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Optimization of extractive removal of formic acid from water by tri-*n*-propyl amine and dibenzyl amine in mono and dibasic ester diluents: LSER modelling

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ABSTRACT

A comparative study of reactive extraction of formic acid from water by tri-*n*-propyl amine (TPA) and dibenzyl amine (DBA) dissolved in ester and alcohol diluents has been carried out at $T = 298.2$ K and $P = 101.3$ kPa. The uptake capacity of the amine/diluent system is ranging in the order, isoamyl alcohol > diethyl malonate > diethyl succinate > diethyl sebacate > ethyl valerate > ethyl caprylate, and TPA > DBA. Different mechanisms control favourably monotype (1:1 or 1:2) and two types (1:2 and 1:3, or 1:1 and 1:3) formic acid-amine aggregation in the organic phase depending on the solvation efficiency of diluent. Monobasic esters are more effective solvating agents for organic complexes, whereas amine/isoamyl alcohol mixture yields larger extraction factors of $D > 1$, $Z_t > 1$, and $E > 50\%$ due to the simultaneous effect of physical extraction and chemical interaction. An optimization structure has been formulated for efficiently identifying the optimum ranges of separation ratio R and synergistic enhancement SE factors based on the derivative variation method. The most compatible optimization ranges for the extractive recovery of formic acid from water are $1 < R < 8$ and $5 < SE < 10$. The correlative performance of LSER and mass action law models has shown considerable success. The deviation statistics testify the ability of LSER to simulate accurately the observed properties with a mean error of 4.7%.

Keywords: Extraction; Formic acid; Amine; Modelling; LSER; Optimization

1. Introduction

Nowadays, priority of the commercialization of the formic acid separation from the fermentation or reaction broth and wastewaters has increased, but work still has to be done in many fields. Effective separation methods employing construction materials need to be developed and optimized in order to improve efficiency, to minimize production costs, and to obtain information on the suitability of these materials as separating agents for formic acid [1]. Formic acid is currently being produced by catalytic partial oxidation of wet biomass or by bacterial fermentation [1, 2]. The operating conditions of the dedicated oxidative routes are usually susceptible to the acid recovering process. Formic acid is an important intermediate in chemical synthesis and occurs naturally, most notably in some ants. It is a strong reducing agent, being commonly used as reducer in dyeing wool fast colours, tanning, electroplating, coagulating rubber latex; aid in regenerating old rubber and also in chemical analysis.

Among various downstream processing options for the recovery of a hydrophilic acid from fermentation broth and wastewater, reactive extraction is actually encountered in practice due to a high acid recovery, an easy reuse of solvents, a low operating temperature, and a controllable pH [3, 4]. Commercial aliphatic amines and phosphorous extractants dissolved in polar diluents have found use to varying degree in extracting C_1–C_5 aliphatic carboxylic acids [3–18]. Typically, tertiary amines are being preferred to primary and secondary amines by reason of decreasing the extractant loss through H_2O solubility and amide formation with the

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acid [3–8]. Experimental findings concerning amine/diluent/acid systems reveal that characterization of the reversible acid-amine complexation is very much dependent on the types and concentrations of the acid, carrier and diluent, temperature, pH, the swing effect of a mixed diluent and the third phase formation [4–18]. As reported by Bízek et al. [7] and Senol et al. [8–13], the acid-amine association is very sensitive to the strength of the complex solvation by an aromatic or aliphatic diluent, allowing the formation of at least two stable acid-amine complexes in the organic phase. From this perspective, the implementation of amine extraction method argues an uncoupling the behaviour relative to the diluent/complex interaction through hydrogen bonding and dipole–dipole interaction from the physical solubility of the acid to establish a sentence structure distinguishing the dominating factors of reversible acid-amine complexation.

The present work aims at generating new liquid-liquid equilibrium data for the reactive extraction of formic acid from water at $T = 298.2$ K and $P = 101.3$ kPa using tri-*n*-propyl amine (TPA)/diluent and dibenzyl amine (DBA)/diluent solvent systems of lower vapour pressure than water and formic acid. The effect of the carrier and diluent structures on the extraction equilibrium of formic acid, as well as the competition between physical extraction and chemical interaction have been elucidated with respect to the solvation efficiency of polar aliphatic diluents diethyl sebacate, diethyl succinate, diethyl malonate, ethyl caprylate, ethyl valerate and isoamyl alcohol. The studied TPA and DBA extractants, and ester and alcohol diluents have higher boiling temperatures than water and formic acid, allowing for an economical regeneration of components by distillation. Experimental data for the present systems composed of TPA/ester or alcohol/formic acid and DBA/ester or alcohol/formic acid are not available in the open literature.

Theoretically based mass-action law and LSER (linear solvation energy relationship) models have been widely used for estimating the properties of extraction systems of hydrogen-bond formation [18–20]. In this study, the properties of relevant systems were correlated in terms of a chemodel, a modified Langmuir model and an extended version of the LSER approach [8, 10, 12, 13]. The distribution data have been subjected to the formulation of an optimization structure for the description of the optimum extraction field. The algorithm optimizes the extraction conditions in terms of the separation ratio *R* and synergistic enhancement *SE* factors, being used as the optimization criteria for a reactive extraction system. To reach an easy and unique solution to the optimization problem, optimum conditions have been analyzed both graphically and analytically along with considering a non-homogeneous differential equation to represent conformably the non-linear variation profile of the optimized quantity. In order to accomplish this task, the derivative variation method described previously by Senol [21, 22] has been applied to identifying the optimization range.

The present study differs from the literature works, as it investigates and compares special amine extractants and ester diluents simultaneously on an efficiency-basis using eight extraction factors, and also analyzes the optimum extraction field with a self-developed optimization approach, which brings a new perspective to literature.

2. Theoretical

2.1. Criteria of extraction equilibria

Here, eight physically definable extraction factors are used for interpreting the extraction results, namely (a) the distribution ratio *D*, (b) the degree of extraction *E*, (c) the overall loading factor of the amine extractant Z_t, (d) the stoichiometric loading factor Z_s, (e) the chemical separation factor s_f^{chem} accounting for the acid-amine chemical interaction, (f) the physical separation factor s_f^{phys} pertaining to the physical extraction of the acid by the diluent, (g) the separation ratio optimization factor *R*, (h) the synergistic enhancement factor *SE*. *D* is the ratio of the overall extracted acid $\overline{C_{TA}}$ in the organic phase to total aqueous phase acid C_{TA}, Eq. (1a). *E* (%) is the ratio of the overall extracted acid to the initial acid, Eq. (1b). The overall loading factor Z_t is the ratio of the total amount of acid extracted $\overline{C_{TA}}$ to the initial organic phase concentration of the amine (AM) $\overline{C^0_{AM}}$, Eq. (1c). The stoichiometric loading factor Z_s is the ratio of the overall complexed acid in the organic phase $\overline{C_{HA}}$ to the initial amount of the amine $\overline{C^0_{AM}}$, Eq. (1d). This factor includes a correction term ($v\overline{C^d_{TA}}$) for the amount of acid extracted by the diluent in the solvent mixture. The chemical separation factor s_f^{chem} represents the ratio of the complexed acid with the amine $\overline{C_{HA}}$ to the overall extracted acid in the organic phase $\overline{C_{TA}}$, Eq. (1e). The physical separation factor s_f^{phys} stands for the ratio of the acid portion extracted by the diluent to the overall extracted acid $\overline{C_{TA}}$, Eq. (1f). The separation ratio optimization factor *R* represents the relative proportion between chemical interaction and physical extraction, Eq. (1g). The synergistic enhancement factor *SE* is a measure of the synergistic extraction power of amine/diluent system, Eq. (1h).

R and *SE* factors are originally intended for the description of the optimum extraction field of relevant systems, whereas s_f^{chem} and s_f^{phys} factors account for the chemical interaction and physical extraction of the distributed acid.

$$D = \overline{C_{TA}} \big/ C_{TA} \tag{1a}$$

$$E = 100\left(1 - \frac{C_{TA}}{C^0_{TA}}\right) = 100\frac{D}{1+D}\ (\%) \tag{1b}$$

$$Z_t = \overline{C_{TA}} \big/ \overline{C^0_{AM}} \tag{1c}$$

$$Z_s = \frac{\overline{C_{TA}} - v\overline{C^d_{TA}}}{\overline{C^0_{AM}}} = \frac{\overline{C_{HA}}}{\overline{C^0_{AM}}} \tag{1d}$$

$$s_f^{chem} = \overline{C_{HA}} \big/ \overline{C_{TA}} \tag{1e}$$

$$s_f^{phys} = 1 - s_f^{chem} \tag{1f}$$

$$R = \frac{s_f^{chem}}{s_f^{phys}} \tag{1g}$$

$$SE = \frac{1}{s_{\mathrm{f}}^{\mathrm{chem}}} + \frac{1}{s_{\mathrm{f}}^{\mathrm{phys}}} \tag{1h}$$

where v and $\overline{C_{\mathrm{TA}}^{\mathrm{d}}}$ designate the volume fraction of diluent in the solvent mixture and the amount of acid extracted by the pure (amine-free) diluent alone, respectively. $\overline{C_{\mathrm{AM}}^{0}}$, C_{TA}^{0}, $\overline{C_{\mathrm{HA}}}$, $\overline{C_{\mathrm{TA}}}$ and C_{TA} stand for the initial concentrations of the extractant and acid, the concentration of the complexed acid, the amount of the overall extracted acid in the organic phase and the aqueous phase acid concentration, respectively. Concentrations are given in (mol dm^{-3}) unit. The species in the organic phase are presented by the overbar.

2.2. Equilibrium mass-action law models

Following the chemical modelling concepts of Senol and co-workers [8, 10, 12, 13], we consider here the overall equilibrium of the amine/diluent/formic acid systems to obey the mass-action law interfacial reactions, Eqs. (2a) and (2b), which conditioned extraction constant β_{pq} in (mol dm^{-3})$^{1-p-q}$ is represented by Eq. (2c):

$$p\mathrm{HA} + q\overline{\mathrm{NR}_3} = \overline{(\mathrm{HA})_p(\mathrm{NR}_3)_q},\ p = 1, k;\ q = 1, l \tag{2a}$$

$$p\mathrm{HA} + q\overline{\mathrm{NR}_2\mathrm{H}} = \overline{(\mathrm{HA})_p(\mathrm{NR}_2\mathrm{H})_q},\ p = 1, k;\ q = 1, l \tag{2b}$$

$$\beta_{pq} = \overline{C_{pq}} \Big/ \left(C_{\mathrm{HA}}{}^{p}\,\overline{C_{\mathrm{AM}}}{}^{q} \right),\ p = 1, k;\ q = 1, l \tag{2c}$$

where HA, $\overline{\mathrm{NR}_3}$ and $\overline{\mathrm{NR}_2\mathrm{H}}$ represent the non-dissociated acid in the aqueous phase, TPA and DBA, respectively. $\overline{(\mathrm{HA})_p(\mathrm{NR}_3)_q}$ and $\overline{(\mathrm{HA})_p(\mathrm{NR}_2\mathrm{H})_q}$ stand for the acid-amine complexes. The overbar denotes species in the organic phase. C_{HA}, $\overline{C_{\mathrm{AM}}}$ and $\overline{C_{pq}}$ designate the equilibrium concentrations of non-dissociated acid in the aqueous phase, non-complexed amine and acid-amine (p, q) complex, respectively. Postulating that the total equilibrium content of complexed acid ($\overline{C_{\mathrm{HA}}}$), is the sum of contributions of the individual complexes given by $\overline{C_{\mathrm{HA}}} = \sum_{p=1}^{k} \sum_{q=1}^{l} p\,\beta_{pq} C_{\mathrm{HA}}{}^{p}\,\overline{C_{\mathrm{AM}}}{}^{q}$, then the overall balance equation for the acid as a function of its molarity is represented by Eq. (3):

$$C_{\mathrm{TA}}^{0} = \overline{C_{\mathrm{d}}} + \overline{C_{\mathrm{HA}}} + C_{\mathrm{TA}} \tag{3}$$

where C_{TA}^{0}, C_{TA} and $\overline{C_{\mathrm{d}}}$ stand for the initial and total aqueous phase acid concentrations, and concentration related to the acid portion physically extracted by the diluent in the solvent mixture, respectively. Conventionally, the non-dissociated aqueous phase acid concentration C_{HA} is being calculated from the dissociation equation of the acid $C_{\mathrm{HA}} = C_{\mathrm{TA}} C_{\mathrm{H}^+} \big/ \left(C_{\mathrm{H}^+} + K_a \right)$ using pH, the dissociation constant of formic acid pK_a = 3.751 [23] and the molar aqueous-phase concentration of proton $C_{\mathrm{H+}}$. Here, the phase behaviour of formic acid has been estimated in terms of the mass action law chemodel Eq. (4), which incorporates $\overline{C_{\mathrm{d}}}$, $\overline{C_{\mathrm{HA}}}$ and C_{TA}^{0} quantities of Eq. (3) into Z_{t}.

$$Z_{\mathrm{t}} = \frac{\overline{C_{\mathrm{d}}} + \overline{C_{\mathrm{HA}}}}{\overline{C_{\mathrm{AM}}^{0}}} = \frac{vD_0 C_{\mathrm{TA}}^{0}}{\left(1 + D_0\right)\overline{C_{\mathrm{AM}}^{0}}} + \frac{\sum_{p=1}^{k} \sum_{q=1}^{l} p\,\beta_{pq} C_{\mathrm{HA}}{}^{p}\,\overline{C_{\mathrm{AM}}}{}^{q}}{\overline{C_{\mathrm{AM}}^{0}}} \tag{4}$$

where $\overline{C_{\mathrm{d}}} = vD_0 C_{\mathrm{TA}}^{0} / \left(1 + D_0\right)$ represents the concentration of the physically extracted acid part by the diluent, ν is the volume fraction of diluent, D_0 is the distribution ratio of the acid referred to the diluent alone. $\overline{C_{\mathrm{AM}}^{0}}$ and C_{TA}^{0} stand for the initial concentrations of the amine and acid, respectively. The extraction constants β_{pq}(mol dm^{-3})$^{1-p-q}$ are calculated by means of a multivariable regression supposing one or two (p, q) acid$_p$-amine$_q$ complex formation.

Starting from the adsorption approach of Bauer et al. [24], we develop a modified Langmuir model Eq. (5), which contains two dependently varying interaction terms. Here, the association number z is related to the maximum loading of the extractant $z = Z_{\mathrm{s,max}} = \left(\overline{C_{\mathrm{HA}}}\right)_{\mathrm{max}} \Big/ \overline{C_{\mathrm{AM}}^{0}}$. In Eq. (5), $\overline{C_{\mathrm{d}}}$, D_0, $\overline{C_{\mathrm{AM}}^{0}}$, C_{TA}^{0} and C_{HA} stand for the same quantities as defined above. The Langmuir extraction constant β_{L} in (mol dm^{-3})$^{-z}$ is attributed to a monotype acid$_z$-amine$_1$ (p:q = z:1) aggregation.

$$Z_{\mathrm{t}} = \frac{\overline{C_{\mathrm{d}}} + \overline{C_{\mathrm{HA}}}}{\overline{C_{\mathrm{AM}}^{0}}} = \frac{vD_0 C_{\mathrm{TA}}^{0}}{\left(1 + D_0\right)\overline{C_{\mathrm{AM}}^{0}}} + \frac{z\beta_{\mathrm{L}} C_{\mathrm{HA}}{}^{z}}{1 + \beta_{\mathrm{L}} C_{\mathrm{HA}}{}^{z}} \tag{5}$$

2.3. Extended LSER approach

To formulate a perceptible model for reactive extraction systems depending on LSER principles [19, 20], we consider here a generalized approach to be represented by $Pr = Pr_0 + F \times Pr_{\mathrm{solvent}}$. Pr, Pr_0 and Pr_{solvent} stand for the modelled property, the limiting value of the observed property and the integration property term involving six molecular descriptors of the solvent (δ_{H}, π, β, α, δ, $\bar{V}$), respectively. F is a concentration–dependent correction factor including the s_f^{chem} quantity to account for the concentration effect of the extractant and acid. δ_{H} (MPa$^{0.5}$) and $\bar{V}$ (cm^3 mol^{-1}) are the Hildebrand solubility parameter and the molar volume of the solvent, respectively. The solvatochromic indices π, β, α and δ are physical descriptors characterizing the ability of the solvent to form hydrogen bond [19, 20].

The extended LSER model is given by Eq. (6) in which the modelled property Pr is composed of two balancing parts, i.e., one part accounted for the limiting observed property Pr_0 and an integration term with respect to the Hildebrand solubility parameter δ_{H}^{*} (MPa$^{0.5}$), the solvatochromic parameters π^*, β^*, α^* and δ^*, and the molar volume $\bar{V}^*$ (cm^3 mol^{-1}) of the solvent mixture. The correction factor $F = s_{\mathrm{f}}^{\mathrm{chem}} \Big/ \left(1 - s_{\mathrm{f}}^{\mathrm{chem}}\right)$ in Eq. (6) accounts for two limiting conditions when either $s_f^{\mathrm{chem}} = 0$ for which $Pr = Pr_0$, or $s_{\mathrm{f}}^{\mathrm{chem}} = 1$ for which an indefinable character of the function appears.

$$Pr = Pr_0 + \left(\frac{s_{\mathrm{f}}^{\mathrm{chem}}}{1\text{-}s_{\mathrm{f}}^{\mathrm{chem}}}\right)\left[C_{\mathrm{H}}\delta_{\mathrm{H}}^{*} + C_{\pi}\left(\pi^{*} - 0.35\delta^{*}\right) + C_{\beta}\beta^{*} + C_{\alpha}\alpha^{*} + C_{V}\bar{V}^{*}\right] \tag{6}$$

where the molecular indices of the solvent mixture (δ_{H}^{*}, π^*, β^*, α^*, δ^* and $\bar{V}^{*}$) are derived from the corresponding parameters ($\delta_{H,i}$, π_i, β_i, α_i, δ_i, $\bar{V}_i$) and volume fractions (v_i) of the individual components by applying a mean value estimation rule, i.e., $\delta_{\mathrm{H}}^{*} = (1/1000)\sum_i v_i\delta_{\mathrm{H},i}^{2}$, $\left(\pi^{*} - 0.35\delta^{*}\right) = \sum_i v_i\left(\pi_i - 0.35\delta_i\right)$, $\beta^{*} = \sum_i v_i\beta_i$, $\alpha^{*} = \sum_i v_i\alpha_i$, and $\bar{V}^{*} = \sum_i v_i\left(\bar{V}_i \times 10^{-2}\right)$. C_{H}, C_{π}, C_{β}, C_{α} and C_V are adjustable coefficients of Eq. (6). Here, the correlative capability of Eq. (6) to reproduce satisfactorily the observed properties has been checked by processing the following Pr and Pr_0 quantities.

$$\begin{aligned}
&Pr = \ln(E);\ Pr_0 = \ln(E_0)\\
&Pr = \ln(D);\ Pr_0 = \ln(D_0)\\
&Pr = \ln\left(s_{\mathrm{f}}^{\mathrm{phys}}\right);\ Pr_0 = \ln\left(s_{\mathrm{f0}}^{\mathrm{phys}}\right)\\
&Pr = \ln(Z_{\mathrm{t}});\ Pr_0 = \ln(Z_{\mathrm{t,max}})\\
&Pr = \ln(SE);\ Pr_0 = \ln(SE_{\mathrm{max}})
\end{aligned} \tag{7}$$

where, E_0, D_0 and $s_{\mathrm{f0}}^{\mathrm{phys}}$ represent the observed properties relative to the pure diluent alone ($s_{\mathrm{f0}}^{\mathrm{phys}} = 1$). The values of $Z_{\mathrm{t,max}}$ and SE_{max} are obtained from the observed curves. Since $\alpha^* = 0$ for the considered solvents, the $C_{\alpha}\alpha^*$ term was excluded from the model.

3. Experimental

Formic acid, as well as the reactive extractants TPA and DBA and six organic solvents diethyl sebacate, diethyl succinate, diethyl malonate, ethyl caprylate, ethyl valerate and isoamyl alcohol of analytical grade purity (0.98–0.99 mass fraction, GC) were furnished from Merck and Aldrich. All the chemicals were used as received without further purification. Deionized and redistilled water was used in all experiments. Table 1 gives a brief summary of the experimentally defined purities of the chemicals in terms of their densities (Anton Paar Density Meter, Model DMA 4500) and refractive indexes (Model RXA 170) measured at $T = 298.2 \pm 0.1$ K and $P = 101.3 \pm 0.7$ kPa within $\pm 10^{-5}$ precision.

The extraction experiments were performed using an equilibrium glass cell equipped with a magnetic stirrer and thermostatted at $T = 298.2 \pm 0.2$ K. Equal volumes (10 cm^3) of initial aqueous formic acid and organic (TPA/diluent or DBA/diluent) phases were agitated for 1 h and then left for 2 h to settle down into aqueous and solvent layers at fixed temperature ($T = 298.2 \pm 0.2$ K) and pressure ($P = 101.3 \pm 0.7$ kPa). The effective separation of the phases was ensured by centrifugation. Aqueous-phase pH was measured using an Orion 601A pH-meter within ±0.01 precision. Aqueous-phase acid concentration was determined by titration with aqueous NaOH (Titrosol A, Merck) and phenolphthalein indicator. The organic phase acid concentration was checked by a mass balance. The initial amine/diluent content in the organic phase was determined gravimetrically by weighing with a Sartorius scale accurate to within $\pm 10^{-4}$ g, in addition to chromatographically analysed using Hewlett-Packard GC Analyzer, Model 6890, equipped with HP1-type capillary column (50 m × 0.2 mm × 0.5 μm) for FID and HP Plot Q column (0.32 mm i.d., 0.2 μm film

Table 1
Densities ρ (g cm^{-3}) and refractive indexes n_D of pure components at $T = 298.2 \pm 0.1$ K and $P = 101.3 \pm 0.7$ kPa

Compound	Supplier	Density ρ (g cm^{-3})		Refractive index n_D		Purity (mass fr.)[a]
		Exp	Lit	Exp	Lit	
Formic acid	Merck	1.21410	1.21380[b]	1.36939	1.36943[b]	0.99
Diethyl sebacate	Merck	0.95918	0.95913[c]	1.43485	1.43480[c]	0.98
Diethyl succinate	Merck	1.03534	1.03530[d]	1.41967	1.41960[d]	≥0.98
Diethyl malonate	Merck	1.04750	1.04960[e]	1.41331	1.41320[e]	≥0.98
Ethyl caprylate	Merck	0.86223	0.86215[f]	1.41572	1.41560[f]	0.98
Ethyl valerate	Merck	0.87236	0.87680[g]	1.39841	1.40100[g]	≥0.98
Isoamyl alcohol	Aldrich	0.80716	0.80710[h]	1.40528	1.40523[h]	0.99
Tri-*n*-propyl amine	Aldrich	0.75265	0.75580[i]	1.41523	1.41710[i]	0.98
Dibenzyl amine	Aldrich	1.02563	1.02600[j]	1.57365	1.57450[j]	≥0.97

[a] The purities refer to the mass fraction as defined by the supplier.
[b] Due to Cases et al. [30].
[c] Due to Lorenzi et al. [31].
[d] Due to Aminabhavi et al. [32].
[e] Due to Baragi et al. [33].
[f] Due to Sheu and Tu [34].
[g] Due to Indraswati et al. [35].
[h] Due to Riggio et al. [36].
[i] Due to Lide [37].
[j] Due to Lide and Kehiaian [38].

thickness) for TCD. The detector temperature was kept at T = 523.2 K, while the injection port temperature was held at T = 473.2 K. Injections were performed on the split 1/100 mode. Nitrogen was used as a carried gas at a flow rate of 5 ml min^{-1}.

The initial acid content in the aqueous phase was kept at C_{TA}^0 = 2.1725 mol dm^{-3} (10% w/w) and that solution was used as a simulated synthetic fermentation sample. It was confirmed from two independent replicates that the extraction experiments were reproducible within at most 3% standard deviation. To eliminate a third phase formation, the initial amine concentration was restricted in the range of 0.2–1.05 mol dm^{-3}. A comparison of extraction equilibria pertaining to TPA/diluent/formic acid and DBA/diluent/formic acid systems has been adequately assessed for the identical experimental conditions of A:O = 1:1 (v/v), T = 298.2 K, P = 101.3 kPa and C_{TA}^0 = 2.1725 mol dm^{-3} initial aqueous acid solution. However, the relative dependence of the extraction efficiency of formic acid on the structural properties and concentrations of the carrier and diluent has been elucidated by comparing eight extraction factors relative to the amine/diluent systems composed of (TPA, or DBA + diethyl sebacate, or diethyl succinate, or diethyl malonate, or ethyl caprylate, or ethyl valerate, or isoamyl alcohol diluent). The physical extraction of the acid by the diluent alone has been also studied.

The mutual solubilities of (water + solvent) and (water + amine) binaries are determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain the temperature within T = 298.2 ± 0.2 K [22], and summarized in Table 2. As marked in Table 2, except for (water + isoamyl alcohol) system, the binary mutual solubility values are relatively small within their experimental uncertainties (1%–5% mean deviation). The mutual solubility results suggest that, except for isoamyl alcohol, the solubilities of the extractant, diluent and organic complex in the aqueous phase are negligible in the range of variables investigated. From Table 2, one may conclude that there is a less tendency of the ester and amine coextraction in the aqueous phase, but as expected the acid should carry a small amount of water in the organic phase. To simplify the complexity of the problem, the change in the phase volume can be neglected.

4. Results and discussion

4.1. Comparative assessment of extraction power of amine/diluent systems

Study of the reactive extraction systems in Table 3 and Figs. 1–3 containing 2.1725 mol dm^{-3} initial aqueous-phase acid solution reveals that the physical extraction of formic acid by pure diluent alone is remarkably small with a distribution ratio D_0 = 0.508 (E_0 = 33.71%) for isoamyl alcohol and less than 0.5 for esters ranging from 0.053 for ethyl caprylate to 0.33 for diethyl succinate, but all disapprovingly not convenient as separating agents. In general, a remarkably small physical extractability of formic acid by conventional solvents could be attributable to the strong hydrophilic nature of the acid due to the absence of a R-chain structure and its high ionizing strength (pK_a = 3.751). These concepts are verified by the results from Table 3 manifesting the fact that the physical extraction of formic acid is very sensitive to the capability of the diluent to hydrogen bonding and dipole-dipole interaction ranging as: isoamyl alcohol > diethyl succinate > diethyl malonate > diethyl sebacate > ethyl valerate > ethyl caprylate.

As seen in Table 3, the synergistic extraction power of TPA/diluent mixture in terms of Z_t, D and E factors, as well as the most probable monotype acid$_p$-amine$_q$ (p, q) complexation appear as follows, isoamyl alcohol (1, 2) > diethyl malonate (1, 2) > diethyl succinate (1, 2) > ethyl valerate (1, 2) > ethyl caprylate (1, 2) > diethyl sebacate (1, 2). Similarly, the Z_t, D and E factors of DBA/diluent system increase in the order, isoamyl alcohol (1, 1) > diethyl malonate (1, 1) > diethyl succinate (1, 1) > ethyl valerate (1, 1) ≈ diethyl sebacate (1, 1) > ethyl caprylate (1, 1). It turns out from Table 3 and Figs. 1–3 that the uptake capacity of amine/isoamyl alcohol system is considerably larger as compared with other systems, yielding $D > 1$, $Z_t > 1$ and $E > 50\%$ due to the simultaneous effect of physical extraction and chemical interaction through hydrogen bonding. In contrast, protic isoamyl alcohol diluent exhibits a moderately streamlined solvating efficiency towards the organic complexes, probably activating (1, 2) acid$_1$-TPA$_2$ and (1, 1) acid$_1$-DBA$_1$ complex formations related to $s_f^{chem} \approx 0.27$–0.60 and $Z_s \approx 0.7$ –1. As shown in Figs. 1 and 2 and Table 3, D and E values proportionally increase with the

Table 2
Mutual solubility of binaries (w_1 water + w_2 solvent) in terms of mass fraction (w) at T = 298.2 K and P = 101.3 kPa[a]

Binary system	Solvent (2) in water (1)		Water (1) in solvent (2)	
	w_1[b]	w_2	w_1[b]	w_2
Water + diethyl sebacate	0.9990 (0.9999)[c]	0.0010 (0.0001)	0.0019 (0.0266)[c]	0.9981 (0.9734)
Water + diethyl succinate	0.9981 (0.9998)	0.0019 (0.0002)	0.0104 (0.0923)	0.9896 (0.9077)
Water + diethyl malonate	0.9806 (0.9978)	0.0194 (0.0022)	0.0200 (0.1537)	0.9800 (0.8463)
Water + ethyl caprylate	0.9979 (0.9998)	0.0021 (0.0002)	0.0036 (0.0334)	0.9964 (0.9666)
Water + ethyl valerate	0.9942 (0.9992)	0.0058 (0.0008)	0.0082 (0.0564)	0.9918 (0.9436)
Water + isoamyl alcohol	0.9784 (0.9955)	0.0216 (0.0045)	0.1030 (0.3599)	0.8970 (0.6401)
Water + tri-*n*-propyl amine	0.99927 (0.99991)	0.00073 (0.00009)	0.00061 (0.00483)	0.99939 (0.99517)
Water + dibenzyl amine	0.99990 (0.99999)	0.00010 (0.00001)	0.00014 (0.00153)	0.99986 (0.99847)

[a] Standard uncertainties u are $u(T)$ = 0.2 K, $u(P)$ = 0.7 kPa, $u(w)$ = 0.002.
[b] Mass fraction of the component.
[c] Mole fraction of the component is given in parenthesis.

amine content, while Z_t and s_f^{chem} factors gradually decrease with increasing the amine concentration in the organic phase. This type of functional variation gives a realistic picture of whether synergism or antagonism would likely proceed during formic acid extraction by the amine/diluent mixture. In the examined overall amine concentration interval (0.20–1.05 mol dm^{-3}), synergistic extraction power with overloading ($Z_t > 1$) were obtained for all the tested TPA/diluent mixtures, and also for DBA/dibasic ester and DBA/isoamyl alcohol. On the contrary, the stoichiometric loading factors Z_s for the studied concentration level are $Z_s \leq 1$, exception for TPA/monobasic ester, being indicative of a simultaneous formation of not overloaded acid$_p$-amine$_q$ complexes, predominantly of the types (p:q = 1:2 and p:q = 1:3) or (p:q = 1:1 and p:q = 1:3).

In general, as shown in Table 3 and Figs. 1 and 2, except for TPA/ethyl caprylate and TPA/ethyl valerate, the examined solvent mixtures typically yield moderately large interaction factors of $Z_s < 1$ ($Z_s \approx 0.30$ –0.97), $s_f^{chem}<0.9$ ($s_f^{chem} \approx 0.20$–0.93) and $s_f^{phys}<0.8$ ($s_f^{phys} \approx 0.10$–0.80), indicating that moderately strong interactive forces dominate during formic acid-amine complex formation. This suggests that the polarity and the ionizing strength of the acid should affect the solvation efficiency and the complex stability of acid-base type structures with a lowered polarity degree. The preference of the formic acid anions for water over the amine could be attributable to a relatively high polarity (dipole moment $\mu_F = 4.7\times10^{-12}$ Cm and dielectric constant $\varepsilon_F = 58.5$) and a large ionizing strength ($pK_F = 3.751$) of the acid molecule, which in turn give rise to an increased mass transfer resistance causing the polar acid molecules to favour the aqueous phase on this account. On the other hand, the reduction in the extraction efficiency with increasing the molecule size of the amine reflects the lessening in the cross–interaction due to a predominant steric effect of larger DBA species, as compared with less polar TPA media working in favour of transfer of the formic acid anions from water into the organic TPA phase. In comparison with DBA, the smaller size of more structured TPA molecule permits the formic acid molecule to approach closer and hence makes its dipole more effective in inducing dipole in the ammonium ions. From Figs. 1 and 2 and Table 3, one may conclude that the polarity and the ionizing strength of the acid are most promising factors in the acid-amine complexation, distinguishing the divergent behaviour relative to the physical extraction and chemical interaction of the hydrophilic formic acid.

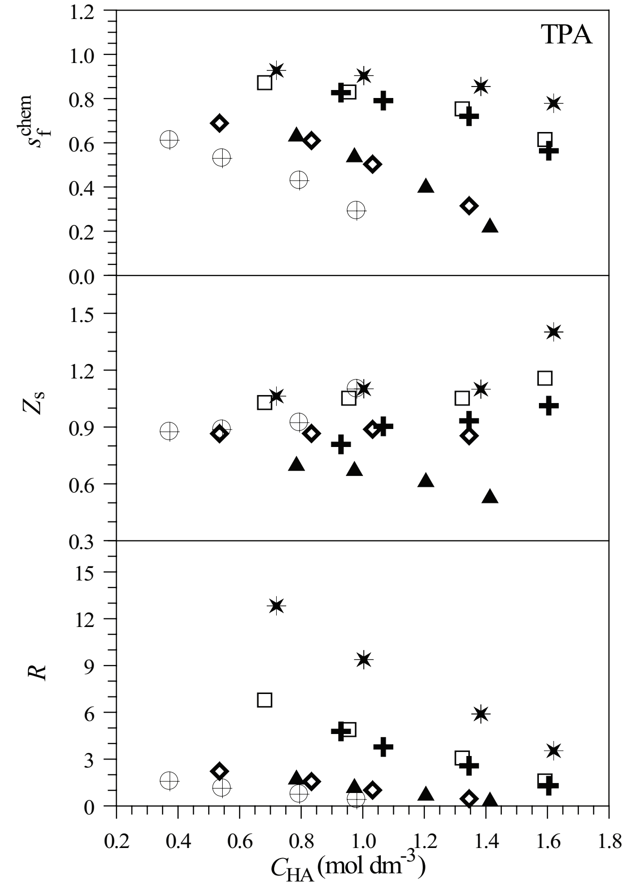

Fig. 1. Variation of separation factor (s_f^{chem}), stoichiometric loading (Z_s) and optimization factor (R) with non-dissociated aqueous phase formic acid concentration (C_{HA}) relative to tri-n-propyl amine (TPA)/diluent system; ✚ diethyl sebacate, ▲ diethyl succinate, ◇ diethyl malonate, ✶ ethyl caprylate, □ ethyl valerate, ⊕ isoamyl alcohol (C_{TA}^0 = 2.1725 mol dm^{-3}).

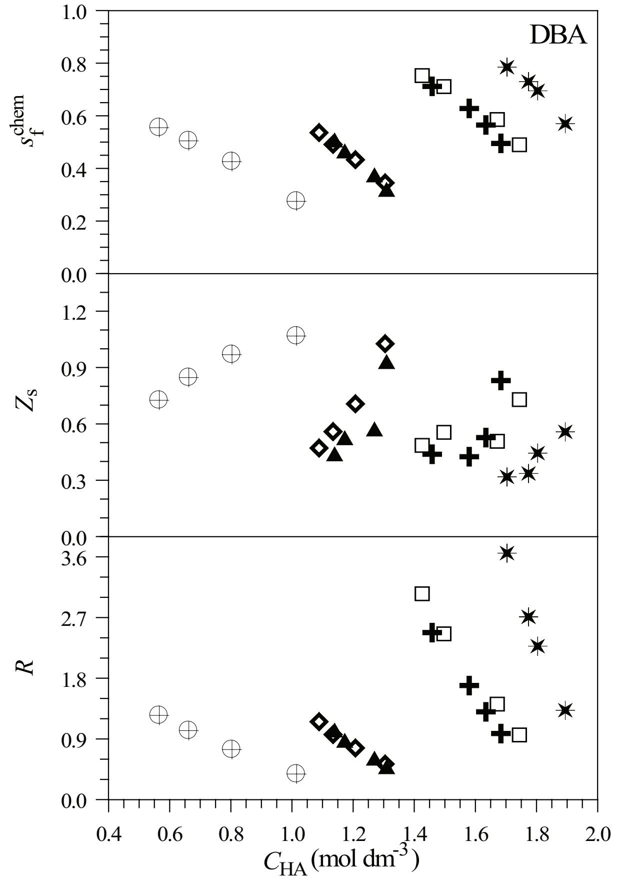

Fig. 2. Variation of separation factor (s_f^{chem}), stoichiometric loading (Z_s) and optimization factor (R) with non-dissociated aqueous phase formic acid concentration (C_{HA}) relative to dibenzyl amine (DBA)/diluent system; ✚ diethyl sebacate, ▲ diethyl succinate, ◇ diethyl malonate, ✶ ethyl caprylate, □ ethyl valerate, ⊕ isoamyl alcohol (C_{TA}^0 = 2.1725 mol dm^{-3}).

Table 3
Variation of the extractability factors (E, D, Z_t, Z_s, s_f^{chem}, R, SE) with the concentration of components for the extraction of formic acid by tri-*n*-propyl amine/diluent, dibenzyl amine/diluent and pure diluent alone at $T = 298.2$ K and $P = 101.3$ kPa ($C_{TA}^0 = 2.1725$ mol dm^{-3}; A:O = 1:1 (v/v))[a]

$\overline{C_{AM}^0}$ [b] (mol dm^{-3})	pH[c]	C_{TA} [d] (mol dm^{-3})	$\overline{C_{TA}}$ [e] (mol dm^{-3})	E	D	Z_t	Z_s	s_f^{chem} [f]	R	SE
TPA[g] + Diethyl sebacate										
0.0000[h]	2.01	1.9505	0.2220	10.22	0.114					
0.2697	2.47	1.6884	0.4841	22.28	0.287	1.795	1.013	0.564	1.295	4.067
0.5499	2.68	1.4597	0.7128	32.81	0.488	1.296	0.933	0.720	2.568	4.957
0.7893	3.03	1.2699	0.9026	41.55	0.711	1.144	0.904	0.791	3.783	6.048
1.0500	3.12	1.1466	1.0259	47.22	0.895	0.977	0.808	0.827	4.776	6.986
TPA + Diethyl succinate										
0.0000[h]	2.50	1.6329	0.5396	24.84	0.330					
0.2710	2.62	1.5180	0.6545	30.13	0.431	2.415	0.524	0.217	0.277	5.890
0.5250	2.88	1.3672	0.8053	37.07	0.589	1.534	0.609	0.397	0.658	4.177
0.7903	3.09	1.1858	0.9867	45.42	0.832	1.249	0.668	0.535	1.151	4.020
1.0512	3.21	1.0102	1.1623	53.50	1.151	1.106	0.695	0.629	1.693	4.283
TPA + Diethyl malonate										
0.0000[h]	2.49	1.6584	0.5141	23.66	0.310					
0.2623	2.68	1.4600	0.7125	32.80	0.488	2.716	0.854	0.315	0.459	4.638
0.5267	3.06	1.2422	0.9303	42.82	0.749	1.766	0.888	0.503	1.011	4.000
0.7891	3.17	1.0519	1.1206	51.58	1.065	1.420	0.866	0.610	1.564	4.204
1.0549	3.52	0.8486	1.3239	60.94	1.560	1.255	0.865	0.689	2.219	4.670
TPA + Ethyl caprylate										
0.0000[h]	1.92	2.0631	0.1094	5.04	0.053					
0.2618	2.45	1.7015	0.4710	21.68	0.277	1.799	1.402	0.779	3.532	5.815
0.5275	2.65	1.4937	0.6788	31.25	0.454	1.287	1.100	0.855	5.894	8.064
0.7904	3.06	1.2081	0.9644	44.39	0.798	1.220	1.102	0.904	9.371	11.478
1.0558	3.28	0.9628	1.2097	55.68	1.256	1.146	1.063	0.928	12.822	14.900
TPA + Ethyl valerate										
0.0000[h]	1.98	1.9727	0.1998	9.20	0.101					
0.2620	2.49	1.6792	0.4933	22.71	0.294	1.883	1.158	0.615	1.599	4.224
0.5246	2.70	1.4410	0.7315	33.67	0.508	1.394	1.052	0.754	3.068	5.394
0.7891	3.11	1.1728	0.9997	46.02	0.852	1.267	1.051	0.830	4.886	7.091
1.0540	3.31	0.9282	1.2443	57.28	1.341	1.181	1.029	0.872	6.785	8.932
TPA + Isoamyl alcohol										
0.0000[h]	2.70	1.4402	0.7323	33.71	0.508					
0.2605	3.08	1.1900	0.9825	45.22	0.826	3.772	1.101	0.292	0.412	4.838
0.5366	3.20	1.0183	1.1542	53.13	1.133	2.151	0.923	0.429	0.751	4.082
0.7904	3.50	0.8492	1.3233	60.91	1.558	1.674	0.887	0.530	1.126	4.014
1.0556	3.64	0.6627	1.5098	69.50	2.278	1.430	0.875	0.612	1.577	4.211
DBA[g] + Diethyl sebacate										
0.0000[h]	2.01	1.9505	0.2220	10.22	0.114					
0.2487	2.38	1.7550	0.4175	19.22	0.238	1.679	0.831	0.495	0.980	4.000
0.4934	2.43	1.7127	0.4598	21.16	0.268	0.932	0.527	0.565	1.301	4.070
0.7504	2.48	1.6647	0.5078	23.37	0.305	0.677	0.425	0.628	1.691	4.282
1.0042	2.57	1.5549	0.6176	28.43	0.397	0.615	0.438	0.712	2.477	4.881
DBA + Diethyl succinate										
0.0000[h]	2.50	1.6329	0.5396	24.84	0.330					
0.2515	2.71	1.4288	0.7437	34.23	0.521	2.957	0.919	0.311	0.451	4.669

(*Continued*)

Table 3 (*Continued*)

$\overline{C^0_{AM}}$ [b] (mol dm^{-3})	pH[c]	C_{TA} [d] (mol dm^{-3})	$\overline{C_{TA}}$ [e] (mol dm^{-3})	*E*	*D*	Z_t	Z_s	s_f^{chem} [f]	*R*	*SE*
0.5013	2.78	1.4060	0.7665	35.28	0.545	1.529	0.560	0.366	0.578	4.307
0.7537	2.87	1.3273	0.8452	38.90	0.637	1.121	0.513	0.457	0.843	4.029
1.0057	2.93	1.3112	0.8613	39.65	0.657	0.856	0.427	0.499	0.995	4.000
DBA + Diethyl malonate										
0.0000[h]	2.49	1.6584	0.5141	23.66	0.310					
0.2509	2.72	1.4264	0.7461	34.34	0.523	2.974	1.027	0.345	0.528	4.423
0.5009	2.84	1.3559	0.8166	37.59	0.602	1.630	0.707	0.433	0.765	4.072
0.7541	2.95	1.3137	0.8588	39.53	0.654	1.139	0.559	0.491	0.965	4.001
1.0075	3.01	1.2862	0.8863	40.80	0.689	0.880	0.471	0.536	1.155	4.021
DBA + Ethyl caprylate										
0.0000[h]	1.92	2.0631	0.1094	5.04	0.053					
0.2465	2.04	1.9310	0.2415	11.12	0.125	0.980	0.558	0.570	1.324	4.079
0.5044	2.16	1.8500	0.3225	14.84	0.174	0.639	0.444	0.695	2.275	4.715
0.7506	2.23	1.8275	0.3450	15.88	0.189	0.460	0.336	0.730	2.710	5.079
1.0057	2.31	1.7652	0.4073	18.75	0.231	0.405	0.318	0.785	3.654	5.927
DBA + Ethyl valerate										
0.0000[h]	1.98	1.9727	0.1998	9.20	0.101					
0.2494	2.26	1.8006	0.3719	17.12	0.207	1.491	0.730	0.490	0.959	4.002
0.5022	2.35	1.7380	0.4345	20.00	0.250	0.865	0.507	0.586	1.416	4.122
0.7519	2.52	1.5852	0.5873	27.03	0.370	0.781	0.555	0.711	2.458	4.865
1.0068	2.59	1.5247	0.6478	29.82	0.425	0.643	0.485	0.753	3.053	5.380
DBA + Isoamyl alcohol										
0.0000[h]	2.70	1.4402	0.7323	33.71	0.508					
0.2475	3.04	1.2126	0.9599	44.18	0.792	3.878	1.068	0.275	0.380	5.013
0.5045	3.19	1.0244	1.1481	52.85	1.121	2.276	0.969	0.426	0.742	4.090
0.7515	3.33	0.9139	1.2586	57.93	1.377	1.675	0.847	0.505	1.022	4.001
1.0072	3.46	0.8555	1.3170	60.62	1.539	1.308	0.726	0.555	1.248	4.049

[a] C^0_{TA} is the initial concentration of formic acid.
[b] Initial concentration of the amine dissolved in oxygen-containing diluent.
[c] Acidity of the aqueous phase at equilibrium.
[d] The equilibrium aqueous phase acid concentration.
[e] The equilibrium organic phase acid concentration.
[f] $s_f^{chem} = 1 - s_f^{phys}$.
[g] TPA tri-*n*-propyl amine, DBA dibenzyl amine.
[h] Properties referred to pure diluent alone.

These findings are comprehensively supported by the results for the relative proportion of physical interaction and chemical reaction in terms of Z_s and s_f^{chem} factors from Table 3 and Figs. 1 and 2, signifying that different mechanisms control favourably monotype (1:1 or 1:2) and two types (1:2 and 1:3, or 1:1 and 1:3) formic acid-amine aggregation depending on the solvation degree of diluent. It is seen from Table 3 and Figs. 1 and 2 that formic acid is physically more easily extracted by protic isoamyl alcohol alone as compared with others, whereas the magnitude of the acid-amine complexation is larger for TPA/monobasic ester (TPA/ethyl caprylate and TPA/ethyl valerate) regarding the Z_s and s_f^{chem} factors. As shown in Table 3 and Fig. 3, the synergistic extraction power of the solvent mixture in terms of the *SE* factor is ranging as follows: ethyl caprylate > ethyl valerate > isoamyl alcohol > diethyl succinate ≈ diethyl malonate ≈ diethyl sebacate, and TPA > DBA. The same remarks hold for the *R* factors of relevant systems listed in Table 3.

The variation profiles of the quantities given in Figs. 1 and 2 illustrate that the maximum stoichiometric loading corresponding to the plateau in the loading curve substantially appears at $Z_{s,max} < 1$ or $Z_{s,max} > 1$, which corroborates the tendency toward the formation of either a more structured acid$_p$-amine$_q$ aggregation related to one acid per multiple amines (p:q = 1:2 and p:q = 1:3), or a less structured acid$_p$-amine$_q$ association (p:q = 1:1 and p:q = 1:3). This fact seems to be a common strategy for designing the reactive extraction of formic acid. Typically, TPA is more effective separation agent than the DBA for the identical diluents checked in terms of Z_s, s_f^{chem}, *D*, *E*, Z_t, *R* and *SE* factors from Table 3. This could be attributable to the steric hindrance and the resonance π electron effect in the DBA structure that take a role in the complexation stage,

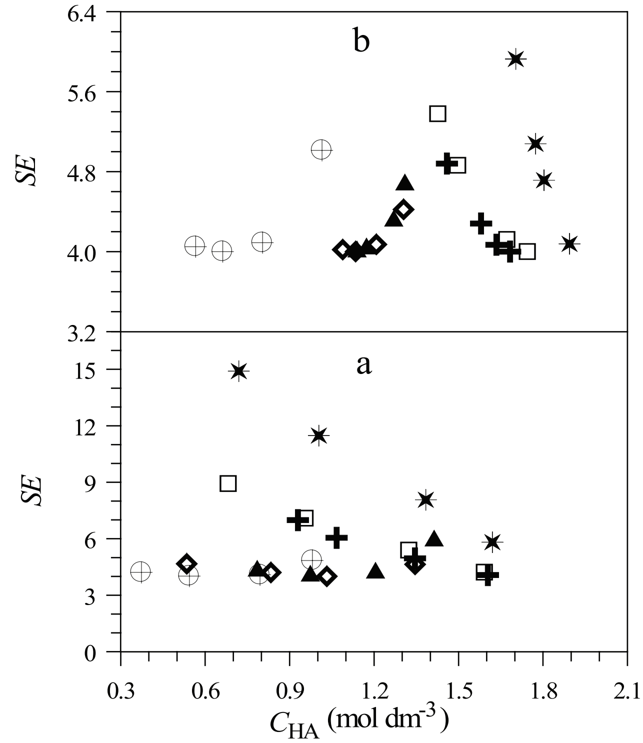

Fig. 3. Variation of synergistic enhancement factor (*SE*) with non-dissociated aqueous phase formic acid concentration (C_{HA}). (a) TPA/diluent; (b) DBA/diluent; ✚ diethyl sebacate, ▲ diethyl succinate, ◇ diethyl malonate, ✶ ethyl caprylate, □ ethyl valerate, ⊕ isoamyl alcohol (C^0_{TA} = 2.1725 mol dm^{-3}).

in contrast to a more structured formula of TPA extractant, which basicity increases in the polar diluent medium allowing the formation of a more solvated acid-amine complex. As seen in Table 3 and Figs. 1 and 2, the effect is more pronounced in the case of polar ethyl caprylate ($Z_{s,\max}$ = 1.50), ethyl valerate ($Z_{s,\max}$ = 1.26), isoamyl alcohol ($Z_{s,\max}$ = 1.20) and diethyl sebacate ($Z_{s,\max}$ = 1.11) for TPA, and isoamyl alcohol ($Z_{s,\max}$ = 1.17), diethyl malonate ($Z_{s,\max}$ = 1.13) and diethyl succinate ($Z_{s,\max}$ = 1.02) for DBA, which eventually promote more readily the diluent-complex aggregation corresponding to larger Z_s and s_f^{chem} factors, as compared with the same quantities of other diluents. It ought to be pointed out that comparably large $Z_{s,\max}$ factors have been obtained for all the tested solvents defined as follows: 1.11, 0.79, 0.99, 1.50, 1.26 and 1.20 for TPA/diluent and 0.84, 1.02, 1.13, 0.66, 0.83 and 1.17 for DBA/diluent for diethyl sebacate, diethyl succinate, diethyl malonate, ethyl caprylate, ethyl valerate and isoamyl alcohol, respectively. In view of the *D*, *E*, Z_t, Z_s, s_f^{chem}, *R* and *SE* factors in Table 3, the extraction power of amine/diluent system is the largest for protic isoamyl alcohol, where a complementary interaction effect of the hydroxyl, carboxyl and amine functional groups would likely proceed. Monobasic esters are more effective solvating agents for organic complexes in comparison with others, allowing the formation of acid$_1$-amine$_2$ and acid$_1$-amine$_3$ structures. The more structured TPA is favourably more effective solvent than DBA for which the aromatic ring is likely responsible for a steric effect. The resonance effect of aromatic π electron system is another controlling factor for DBA.

Consequently, the most common behaviour for a reactive extraction of formic acid is focused on a tendency toward an acid-amine complexation related to $s_f^{chem} < 0.95$. This fact would call for the assumption that a more complicate chemical aggregation should be affected by the diluent in different ways regarding its polarity and hydrogen-bonding ability.

4.2. Optimization of amine extraction of formic acid

A survey of the literature reveals that there is gained a little insight into the problem covering the prediction of optimum extraction limits relative to LLE systems [21, 22]. The solution algorithms and procedures for these kinds of problems including especially optimization of reactive extraction systems are complex and time consuming [21, 25]. To find a global optimum point on the search without converging to the local minimum or maximum points, the selection of the search algorithm is very crucial. This type of optimization problem is usually solved by an optimization approach which tries to find out an optimum point by considering conflicting objectives and lets us to not to make a trade of between objectives where to find a point that globally satisfies the problem [25, 26]. Since the size and complexity of the problem increases when it is defined in a multi-objective way, simplified solution methods and approaches are needed.

In this study, the goal is to determine the most suitable extract composition for the acid recovery against practically permissible optimum concentration range of the solvent mixture with respect to the *R* and *SE* factors, being used as the optimization criteria. To achieve this goal, the derivative variation method, described previously by Senol [21, 22], has been processed to analyze the variation profiles of *R* and *SE* factors. This method implies that (1) the contribution of the derivatives to the optimized property is validated by the slope analysis, and (2) the identification of the optimum conditions is governed by the range of changes in the derivative value. Here, for a quantitative description of optimum conditions both experimentally and analytically, firstly modelling of $R = f(x_{iv})$ and $SE = f(x_{iv})$ curves by a differential equation is necessarily required, then the optimization approach which depends on the variation profiles of *R* and *SE* quantities is solved using the derivative variation technique. As shown in Table 3, *R* and *SE* are inversely proportional to C_{TA} and varying proportionally with $\overline{C^0_{AM}}$, so the analysis of optimum conditions is performed in terms of the independent variable $x_{iv} = \overline{C^0_{AM}}/C_{TA}$. For the sake of simplicity, the variation profile of the modelled performance, *R* or *SE*, is expressed by a non-homogeneous differential Eq. (8):

$$R = R_{\max}\left[1-\exp\left(rx_{iv}\right)\right];\ SE = SE_{\max}\left[1-\exp\left(sx_{iv}\right)\right] \tag{8}$$

$R_{\max}$ and $SE_{\max}$ stand for the maximum values of extraction factors defined as follows, (a) for TPA: $R_{\max}$ = 5.27, $SE_{\max}$ = 7.38 (*r* = –2.2098, *s* = –3.1615, diethyl sebacate); $R_{\max}$ = 2.19, $SE_{\max}$ = 6.30 (*r* = –1.1990, *s* = –2.6327, diethyl succinate); $R_{\max}$ = 2.72, $SE_{\max}$ = 5.07 (*r* = –1.2311, *s* = –3.2054 diethyl malonate); $R_{\max}$ = 13.32, $SE_{\max}$ = 15.30 (*r* = –2.3893, *s* = –2.7717, ethyl caprylate); $R_{\max}$ = 7.28, $SE_{\max}$ = 9.63 (*r* = –1.9737, *s* = –2.3004, ethyl valerate); $R_{\max}$ = 2.08, $SE_{\max}$ = 5.24

(r=–8.7710, s=–2.1892, isoamyl alcohol), (b) for DBA: $R_{\max}$=2.98, $SE_{\max}$=5.28 (r=–2.3517, s=–4.6776, diethyl sebacate); $R_{\max}$=1.49, $SE_{\max}$ = 5.07 (r = –1.4927, s = –4.0542, diethyl succinate); $R_{\max}$ = 1.65, $SE_{\max}$ = 4.82 (r = –1.6249, s = –4.1674, diethyl malonate); $R_{\max}$=4.15, $SE_{\max}$=6.33 (r=–3.1588, s=–4.9079, ethyl caprylate); $R_{\max}$ = 3.55, $SE_{\max}$ = 5.78 (r = –2.5407, s = –4.4444 , ethyl valerate); $R_{\max}$= 1.75, $SE_{\max}$= 5.41 (r = –1.0839, s = –2.5025, isoamyl alcohol). The substance-dependent adjustable coefficients r and s have been estimated by means of linear regression. The derivative variation test (slope analysis) of the considered variables has been performed using linear programming algorithm of QSB+ (V 2.0) software [26]. By presuming that the slope variation profile of the R quantity gives evidence for the suitability of the carrier concentration for a reliable reactive extraction, an interpretation of the optimum conditions in terms of the derivative variation profile of the observed (Figs. 1 and 2) and modelled (Eq. (8)) properties results in the following quantitative ranges of the R factor attributed to the amine/diluent/formic acid systems studied:

$0 < R < 0.5$	(the extractant is a poor separating agent)
$0.5 < R < 1$	(the extractant is moderately effective)
$1 < R < 8$	(the extractant is excellent separating agent)
$R > 8$	(a very large extractant load is used)

In a similar way, the synergism in the extraction power of amine/diluent system can be optimized adequately in terms of the SE factor. Since the physical extraction of formic acid by the pure diluent alone is almost invariably small, the ranges of the synergistic enhancement factor SE generally increase with increasing the volume fraction of the amine, whereas Z_t is varying inversely with the amine content. In this case, the most appropriate synergistic extraction power of relevant amine/diluent system can be identified due to the SE ranges regarding the slope variation profile (slope changes) of the observed (Fig. 3) and modelled (Eq. (8)) curves defined as follows:

$0 < SE < 2$	(the solvent system is a poor separating agent)
$2 < SE < 5$	(the solvent system is moderately effective)
$5 < SE < 10$	(the solvent system is excellent separating agent)
SE > 10	(a very large extractant load is used)

It seems clear that R and SE factors are devoid of the physical meaning for a practically insoluble acid in the selected diluent alone. It turns out from the variation profiles of the quantities in question that the curve slope is changed more variably in the ranges $1 < R < 8$ and $5 < SE < 10$. However, both R and SE factors are varying with the extractant content in the solvent mixture and their optimum values are intimately connected to the physical solubility of the acid in pure diluent alone. This leaves us with the conclusion that R and SE factors are capable of representing reliably optimum behaviour of a reactive extraction system involving hydrophilic formic acid with $D_0 < 0.52$ for pure diluent.

As described above, the optimum R and SE conditions for the observed (Table 3, Figs. 1–3) and modelled (Eq. (8)) performance give rise to a preferable use of monobasic esters and isoamyl alcohol as the most appropriate diluents for DBA and TPA. It is recognized from the R profile that monobasic esters (ethyl caprylate, ethyl valerate) and isoamyl alcohol are most appropriate diluents for DBA, whereas TPA is an effective carrier for all the studied diluents. On the other hand, the variation profile of SE comprises favourably the monobasic ester diluent to be an appropriate medium for organic formic acid-amine complexes leading to a high distribution coefficient as compared with a less effective dibasic ester. In contrast to moderately large R and SE factors, amine/isoamyl alcohol yields the largest Z_t factors, thus this system is categorized as an effective synergistic solvent mixture. These concepts are supported by the observed R, SE and Z_t factors from Table 3 and Figs. 1–3, dictating that an effective synergistic separation of formic acid by amine/monobasic ester and amine/isoamyl alcohol systems is predominantly achieved. Consequently, due to the synergistic effect of physical extraction and chemical interaction, the studied amine/diluent systems can improve the extraction efficiency of the considered acid especially when a monobasic ester or isoamyl alcohol diluent takes place in the solvent mixture.

4.3. Reliability analysis of existing models

Comparisons of experimental and calculated distribution data for the studied reactive extraction systems are used to analyze statistically the reliability of the equilibrium models, Eqs. (4)–(6), in terms of the mean relative error $\bar{e}=(100/N)\sum_{i=1}^{N}\left|\left(Y_{i,\mathrm{obs}}-Y_{i,\mathrm{mod}}\right)/Y_{i,\mathrm{obs}}\right|$ (%) and root-mean-square deviation $\sigma=\left(\sum_{i=1}^{N}\left(Y_{i,\mathrm{obs}}-Y_{i,\mathrm{mod}}\right)^2/N\right)^{0.5}$. Firstly, the application of Eqs. (4)–(6) generates the corresponding model coefficients

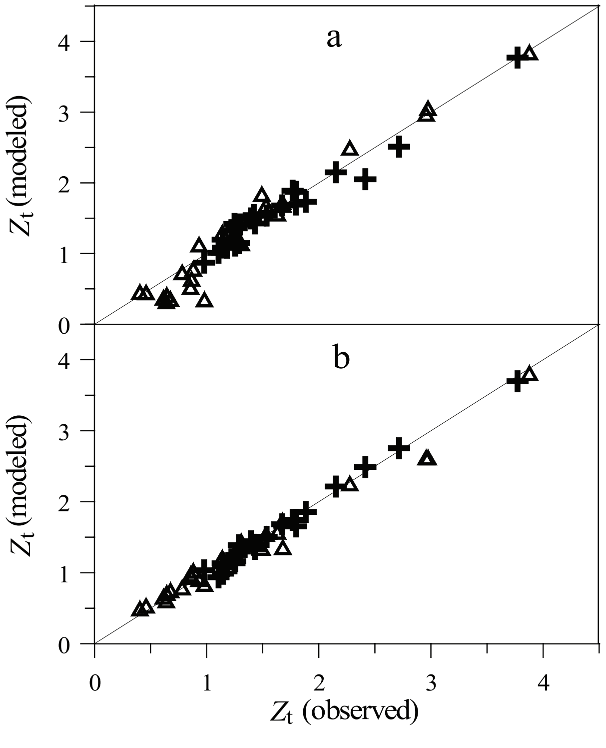

Fig. 4. Graphical confidence test of the models as a plot of the modelled performance (Z_t) against the observed properties: ✚ TPA/diluent, △ DBA/diluent. (a) Chemodel, Eq. (4); (b) Langmuir model, Eq. (5).

β_{pq}(mol dm^{-3})$^{1-p-q}$, β_L(mol dm^{-3})$^{-z}$ and C_i, being regressed by means of linear programming [27].

Fig. 4 and Table 4 demonstrate the graphical confident tests and the consistency of calculations achieved for Eqs. (4) and (5). The chemodel, Eq. (4), has been performed in terms of one, two or three selected appropriate complex combinations regarding Z_s. The best fits of the experimental data display the approach comprising the acid$_p$-amine$_q$ (p, q) complex formation of one (1:2 for TPA, 1:1 for DBA) or simultaneous two associated structures as follows: (a) TPA, (1:1 and 1:2) for ethyl caprylate and isoamyl alcohol and (1:2 and 1:3) for other diluents; (b) DBA, (1:1 and 1:3) for ethyl caprylate and (1:2 and 1:3) for other diluents. The Langmuir model, Eq. (5), was performed considering the formation of only one associated structure $p{:}q = z{:}1 = Z_{s,\max}$. The equilibrium extraction constants β_{pq} and β_L obtained for the above mentioned individual complexes are listed in Table 4. From that table, the chemodel reproduces the overall Z_t data moderately accurate with the mean deviations of $\bar{e}(Z_t) = 12.7\%$ (σ (Z_t) = 0.29) and $\bar{e}(Z_t) = 13.2\%$ (σ (Z_t) = 0.17) for the selected one and two complex formations, respectively. As shown in Table 4, Eq. (4) coincides with the experimental data for one selected complex formation slightly more precisely than those for two complexes due to a reduced number of degrees of freedom. The β_L constants from Table 4 have been estimated by processing the maximum loading values ($z = Z_{s,\max}$) of 1.11, 0.79, 0.99, 1.50, 1.26 and 1.20 for TPA/diluent and 0.84, 1.02, 1.13, 0.66, 0.83 and 1.17 for DBA/diluent pertaining to diethyl sebacate, diethyl succinate, diethyl malonate, ethyl caprylate, ethyl valerate and isoamyl alcohol, respectively. The reliability analysis of Eq. (5) results in an average error of $\bar{e}(Z_t) = 6.1\%$ (σ (Z_t) = 0.11). As illustrated in Fig. 4, the Langmuir model (Eq. (5)) is slightly more accurate than chemodel (Eq. (4)) with respect to the selected two (T) complexes for the later. It is apparent from Fig. 4 that both Eqs. (4) and (5) are almost free of systematical errors, yielding a relatively fair distribution verifying the goodness-of-fit.

The reliability analysis of LSER, Eq. (6), has been performed using the solubility, solvatochromic and molar volume indices

Table 4

Extraction constants β_{pq} and β_L of Eqs. (4) and (5), and root-mean-square deviation $\sigma(Z_t)$[a] and mean relative error $\bar{e}(Z_t)$[a] of model estimates for formic acid-amine complexation

System		Langmuir model, Eq. (5)			Chemodel, Eq. (4)			
		β_L; ($z = Z_{s,\max}$)[b]	$\sigma(Z_t)$	$\bar{e}(Z_t)$[a]	β_{pq1}; (p,q)[c]	β_{pq2}; (p,q)[c]	$\sigma(Z_t)$	$\bar{e}(Z_t)$[a]
TPA[e] + Diethyl	S[d]	0.3837×10^1; (1.11)	0.039	2.46	0.1858×10^1; (1, 2)		0.129	9.90
sebacate	T[d]				0.1027×10^1; (1, 2)	0.3124×10^0; (1, 3)	0.112	7.51
TPA + Diethyl	S	0.2380×10^1; (0.79)	0.111	7.44	0.6958×10^1; (1, 2)		0.340	17.16
succinate	T				0.4760×10^1; (1, 2)	0.4412×10^1; (1, 3)	0.206	9.34
TPA + Diethyl	S	0.6678×10^1; (0.99)	0.052	2.94	0.2859×10^1; (1, 2)		0.189	6.48
malonate	T				0.1581×10^1; (1, 2)	0.5157×10^0; (1, 3)	0.175	8.60
TPA + Ethyl	S	0.2478×10^1; (1.50)	0.121	8.18	0.1025×10^1; (1, 2)		0.056	3.87
caprylate	T				0.4678×10^0; (1, 1)	0.4479×10^1; (1, 2)	0.116	7.29
TPA + Ethyl	S	0.4864×10^1; (1.26)	0.051	3.37	0.1281×10^1; (1, 2)		0.132	6.06
valerate	T				0.7341×10^0; (1, 2)	0.1265×10^0; (1, 3)	0.131	7.71
TPA + Isoamyl	S	0.6041×10^1; (1.20)	0.068	2.99	0.3268×10^1; (1, 2)		0.101	4.86
alcohol	T				0.4330×10^1; (1, 1)	0.3566×10^2; (1, 2)	0.004	0.19
DBA[e] + Diethyl	S	0.8472×10^0; (0.84)	0.180	8.80	0.5630×10^0; (1, 1)		0.341	16.57
sebacate	T				0.1814×10^2; (1, 2)	0.6154×10^2; (1, 3)	0.239	29.00
DBA + Diethyl	S	0.8893×10^0; (1.02)	0.190	6.14	0.8194×10^0; (1, 1)		0.423	12.84
succinate	T				0.1478×10^2; (1, 2)	0.4030×10^2; (1, 3)	0.196	14.43
DBA + Diethyl	S	0.9765×10^0; (1.13)	0.206	8.68	0.1016×10^1; (1, 1)		0.562	18.59
malonate	T				0.1696×10^2; (1, 2)	0.3971×10^2; (1, 3)	0.104	8.26
DBA + Ethyl	S	0.9244×10^0; (0.66)	0.098	12.73	0.3308×10^0; (1, 1)		0.157	18.61
caprylate	T				0.4747×10^0; (1, 1)	0.4869×10^0; (1, 3)	0.375	33.85
DBA + Ethyl	S	0.1272×10^1; (0.83)	0.093	6.41	0.7338×10^0; (1, 1)		0.203	13.52
valerate	T				0.5282×10^1; (1, 2)	0.8497×10^1; (1, 3)	0.246	25.48
DBA + Isoamyl	S	0.4699×10^1; (1.17)	0.077	3.50	0.4549×10^1; (1, 1)		0.834	24.43
alcohol	T				0.1465×10^1; (1, 2)	0.7963×10^{-1}; (1, 3)	0.140	6.54

[a] $\bar{e} = (100/N)\sum_{i=1}^{N}\left|\left(Z_{t,\mathrm{obs}} - Z_{t,\mathrm{mod}}\right)/Z_{i,\mathrm{obs}}\right|$ (%), $\sigma = \left[\sum_{i=1}^{N}\left(Z_{\mathrm{t,obs}} - Z_{\mathrm{t,mod}}\right)^2/N\right]^{0.5}$.

[b] Langmuir extraction constant β_L in (mol dm^{-3})$^{-z}$ for a given association number ($z = Z_{s,\max}$) due to Eq. (5).

[c] Equilibrium extraction constant β_{pq} in (mol dm^{-3})$^{1-p-q}$ for a given acid$_p$-amine$_q$ (p, q) aggregation due to Eq. (4).

[d] One (S) or two (T) complex formation considered.

[e] TPA = tri-*n*-propyl amine; DBA = dibenzyl amine.

Table 5

The Hildebrand solubility parameter (δ_H), solvatochromic parameters (π, β, α, δ) and molar volumes ($\bar{V}$) of compounds

Compound	$\pi^{a,b}$	$\beta^{a,b}$	$\alpha^{a,b}$	$\delta_H^{c,d}$ (MPa$^{0.5}$)	$\delta^{a,b}$	$\bar{V}\times10^{-2}$ ^{e} (cm^3 mol^{-1})
Formic acid	0.65	0.38	0.65	24.8	0	0.377
Tri-*n*-propyl amine	0.14	0.69	0	26.8[e]	0	1.895
Dibenzyl amine[f]	0.82	0.47	0	22.5[e]	1	1.923
Diethyl sebacate[g]	0.49	0.45	0	18.8[e]	0	2.682
Diethyl succinate[h]	0.55	0.45	0	18.1[e]	0	1.702
Diethyl malonate	0.64	0.45	0	19.4[e]	0	1.520
Ethyl caprylate	0.49	0.45	0	19.8[e]	0	1.987
Ethyl valerate	0.51	0.45	0	16.0	0	1.490
Isoamyl alcohol	0.40	0.45	0.33	25.1	0	1.090

[a] Due to Kamlet et al. [19].
[b] Due to Marcus [20].
[c] Due to Barton [28].
[d] Due to Riddick et al. [29].
[e] Calculated.
[f] Parameters of phenylethyl amine ($C_6C_5NHC_2H_5$).
[g] Parameters of butyl propanoate (n-$C_4H_9COOC_2H_5$).
[h] Parameters of ethyl propanoate ($C_2H_5COOC_2H_5$).

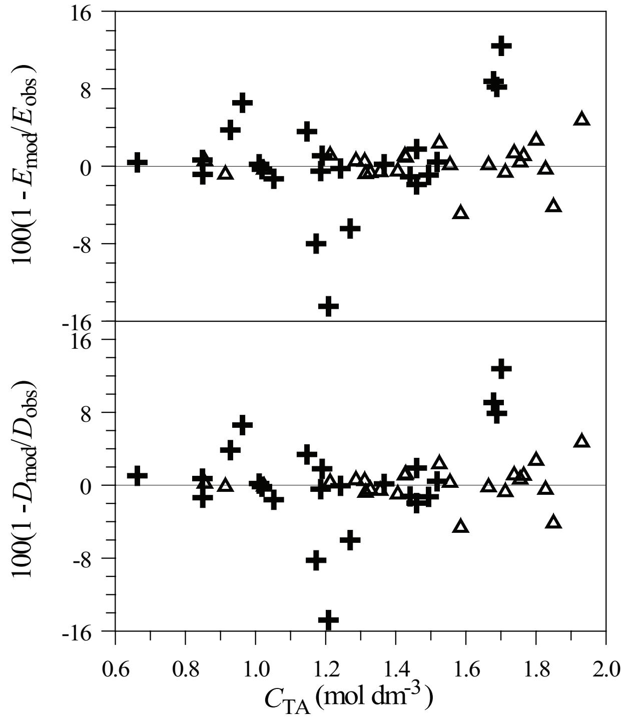

Fig. 5. Mean deviations of the modelled properties *D* and *E* due to the LSER model, Eq. (6), varying against aqueous acid concentration: ✚ tri-*n*-propyl amine (TPA)/diluent, △ dibenzyl amine (DBA)/diluent.

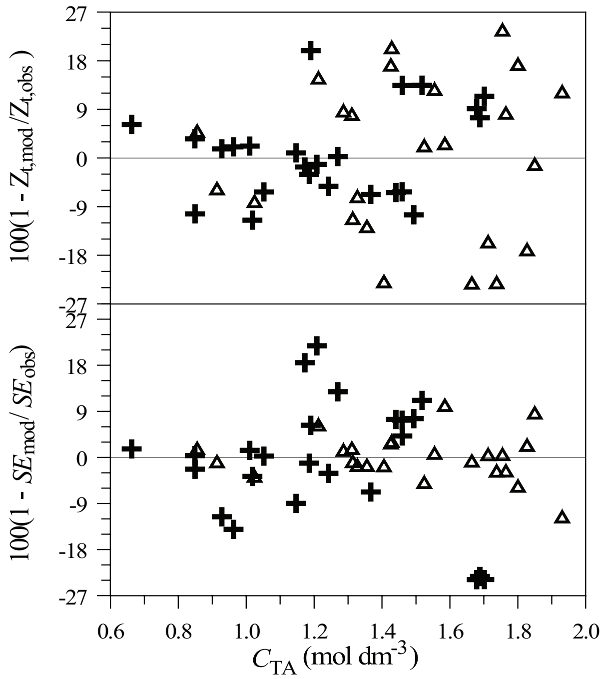

Fig. 6. Mean deviations of the modelled properties Z_t and *SE* due to the LSER model, Eq. (6), varying against aqueous acid concentration: ✚ tri-*n*-propyl amine (TPA)/diluent, △ dibenzyl amine (DBA)/diluent.

of the solvents (δ_H, π, β, α, δ, $\bar{V}$) listed in Table 5 [19, 20, 28, 29], and the coefficients C_i (C_H, C_π, C_β, C_V) corresponding to *D*, *E*, s_f^{phys}, *SE* and Z_t factors from Table 6. Inspection of Figs. 5 and 6 and Table 6 reveals that LSER matches reliably the observed performance over the entire composition range, yielding mean deviations of $\bar{e}(D) = 2.4\%$ ($\sigma(D) = 0.02$), $\bar{e}(E) = 2.4\%$ ($\sigma(E) = 0.95$), $\bar{e}(s_f^{phys}) = 2.5\%$ ($\sigma(s_f^{phys}) = 0.01$), $\bar{e}(SE) = 6.5\%$ ($\sigma(SE) = 0.46$), and $\bar{e}(Z_t) = 9.5\%$ ($\sigma(Z_t) = 0.20$) considering all of the systems studied. The values of $Z_{t,max}$ and SE_{max} used in Eq. (6) are provided completely in Table 6.

Table 6
Coefficients C_i (C_H, C_π, C_β, and C_V) of the LSER model, Eq. (6), and root-mean-square deviation (σ)[a] and mean relative error ($\bar{e}$)[a] evaluated for different properties Pr (D, E, s_f^{phys}, SE, Z_t)

System	C_H	C_π	C_β	C_V
$Pr = \ln(D)$; $Pr_0 = \ln(D_0)$[b]; $\sigma(D)$; $\bar{e}(D)$				
TPA[c] + Diethyl sebacate ($\sigma = 0.029$; $\bar{e} = 4.81\%$)	-0.28817×10^1	0.62704×10^0	0.50906×10^0	0.45012×10^0
TPA + Diethyl succinate ($\sigma = 0.002$; $\bar{e} = 0.30\%$)	-0.79086×10^1	-0.13989×10^1	0.32942×10^1	0.17000×10^1
TPA + Diethyl malonate ($\sigma = 0.011$; $\bar{e} = 1.06\%$)	-0.52763×10^1	0.53800×10^0	-0.53433×10^0	0.19104×10^1
TPA + Ethyl caprylate ($\sigma = 0.074$; $\bar{e} = 8.86\%$)	-0.46533×10^1	-0.25069×10^0	0.11198×10^1	0.97380×10^0
TPA + Ethyl valerate ($\sigma = 0.046$; $\bar{e} = 5.59\%$)	-0.33063×10^1	0.44654×10^0	-0.17402×10^1	0.13997×10^1
TPA + Isoamyl alcohol ($\sigma = 0.018$; $\bar{e} = 1.09\%$)	-0.44557×10^1	0.56777×10^1	0.711146×10^1	-0.13487×10^1
DBA[c] + Diethyl sebacate ($\sigma = 0.001$; $\bar{e} = 0.47\%$)	-0.35734×10^1	-0.81507×10^1	0.33023×10^1	0.17143×10^1
DBA + Diethyl succinate ($\sigma = 0.005$; $\bar{e} = 0.79\%$)	-0.87409×10^1	0.54544×10^1	0.24954×10^1	-0.10535×10^0
DBA + Diethyl malonate ($\sigma = 0.005$; $\bar{e} = 0.77\%$)	-0.30452×10^1	0.34985×10^1	0.90350×10^1	-0.26928×10^1
DBA + Ethyl caprylate ($\sigma = 0.005$; $\bar{e} = 2.61\%$)	-0.44517×10^1	0.34932×10^2	-0.19748×10^2	-0.29201×10^1
DBA + Ethyl valerate ($\sigma = 0.010$; $\bar{e} = 2.69\%$)	-0.82698×10^1	0.49837×10^1	-0.43181×10^1	0.15550×10^1
DBA + Isoamyl alcohol ($\sigma = 0.002$; $\bar{e} = 0.20\%$)	0.10603×10^2	-0.98123×10^1	-0.41410×10^1	0.32698×10^0
$Pr = \ln(E)$; $Pr_0 = \ln(E_0)$[b]; $\sigma(E)$; $\bar{e}(E)$				
TPA[c] + Diethyl sebacate ($\sigma = 1.85$; $\bar{e} = 5.02\%$)	-0.12587×10^1	0.14836×10^1	-0.11100×10^1	0.30864×10^0
TPA + Diethyl succinate ($\sigma = 0.15$; $\bar{e} = 0.34\%$)	-0.93259×10^1	-0.19214×10^1	0.40955×10^1	0.17785×10^1
TPA + Diethyl malonate ($\sigma = 0.49$; $\bar{e} = 0.99\%$)	0.15574×10^0	0.31273×10^1	0.13427×10^1	-0.12560×10^1
TPA + Ethyl caprylate ($\sigma = 3.93$; $\bar{e} = 8.59\%$)	-0.63443×10^1	-0.13054×10^1	0.18667×10^1	0.13725×10^1
TPA + Ethyl valerate ($\sigma = 2.36$; $\bar{e} = 5.40\%$)	-0.28369×10^1	0.10849×10^1	-0.10214×10^1	0.81992×10^0
TPA + Isoamyl alcohol ($\sigma = 0.39$; $\bar{e} = 0.66\%$)	-0.60342×10^1	0.57448×10^1	0.12792×10^2	-0.32016×10^1
DBA[c] + Diethyl sebacate ($\sigma = 0.083$; $\bar{e} = 0.33\%$)	-0.41407×10^1	-0.67278×10^1	0.35803×10^1	0.14413×10^1
DBA + Diethyl succinate ($\sigma = 0.24$; $\bar{e} = 0.65\%$)	-0.72848×10^1	0.37726×10^1	0.12110×10^1	0.31358×10^0
DBA + Diethyl malonate ($\sigma = 0.29$; $\bar{e} = 0.75\%$)	-0.13904×10^1	0.30993×10^1	0.57190×10^1	-0.21545×10^1
DBA + Ethyl caprylate ($\sigma = 0.42$; $\bar{e} = 2.59\%$)	-0.45402×10^1	0.32946×10^2	-0.18238×10^2	-0.27815×10^1
DBA + Ethyl valerate ($\sigma = 0.80$; $\bar{e} = 2.82\%$)	-0.78845×10^1	0.30973×10^1	-0.13739×10^1	0.11794×10^1
DBA + Isoamyl alcohol ($\sigma = 0.40$; $\bar{e} = 0.72\%$)	0.78276×10^1	-0.41619×10^1	-0.53424×10^1	-0.98253×10^{-1}
$Pr = \ln\left(s_f^{phys}\right)$; $Pr_0 = \ln\left(s_{f0}^{phys}\right)$; $\sigma\left(s_f^{phys}\right)$; $\bar{e}\left(s_f^{phys}\right)$				
TPA[c] + Diethyl sebacate ($\sigma = 0.021$; $\bar{e} = 5.26\%$)	0.11385×10^1	-0.14612×10^1	0.10958×10^1	-0.30767×10^0
TPA + Diethyl succinate ($\sigma = 0.004$; $\bar{e} = 0.60\%$)	0.81446×10^1	0.90462×10^0	-0.28577×10^1	-0.16591×10^1
TPA + Diethyl malonate ($\sigma = 0.007$; $\bar{e} = 1.05\%$)	-0.29563×10^0	-0.33486×10^1	-0.15725×10^1	0.13786×10^1
TPA + Ethyl caprylate ($\sigma = 0.016$; $\bar{e} = 8.27\%$)	0.61241×10^1	0.10277×10^1	-0.19498×10^1	-0.12500×10^1
TPA + Ethyl valerate ($\sigma = 0.019$; $\bar{e} = 5.35\%$)	0.20400×10^1	-0.18674×10^1	0.43485×10^0	-0.26101×10^0
TPA + Isoamyl alcohol ($\sigma = 0.002$; $\bar{e} = 0.34\%$)	0.11855×10^2	-0.83035×10^1	-0.21764×10^2	0.43573×10^1
DBA[c] + Diethyl sebacate ($\sigma = 0.005$; $\bar{e} = 1.01\%$)	0.35635×10^1	0.62847×10^1	-0.35209×10^1	-0.13164×10^1
DBA + Diethyl succinate ($\sigma = 0.003$; $\bar{e} = 0.44\%$)	0.42585×10^1	-0.23811×10^1	-0.16425×10^1	-0.12636×10^0
DBA + Diethyl malonate ($\sigma = 0.003$; $\bar{e} = 0.46\%$)	-0.12182×10^0	-0.20164×10^1	-0.40181×10^1	0.15203×10^1
DBA + Ethyl caprylate ($\sigma = 0.012$; $\bar{e} = 2.60\%$)	0.45130×10^1	-0.27970×10^2	0.14802×10^2	0.23206×10^1
DBA + Ethyl valerate ($\sigma = 0.011$; $\bar{e} = 3.14\%$)	0.78006×10^1	-0.32778×10^1	0.20781×10^1	-0.13545×10^1
DBA + Isoamyl alcohol ($\sigma = 0.006$; $\bar{e} = 0.90\%$)	-0.65166×10^1	0.51042×10^1	0.30181×10^1	-0.14556×10^0

(*Continued*)

Table 6 (*Continued*)

System	C_H	C_π	C_β	C_V
$Pr = \ln(SE)$; $Pr_0 = \ln(SE_{\max})$[d]; $\sigma(SE)$; $\bar{e}(SE)$				
TPA[c] + Diethyl sebacate ($\sigma = 0.75$; $\bar{e} = 13.84\%$)	0.21565×10^1	-0.14272×10^1	0.13295×10^1	-0.38646×10^0
TPA + Diethyl succinate ($\sigma = 0.36$; $\bar{e} = 5.09\%$)	0.14526×10^2	0.24432×10^1	-0.52852×10^1	-0.26664×10^1
TPA + Diethyl malonate ($\sigma = 0.12$; $\bar{e} = 1.97\%$)	-0.81744×10^0	-0.30738×10^1	-0.55637×10^0	0.14181×10^1
TPA + Ethyl caprylate ($\sigma = 1.96$; $\bar{e} = 17.82\%$)	0.50297×10^1	0.44963×10^0	-0.11283×10^1	-0.97467×10^0
TPA + Ethyl valerate ($\sigma = 1.15$; $\bar{e} = 16.35\%$)	0.36718×10^1	-0.13068×10^1	0.17209×10^1	-0.99400×10^0
TPA + Isoamyl alcohol ($\sigma = 0.18$; $\bar{e} = 3.49\%$)	0.40528×10^1	-0.42607×10^1	-0.88451×10^1	0.24889×10^1
DBA[c] + Diethyl sebacate ($\sigma = 0.026$; $\bar{e} = 0.49\%$)	0.39016×10^1	-0.21777×10^1	0.57319×10^1	-0.12159×10^1
DBA + Diethyl succinate ($\sigma = 0.091$; $\bar{e} = 2.02\%$)	-0.42582×10^0	-0.29861×10^0	0.29924×10^{-1}	0.27477×10^{-1}
DBA + Diethyl malonate ($\sigma = 0.074$; $\bar{e} = 1.65\%$)	0.69770×10^0	-0.59193×10^0	-0.13576×10^1	0.33004×10^0
DBA + Ethyl caprylate ($\sigma = 0.33$; $\bar{e} = 6.33\%$)	0.55248×10^1	-0.36645×10^2	0.20637×10^2	0.31092×10^1
DBA + Ethyl valerate ($\sigma = 0.31$; $\bar{e} = 6.01\%$)	0.10260×10^2	-0.40691×10^1	0.30430×10^1	-0.15766×10^1
DBA + Isoamyl alcohol ($\sigma = 0.18$; $\bar{e} = 3.16\%$)	-0.38424×10^1	0.19414×10^1	0.23207×10^1	0.17892×10^0
$Pr = \ln(Z_t)$; $Pr_0 = \ln(Z_{t,\max})$[d]; $\sigma(Z_t)$; $\bar{e}(Z_t)$				
TPA[c] + Diethyl sebacate ($\sigma = 0.078$; $\bar{e} = 3.73\%$)	-0.36467×10^0	-0.13491×10^{-1}	0.14080×10^0	-0.23717×10^{-1}
TPA + Diethyl succinate ($\sigma = 0.17$; $\bar{e} = 6.36\%$)	0.10304×10^2	0.18435×10^1	-0.41924×10^1	-0.19972×10^1
TPA + Diethyl malonate ($\sigma = 0.19$; $\bar{e} = 7.13\%$)	-0.35899×10^0	-0.13737×10^1	-0.14916×10^1	0.78203×10^0
TPA + Ethyl caprylate ($\sigma = 0.12$; $\bar{e} = 6.29\%$)	0.53160×10^0	0.41763×10^{-1}	-0.17122×10^0	-0.11198×10^0
TPA + Ethyl valerate ($\sigma = 0.098$; $\bar{e} = 4.72\%$)	0.33402×10^0	-0.25644×10^0	0.14078×10^0	-0.10229×10^0
TPA + Isoamyl alcohol ($\sigma = 0.41$; $\bar{e} = 11.99\%$)	-0.90576×10^0	-0.76079×10^{-1}	0.78086×10^0	-0.37071×10^0
DBA[c] + Diethyl sebacate ($\sigma = 0.23$; $\bar{e} = 17.52\%$)	-0.44107×10^1	0.11350×10^1	0.68603×10^0	0.12895×10^0
DBA + Diethyl succinate ($\sigma = 0.35$; $\bar{e} = 14.64\%$)	-0.23296×10^2	0.10643×10^2	0.39944×10^1	-0.24381×10^0
DBA + Diethyl malonate ($\sigma = 0.28$; $\bar{e} = 12.44\%$)	-0.10515×10^2	0.78476×10^1	0.17306×10^2	-0.59777×10^1
DBA + Ethyl caprylate ($\sigma = 0.073$; $\bar{e} = 9.67\%$)	-0.22164×10^1	0.10485×10^2	-0.60427×10^1	-0.88554×10^0
DBA + Ethyl valerate ($\sigma = 0.16$; $\bar{e} = 11.18\%$)	0.37480×10^0	-0.34830×10^0	0.19243×10^0	-0.22202×10^0
DBA + Isoamyl alcohol ($\sigma = 0.30$; $\bar{e} = 8.37\%$)	0.42069×10^1	-0.61721×10^1	-0.25731×10^1	0.52617×10^0

[a] $\bar{e} = (100/N)\sum_{i=1}^{N}\left|\left(Y_{i,\text{obs}} - Y_{i,\text{mod}}\right)/Y_{i,\text{obs}}\right|$ (%) ; $\sigma = \left[\sum_{i=1}^{N}\left(Y_{i,\text{obs}} - Y_{i,\text{mod}}\right)^2/N\right]^{0.5}$.

[b] D_0, E_0 and s_{f0}^{phys} ($s_{f0}^{\text{phys}} = 1$) stand for the properties attributed to the pure diluent alone.

[c] TPA, tri-*n*-propyl amine; DBA, dibenzyl amine.

[d] $Z_{t,\max}$ and $SE_{\max}$ represent the maximum values of extraction factors defined as follows, (a) for TPA: $Z_{t,\max} = 1.99$, $SE_{\max} = 7.38$ (diethyl sebacate); $Z_{t,\max} = 2.61$, $SE_{\max} = 6.30$ (diethyl succinate); $Z_{t,\max} = 2.92$, $SE_{\max} = 5.07$ (diethyl malonate); $Z_{t,\max} = 2.00$, $SE_{\max} = 15.30$ (ethyl caprylate); $Z_{t,\max} = 2.08$, $SE_{\max} = 9.63$ (ethyl valerate); $Z_{t,\max} = 3.97$, $SE_{\max} = 5.24$ (isoamyl alcohol), (b) for DBA: $Z_{t,\max} = 1.88$, $SE_{\max} = 5.28$ (diethyl sebacate); $Z_{t,\max} = 3.16$, $SE_{\max} = 5.07$ (diethyl succinate); $Z_{t,\max} = 3.17$, $SE_{\max} = 4.82$ (diethyl malonate); $Z_{t,\max} = 1.18$, $SE_{\max} = 6.33$ (ethyl caprylate); $Z_{t,\max} = 1.69$, $SE_{\max} = 5.78$ (ethyl valerate); $Z_{t,\max} = 4.07$, $SE_{\max} = 5.41$ (isoamyl alcohol).

Figs. 5 and 6 illustrate clearly that Eq. (6) reproduces precisely the observed curve over the entire composition range for all the considered systems, yielding an overall deviation of $\bar{e} = 4.7\%$ ($\sigma = 0.32$). The model coincides with the observed performance for the TPA/diluent systems slightly less accurate, yielding $\bar{e} = 5.4\%$ ($\sigma = 0.50$) as compared with $\bar{e} = 3.9\%$ ($\sigma = 0.14$) for the DBA/diluent ones. The reliability of Eq. (6) has proven to be disapprovingly less accurate for Z_t factor, yielding $\bar{e} = 9.5\%$ ($\sigma = 0.2$). Conversely, except for the latter, any drastic deviation of estimates has not been observed for any of the modelled property and systems examined. The results suggest an underlying physical significance for the model variables and show an excellent potential for generalized predictions by LSER.

5. Conclusion

Comparative assessment of the reactive extraction of formic acid from water by TPA/diluent and DBA/diluent has been elucidated on the basis of simultaneous effect of chemical interaction and physical extraction. The results suggest that the extraction of formic acid by the amine/ester solvent mixture is feasible. The extracted data agree well with Eqs. (4)–(6), and the model coefficients support the conditions of favourable extraction. The proposed optimization approach is applied successfully to the description of the optimum extraction field. The work draws the following conclusions:

- The uptake capacity of amine/diluent systems is ranging as follows, TPA > DBA, and isoamyl alcohol > diethyl malonate > diethyl succinate > diethyl sebacate > ethyl valerate > ethyl caprylate. Different mechanisms control favourably monotype (1:1 or 1:2) and two types (1:2 and 1:3, or 1:1 and 1:3) formic acid-amine aggregation in the organic phase depending on the solvation degree of diluent. Monobasic esters are more effective solvating agents for organic complexes, whereas amine/isoamyl alcohol mixture yields larger overall extraction factors of $D > 1$, $Z_t > 1$ and $E > 50\%$ due to the simultaneous effect of physical extraction and chemical interaction. In view of the results in Table 3, the examined amine/diluent mixtures yield moderately large interaction factors of $Z_s < 1$ ($Z_s \approx 0.30–0.97$), $s_f^{chem} < 0.9$ ($s_f^{chem} \approx 0.20–0.93$) and $s_f^{phys} < 0.8$ ($s_f^{phys} \approx 0.10–0.80$), indicating that moderately strong interactive forces dominate during formic acid-amine complex formation.
- The optimization structure utilizing R and SE factors is able to identify the optimum extraction field. It turns out from the variation profiles of the quantities in question that the most appropriate optimization ranges are $1 < R < 8$ and $5 < SE < 10$. The optimization approach is applicable to any reactive extraction system for which the complex solute-carrier interaction phenomenon is being definable in the whole working range.
- The deviation statistics obtained for LSER, Eq. (6), testify its ability to simulate the observed performance satisfactorily with a mean error of 4.7%. The chemodel Eq. (4) and Langmuir model Eq. (5) are slightly less accurate yielding mean errors of 12.1% and 5.7%, respectively.

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Nomenclature

$\overline{C}_{AM}$ — Concentration of non-complexed amine, mol dm^{-3}

$\overline{C}_{AM}^{0}$ — Initial concentration of amine in the solvent mixture, mol dm^{-3}

$\overline{C}_{d}$ — Concentration of acid extracted by the diluent, mol dm^{-3}

C_{H^+} — Proton concentration of acid in the aqueous phase, mol dm^{-3}

C_{HA} — Concentration of undissociated acid in the aqueous phase, mol dm^{-3}

$\overline{C}_{HA}$ — Overall concentration of complexed acid, mol dm^{-3}

C_i — Coefficient

$\overline{C}_{pq}$ — Concentration of acid$_p$-amine$_q$ complex, mol dm^{-3}

C_{TA} — Overall concentration of acid in the aqueous phase, mol dm^{-3}

$\overline{C}_{TA}$ — Overall concentration of acid in the organic phase, mol dm^{-3}

C_{TA}^{0} — Initial concentration of acid, mol dm^{-3}

$\overline{C}_{TA}^{d}$ — Concentration of acid extracted by the diluent alone, mol dm^{-3}

D — Distribution ratio of the acid referred to the solvent mixture

D_0 — Distribution ratio of the acid referred to the diluent alone

E — Extraction degree of the acid referred to the solvent mixture, %

E_0 — Extraction degree of the acid referred to the diluent alone, %

$\bar{e}$ — Mean relative error

$$\bar{e}=(100/\mathrm{N})\sum_{i=1}^{N}\left|\left(Y_{i,\mathrm{obs}}-Y_{i,\mathrm{mod}}\right)/Y_{i,\mathrm{obs}}\right|,\ \%$$

F — Correction factor

HA — Monocarboxylic acid

$\overline{(\mathrm{HA})_p(\mathrm{NR}_3)_q}$ Acid-amine complex

$\overline{(\mathrm{HA})_p(\mathrm{NR}_2\mathrm{H})_q}$ Acid-amine complex

K_a — Dissociation constant of acid

N — Number of observation

NR_3, NR_2H Tertiary and secondary amines

P — Pressure, kPa

p,q — Number of acid and extractant molecules involved in the complex

R — Separation ratio optimization factor

Pr, Pr_0 — Properties as defined by Eq. (6)

r, s — Coefficients

s_f^{chem}, s_f^{phys} Chemical and physical separation factors of the solvent mixture

SE — Synergistic enhancement factor

T — Temperature, K

$\bar{V}$ — Molar volume, cm^3 mol^{-1}

v; v_i — Volume fraction of diluent or a component in the solvent mixture

x_{iv} — Independent variable

Y — Independent variable

Z_s — Stoichiometric loading factor

Z_t — Overall loading factor of extractant

z — Associated number

$\left(\overline{\text{overbar}}\right)$ – Species in the organic phase

Greek letters

α^*; α — Solvatochromic parameters
β^*; β — Solvatochromic parameters
β_L — Langmuir extraction constant, $(\text{mol dm}^{-3})^{-z}$
β_{pq} — Apparent equilibrium extraction constant, $(\text{mol dm}^{-3})^{1-p-q}$
δ^*; δ — Solvatochromic parameters
δ^*_H; δ_H — Hildebrand solubility parameters, $\text{MPa}^{0.5}$
π^*; π — Solvatochromic parameters
σ — Root-mean-square deviation

$$\sigma=\left[\sum_{i=1}^{N}\left(Y_{i,\text{obs}}-Y_{i,\text{mod}}\right)^2 \Big/ N\right]^{0.5}$$

Subscripts

mod — Modelled
obs — Observed

References

[1] B. Kamm, P.R. Gruber, M. Kamm, *Biorefineries – Industrial processes and products: status quo and future directions*, Willey-VCH, Weinheim, Germany (2010).

[2] R. Wölfel, N. Taccardi, A. Bösmann, P. Wasserscheid, Selective catalytic conversion of biobased carbohydrates to formic acid using molecular oxygen, Green Chem., 13 (2011) 2759–2763.

[3] H.G. Joglekar, I. Rahman, S. Babu, B.D. Kulkarni, A. Joshi, Comparative assessment of downstream processing options for lactic acid, Sep. Purif. Technol., 52 (2006) 1–17.

[4] A.S. Kertes, C.J. King, Extraction chemistry of fermentation product carboxylic acids, Biotechnol. Bioeng., 28 (1986) 269–282.

[5] J.A. Tamada, A.S. Kertes, C.J. King, Extraction of carboxylic acids with amine extractants. 1. Equilibria and law of mass action modeling, Ind. Eng. Chem. Res., 29 (1990) 1319–1326.

[6] S.T. Yang, S.A. White, S.T. Hsu, Extraction of carboxylic acids with tertiary and quaternary amines: effect of pH, Ind. Eng. Chem. Res., 30 (1991) 1335–1342.

[7] V. Bízek, J. Horácek, M. Koušová, Amine extraction of citric acid: Effect of diluent, Chem. Eng. Sci., 48 (1993) 1447–1457.

[8] A. Senol, Extraction equilibria of formic, levulinic and acetic acids using (Alamine 336/diluent) and conventional solvent systems: modeling considerations, J. Chem. Eng. Japan, 32 (1999) 717–731.

[9] A. Senol, Extraction equilibria of nicotinic acid using Alamine 336 and conventional solvents: effect of diluent, Chem. Eng. J., 83 (2001) 155–163.

[10] A. Senol, Effect of diluent on amine extraction of acetic acid: modeling considerations, Ind. Eng. Chem. Res., 43 (2004) 6496–6506.

[11] A. Senol, Influence of diluent on amine extraction of pyruvic acid using Alamine system, Chem. Eng. Process., 45 (2006) 755–763.

[12] A. Senol, U. Dramur, Predicting liquid–liquid equilibria of amine extraction of carboxylic acid through solvation energy relation, Solv. Extr. Ion Exch., 22 (2004) 865–883.

[13] A. Senol, M. Lalikoglu, M. Bilgin, Modeling extraction equilibria of butyric acid distributed between water and tri-*n*-butyl amine/diluent or tri-*n*-butyl phosphate/diluent system: extension of the LSER approach, Fluid Phase Equilib., 385 (2015) 153–165.

[14] Z. Li, W. Qin, Y. Dai, Liquid-liquid equilibria of acetic, propionic, butyric, and valeric acids with trioctylamine as extractant, J. Chem. Eng. Data, 47 (2002) 843–848.

[15] J. Zhou, W. Bi, K.H. Row, Extraction and separation of D/L-lactic acid in simulated fermentation broth, Korean J. Chem. Eng., 28 (2011) 1608–1612.

[16] R.S. Juang, W.T. Huang, Equilibrium studies on the extraction of citric acid from aqueous solutions with tri-*n*-octylamine, J. Chem. Eng. Japan, 27 (1994) 498–504.

[17] D. Datta, H. Uslu, S. Kumar, Intensification of picolinic acid extraction with tri-n-butylphosphate and tri-n-octylamine in three different diluents, Chem. Eng. Res. Des., 95 (2015) 105–112.

[18] T. Kirsch, G. Maurer, Distribution of oxalic acid between water and organic solutions of tri-*n*-octylamine, Ind. Eng. Chem. Res., 35 (1996) 1722–1735.

[19] M.J. Kamlet, R.M. Doherty, M.H. Abraham, Y. Marcus, R.W. Taft, Linear solvation energy relationships. 46. An improved equation for correlation and prediction of octanol/water partition coefficients of organic nonelectrolytes (including strong hydrogen bond donor solutes), J. Phys. Chem., 92 (1988) 5244–5255.

[20] Y. Marcus, Linear solvation energy relationships. Correlation and prediction of the distribution of organic solutes between water and immiscible organic solvents, J. Phys. Chem., 95 (1991) 8886–8891.

[21] A. Senol, Optimal extractive separation of chromium(VI) from acidic chloride and nitrate media by commercial amines: equilibrium modeling through linear solvation energy relation, Ind. Eng. Chem. Res., 52 (2013) 16321–16334.

[22] A. Senol, B. Baslıoglu, Phase equilibria of ternary systems (water + pyruvic acid + high boiling alcohol). Thermodynamic modeling and optimization of extraction, J. Chem. Thermodyn., 55 (2012) 92–101.

[23] J.A. Dean, *Lange's handbook of chemistry*, 30th ed., McGraw-Hill, New York (1985).

[24] U. Bauer, R. Marr, W. Ruckl, M. Siebenhofer, Reactive extraction of citric acid from aqueous fermentation broth, Ber. Bunsen-Ges. Phys. Chem., 93 (1989) 980–984.

[25] N.H. Timm, *Applied multivariate analysis*, Springer, New York (2002).

[26] Y.-L. Chang, R.S. Sullivan, Quantitative Systems for Business Plus (QSB+) V 2.0, Prentice–Hall Inc., Englewood Cliffs, New Jersey (1991).

[27] D.M. Himmelblau, J. Riggs, *Basic principles and calculations in chemical engineering*, 8th ed., Prentice Hall Inc., Englewood Cliffs, New Jersey (2012).

[28] A.F.M. Barton, Solubility parameters, Chem. Rev., 75 (1975) 731–753.

[29] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic solvents. Physical properties and methods of purification*, 4th ed., Willey-Interscience, New York (1986).

[30] A.M. Cases, A.C.G. Marigliano, C.M. Bonatti, H.N. Sólimo, Density, viscosity, and refractive index of formamide, three carboxylic acids, and formamide + carboxylic acid binary mixtures, J. Chem. Eng. Data, 46 (2001) 712–715.

[31] L.D. Lorenzi, M. Fermeglia, G. Torriano, Density, refractive index, and kinematic viscosity of diesters and triesters, J. Chem. Eng. Data, 42 (1997) 919–923.

[32] T.M. Aminabhavi, H.T.S. Phayde, R.S. Khinnavar, B. Gopalakrishna, K.C. Hansen, Densities, refractive indices, speeds of sound, and shear viscosities of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, and diethyl succinate in the temperature range from 298.15 to 318.15 K, J. Chem. Eng. Data, 39 (1994) 251–260.

[33] J.G. Baragi, M.I. Aralaguppi, T.M. Aminabhavi, M.Y. Kariduraganavar, S.S. Kulkarni, Density, viscosity, refractive index, and speed of sound for binary mixtures of 1,4-dioxane with different organic liquids at (298.15, 303.15, and 308.15) K, J. Chem. Eng. Data, 50 (2005) 917–923.

[34] Y.W. Sheu, C.H. Tu, Densities, viscosities, refractive indices, and surface tensions for 12 flavor esters from T = 288.15 K to T = 358.15 K, J. Chem. Eng. Data, 50 (2005) 1706–1710.

[35] N. Indraswati, M. Mudjijati, F. Wicaksana, H. Hindarso, S. Ismadji, Density and viscosity for a binary mixture of ethyl valerate and hexyl acetate with 1-pentanol and 1-hexanol at 293.15 K, 303.15 K, and 313.15 K, J. Chem. Eng. Data, 46 (2001) 134–137.

[36] R. Riggio, H.E. Martinez, H.N. Sólimo, Densities, viscosities, and refractive indexes for the methyl isobutyl ketone + pentanols systems: measurements and correlations, J. Chem. Eng. Data, 31 (1986) 235–238.

[37] D.R. Lide, *CRC handbook of chemistry and physics*, 79th ed., CRC Press, Boca Raton, FL (1998–1999).

[38] D.R. Lide, H.V. Kehiaian, *CRC handbook of thermophysical and thermochemical data*, CRC Press, Boca Raton, FL (1994).