extraction of phenyl acetic acid by Alamine 336. *Chem. Eng. Sci.*, 57: 1979.
23. Kertes, A.S.; King, C.J. (1986) Extraction chemistry of fermentation product carboxylic acids. *Biotechnol. Bioeng.*, 28: 262.
24. Kiani, A.; Bhave, R.; Sirkar, K.K. (1984) Solvent extraction with immobilized interface in a microporous hydrophobic membrane. *J. Membr. Sci.*, 20: 125.
25. Juang, R.S.; Lo, R.H. (1994) Mass-transfer characteristics of a membrane permeation cell and its application to the kinetic studies of solvent extraction. *Ind. Eng. Chem. Res.*, 33: 1001.
26. Komasawa, I.; Otake, T.; Yamada, A. (1980) Diffusional resistance in extraction rate of copper with hydroxyoxime extractant. *J. Chem. Eng. Jpn.*, 13: 209.
27. Levich, V.G. (1962) *Physicochemical Hydrodynamics*; Prentice Hall, Inc.: Englewood Cliffs, NJ.
28. Prasad, R.; Kiani, A.; Bhave, R.R.; Sirkar, K.K. (1986) Further studies on solvent extraction with immobilized interfaces in a microporous hydrophobic membrane. *J. Membr. Sci.*, 26: 79.
29. Juang, R.S. Huang, R.H. (1997) Kinetic studies on lactic acid extraction with amine using a microporous membrane-based stirred cell. *J. Membr. Sci.*, 129: 185.
30. Whitman, W.G. (1923) The two-film theory of gas absorption. *Chem. Met. Eng.*, 29: 147.
31. Matsumoto, M.; Uenoyama, S.; Hano, T.; Hirata, M.; Miura, S. (1996) Extraction kinetics of organic acids with tri-n-octylphosphine Oxide. *J. Chem. Tech. Biotechnol.*, 67: 260.
32. Herrero, A.A. (1983) End-product inhibition in anaerobic fermentation. *Trends Biotechnol.*, 1: 49.
33. Prochazka, J.; Heyberger, A.; Bizek, V.; Kousova, M.; Volaufova, E. (1994) Amine extraction of hydroxycarboxylic acids 2. Comparison of equilibria for lactic, malic and citric acids. *Ind. Eng. Chem. Res.*, 33: 1565.
34. Reid, R.C.; Prausnitz, J.M.; Poling, B.E. (1988) *The Properties of Gases and Liquids*, 4th Ed.; McGraw-Hill Book Co.: Singapore.
35. Levenspiel, O. (2001) *Chemical Reaction Engineering*, 3rd Ed.; John Wiley & Sons: Singapore.
36. Doraiswamy, L.K.; Sharma, M.M. (1984) *Heterogeneous Reaction: Analysis, Examples and Reactor Design, Vol. 2, Fluid–Fluid–Solid-Reactions*; 1st Ed.; John Wiley & Sons: New York.