


Research article

Optimization of reactive extraction of C1–C4 aliphatic monocarboxylic acids from aqueous solutions: modeling solvation effect with extended-LSER, A-UNIFAC and SPR

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ABSTRACT: This paper studies reactive extraction of formic (FA), acetic (AA), propionic (PA) and butyric (BA) acids from aqueous solutions by tri-*n*-butyl amine/diluent, with particular focus on proper optimization and modeling of extraction equilibria. The uptake capacities of amine/diluent and diluent alone approximate the following order: oleyl alcohol > octyl acetate > diisobutyl ketone and BA > PA > AA ≈ FA. An intrinsic optimization structure has been applied to the description of optimum extraction field of relevant systems, based on analyzing the variation profiles of separation ratio *R* and synergistic enhancement *SE* factors through the derivative variation method. We present new solvation molecular models extended-linear solvation energy relation (e-LSER), SPR1 and SPR2 (solvation probability relation), and an extension to group-contribution approach A-UNIFAC (Association-UNIFAC). A-UNIFAC predicts phase equilibria using new group interaction parameters regressed from vapor-liquid equilibrium data. The e-LSER model involves eight descriptors used for expressing solvent effects. By performing SPR1 and SPR2, we are able to scale up the probability range and activation energy of solvation effect. The strength of acid-amine association is calculated with chemodel. e-LSER, A-UNIFAC, SPR and chemodel simulate accurately the observed performance with average deviations inferior to 4.8%, 24.1%, 0.8% and 16.2%, respectively. © 2017 Curtin University and John Wiley & Sons, Ltd.

KEYWORDS: extraction; monocarboxylic acid; tri-*n*-butyl amine; modeling; optimization

INTRODUCTION

Formic (FA), acetic (AA), propionic (PA) and butyric (BA) acids can be produced commercially either by chemical synthesis or by bacterial fermentation.^[1,2] FA, AA and PA are currently being synthesized on a commercial scale by catalytic partial oxidation of wet biomass, alkanes or alkenes at aerobic conditions, by a process that co-generates significant C1–C4 acids as a byproduct.^[2,3] Biologically, FA, AA, PA and BA can be produced by anaerobic metabolism of carbohydrates, fatty acids, sugar and starch, brought about by the direct addition of anaerobic bacteria.^[1,3] However, in a special oxidative degradation of biomass, C1–C4 aliphatic monocarboxylic acids are formed simultaneously, and their extraction from the broth is an industrial concern providing the opportunity

for developing crucial processes for the synthesis of integrated biorefineries.^[1]

Reactive extraction preferably by a tertiary amine is a promising method for the recovery of C1–C4 monocarboxylic acids from fermentation broth because tertiary amine/diluent system has an excessive affinity for carboxylic acids and a high selectivity towards formation of steady acid-amine complexes, leading to a large distribution coefficient.^[4–11] The acid-amine association is reversible, enabling recovery of the acid and recycling of the solvent. Practically, the organic diluent can affect the basicity of the amine and the stability of ion-pair complexes, causing the extraction equilibrium of acid/amine/diluent system to be very sensitive to the solvation efficiency of diluent.^[5–11] Over the past few years, commercial supramolecular complexation agents like Alamine 336, *N,N*-didodecylpyridin-4-amine, trialkylphosphine oxide, di(2-ethylhexyl)phosphoric acid, phosphonium-based ionic liquids and sustainable low molecular weight extractants have been extensively employed as attractive carriers for the acid separation.^[12–17] These

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carriers possess hydrophilic cavities and interactive abilities that enable them to incorporate acid molecules from the aqueous solution with a high product purity and yield.^[12–17] A survey of the literature reveals that the equilibrium characteristics of reactive extraction systems are very sensitive to the types and concentrations of the acid, carrier and diluent, temperature, the aqueous phase pH and the third-phase formation.^[5,6] These dependences are usually rationalized in terms of acid-amine and diluent-complex interactions that take place in the organic phase. Overall, the experimental findings of Bizek *et al.*^[7] and Senol^[8,9] corroborate the fact that the strength of acid-amine complexation is very much dependent on the ability of diluent to solvate acid-amine ion-pair species through dipole–dipole interaction or hydrogen bonding following the order: inert diluent (hydrocarbons) < nonprotic active diluent (halogenated hydrocarbons, esters and ketones) < polar diluent (nitrobenzene) < protic diluent (alcohols).

The present work aims at generating new liquid–liquid equilibrium (LLE) data for the extraction of FA, AA, PA and BA from water by tri-*n*-butyl amine (TBA)/aliphatic diluent at $T=298.2$ K and $P=101.3$ kPa, using the oxygenated diluent diisobutyl ketone (2,6-dimethyl-4-heptanone), or oleyl alcohol (9-octadecen-1-ol), or octyl acetate. Here, it will be discussed the acid-amine complexation and the competition between physical and chemical extractions of C1–C4 acids on an efficiency basis using eight extraction factor as comparison criteria. In order to make the regeneration of components by distillation more manageable, we select TBA and aliphatic diluents of higher boiling temperatures than water and acids. Experimental data for the present systems composed of (TBA + polar ester, or nonprotic ketone, or protic alcohol +10% (w/w) initial aqueous content of FA, or AA, or PA, or BA) are not available in the open literature.

The phase behavior of a reactive extraction system can be estimated by equilibrium models based on the mass action law methodology,^[8,9,13] linear solvation energy relationship (LSER) principles^[10,18,19] and group-contribution theory,^[20–23] all these aim to capture the physics of the hydrogen bond. Here, the strength of acid-amine association is calculated with chemodel. The proposed solvation probability relation (SPR) models are concerned with the probability theory applied to the activation energy of solvation. Special attention was paid to estimate LLE of relevant systems using molecular solvation model extended-LSER (e-LSER) and group-contribution approach Association-UNIFAC (A-UNIFAC), with particular focus on their proper parameterization. Here, the capabilities of e-LSER, SPR1, SPR2, A-UNIFAC and chemodel to simulate the observed performance have been stringently tested.

The study deals with a new conceptual definition for optimum extraction as the locus of the proposed separation ratio R and synergistic enhancement SE factors being fundamentally suited for the optimal tests of reactive extraction of C1–C4 acids. To accomplish this goal, Senol's derivative variation method (DVM)^[24] was successfully applied to the description of the optimum extraction field by analyzing the variation profiles of the derivatives of the optimization factor in question. Because optimum extraction conditions are being very sensitive to the composition levels of amine, acid and diluent and the acid hydrophobicity,^[5,11] it is worthwhile to gain the idea of using only R and SE as separate factors of performance for building up the main optimization structure. Essentially, the main objectives of this work are placed on (1) comparing the LLE behavior of reactive extraction of C1–C4 acids, (2) optimizing the observed and modeled extraction conditions by means of Senol's optimization method, (3) modeling LLE of reactive extraction systems with various thermodynamically compatible solvation models originated from the mass action law, group-contribution theory, solvation principles and probability theory.

THEORETICAL

Physical criteria of extraction equilibria

In a recent paper by Senol *et al.*,^[11] it was reported eight extraction factors to be exactly adequate for interpreting the phase behavior of a reactive LLE system, namely, (1) distribution ratio $D = \overline{C_{TA}}/C_{TA}$; (2) degree of extraction $E = 100(1 - C_{TA}/C_{TA}^0) = 100[D/(1 + D)]$ (%); (3) the overall loading factor of amine $Z_t = \overline{C_{TA}}/C_{NR_3}^0$; (4) stoichiometric loading factor $Z_s = (\overline{C_{TA}} - \nu C_{TA}^d)/\overline{C_{NR_3}^0} = \overline{C_{HA}}/C_{NR_3}^0$; (5) chemical separation factor $s_f^{\text{chem}} = \overline{C_{HA}}/\overline{C_{TA}}$; (6) physical separation factor $s_f^{\text{phys}} = 1 - s_f^{\text{chem}}$; (7) separation ratio optimization factor $R = s_f^{\text{chem}}/s_f^{\text{phys}}$; and (8) synergistic enhancement factor $SE = 1/s_f^{\text{chem}} + 1/s_f^{\text{phys}}$.

Here, ν and $\overline{C_{TA}^d}$ designate the volume fraction of diluent and the amount of acid extracted by the pure (amine-free) diluent alone, respectively. $\overline{C_{NR_3}^0}$, C_{TA}^0 , $\overline{C_{HA}}$, $\overline{C_{TA}}$ and C_{TA} stand for the initial concentrations of amine and acid, the concentration of the complexed acid, the overall acid extracted into the organic phase and the aqueous phase acid content, respectively. The concentration is expressed on (mol dm⁻³) scale, and overbar represents the organic phase species. D , E

and Z_t represent both the distribution effect of acid and the contribution of the amine loading to the extraction. Z_s and s_f^{chem} are typical scales for acid-amine aggregation, and so is s_f^{phys} for the physical extraction. R and SE are fair measures of the synergistic effect of chemical and physical extractions. In fact, the main goal is placed on building up the optimization scheme for effective acid recovery based solely on R and SE factors, because they are brought out opposite variation profiles and different curve slopes with increasing the amine concentration.

Mass action law models

Following Senol,^[8,9] LLE of a reactive extraction system can be successfully described by the interfacial reaction Eqn (1) and the extraction constant β_{pq} in $(\text{mol dm}^{-3})^{1-p-q}$ given by Eqn (2). In the development of chemodel, Eqn (3), it has been brought forward the hypothesis that the overall complexed acid ($\overline{C_{HA}}$) is a linear combination of the individual complexes, which should obey the balance equation $C_{TA}^0 = \overline{C_d} + \overline{C_{HA}} + C_{TA}$.



$$\beta_{pq} = \overline{C_{pq}} / (C_{HA}^p \overline{C_{NR_3}}^q), p = 1, k; q = 1, l \quad (2)$$

$$Z_t = \frac{\overline{C_d} + \overline{C_{HA}}}{C_{NR_3}^0} = \frac{vD_0 C_{TA}^0}{(1 + D_0) C_{NR_3}^0} + \frac{\sum_{p=1}^k \sum_{q=1}^l p \beta_{pq} C_{HA}^p \overline{C_{NR_3}}^q}{C_{NR_3}^0} \quad (3)$$

Here, HA , $\overline{\text{NR}_3}$ and $\overline{(\text{HA})_p(\text{NR}_3)_q}$ stand for the non-dissociated acid in the aqueous phase, the tertiary amine (TBA) and the acid-amine complex, respectively. $\overline{C_d} = vD_0 C_{TA}^0 / (1 + D_0)$ denotes the concentration of the acid portion physically extracted by the diluent in the solvent mixture, and D_0 represents the distribution ratio of the acid referred to the diluent alone. The aqueous phase acid concentration at equilibrium C_{HA} is typically calculated from the dissociation equation $C_{HA} = C_{TA} C_{H^+} / (C_{H^+} + K_a)$ using the dissociation constant of the acid K_a ($pK_{a,FA} = 3.751$, $pK_{a,AA} = 4.756$, $pK_{a,PA} = 4.860$, $pK_{a,BA} = 4.830$).^[25] The extraction constants β_{pq} are calculated by linear regression considering the formation of one, two or three acid-amine_q complexes.

Postulating that acid_z-amine₁ aggregation goes in for the maximum stoichiometric loading $z = Z_{s, \text{max}} =$

$(\overline{C_{HA}})_{\text{max}} / \overline{C_{NR_3}^0}$, the Langmuir adsorption model of Bauer *et al.*^[26] can be rearranged to establish a relation including physical and chemical interaction terms, Eqn (4). Here β_L , expressed on $(\text{mol dm}^{-3})^{-z}$, stands for the Langmuir extraction constant.

$$Z_t = \frac{\overline{C_d} + \overline{C_{HA}}}{C_{NR_3}^0} = \frac{vD_0 C_{TA}^0}{(1 + D_0) C_{NR_3}^0} + \frac{z \beta_L C_{HA}^z}{1 + \beta_L C_{HA}^z} \quad (4)$$

Extended-LSER approach

The proposed e-LSER model is an extension to the Kamlet-Taft approach^[18,19,27-29] with which we are able to quantify solvent effects in the reactive extraction. One might expect solvent effects to be more complicated functions than that represented by Kamlet-Taft LSER expression based on a linear combination of four solvatochromic indices. A host of physical solvent polarity indicators have been proposed over the years to express solvent effects in this context.^[27-29] Of widespread use are many of these, including Reichardt's^[29] polarity parameter ($E_T(30)$), Swain *et al.*'s^[30] Acity (A) and Bacity (B), and Koppel and Palm's^[27,28] polarization ($R_s = (\epsilon - 1) / (\epsilon + 2)$) and polarizability ($P_s = (n_D^2 - 1) / (n_D^2 + 2)$) descriptors, to mention but a few that describe various aspects of polarity and solvation behavior.

We consider here a generalized LSER approach to be represented by $Pr = Pr_0 + F \times \sum Pr_{\text{solvent}}$, including serially contributed physical terms, namely, \sum [solubility term (δ_H) + cavity term (\overline{V}) + solvatochromic term ($\pi, \beta, \alpha, \delta$) + solvent polarity term (P_s, E_T^N)]. Pr , Pr_0 and Pr_{solvent} stand for the modeled property, the limiting observed property and the integration term involving eight molecular descriptors of the solvent, that is, the Hildebrand solubility parameter δ_H ; the molar volume \overline{V} ; the solvatochromic indices of hydrogen-bonding^[18,19] π, β, α and δ ; polarizability P_s ; and the normalized dimensionless scale of the molar transition energy E_T^N . F is a correction factor. E_T^N is calculated from the $E_T(30)$ / (kcal mol^{-1}) values, wherein tetramethylsilane (TMS) and water are selected as extreme reference solvents, ($E_T^N(\text{solvent}) = [E_T(\text{solvent}) - E_T(\text{TMS})] / [E_T(\text{water}) - E_T(\text{TMS})]$).^[28,29] P_s is obtained from the refractive index of the solvent, as defined previously.

The e-LSER model Eqn (5) is made up of a limiting observed property Pr_0 and an integration term with respect to the solvatochromic and solvent polarity indicators pertaining to the solvent mixture ($\delta_H^*, \pi^*, \beta^*, \alpha^*, \delta^*, \overline{V}^*, P_s^*, E_T^{N*}$). The correction factor $F = s_f^{\text{chem}} / (1 - s_f^{\text{chem}})$ in Eqn (5) accounts for two limiting

conditions when either $s_f^{\text{chem}} = 0$ for which $Pr = Pr_0$, or $s_f^{\text{chem}} = 1$ for which an indefinable character of the function appears.

$$Pr = Pr_0 + \left(\frac{s_f^{\text{chem}}}{1 - s_f^{\text{chem}}} \right) \sum_i \left[C_{H,i} (\delta_H^*)^i + C_{\pi,i} (\pi^* - 0.35\delta^*)^i + C_{\beta,i} (\beta^*)^i + C_{\alpha,i} (\alpha^*)^i + C_{V,i} (\bar{V}^*)^i + C_{P,i} (P_s^*)^i + C_{E,i} (E_T^{N*})^i \right] \quad (5)$$

The molecular indices of the solvent mixture (δ_H^* , π^* , β^* , α^* , δ^* , \bar{V}^* , P_s^* , E_T^{N*}) are calculated from the corresponding parameters ($\delta_{H,i}$, π_i , β_i , α_i , δ_i , \bar{V}_i , $P_{s,i}$, $E_{T,i}^N$) and volume fractions (v_i) of the individual components by applying a mean value estimation rule, that is, $\delta_H^* = (1/1000) \sum_i v_i \delta_{H,i}^2$, $(\pi^* - 0.35\delta^*) = \sum_i v_i (\pi_i - 0.35\delta_i)$, $\beta^* = \sum_i v_i \beta_i$, $\alpha^* = \sum_i v_i \alpha_i$, $\bar{V}^* = \sum_i v_i (\bar{V}_i \times 10^{-2})$, $P_s^* = \sum_i v_i P_{s,i}$ and $E_T^{N*} = \sum_i v_i E_{T,i}^N$. C_i are adjustable coefficients of Eqn (5). Here, the capability of Eqn (5) to reproduce satisfactorily the observed properties has been checked in terms of the following Pr and Pr_0 quantities.

$$\begin{aligned} Pr &= \ln(E); Pr_0 = \ln(E_0) \\ Pr &= \ln(D); Pr_0 = \ln(D_0) \\ Pr &= \ln(s_f^{\text{phys}}); Pr_0 = \ln(s_{f_0}^{\text{phys}}) \\ Pr &= \ln(Z_t); Pr_0 = \ln(Z_{t,\max}) \\ Pr &= \ln(SE); Pr_0 = \ln(SE_{\max}) \end{aligned} \quad (6)$$

where E_0 , D_0 and $s_{f_0}^{\text{phys}}$ represent the observed properties pertained to the pure diluent alone ($s_{f_0}^{\text{phys}} = 1$). The values of $Z_{t,\max}$ and SE_{\max} are obtained from the observed curves. Because $\alpha^* = 0$ for the considered solvents, the $C_{\alpha}\alpha^*$ term was excluded from the fit. Overall, the model has been performed for the expansion degree $i=1$ along with generating the coefficients C_H , C_{π} , C_{β} , C_V , C_P and C_E for each of the above-mentioned quantities.

A-UNIFAC model

Basically, A-UNIFAC is concerned with the group contribution according to the combinatorial and residual activity coefficient terms of UNIFAC-original framework in combination with an association term derived from the statistical Wertheim theory.^[20–22] The general expression for the group-contribution association term of the activity coefficient is a function

of the fraction of non-bonded sites in the solution (X^{A_k}) and in pure-component i ($X_i^{A_k}$), as described elsewhere.^[20–22]

$$\ln \gamma_i^{\text{assoc}} = \sum_{i=1}^{NGA} \left\{ v_k^i \sum_{A_k} \left[\ln \left(\frac{X^{A_k}}{X_i^{A_k}} \right) + \frac{X_i^{A_k} - 1}{2} \right] + r_i \rho_k \sum_{A_k} \left(\frac{1 - X^{A_k}}{2} \right) \right\} \quad (7)$$

where v_k^i is the number of groups of type k in a molecule of component i , ρ_k represents the density of associating group k in the mixture and r_i represents the molecular volume of species i evaluated from UNIFAC group volume parameters R_k by summation over all NG groups within molecule i , $r_k = \sum_{k=1}^{NG} v_k^i R_k$.

As reported by Bottini and co-workers,^[20–22] the fraction of non-bonded sites (X^{A_k} or $X_i^{A_k}$) is a function of the associating group density ρ_j , and the association strength $\Delta^{A_k B_j}$ between site A of group k and site B of group j . The association strength given by $\Delta^{A_k B_j} = \kappa^{A_k B_j} [\exp(\epsilon^{A_k B_j}/kT) - 1]$ is a function of two association parameters: the energy ($\epsilon^{A_k B_j}$) and volume ($\kappa^{A_k B_j}$) of association.^[20–22] Essentially, a new set of A-UNIFAC association and interaction parameters between associating and non-associating functional groups is reported. Here, we particularly focus on the parameterization of residual interaction energy between cross-associating binaries (amine + water or acid or alcohol or ester or ketone) and (ketone + water or acid or alcohol) obtained from VLE and LLE data. Although it might be risky to solve the parameter estimation problem using binary VLE data only, A-UNIFAC prediction was surprisingly good even for extremely non-ideal system with acid–base-type interaction. To the best of our knowledge, this is the first time that A-UNIFAC is applied to the amine/diluent/carboxylic acid systems.

EXPERIMENTAL

FA (99% wt GC, Merck), AA (99% wt GC, Merck), PA (99% wt GC, Merck), BA (99% wt GC, Sigma-Aldrich), the extractant TBA (98.5% wt GC, Sigma-Aldrich) and organic solvents diisobutyl ketone (99% wt, Sigma-Aldrich), oleyl alcohol (98% wt, Merck) and octyl acetate (98% wt, Merck) of analytical grade purity were used as received without further purification. Deionized and redistilled water was used in all experiments.

The extraction experiments were carried out using an equilibrium glass cell equipped with a magnetic stirrer and a water jacket to maintain isothermal conditions. The sample temperature in the cell was kept constant at $T=(298.2\pm 0.2)$ K by means of a water bath (Julago Labortechnik GMBH-Germany) equipped with a temperature controller. Equal volumes (10 cm^3) of aqueous (acid) and organic (TBA/diluent) phases were agitated for 50–60 min and then left for 1 h to settle down into water and solvent layers at a fixed temperature ($T=298.2$ K) and pressure ($P=101.3$ kPa).^[31] The atmospheric pressure was measured by Fortin's mercury barometer with an average uncertainty of ± 0.5 kPa. The contact time enough to reach equilibrium and the waiting time required to separate completely the conjugate phases were determined in preliminary analysis.^[31] The effective separation of the phases was ensured by centrifugation. The equilibrium aqueous-phase pH value was measured by WTW 3310 IDS pH meter within an uncertainty of ± 0.005 . The equilibrium aqueous acid concentration was determined by titration with aqueous 0.1 N NaOH (Titrosol A, Merck) and phenolphthalein indicator. The organic phase acid concentration was analyzed by Hewlett-Packard GC Analyzer, Model 6890, equipped with FI and TC detectors and capillary columns HP Plot Q ($15\text{ m} \times 0.32\text{ mm} \times 0.2\text{ }\mu\text{m}$) for TCD and HP-Innowax polyethylene glycol ($30\text{ m} \times 0.32\text{ mm} \times 0.5\text{ }\mu\text{m}$) for FID. Nitrogen was used as a carrier gas at a flow rate of 5 mL min^{-1} . The acid content was checked by mass balance within at most 3% standard deviation. The initial amine/diluent concentration was determined by weighing with a Sartorius scale accurate to within $\pm 10^{-4}$ g. To attain an effective parameterization process, the equilibrium mole fractions of components in both phases were also defined by GC analysis. Exceptions are the composition of TBA/oleyl alcohol mixture in the organic phase and, also, the composition of TBA/diluent mixture in the aqueous phase that had to be determined by mass balance. The initial acid content in the aqueous phase was kept at 10% w/w to represent a simulated fermentation acid sample (i.e., $C_{\text{TA}}^0 = 2.1727\text{ mol dm}^{-3}$ for FA, $C_{\text{TA}}^0 = 1.6652\text{ mol dm}^{-3}$ for AA, $C_{\text{TA}}^0 = 1.3499\text{ mol dm}^{-3}$ for PA and $C_{\text{TA}}^0 = 1.1349\text{ mol dm}^{-3}$ for BA).^[31] However, the dependence of reactive extraction equilibria on the structural characteristics of amine, diluent and acid has been explored by comparing TBA/diluent/acid systems for similar experimental conditions, that is, A:O = 1:1 (v/v), $T=298.2$ K, $P=101.3$ kPa, the initial amine content restricted between $0.25\text{--}1.1\text{ mol dm}^{-3}$ and the initial aqueous acid solution of 10% (w/w). The mutual solubilities of TBA-water and diluent-water binaries are negligible in the range of variables investigated.^[32]

RESULTS AND DISCUSSION

Evaluation of extraction equilibria of C1–C4 acids

The experimental results provided in Table S1 indicate that the distribution ratio (D_0) and extraction degree (E_0) of C1–C4 acids by pure diluent alone are very much dependent on the R-chain structure of the acid following the order: FA ($D_0 \approx 0.12$, $E_0 \approx 10\%$) < AA ($D_0 \approx 0.18$, $E_0 \approx 15\%$) < PA ($D_0 \approx 0.85$, $E_0 \approx 45\%$) < BA ($D_0 \approx 2.7$, $E_0 \approx 73\%$). Evidently, none of the examined conventional solvents is proper separating agent for FA and AA, but all these are fairly effective in extracting PA and BA. This behavior could be attributable to the strong hydrophilic nature and high ionizing strength of FA and AA ($\text{p}K_{a,\text{FA}}=3.75$; $\text{p}K_{a,\text{AA}}=4.756$), as compared with those of PA and BA ($\text{p}K_{a,\text{PA}}=4.86$; $\text{p}K_{a,\text{BA}}=4.83$) exhibiting a high hydrophobicity. Checking physical extraction is fundamental to a reliable analysis of amine extraction. The physical extraction of C1–C4 acids by the diluent alone approximates the order: oleyl alcohol > octyl acetate > diisobutyl ketone.

A comparative assessment of experimental factors D , E and Z_t from Figs 1 and 2, and Table S1 shows that the uptake capacity of TBA/diluent system is intimately connected to the structural characteristics of acid and diluent following the order: oleyl alcohol \approx octyl acetate > diisobutyl ketone and BA > PA > AA \approx FA. It is observed that the extraction equilibrium is very sensitive to the hydrophobicity of the acid and the solvation effect of the diluent, but the later is thought to be no dominating factor. These dependences are rationalized in terms of a simultaneous formation of at least two acid-amine complexes regarding the ability of diluent to hydrogen bonding and dipole–dipole interaction. Referring to Z_t and Z_s data from Figs 1–3, it is recognized that the synergistic extraction power of TBA/diluent mixture and the most probable acid_{*p*}-amine_{*q*} (*p*, *q*) complex formation should keep to the following order: oleyl alcohol (1, 2) \geq octyl acetate (1, 2) > diisobutyl ketone (1, 2). This was because in the media of more structured oleyl alcohol or octyl acetate it is a solvation of the acid–amine complex by the diluent that plays the role, whereas in the media of less structured diisobutyl ketone, it is a mass transfer resistance of the acid molecule that does so. As depicted in Figs 1 and 2 and Table S1, for a given TBA/diluent both FA and AA act on achieving about equally largely removal efficiencies, BA is almost invariably sensitive, perhaps imperceptible, to the diluent structure, while PA plays an intermediate role on this account. This may be ascribed to the relatively higher polarities and smaller molecule sizes of FA and AA as compared with those of PA and BA (dipole moment μ and dielectric constant ϵ of C1–C4 acids:

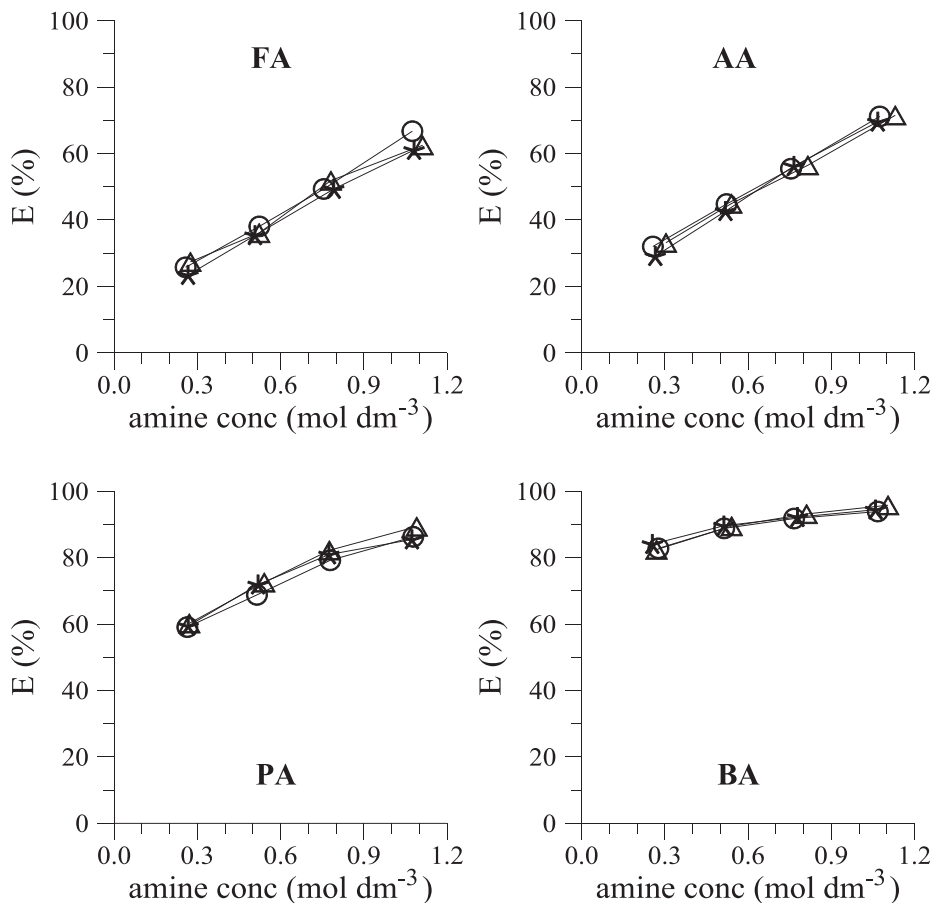


Figure 1. Variation of extraction degrees (E) with the initial amine concentration ($\overline{C_{NR_3}^0}$) of TBA/diluent mixture pertaining to C1–C4 acids (FA, AA, PA, BA); \star diisobutyl ketone; \triangle oleyl alcohol; \circ octyl acetate.

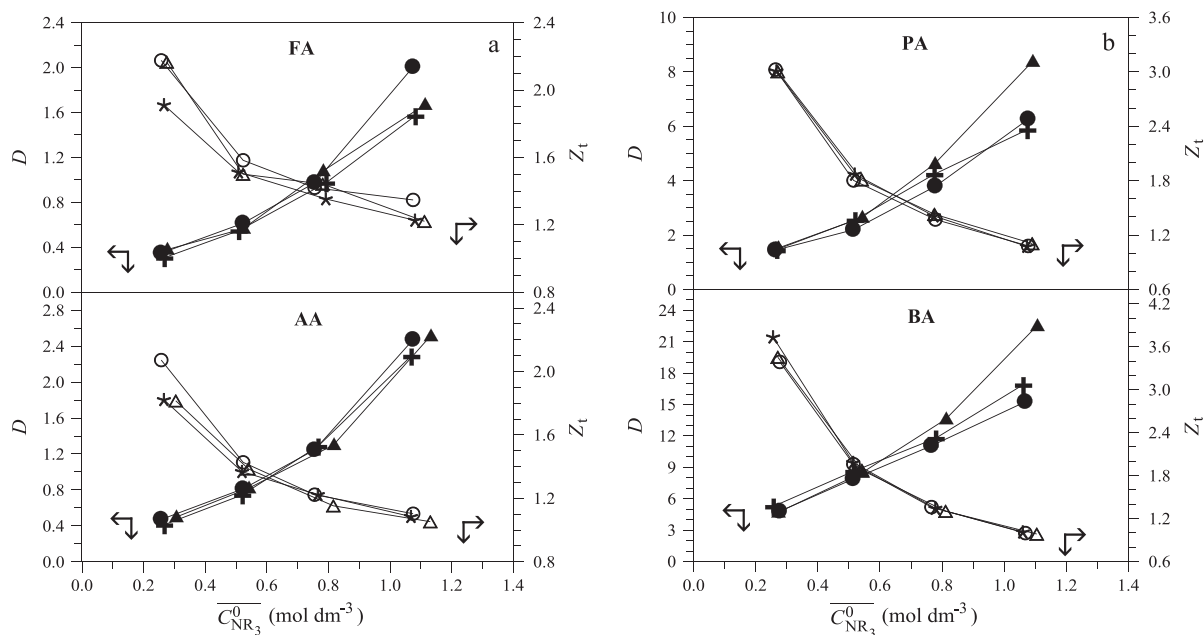


Figure 2. Variation of distribution ratio (D) and loading factor (Z_t) with the initial amine concentration ($\overline{C_{NR_3}^0}$) of TBA/diluent mixture relative to (a) FA and AA and (b) PA and BA: \star diisobutyl ketone; \triangle oleyl alcohol; \bullet , \circ octyl acetate.

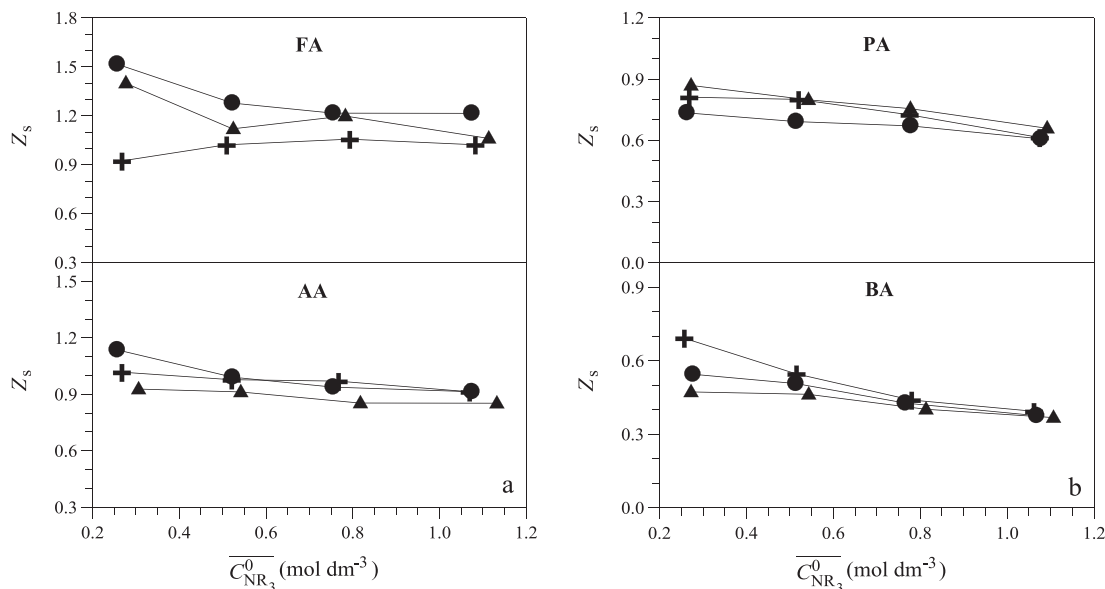


Figure 3. Variation of stoichiometric loading factor (Z_s) with the initial amine concentration ($\overline{C_{NR_3}^0}$) of TBA/diluent mixture relative to (a) FA and AA and (b) PA and BA: \times diisobutyl ketone; \blacktriangle oleyl alcohol; \bullet octyl acetate.

$\mu_{FA} = 4.0 \times 10^{-12}$ C m, $\varepsilon_{FA} = 58.5$; $\mu_{AA} = 2.8 \times 10^{-12}$ C m, $\varepsilon_{AA} = 6.15$; $\mu_{PA} = 2.1 \times 10^{-12}$ C m, $\varepsilon_{PA} = 3.44$; $\mu_{BA} = 2.0 \times 10^{-12}$ C m, $\varepsilon_{BA} = 2.97$ [25], causing the acid-amine aggregation for C1–C2 acids to be dominated over that for C3–C4 acids.

Overall, from an acid–amine association perspective, less structured FA and AA yield relatively larger $Z_s \approx 1 - 1.5$ as compared with $Z_s \approx 0.5 - 0.8$ for PA and BA, being indicative of the formation of willingly solvated (C1/C2 acid-amine) species, but oppositely weaker interactive forces should be dominant during (C3/C4 acid-amine) complexation. In particular, as shown in Fig. 3, the preference of FA acidic anions for the amine over water could be attributable to a high polar structure of that acid. There is a parallelism between the reduction in acid-amine association and augmentation in the magnitude of diluent-acid interaction as the molecule size of the acid increases, manifesting the fact that the steric effect of larger acid species like dimers or oligomers (PA and BA) in the TBA media works in favor of cross-interaction of smaller acid anions (FA and AA) with the amine.

This deduction is verified by the results from Fig. 4 signifying that the oxygenated diluent eventually favors the formation of well-solvated specific (C1/C2 acid-amine) complexes with $s_f^{\text{chem}} \approx 0.50 - 0.85$ being indicative of a preferable chemical association. Conversely, weaker interactive forces should dominate in (C3/C4 acid-amine) aggregation relative to $s_f^{\text{chem}} \approx 0.15 - 0.55$ hinting that a preferable physical association would likely proceed. No evidence of overloading ($Z_s > 1$) is observed in any of the examined amine/diluent/AA or PA or BA systems.

These findings are comprehensively supported by the results for the relative proportion of physical extraction and chemical association in terms of Z_s and s_f^{chem} factors from Figs 3 and 4, indicating that different mechanisms control predominantly monotype (1, 2) or two types (1, 1 and 1, 2, or 1, 2 and 1, 3) acid-amine complex formation with regard to the diluent examined. This fact seems to be a common strategy for designing the reactive extraction of C1–C4 aliphatic acids. The results emphasize clearly the fact that the synergistic extraction power (D , Z_t , R and SE) of amine/diluent system is the largest for protic oleyl alcohol diluent because of a complementary interaction effect of carboxyl (COOH), hydroxyl (OH) and amine (NR₃) groups. Besides the diluent solvation efficiency, an inherent concern is the group-contribution effect of the TBA structure, allowing the formation of strongly saturated acid-amine structures that are prerequisite for proceeding the extraction method. Nevertheless, relatively large differences among D , E , Z_t , Z_s , R and SE values indicate that the complex solvation by the diluent is a critical factor in amine extraction of the acids studied.

Optimization framework for reactive extraction of C1–C4 monocarboxylic acids

A survey of the literature reveals that there is gained a little insight into the problem concerning the prediction of optimum extraction field of a reactive extraction system. [11,24] Multi-objective optimization is usually used to define a global optimum point

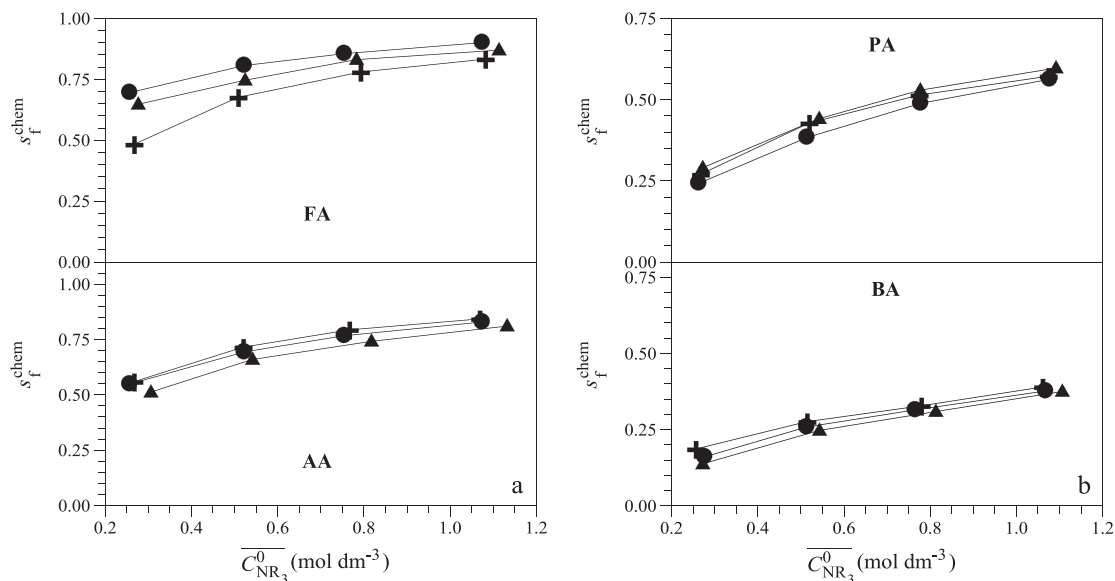


Figure 4. Variation of chemical separation factor (s_f^{chem}) with the initial amine concentration ($\overline{C_{\text{NR}_3}^0}$) of TBA/diluent mixture relative to (a) FA and AA and (b) PA and BA: \times diisobutyl ketone; \blacktriangle oleyl alcohol; \bullet octyl acetate.

without converging to the local minimum or maximum points, wherein conflicting in nature objective functions are brought together for achieving a set of candidate solutions.^[33,34] In such cases, the objective functions are non-linear with several local minima/maxima/saddle points within the specified bounds of the variables and quite often the convergence process is finalized without a unique solution. Here, we particularly focus on optimizing analytically the operating conditions of a reactive extraction system by means of Senol's DVM algorithm,^[11,24] which guarantees a global optimum point to be quantified. Note that a very common assumption inherent in DVM algorithm is that generalized convexity of a differentiable function is being characterized by generalized monotonicity of its gradient. Specifically, the technique of DVM originated from the slope analysis of the derivative variation profile of R and SE factors, which gave an existence result for optimum point by analyzing monotonicity of the derivative curve. Procedurally, the optimization algorithm searches for the optimum point by analyzing the variation profiles of $R=f(x_{iv})$ and $SE=f(x_{iv})$ functions both experimentally and analytically, where $x_{iv} = \overline{C_{\text{NR}_3}^0}/C_{\text{TA}}$ stands for the independent variable. For the sake of simplicity, we consider here two non-homogenous differential functions of R and SE to be adequately assessed for this purpose, namely, Eqns (8) and (9) for C1–C2 and C3–C4 acids, respectively. R_{max} and SE_{max} stand for the maximum values obtained from the experimental curve, whereas r and s are adjustable

coefficients of Eqns (8) and (9) regressed by linear analysis and tabulated in Table S2.

$$R = R_{\text{max}}[1 - \exp(rx_{iv})]; SE = SE_{\text{max}}[1 - \exp(sx_{iv})] \quad (\text{C1-C2 acids}) \quad (8)$$

$$R = R_{\text{max}}[1 - \exp(rx_{iv})]; SE = SE_{\text{max}}[1 - \exp(sx_{iv}^{-1})] \quad (\text{C3-C4 acids}) \quad (9)$$

However, the calculation procedures are analogous for the selected R and SE factors, allowing a continuous predictive process to be accomplished. Evidently, an erroneous conclusion may be implemented by conventional searching techniques based solely on a supreme point convergence, that is, any optimum point does not exist if no zero derivative value is found. Therefore, a slope analysis of the non-linear section of the derivative curve as a test case is necessarily required for achieving an optimum point, which actually occurs at that section, as depicted in Fig. 5a–d. For the sake of clarity, only the experimental R and SE values and the modeled dR/dx_{iv} and dSE/dx_{iv} derivative values calculated from Eqns (8) and (9) are plotted on Fig. 5a–d. Following Senol,^[24] currently the optimal tests are carried out with optimality criterion as the size in the derivative changes should approximate the maximum slope range within the specified lower and upper bounds of the optimized quantity. If more than one position for the optimum point uncontrollably is brought to pass then linearization of the upper and lower parts of the

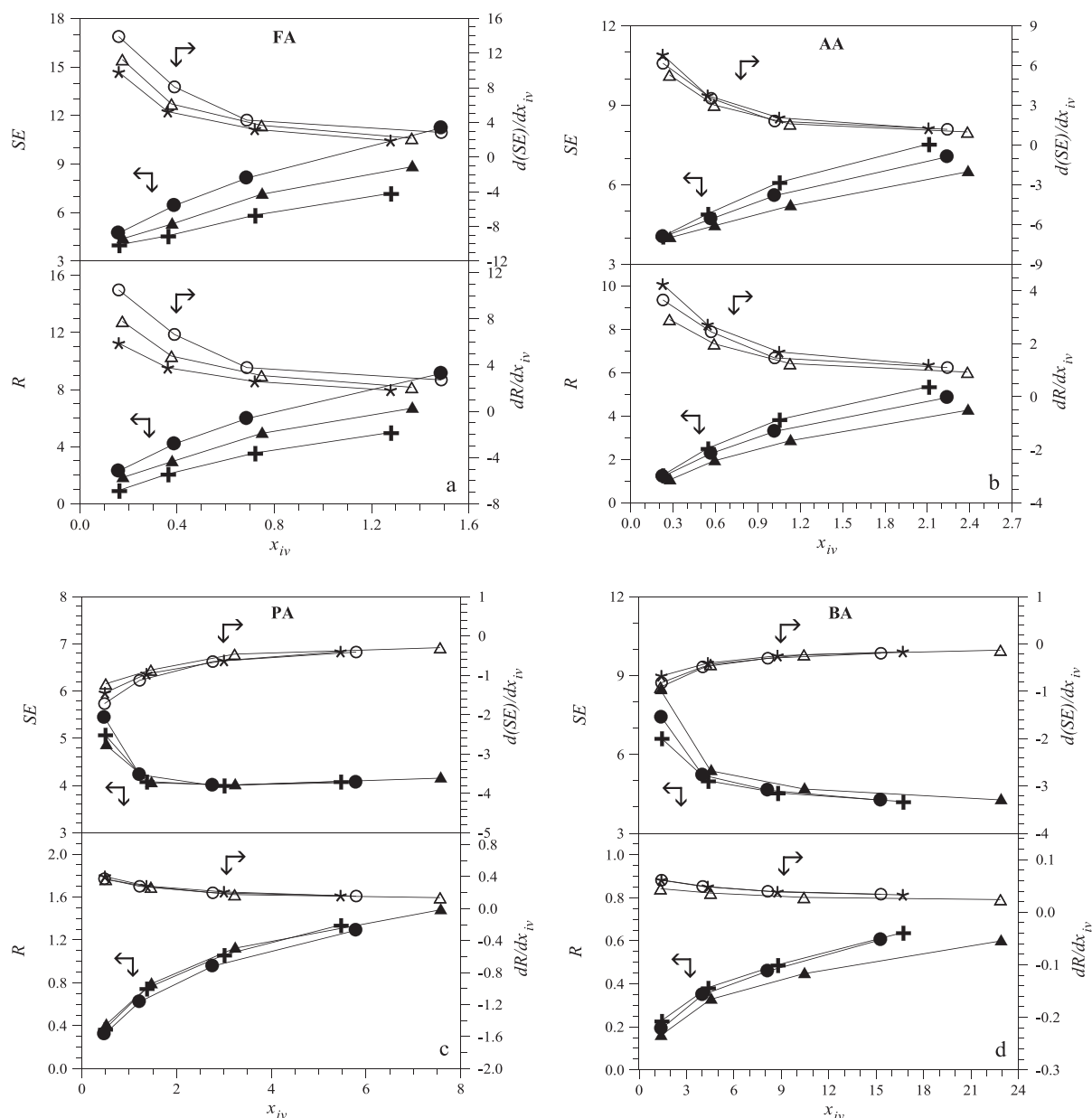


Figure 5. Optimal tests in terms of variation profiles of experimental R and SE factors and modeled dR/dx_{iv} and $d(SE)/dx_{iv}$ derivatives according to Eqns (8) and (9) as a function of the independent variable $x_{iv} = C_{NR_3}^0/C_{TA}$ pertained to (a) FA, (b) AA, (c) PA and (d) BA. For R and SE curves \blacktriangleleft diisobutyl ketone; \blacktriangle oleyl alcohol; \bullet octyl acetate. For derivative curves \star diisobutyl ketone; \triangleleft oleyl alcohol; \circ octyl acetate.

derivative curve to find their intercepting point has to be carried out, causing an unworkable searching process to be eventually avoided.

Procedurally, the optimization algorithm first calculates dR/dx_{iv} and dSE/dx_{iv} for all the data points throughout the working range and then analyzes the variation profiles of the observed and modeled (Eqns (8) and (9)) derivatives restricted between lower and upper x_{iv} bounds corresponding to lower and upper amine loads, which circumscribe the calculation limits. As illustrated in Fig. 5a–d, R and SE are proportionally varying with x_{iv} for C1–C2 acids, but they exhibit

inversely proportionality against increasing x_{iv} for C3–C4 acids. Computationally, DVM moves step by step from a derivative value to its neighboring client generating the differences between them and selecting larger slope values until a termination criterion is met. The optimization criterion is the working range with the largest derivative slope changes. Before implementing DVM, we first build up a scheme for the solvation effects of components in which propionic acid plays an intermediate role.

Following Swain *et al.*,^[30] it seems preferable to associate the optimization scheme with the solvent

effects categorized as ‘acity’ or anion-solvating tendency (A) and ‘basity’ or cation-solvating tendency (B), because they are neat (bulk) solvent properties involved in solvations. Likewise, Swain *et al.*^[30] have reported a remarkable parallelism among the solvent properties anion-solvating or cation-solvating tendency, hydrogen-bonding acidity or basicity, and electrophilicity or nucleophilicity that can all be adequately represented by A and B numbers. This is equivalent to the assumptions that A and B are contributed cumulatively to the solvation process following the scheme:

$$\begin{array}{ll}
 A + B \geq 1.05 \text{ (for FA and AA)} & A + B < 0.9 \text{ (for acetates)} \\
 A + B \approx 0.9 - 1 \text{ (for PA)} & A + B \approx 1.05 - 1.1 \text{ (for aliphatic alcohols)} \\
 A + B < 0.9 \text{ (for BA)} & A + B < 0.9 \text{ (for ketones)} \\
 A + B = 2 \text{ (for water)} & A + B \approx 1.3 - 1.4 \text{ (for aliphatic amines)}
 \end{array}$$

On this account, FA ($A=1.18$; $B=0.51$) and AA ($A=0.93$; $B=0.13$) are better cation solvators (outliers) than PA and BA, as well as being better anion solvators. In the case of A , formic acid is an outlier, probably because it is a sufficiently strong acid to protonate, rather than hydrogen bond to the probe base, tertiary amine. Water is an excellent universal solvator. In the case of B the reported value for the aliphatic amine is obviously too high, causing it to be a strong outlier; thereby, the later is much readily aggregated with FA and AA, but not so effectively with PA and BA. Aliphatic alcohol is a bilateral solvator in the case of $A+B$, but its basity should certainly not be as good as the aliphatic amine. In the case of basity, acetate and ketone are moderate solvators to which the arbitrary value of $A+B \approx 0.9$ was assigned, but their proton-accepting ability is being exceedingly smaller than that of amines. This is perhaps not surprising considering the hydrophobicity ranges of solutes and solvents studied. In this scheme, PA is contributed to a composite solvation behavior bilaterally.

Practically, however, the main consideration should still be the sense that R and SE are efficient predictors of the solvent effects on the behavior of divers kinds of solutes. For this case, the correlations according to Eqns (8) and (9) are sufficiently good to claim that the optimization quantity Y is non-linearly correlated with x_{iv} for R and with x_{iv}^{-1} for SE . Although R and SE are about equally strongly

dependent on s_f^{chem} , especially for C3–C4 acids, they exhibit opposite variation profiles, allowing the optimum extraction power of the solvent mixture to be quantified distinctly. Here considering R to be a test case for the extractant behavior, the optimization scheme A is built up, hinting the suitability of the carrier for the acid recovery. Similarly, the synergistic extraction power of solvent mixture is optimized with respect to the optimization scheme B, reflecting formally the effectiveness with which the extraction process would likely proceed. However, Fig. 5a–d is used as the database for constructing schemes A

and B. The optimization results from Fig. 5a–d indicate that the variation profiles of relevant derivatives separate the location of the optimum extraction field restricted strictly between upper and lower parts of the functional curve for which the largest changes in the slope size are substantial. Openly, outside the optimized range conflicting unacceptable behavior due to the almost invariably small changes of the slope size should be dominated. Logically, R and SE factors are devoid of the physical meaning when the acid is practically insoluble in the selected diluent or amine.

In view of the results presented in scheme A, with increasing the carbon C-chain in the acid structure, the size of the optimal x_{iv} working range increases, but the size of the optimal R range in which the extractant functions in favor of chemical association with the acid decreases reciprocally. The same functional behavior holds for the variation of Z_i .

In the case of scheme B for the synergism of the solvent mixture, the variation profile of SE exhibits a bilateral character; that is, the optimal x_{iv} working range increases proportionally with increasing the carbon C-chain of acid, but the size of the SE range reflecting the optimal synergistic extraction power of the solvent mixture decreases for C1–C2 acids and remains almost invariably constant for C3–C4 acids. This leaves us with the conclusion that the resulting optimum extraction conditions for the acid recovery are being outdone markedly at the following ranges:

$$0.5 < x_{iv} < 1.5; 2 < R < 7 \text{ (for C1-C2 acids)} \quad 0.5 < x_{iv} < 1.5; 5 < SE < 8 \text{ (for C1-C2 acids)}$$

$$2 < x_{iv} < 6; 0.3 < R < 1.5 \text{ (for C3-C4 acids)} \quad 1 < x_{iv} < 5; 4 < SE < 6 \text{ (for C3-C4 acids)}$$

A. Optimization scheme for C1–C4 acids with respect to R factors.

Acid	Theoretical	Experimental	x_{iv} range	R range	Remarks
C1 acid-FA	Eqn (8)	Fig. 5a	$0 < x_{iv} < 0.1$	$0 < R < 0.5$	I
			$0.1 < x_{iv} < 0.4$	$0.5 < R < 3$	II
			$0.4 < x_{iv} < 1$	$3 < R < 7$	III
			$x_{iv} > 1$	$R > 7$	IV
C2 acid-AA	Eqn (8)	Fig. 5b	$0 < x_{iv} < 0.2$	$0 < R < 0.5$	I
			$0.2 < x_{iv} < 0.6$	$0.5 < R < 2.5$	II
			$0.6 < x_{iv} < 1.6$	$2.5 < R < 5$	III
			$x_{iv} > 1.6$	$R > 5$	IV
C3 acid-PA	Eqn (9)	Fig. 5c	$0 < x_{iv} < 0.5$	$0 < R < 0.3$	I
			$0.5 < x_{iv} < 1.5$	$0.3 < R < 0.7$	II
			$1.5 < x_{iv} < 4.5$	$0.7 < R < 1.3$	III
			$x_{iv} > 4.5$	$R > 1.3$	IV
C4 acid-BA	Eqn (9)	Fig. 5d	$0 < x_{iv} < 1$	$0 < R < 0.1$	I
			$1 < x_{iv} < 3.5$	$0.1 < R < 0.3$	II
			$3.5 < x_{iv} < 16$	$0.3 < R < 0.7$	III
			$x_{iv} > 16$	$R > 0.7$	IV

The numbers refer to the following: I, extractant is a poor separating agent; II, extractant is moderately effective; III, extractant is excellent separating agent; IV, very large extractant load is used.

B. Optimization scheme for C1–C4 acids with respect to SE factors.

Acid	Theoretical	Experimental	x_{iv} range	SE range	Remarks
C1 acid-FA	Eqn (8)	Fig. 5a	$0 < x_{iv} < 0.1$	$0 < SE < 3$	I
			$0.1 < x_{iv} < 0.4$	$3 < SE < 5$	II
			$0.4 < x_{iv} < 1$	$5 < SE < 10$	III
			$x_{iv} > 1$	$SE > 10$	IV
C2 acid-AA	Eqn (8)	Fig. 5b	$0 < x_{iv} < 0.2$	$0 < SE < 3.5$	I
			$0.2 < x_{iv} < 0.6$	$3.5 < SE < 5$	II
			$0.6 < x_{iv} < 1.6$	$5 < SE < 8$	III
			$x_{iv} > 1.6$	$SE > 8$	IV
C3 acid-PA	Eqn (9)	Fig. 5c	$0 < x_{iv} < 0.5$	$SE > 5.5$	I
			$0.5 < x_{iv} < 2$	$4 < SE < 5.5$	II
			$2 < x_{iv} < 4.5$	$3.8 < SE < 4$	III
			$x_{iv} > 4.5$	$SE < 3.8$	IV
C4 acid-BA	Eqn (9)	Fig. 5d	$0 < x_{iv} < 1$	$SE > 9$	I
			$1 < x_{iv} < 6$	$4.5 < SE < 9$	II
			$6 < x_{iv} < 16$	$4 < SE < 4.5$	III
			$x_{iv} > 16$	$SE < 4$	IV

The numbers refer to the following: I, solvent system works in favor of physical extraction; II, solvent system is moderately effective; III, solvent system is excellent separating agent; IV, very large extractant load is used.

By analyzing the variation profiles of the quantities in question, it is recognized that the most appropriate ranges for amine extraction of C1–C4 acids should be $1 < R < 7$ and $4 < SE < 8$ where the curve slope is changed considerably. Because of the synergistic effect of physical extraction and chemical interaction, TBA/diluent system can improve the extraction efficiency of the considered acids. The existing information on the observed and modeled performance, presented in Schemes A and B, Fig. 5a–d and Table S1, gives evidence for the optimal extraction conditions dictating preferably the use of octyl acetate and oleyl alcohol as proper diluents for TBA. However, the evaluated optimal R limits call for using favorably TBA/alcohol and TBA/ester for the recovery of FA and AA, respectively, whereas all the examined TBA/diluent systems are effective separating agents for C3–C4 acids. The same remarks hold for the variation profile of the SE factor, comprising dominantly ester or alcohol diluent to be appropriate solvation medium for the organic acid-amine complexes rather than ketone. Although TBA/octyl acetate gives rise to moderate R and SE factors for AA, it is being regarded as a potential synergistic solvent mixture yielding the largest Z_t factors for AA. These concepts are supported by the experimental values of R , SE and Z_t factors from Table S1 and Fig. 5a–d, manifesting the fact that the synergistic separation of C1–C4 acids by TBA/monoester or TBA/alcohol favors over that of TBA/ketone. The evaluated optimization conditions are opening up new possibilities for the recovery of organic acids from aqueous solutions by reactive extraction.

Reliability analysis of molecular and group-contribution models

Statistics for mass action law and e-LSER models

Here, comparisons of observed and calculated equilibrium properties of relevant systems are substantial for the reliability analysis of Eqns (3)–(5) in terms of statistical factors mean relative error $\bar{e} = (100/N) \sum_{i=1}^N |(Y_{i,obs} - Y_{i,mod})/Y_{i,obs}|$ (%) and root-mean-square deviation $\sigma =$

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

Firstly, statistical checking the reliability of chemodel (Eqn (3)) and Langmuir approach (Eqn (4)) has been carried out using the apparent extraction constants β_{pq} and β_L from Table S3 obtained by linear regression of the equilibrium data for the examined diluents and acids. As shown in Table S3, the best fits display the approach comprising the formation of one (1, 2) or simultaneous two (1, 1 and 1, 2, or 1, 2 and 1, 3) acid_p-amine_q structures for chemodel, and one

associated structure ($p:q=z:1=Z_{s,max}$) corresponding to the maximum loading values $z=Z_{s,max}$ for the Langmuir model. The statistical results from Table S3 and Fig. 6 indicate that both Eqns (3) and (4) reproduce the observed Z_t property moderately precisely yielding mean deviations of $\bar{e}(Z_t) = 16.8\%$ ($\sigma(Z_t)=0.273$) and $\bar{e}(Z_t) = 7.3\%$ ($\sigma(Z_t)=0.127$), respectively. In comparison with Eqn (3), Eqn (4) has proven to be slightly more accurate because of a reduced number of degrees of freedom.

The application of e-LSER (Eqn (5)) to the present extraction systems generates six adjustable parameters C_H , C_π , C_β , C_V , C_P and C_E . The coefficients C_i of Eqn (5) are regressed by linear analysis using the values of seven molecular descriptors (δ_H , π , β , δ , \bar{V} , P_s and E_T^N) given in Table 1. Note that the parameterization test with the expansion degree of Eqn (5) $i=1$ provides statistics similar to those obtained by compiling Eqn (5) with an integration term pertained to $i=2,3$. The resulting coefficients C_i relative to E , D , s_f^{phys} , Z_t and SE properties, as well as the statistical deviation factors \bar{e} and σ of Eqn (5) are provided in Table S4. It is seen from Table S4 that the terms in β^* and E_T^{N*} of Eqn (5) make generally negative contributions, because their coefficients C_β and C_E are almost invariably negative, while the terms in δ_H^* and π^* are about constantly positive regarding the sign of C_H and C_π coefficients. The terms in \bar{V}^* and P_s^* make generally bilateral contributions to the modeled quantity because of positive and negative signs of C_V and C_P coefficients

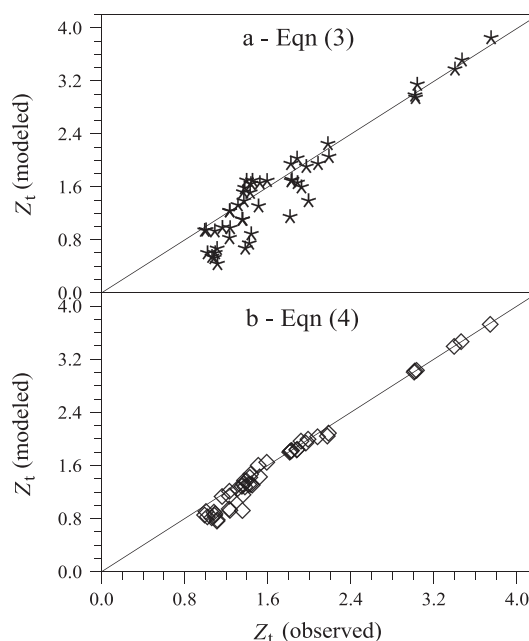


Figure 6. Presentation of cross-validated diagonal test results for chemodel Eqn (3) (*) and modified Langmuir model Eqn (4) (◇).

Table 1. Hildebrand solubility (δ_H), solvatochromic (π , β , α , δ), molar volume (\bar{V}) and solvent polarity (P_s , E_T^N) indices (descriptors) of compounds.

Compound	$\pi^{a,b}$	$\beta^{a,b}$	$\alpha^{a,b}$	δ_H^c (MPa ^{0.5})	$\delta^{a,b}$	$\bar{V} \times 10^{-2d}$ (cm ³ mol ⁻¹)	P_s	E_T^N
Tri- <i>n</i> -butyl amine	0.16	0.62	0	18.2	0	2.395	0.257	0.043
Diisobutyl ketone	0.63 ^e	0.48 ^e	0	16.0	0	1.774	0.249	0.225
Oleyl alcohol	0.42 ^f	0.45 ^f	0.33	17.2	0	3.163	0.274	0.519 ^f
Octyl acetate	0.49 ^g	0.45 ^g	0	16.7	0	1.979	0.250	0.241 ^g

^aDue to Kamlet *et al.*^[18]^bDue to Marcus.^[19]^cDue to Barton.^[51]^dCalculated.^eParameters of butyl methyl ketone.^fParameters of 1-dodecanol (*n*-C₁₂H₂₅OH).^gParameters of hexyl acetate (C₆H₁₃COOCH₃).

being about equally dominant. As seen in Table S4, the term in π^* exhibits extremely small contribution to the modeled property, but it cannot provide a physical explanation for that evidence. Overall, the deviation statistics from Fig. 7 and Table S4 indicate that e-LSER simulates satisfactorily the observed performance with a global average deviation inferior to $\bar{\epsilon} = 4.8\%$ ($\sigma = 0.456$) for E , D , s_f^{phys} , Z_t and SE factors. As shown in Fig. 7, e-LSER has proven to be more accurate in reproducing E , D and s_f^{phys} ($\bar{\epsilon}(D) = 3.0\%$ and $\sigma(D) = 0.1$, $\bar{\epsilon}(E) = 2.5\%$ and $\sigma(E) = 1.4$, $\bar{\epsilon}(s_f^{\text{phys}}) = 2.6\%$ and $\sigma(s_f^{\text{phys}}) = 0.01$)

as compared with Z_t and SE ($\bar{\epsilon}(Z_t) = 6.5\%$ and $\sigma(Z_t) = 0.2$, $\bar{\epsilon}(SE) = 9.6\%$ and $\sigma(SE) = 0.6$), considering all of the systems studied. The results suggest an underlying physical significance for the selected model variables and show an excellent potential for generalized predictions by e-LSER.

Parameterization of A-UNIFAC and correlation results

The usual approach to estimate LLE of reactive mixtures by A-UNIFAC is based on quantifying residual, combinatorial and association terms of the activity coefficient as a function of the fraction of

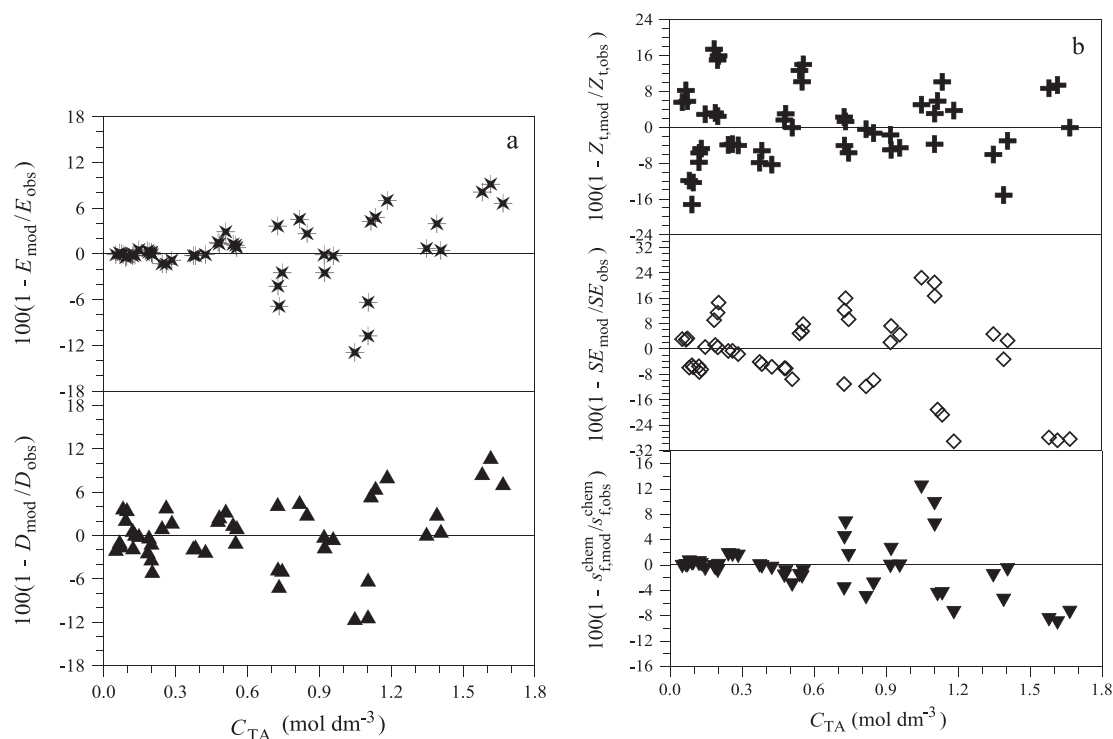


Figure 7. Graphical reliability analysis of e-LSER model (Eqn (5)) in terms of a per cent error: (a) D , E , (b) s_f^{chem} , SE , Z_t .

interactive groups in the solution and in pure-component. To do this, it is necessarily required to extend the current parameter database^[21] including the molecules of the present mixtures as well. We consider here the general case of LLE to be solved by A-UNIFAC in terms of the isoactivity equations ($\hat{x}_i \hat{\gamma}_i = \hat{x}_i^* \hat{\gamma}_i^*$, $i = 1, 2, 3, 4$) under constraints of mass balance without considering the real activity of components.^[35–37] However, A-UNIFAC prediction calls for using both association parameters of self-associating and cross-associating groups and residual group interaction parameters between amine, acid, alcohol, ketone, ester and water. Values of pure-component volume r_i and surface area q_i parameters were selected from the literature.^[35–37]

Here, the following associating groups were put in action to represent the association effect in relevant systems: (1) the carboxylic acid possesses the one-site carboxylic acid group COOH, which can self-associate and cross-associate; (2) the hydroxyl group OH with two associating sites, being capable of both self and cross-associating, is used to represent hydrogen bonding in alcohol and water; and (3) the one-site electronegative ester group COOR, which does not self-associate but can cross-associate with electropositive sites. Although both amine and ketone groups possess an electronegative site, they were

excluded from the parameterization of self-association and cross-association by reason of avoiding the overestimation of parameters on this account. Except for the later groups, Table 2 reports the values of self-association and cross-association parameters ε_a/k and κ of groups involving in the reactive mixtures studied.^[21]

Because no firmly established data for the residual interaction parameters of the tertiary amine (C₃N) are available in the open literature, we have calculated new binary interaction parameters for the pair groups C₃N–OH, C₃N–H₂O and C₃N–COOH, as well as for binaries with a ketone group CH₂CO–H₂O and CH₂CO–COOH. The binary interaction parameters between C₃N and H₂O were obtained by fitting VLE and LLE data on the binary systems (water + tertiary amine)^[32,38,39] with a convergence yielding the average absolute deviation of %AAD = 3.6 for the selected number of experimental points $N_p = 89$. The interaction parameters of C₃N–OH and C₃N–COOH groups were determined by fitting VLE data for binaries tertiary amine + alkanol^[38,40–43] ($N_p = 101$, %AAD = 4.6), and tertiary amine + monocarboxylic acid^[38,44,45] ($N_p = 38$, %AAD = 11), respectively. The binary interaction parameters of CH₂CO–H₂O and CH₂CO–COOH groups were calculated by regressing VLE and LLE data on the binary systems ketone + water^[46,47] ($N_p = 72$, %AAD = 9.1) and ketone + monocarboxylic acid^[48,49] ($N_p = 67$, %AAD = 8.4). Table 3 reports the new residual group interaction parameters determined in this work. The remaining parameters of the interactive groups involving in the mixtures (tri-*n*-butyl amine + diluent + carboxylic acid + water) were taken from elsewhere.^[21,36,37]

The experimental LLE data provided in Table S5 were successfully simulated with A-UNIFAC with global mean deviations in terms of the acid mole fraction inferior to $\bar{e}(x_2) = 24.1\%$ and $\sigma(x_2) = 0.018$ for all of the systems considered. Figure 8 compares experimental data with A-UNIFAC prediction. As illustrated in that figure, all the mole fraction data for

Table 2. Energy ε_a/k and volume κ self-association and cross-association parameters for the A-UNIFAC model.^[21]

Group	ε_a/k (K)	κ
Self-association COOH	4100.0	0.002
Self-association OH	3125.0	0.0062
Self-association H ₂ O	3125.0	0.0062
Cross-association COOH–OH	3612.5	0.0035
Cross-association COOH–H ₂ O	3612.5	0.0022
Cross-association COOH–COOC	2912.0	0.0038
Cross-association OH–COOC	1975.0	0.071
Cross-association OH–H ₂ O	3125.0	0.0062
Cross-association H ₂ O–COOC	1975.0	0.071

Table 3. Residual group interaction parameters $a_{m,n}$ (K) for the A-UNIFAC model.

Groups		$a_{m,n}$	$a_{n,m}$	References
m	n	(K)	(K)	
C ₃ N	CH ₂	–83.98	206.6	Gmehling <i>et al.</i> ^[36]
C ₃ N	OH	–400.8	–481.1	This work
C ₃ N	H ₂ O	–697.4	–311.4	This work
C ₃ N	COOH	–1392.0	–770.2	This work
C ₃ N	COOC	2889.0	–196.7	Magnussen and Pretel ^[37]
C ₃ N	CH ₂ CO	225.3	–169.0	Magnussen and Pretel ^[37]
CH ₂ CO	CH ₂	26.76	476.4	Gmehling <i>et al.</i> ^[36]
CH ₂ CO	H ₂ O	–261.6	–179.4	This work
CH ₂ CO	COOH	334.2	–340.2	This work

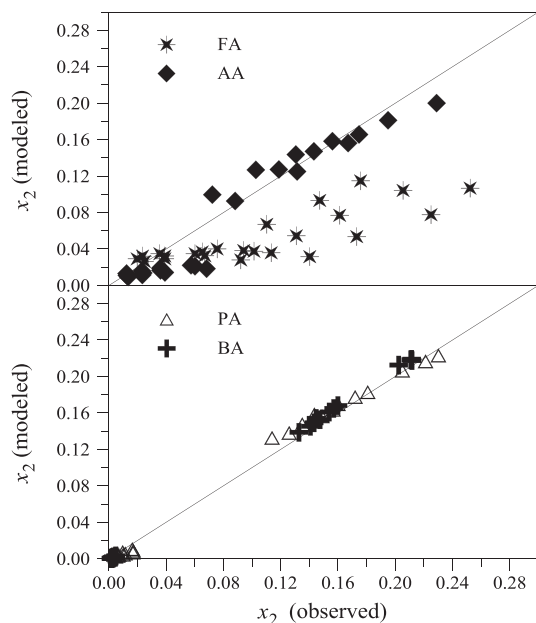


Figure 8. Presentation of cross-validated diagonal test results for A-UNIFAC in terms of x_2 acid mole fraction.

AA, PA and BA show good compliance with A-UNIFAC prediction based on the newly proposed parameters from Tables 2 and 3. But unexpectedly, modeling of phase behavior of FA is moderately accurate being indicative of a complex cross-aggregation concerning FA molecules with no *R*-chain structure.

Solvation probability relations *SPR1* and *SPR2* for estimating solvation effect

The solvation effect is thought to be a complex function of cross-interaction and self-interaction among all the components of the system. As a first approximation, we assume that all the interactions in the aqueous phase, as well as of water molecules in the organic phase, should be neglected because of their indefinable contribution to the mass transfer. Particularly, we consider here the extraction process to be controlled only by the interactions attributed to the organic phase including diluent-acid, amine-acid, diluent-complex, diluent-amine and amine-complex associations. In this perspective, there are attempts intended so far to address modeling the solvation effect of a reactive extraction system by assembling a functionality between solvation probability (*SP*), separation factor (S_c) and activation energy (E_A^*) expressed in the form of Arrhenius type equation, namely, separation probability relation (*SPR1*), Eqn (10). Because no firmly established measured values are available for the activation energy of association concerning the above-mentioned species, it has not been possible to examine separately each individual aggregation in the model development;

therefore, a generalized function had to be compliantly carried out

$$\ln(SP^{-1.7325t}) = S_c^{-0.0578t} \times \exp\left(-\frac{E_A^*}{RT}\right) \quad (10)$$

$$E_A^* = E_{A1} + E_{A2} + E_{A3} + E_{A4} \quad (10a)$$

Here, *SP* stands for the solvation probability of acid, S_c is the cumulative separation factor ($S_c = s_f^{\text{chem}} \times s_f^{\text{phys}}$), $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant, t is Student's t for a certain degree of confidence, and T (K) is the extraction temperature. For a selected 95% probability of success (1 chance in 20 of failures) and an infinite number of degrees of freedom related to a 90% confidence band Student's $t = 1.645$.^[50] E_A^* (J mol^{-1}) denotes the overall activation energy of the solvation effect that takes place in the organic phase. Essentially, this quantity is being composed of four components, namely, E_{A1} is the activation energy of acid-carrier complex formation, E_{A2} designates the activation energy of solvation of acid-carrier complexes by the diluent, E_{A3} stands for the activation energy of solvation of acid molecules by the diluent and E_{A4} is a quantity accounted for the activation energy of solvation of complexes by the carrier itself. The solvation probability (*SP*) is a fairly measure of the degree with which the overall solvation effect would likely proceed in the organic phase. More specifically, *SP* is thought to be fundamental to scaling up the effectiveness with which the solute molecules can stay solvated in the organic phase infinitely. As a first approximation, we consider here the terms E_{A2} and E_{A3} to be the dominant factors of solvation process. Evidently, for a practically insoluble acid in the pure carrier ($s_f^{\text{chem}} = 0$) or pure diluent ($s_f^{\text{phys}} = 0$), Eqn (10) is devoid of the physical meaning. The solvation characteristics *SP* and E_A^* are regressed by linear analysis of Eqn (10).

The results from Table 4 and Fig. 9 indicate that the *SP* profile calculated from *SPR1* firstly tends to go to a maximum value at C3 acid as the C-chain of acid increases from C1 to C3, and then slowly goes down at C4 acid. Intuitively, because of a higher polarity and ionizing strength of FA, the amine-FA aggregation is energetically more prevalent, and thus, the formed polar complexes are more readily solvated as compared with other acids, which in turn has lowered the overall activation energy of solvation. But unexpectedly, the *SP* value of FA is smaller than that of C2–C4 acids eventually because of a high hydrophilic character and a great tendency to a monotype complexation of FA. It is clear that a high physical solubility of BA in pure diluent alone makes its structure less susceptible to interacting with the amine, and this process logically

Table 4. Solvation probability (*SP*) and activation energy (E_A^*) of acid-solvent association calculated from Eqns (10) and (11).

Solvent system	Formic acid		Acetic acid		Propionic acid		Butyric acid	
	<i>SP</i>	$E_A^*/(\text{J mol}^{-1})$	<i>SP</i>	$E_A^*/(\text{J mol}^{-1})$	<i>SP</i>	$E_A^*/(\text{J mol}^{-1})$	<i>SP</i>	$E_A^*/(\text{J mol}^{-1})$
Eqn (10) ^a								
Diisobutyl ketone	0.681	162.14	0.677	140.25	0.691	209.93	0.677	111.97
Oleyl alcohol	0.662	24.08	0.684	176.71	0.691	203.55	0.677	138.55
Octyl acetate	0.670	139.60	0.691	251.02	0.686	170.93	0.700	339.37
Eqn (11) ^a								
Diisobutyl ketone	0.686	250.49	0.688	268.80	0.683	105.75	0.690	190.38
Oleyl alcohol	0.688	263.57	0.684	229.09	0.680	77.29	0.695	249.77
Octyl acetate	0.689	260.21	0.685	231.21	0.686	140.16	0.693	217.13

^aMean relative errors of multivariable regression are defined as follows: $\bar{e} = 1.6\%$ for Eqn (10) and $\bar{e} = 0.07\%$ for Eqn (11).

enhances the overall activation energy of solvation. On the other hand, together with a simple acid molecule, self-associated molecules of C2–C3 acids, such as dimers or oligomers, can also act with the amine and diluent leading to an enhanced solvation probability of relevant acids. In opposite to this, the steric hindrance of self-associated acid molecules of dimers or oligomers energetically can bring difficulties for both acid-amine association and complex solvation by the diluent, so that the energy level of solvation is markedly tending to increase. However, the estimated results according to SPR1 (Table 4 and Fig. 9) come to an agreement with the aforementioned hypothesis; in fact,

except for PA exhibiting a bilateral behavior, the calculated energetic parameters (*SP* and E_A^*) of all other acids corroborate fiducially the concepts of a complex solvation mechanism and, also, provide opportunity to quantify its level.

Unfortunately, because of a lack of parameterization data set at different temperatures, SPR1 prediction surprisingly tends to a convergence going straight ahead a middle field confidence level of relevant quantity, as depicted in Fig. 9. However, this would call for the assumption that a specific benchmarking criterion should be originally intended to the SPR2 model (Eqn (11)) to establish a theoretical functionality between four physical characteristics of the solvation effect, namely, *SP*, E_A^* , S_c and cumulative volume factor $V_c = v_{\text{diluent}} \times v_{\text{extractant}}$. Here, v_{diluent} and $v_{\text{extractant}}$ stand for the initial volume fractions of diluent and extractant, respectively. The diagnostic checking of their contributions is fundamental to the formulation of SPR2, Eqn (11). It is worth mentioning here that there is a competitive effect between the term in *SP* and that in S_c regarding the acid structure; thereby, the term $(1 - S_c)$ has a negative exponent ($-0.05t$) for C1–C2 acids and a positive exponent ($+0.05t$) for C3–C4 acids. In fact, both Eqns (10) and (11) are originally suited for calculating *SP* and E_A^* by linear regression, but they have different structures and parameterized coefficients.

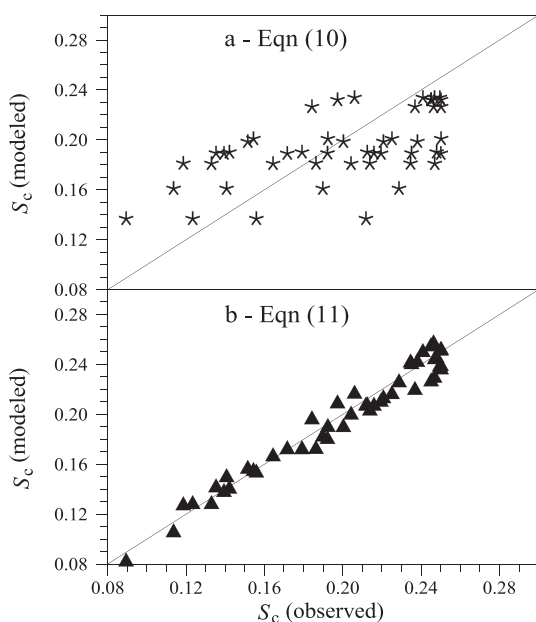


Figure 9. Presentation of cross-validated diagonal test results for SPR1 model Eqn (10) (*) and SPR2 model Eqn (11) (▲).

$$\ln(SP^{-1.5t}) = (1 - S_c)^{\pm 0.05t} \times \left[\exp\left(-\frac{E_A^*}{RT}\right) \right]^{1-V_c} \quad (11)$$

As shown in Table 4 and Fig. 9, the fairly accurate reproducibility of the experimental data by SPR2 implies that the reaction extraction of C1–C4 acids should be diffusion-controlled process being strongly dependent on the aggregation ability and structural

characteristics of carrier, diluent and acid. In general, the highest solvation probability and lowest activation energy are estimated for BA according to SPR2, Eqn (11), signifying that the synergism of physical and reaction extractions is achieved completely for that acid.

CONCLUDING REMARKS

The extractive removal of C1–C4 acids from water by TBA/diluent system has been elucidated by simultaneous effect of chemical and physical interactions closely related to the structural characteristics of amine, diluent and acid. The extraction data agree well with chemodel, e-LSER, SPR and A-UNIFAC models. The optimization algorithm has been successfully applied to the description of the optimum extraction field. The work draws the following conclusions:

- The uptake capacity of TBA/diluent system is intimately connected to the structural characteristics of the acid and diluent following the order, oleyl alcohol > octyl acetate > diisobutyl ketone and BA > PA > AA ≈ FA. The amine extraction of FA and AA is very much dependent on the hydrogen-bonding ability of diluent, while BA and PA exhibit distribution behavior generally being insensitive to the diluent structure. The acid_p-amine_q aggregation works in favor of forming 1:1 and 1:2 structures.
- The effectiveness of the optimization method is demonstrated on several practical case extraction systems. A fundamental distinction between the slopes of dR/dx_{iv} and dSE/dx_{iv} brings about two optimization schemes to be established separately concerning the suitability of the extractant and the solvent mixture for the acid recovery. Our results indicate that the most appropriate extraction ranges are $2 < R < 7$ and $5 < SE < 8$ for C1–C2 acids, and $0.3 < R < 1.5$ and $4 < SE < 6$ for C3–C4 acids. In conclusion, the evaluated optimization structure makes way for creating new perspectives in optimal tests. Particularly, DVM provides a useful basis for optimal tests of reactive extraction systems by compiling a derivative inequality.
- The deviation statistics show that e-LSER, A-UNIFAC and SPR models are able to simulate accurately the observed performance with mean errors of 4.8%, 24.1% and 0.8%, respectively. The results emphasize the fact that the parameterization of solvation models is adequately accomplished, enabling a correct prediction of reaction extraction. The mass action law models have proven moderately precise with an average deviation inferior to 12.1%.

NOMENCLATURE

$a_{m,n}$	A-UNIFAC residual group interaction parameter (K)
A	Acity
B	Basity
\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 as defined by Eqn (5)
\overline{C}_{NR_3}	Concentration of non-complexed amine (mol dm ⁻³)
$\overline{C}_{NR_3}^0$	Initial concentration of amine in the solvent mixture (mol dm ⁻³)
\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 (%)
E_A^*	Overall activation energy (J mol ⁻¹)
$E_T(30)$	Molar transition energy quantity (kcal mol ⁻¹)
$E_T^{N*}; E_T^N$	Normalized scale of $E_T(30)$
\bar{e}	Mean relative error $\bar{e} = (100/N) \sum_{i=1}^N (Y_{i,obs} - Y_{i,mod})/Y_{i,obs} $ (%)
F	Correction factor
HA	Monocarboxylic acid
$(HA)_p(NR_3)_q$	Acid-amine complex
k	Boltzmann's constant
K_a	Dissociation constant of acid
N	Number of observation
n_D	Refractive index
NR ₃	Tertiary amine

P	Pressure (kPa)
P_s^* ; P_s	Polarizability scale
p ; q	Number of acid and extractant molecules involved in the complex
Pr ; Pr_0	Properties as defined by Eqn (6)
R	Separation ratio optimization factor
R'	Universal gas constant ($R' = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
R_s	Polarization scale
S_c	Cumulative separation factor ($S_c = s_f^{\text{chem}} \times s_f^{\text{phys}}$)
r , s	Coefficients
s_f^{chem} ; s_f^{phys}	Chemical and physical separation factors of the solvent mixture
SE	Synergistic enhancement factor
SP	Solvation probability
T	Temperature (K)
t	Student's t number
\bar{V}	Molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
V_c	Cumulative volume factor ($V_c = v_{\text{diluent}} \times v_{\text{extractant}}$)
v ; v_i	Volume fraction of diluent or a component in the solvent mixture
x	Mole fraction
x_{iv}	Independent variable
Y	Independent variable
Z_s	Stoichiometric loading factor
Z_t	Overall loading factor of extractant
z	Associated number
$\overline{(\text{overbar})}$	Species in the organic phase

GREEK LETTERS

α ; α^*	Solvatochromic parameters
β ; β^*	Solvatochromic parameters
β_L	Langmuir extraction constant (mol dm^{-3}) ^{-z}
β_{pq}	Apparent equilibrium extraction constant (mol dm^{-3}) ^{1-p-q}
γ	Activity coefficient
δ ; δ^*	Solvatochromic parameters
δ_H	Hildebrand solubility parameter ($\text{MPa}^{0.5}$)
δ_H^*	
ϵ	Dielectric constant
ϵ_a	A-UNIFAC parameter for energy of association
κ	A-UNIFAC dimensionless parameter for volume of association
π ; π^*	Solvatochromic parameters
σ	Root-mean-square deviation
	$\sigma = \left[\frac{\sum_{i=1}^N (Y_{i,\text{obs}} - Y_{i,\text{mod}})^2}{N} \right]^{0.5}$

SUBSCRIPTS

mod	Modeled
obs	Observed

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

SUPPLEMENTARY MATERIAL

Table S1. Variation of the extraction factors E , D and Z_t with the concentration of components for the extraction of C1-C4 acids by tri-*n*-butyl amine/diluent and pure diluent alone at $T = 298.2$ K ($C_{TA}^0 = 2.1727$ mol dm⁻³ for formic acid; $C_{TA}^0 = 1.6652$ mol dm⁻³ for acetic acid; $C_{TA}^0 = 1.3499$ mol dm⁻³ for propionic acid; $C_{TA}^0 = 1.1349$ mol dm⁻³ for butyric acid)^a

$\overline{C_{NR_3}^0}^b$ (mol dm ⁻³)	pH ^c	C_{TA}^d (mol dm ⁻³)	$\overline{C_{TA}^d}$ (mol dm ⁻³)	E (%)	D	Z_t
TBA ^e + diisobutyl ketone + formic acid						
0.0000 ^f	2.017	1.8959	0.2768	12.74	0.146	
0.2660	2.489	1.6641	0.5086	23.41	0.306	1.912
0.5075	2.852	1.4047	0.7680	35.35	0.547	1.513
0.7913	3.154	1.1010	1.0717	49.33	0.973	1.354
1.0810	3.534	0.8458	1.3269	61.07	1.569	1.227
TBA + oleyl alcohol + formic acid						
0.0000 ^f	1.795	1.9490	0.2237	10.30	0.115	
0.2749	2.538	1.5772	0.5955	27.41	0.378	2.166
0.5227	2.867	1.3883	0.7844	36.10	0.565	1.501
0.7813	3.197	1.0457	1.1270	51.87	1.078	1.442
1.1119	3.587	0.8146	1.3581	62.51	1.667	1.221
TBA + octyl acetate + formic acid						
0.0000 ^f	1.787	1.9937	0.1790	8.24	0.090	
0.2573	2.498	1.6127	0.5600	25.77	0.347	2.176
0.5229	2.927	1.3452	0.8275	38.09	0.615	1.583
0.7553	3.184	1.1004	1.0723	49.35	0.974	1.420
1.0750	3.610	0.7231	1.4496	66.72	2.005	1.348
TBA + diisobutyl ketone + acetic acid						
0.0000 ^f	2.565	1.4402	0.2250	13.51	0.156	
0.2639	3.870	1.1808	0.4844	29.09	0.410	1.822
0.5191	4.260	0.9552	0.7100	42.64	0.743	1.368
0.7656	4.684	0.7291	0.9361	56.22	1.284	1.223

	1.0681	4.989	0.5087	1.1585	69.57	2.286	1.085
TBA + oleyl alcohol + acetic acid	0.0000 ^f	2.612	1.3750	0.2902	17.43	0.211	
	0.3043	3.961	1.1129	0.5523	33.17	0.496	1.815
	0.5400	4.346	0.9167	0.7485	44.95	0.817	1.386
	0.8160	4.648	0.7245	0.9407	56.49	1.298	1.153
	1.1380	5.129	0.4744	1.1908	71.51	2.510	1.053
TBA + octyl acetate + acetic acid	0.0000 ^f	2.583	1.4119	0.2533	15.21	0.179	
	0.2573	3.892	1.1322	0.5330	32.01	0.471	2.072
	0.5229	4.301	0.9192	0.7460	44.80	0.812	1.427
	0.7553	4.576	0.7418	0.9234	55.45	1.245	1.223
	1.0750	5.041	0.4796	1.1856	71.20	2.472	1.103
TBA + diisobutyl ketone + propionic acid	0.0000 ^f	3.905	0.7335	0.6164	45.66	0.840	
	0.2665	4.357	0.5480	0.8019	59.40	1.463	3.009
	0.5183	4.822	0.3802	0.9697	71.83	2.550	1.871
	0.7738	5.247	0.2581	1.0918	80.88	4.230	1.411
	1.0733	5.638	0.1965	1.1534	85.44	5.870	1.075
TBA + oleyl alcohol + propionic acid	0.0000 ^f	3.810	0.7421	0.6078	45.03	0.819	
	0.2706	4.244	0.5372	0.8127	60.20	1.513	3.008
	0.5407	4.735	0.3711	0.9788	72.51	2.638	1.810
	0.7756	5.160	0.2405	1.1084	82.18	4.613	1.430
	1.0903	5.616	0.1441	1.2058	89.33	8.368	1.106
TBA + octyl acetate + propionic acid	0.0000 ^f	3.978	0.7146	0.6353	47.06	0.889	
	0.2635	4.382	0.5527	0.7972	59.06	1.442	3.025
	0.5147	4.837	0.4215	0.9280	68.75	2.200	1.803
	0.7784	5.209	0.2816	1.0683	79.14	3.794	1.372
	1.0776	5.639	0.1860	1.1639	86.22	6.258	1.080
TBA + diisobutyl ketone + butyric acid							

0.0000 ^f	4.120	0.3170	0.8175	72.03	2.576	
0.2553	4.554	0.1814	0.9535	84.02	5.256	3.735
0.5334	5.245	0.1181	1.0168	89.59	8.610	1.981
0.7786	5.615	0.0889	1.0460	92.17	11.766	1.343
1.0601	5.750	0.0635	1.0714	94.40	16.872	1.011
TBA + oleyl alcohol + butyric acid						
0.0000 ^f	4.064	0.2835	0.8494	74.84	2.975	
0.2706	4.412	0.1999	0.9350	82.39	4.677	3.455
0.5414	5.009	0.1198	1.0151	89.44	8.473	1.875
0.8111	5.479	0.0778	1.0571	93.14	13.587	1.303
1.1049	5.834	0.0483	1.0866	93.74	22.497	0.983
TBA + octyl acetate + butyric acid						
0.0000 ^f	4.095	0.3033	0.8296	73.10	2.737	
0.2772	4.568	0.1958	0.9391	82.75	4.796	3.388
0.5141	5.099	0.1277	1.0072	88.75	7.887	1.959
0.7661	5.542	0.0941	1.0408	91.71	11.061	1.359
1.0682	5.714	0.0698	1.0651	93.85	15.259	0.997

^a Initial concentration (C_{TA}^0) of acid. ^b Initial concentration of amine dissolved in oxygen-containing diluent. ^c Acidity of the aqueous phase at equilibrium. ^d C_{TA} and $\overline{C_{TA}}$ stand for the overall aqueous phase and organic phase acid concentrations at equilibrium. ^eTBA, tri-*n*-butyl amine. ^f Properties referred to the pure diluent alone (i.e., diisobutyl ketone, oleyl alcohol, octyl acetate).

Table S2. Values of R_{\max} and SE_{\max} quantities and coefficients r and s of Eqns (8) and (9) calculated by means of linear regression

Acid ^a	Diisobutyl ketone				Oleyl alcohol				Octyl acetate			
	R_{\max}	SE_{\max}	r	s	R_{\max}	SE_{\max}	r	s	R_{\max}	SE_{\max}	r	s
FA	5.49	7.69	-1.6308	-2.3014	7.18	9.34	-1.7480	-2.1872	9.62	11.73	-1.7550	-2.0779
AA	5.86	8.04	-1.1004	-1.4894	4.76	6.99	-0.9015	-1.3441	5.35	7.56	-1.0199	-1.4292
PA	1.84	5.58	-0.2818	-1.9062	1.98	5.36	-0.2314	-2.1402	1.79	5.94	-0.2597	-1.7343
BA	1.14	7.12	-0.0644	-5.1791	1.10	8.96	-0.0464	-4.7176	1.11	7.91	-0.0654	-4.8098

^a FA - formic acid; AA – acetic acid; PA – propionic acid; BA – butyric acid.

Table S3. Extraction constants β_{pq} and β_L of Eqns (3) and (4), and root-mean-square deviation (σ) and mean relative error (\bar{e})^a of model estimates relative to the acid_p-amine_q complexation considered

System		Modified Langmuir model, Eqn (4)			Chemodel, Eqn (3)			
		$\beta_L; (z = Z_{s,max})^b$ (mol dm ⁻³) ^{-z}	$\sigma(Z_t)$	$\bar{e}(Z_t)$ (%)	$\beta_{pq1}; (p, q)^c$ (mol dm ⁻³) ^{1-p-q}	$\beta_{pq2}; (p, q)^c$ (mol dm ⁻³) ^{1-p-q}	$\sigma(Z_t)$	$\bar{e}(Z_t)$ (%)
FA ^e + Diisobutyl ketone	S ^d	0.36406×10 ¹ ; (1.15)	0.180	11.45	0.15174×10 ¹ ; (1, 2)	0.22131×10 ⁰ ; (1, 3)	0.268	12.80
	T ^d				0.94919×10 ⁰ ; (1, 2)			
FA + Oleyl alcohol	S	0.33794×10 ¹ ; (1.50)	0.167	10.80	0.11081×10 ¹ ; (1, 2)	0.41642×10 ¹ ; (1, 2)	0.184	10.77
	T				0.34354×10 ⁰ ; (1, 1)			
FA + Octyl acetate	S	0.39668×10 ¹ ; (1.62)	0.216	10.07	0.95590×10 ⁰ ; (1, 2)	0.38591×10 ¹ ; (1, 2)	0.184	9.88
	T				0.53812×10 ⁰ ; (1, 1)			
AA ^e + Diisobutyl ketone	S	0.11388×10 ² ; (1.12)	0.108	6.69	0.34806×10 ¹ ; (1, 2)	0.18811×10 ² ; (1, 2)	0.245	15.14
	T				0.96164×10 ⁰ ; (1, 1)			
AA + Oleyl alcohol	S	0.11559×10 ² ; (1.03)	0.115	5.91	0.45952×10 ¹ ; (1, 2)	0.36187×10 ² ; (1, 2)	0.269	17.95
	T				0.21346×10 ¹ ; (1, 1)			
AA + Octyl acetate	S	0.84384×10 ¹ ; (1.24)	0.167	8.68	0.32296×10 ¹ ; (1, 2)	0.30734×10 ² ; (1, 2)	0.292	18.48
	T				0.40976×10 ¹ ; (1, 1)			
PA ^e + Diisobutyl ketone	S	0.24996×10 ² ; (0.91)	0.096	5.97	0.22541×10 ² ; (1, 2)	0.34914×10 ³ ; (1, 2)	0.379	23.44
	T				0.11778×10 ² ; (1, 1)			
PA + Oleyl alcohol	S	0.22956×10 ² ; (0.97)	0.165	9.22	0.17650×10 ² ; (1, 2)	0.65712×10 ³ ; (1, 2)	0.407	25.19
	T				0.47518×10 ² ; (1, 1)			
PA + Octyl acetate	S	0.18075×10 ² ; (0.84)	0.118	6.88	0.39505×10 ² ; (1, 2)	0.18779×10 ⁴ ; (1, 2)	0.349	21.78
	T				0.30132×10 ² ; (1, 1)			
BA ^e + Diisobutyl ketone	S	0.39193×10 ² ; (0.79)	0.090	5.45	0.17345×10 ³ ; (1, 2)	0.26340×10 ⁵ ; (1, 3)	0.385	24.16
	T				0.49735×10 ⁴ ; (1, 2)			
BA + Oleyl alcohol	S	0.19643×10 ² ; (0.57)	0.064	4.19	0.12589×10 ⁴ ; (1, 2)	0.35710×10 ⁴ ; (1, 3)	0.232	9.84
	T				0.70366×10 ² ; (1, 1)			

BA + Octyl acetate	S	0.24215×10 ² ; (0.65)	0.043	2.76	0.13201×10 ⁴ ; (1, 2)	0.276	12.47
	T				0.96263×10 ¹ ; (1, 1)	0.27952×10 ³ ; (1, 2)	0.033

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

^b Langmuir extraction constant (β_L) in $(\text{mol dm}^{-3})^{-z}$ for a given association number ($z = Z_{s,max}$) according to Eqn (4). The maximum loading values ($z = Z_{s,max}$) used in the regression are 1.15, 1.50 and 1.62 for FA, 1.12, 1.03 and 1.24 for AA, 0.91, 0.97 and 0.84 for PA, and 0.79, 0.57 and 0.65 pertaining to diisobutyl ketone, oleyl alcohol and octyl acetate, respectively.

^c Extraction constant (β_{pq}) in $(\text{mol dm}^{-3})^{1-p-q}$ for a given acid-amine (p, q) aggregation according to Eqn (3).

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

^e FA formic acid, AA acetic acid, PA propionic acid, BA butyric acid, TBA tri-*n*-butyl amine.

Table S4. Coefficients C_i of the e-LSER model, Eqn (5), and root-mean-square deviation (σ) and mean relative error (\bar{e})^a evaluated for different properties Pr of TBA/diluent/acid systems

System	C_H	C_π	C_β	C_V	C_P	C_E
$Pr = \ln(D); Pr_0 = \ln(D_0)^b; \sigma(D); \bar{e}(D)$						
FA ^c + TBA/Diisobutyl ketone ($\sigma = 0.04$; $\bar{e} = 4.16\%$)	0.15136E+02	-0.42464E-04	0.50944E+00	-0.16677E+01	-0.10004E+02	0.94426E+01
FA + TBA/Oleyl alcohol ($\sigma = 0.07$; $\bar{e} = 6.80\%$)	-0.23109E+02	-0.25036E-04	0.74349E+00	0.73179E+00	0.18496E+02	-0.37604E+00
FA + TBA/Octyl acetate ($\sigma = 0.07$; $\bar{e} = 6.69\%$)	-0.68810E+02	0.40817E-03	0.48458E+02	-0.73520E+01	0.34606E+02	0.16156E+02
AA ^c + TBA/Diisobutyl ketone ($\sigma = 0.06$; $\bar{e} = 4.76\%$)	-0.41055E+01	0.17258E-04	0.31908E+01	-0.11370E+01	0.47208E+01	0.50231E+01
AA + TBA/Oleyl alcohol ($\sigma = 0.04$; $\bar{e} = 3.08\%$)	-0.87931E+00	-0.39799E-05	-0.10816E+01	-0.12016E+00	0.29181E+01	0.22735E+01
AA + TBA/Octyl acetate ($\sigma = 0.05$; $\bar{e} = 3.88\%$)	0.20448E+01	-0.29870E-04	0.65187E+00	-0.29600E+00	-0.48024E+01	0.71812E+01
PA ^c + TBA/Diisobutyl ketone ($\sigma = 0.09$; $\bar{e} = 2.05\%$)	-0.12030E+02	0.59178E-04	0.17051E+02	0.82392E+00	-0.31309E+02	0.12416E+02
PA + TBA/Oleyl alcohol ($\sigma = 0.03$; $\bar{e} = 1.06\%$)	0.17148E-01	0.49354E-04	0.15886E+01	-0.13964E+01	0.17172E+02	0.83132E+00
PA + TBA/Octyl acetate ($\sigma = 0.04$; $\bar{e} = 1.34\%$)	-0.16016E+01	0.63785E-04	-0.40374E+01	0.16347E+01	0.34958E+01	-0.15725E+01
BA ^c + TBA/Diisobutyl ketone ($\sigma = 0.16$; $\bar{e} = 1.50\%$)	0.36861E+02	0.16729E-03	-0.65576E+01	-0.70299E+01	0.39903E+02	-0.18793E+01
BA + TBA/Oleyl alcohol ($\sigma = 0.39$; $\bar{e} = 2.90\%$)	-0.15155E+03	0.10008E-03	0.41245E+02	0.16885E+02	-0.37902E+02	-0.26439E+02
BA + TBA/Octyl acetate ($\sigma = 0.24$; $\bar{e} = 2.11\%$)	0.65913E+01	0.15351E-04	-0.15527E-01	-0.26192E+00	-0.18926E+01	0.99072E+01
$Pr = \ln(E); Pr_0 = \ln(E_0)^b; \sigma(E); \bar{e}(E)$						

FA + TBA/Diisobutyl ketone ($\sigma = 1.93$; $\bar{e} = 4.07\%$)	0.84588E+01	-0.32889E-04	0.22675E+00	-0.12480E+01	-0.57079E+01	0.90122E+01
FA + TBA/Oleyl alcohol ($\sigma = 3.87$; $\bar{e} = 7.41\%$)	-0.18397E+02	-0.37752E-04	0.11303E+01	0.45487E+00	0.12994E+02	0.98763E+00
FA + TBA/Octyl acetate ($\sigma = 3.19$; $\bar{e} = 6.12\%$)	-0.31207E+02	0.17500E-03	0.21244E+02	-0.36481E+01	0.17258E+02	0.10711E+02
AA + TBA/Diisobutyl ketone ($\sigma = 2.41$; $\bar{e} = 4.27\%$)	-0.47106E+01	0.11079E-04	0.14202E+01	-0.96223E+00	0.62315E+01	0.58469E+01
AA + TBA/Oleyl alcohol ($\sigma = 1.49$; $\bar{e} = 2.53\%$)	-0.71661E+00	0.41929E-05	-0.22850E+01	0.11654E-01	0.22334E+01	0.24629E+01
AA + TBA/Octyl acetate ($\sigma = 1.26$; $\bar{e} = 2.77\%$)	0.56970E+00	-0.17028E-04	0.33507E+01	-0.79119E+00	-0.71496E+01	0.97202E+01
PA + TBA/Diisobutyl ketone ($\sigma = 0.62$; $\bar{e} = 0.74\%$)	-0.66892E+01	0.57497E-04	0.81104E+01	0.32051E+00	-0.18526E+02	0.11617E+02
PA + TBA/Oleyl alcohol ($\sigma = 0.70$; $\bar{e} = 0.81\%$)	-0.19499E+01	-0.99129E-05	0.28018E+00	0.20203E+00	-0.32648E+01	0.28073E+01
PA + TBA/Octyl acetate ($\sigma = 0.42$; $\bar{e} = 0.50\%$)	0.14560E+01	-0.53672E-04	0.57439E+01	-0.17378E+01	-0.35930E+01	0.87004E+01
BA + TBA/Diisobutyl ketone ($\sigma = 0.31$; $\bar{e} = 0.33\%$)	0.14714E+02	0.69379E-04	-0.38253E+01	-0.32742E+01	0.17358E+02	0.12761E+01
BA + TBA/Oleyl alcohol ($\sigma = 0.03$; $\bar{e} = 0.03\%$)	-0.31488E+01	0.39338E-05	-0.53706E+00	-0.96284E-01	0.33781E+01	0.23608E+01
BA + TBA/Octyl acetate ($\sigma = 0.17$; $\bar{e} = 0.18\%$)	-0.13023E+00	0.26176E-05	-0.21579E+00	0.32208E+00	-0.65581E+01	0.76358E+01
	$Pr = \ln(s_f^{\text{chem}}); Pr_0 = \ln(s_{f0}^{\text{chem}})^b; \sigma(s_f^{\text{chem}}); \bar{e}(s_f^{\text{chem}})$					
FA + TBA/Diisobutyl ketone ($\sigma = 0.02$; $\bar{e} = 4.39\%$)	-0.97478E+01	0.31780E-04	-0.10239E+00	0.13648E+01	0.60261E+01	-0.93277E+01
FA + TBA/Oleyl alcohol ($\sigma = 0.02$; $\bar{e} = 7.89\%$)	0.16612E+02	0.19646E-04	-0.10210E+01	-0.46455E+00	-0.10966E+02	-0.11450E+01
FA + TBA/Octyl acetate ($\sigma = 0.02$; $\bar{e} = 5.96\%$)	0.74953E+02	-0.44299E-03	-0.52533E+02	0.79162E+01	-0.36774E+02	-0.17833E+02

AA + TBA/Diisobutyl ketone ($\sigma = 0.02$; $\bar{e} = 4.36\%$)	0.35092E+01	-0.55233E-05	0.67745E+00	0.58109E+00	-0.62469E+01	-0.61211E+01
AA + TBA/Oleyl alcohol ($\sigma = 0.01$; $\bar{e} = 2.73\%$)	0.16972E+01	-0.28003E-05	0.20994E+01	0.13522E+00	-0.43846E+01	-0.27615E+01
AA + TBA/Octyl acetate ($\sigma = 0.01$; $\bar{e} = 2.39\%$)	-0.16607E+01	0.14993E-04	-0.14316E+01	0.53215E+00	0.60364E+01	-0.89548E+01
PA + TBA/Diisobutyl ketone ($\sigma = 0.008$; $\bar{e} = 1.12\%$)	0.47408E+01	-0.46687E-04	-0.60433E+01	-0.19440E+00	0.13003E+02	-0.91879E+01
PA + TBA/Oleyl alcohol ($\sigma = 0.007$; $\bar{e} = 1.02\%$)	0.16654E+01	0.18200E-04	0.12914E+01	-0.71469E-01	-0.27156E+01	-0.18607E+01
PA + TBA/Octyl acetate ($\sigma = 0.006$; $\bar{e} = 0.88\%$)	-0.38554E+01	0.85112E-04	-0.82770E+01	0.26886E+01	0.29934E+01	-0.90036E+01
BA + TBA/Diisobutyl ketone ($\sigma = 0.001$; $\bar{e} = 0.17\%$)	-0.27063E+00	0.87585E-05	-0.19930E+01	0.15572E+00	0.40046E+01	-0.52228E+01
BA + TBA/Oleyl alcohol ($\sigma = 0.002$; $\bar{e} = 0.19\%$)	0.29492E+02	-0.68520E-04	-0.10424E+02	-0.41248E+01	0.24785E+02	0.24459E+01
BA + TBA/Octyl acetate ($\sigma = 0.002$; $\bar{e} = 0.18\%$)	0.78457E+00	-0.91984E-05	-0.24448E+01	-0.13252E+01	0.18026E+02	-0.80569E+01
$Pr = \ln(Z_t)$; $Pr_0 = \ln(Z_{t,\max})^d$; $\sigma(Z_t)$; $\bar{e}(Z_t)$						
FA + TBA/Diisobutyl ketone ($\sigma = 0.03$; $\bar{e} = 1.82\%$)	-0.40249E+01	0.12824E-04	-0.10550E+00	0.55263E+00	0.28398E+01	-0.39711E+01
FA + TBA/Oleyl alcohol ($\sigma = 0.15$; $\bar{e} = 7.31\%$)	0.26110E+01	0.59415E-05	-0.24827E+00	-0.64860E-01	-0.15654E+01	-0.40522E+00
FA + TBA/Octyl acetate ($\sigma = 0.12$; $\bar{e} = 5.34\%$)	0.13829E+02	-0.81214E-04	-0.95356E+01	0.14655E+01	-0.69946E+01	-0.36141E+01
AA + TBA/Diisobutyl ketone ($\sigma = 0.05$; $\bar{e} = 2.45\%$)	0.18315E+01	-0.43209E-05	-0.86094E+00	0.41463E+00	-0.26041E+01	-0.17490E+01
AA + TBA/Oleyl alcohol ($\sigma = 0.06$; $\bar{e} = 3.30\%$)	-0.22593E+01	-0.14356E-04	0.36721E+01	-0.25239E+00	-0.22611E+01	0.17714E+00
AA + TBA/Octyl acetate ($\sigma = 0.12$; $\bar{e} = 5.95\%$)	0.19097E+00	0.35238E-05	-0.46493E+00	0.16274E+00	0.90893E+00	-0.28565E+01

PA + TBA/Diisobutyl ketone ($\sigma = 0.16$; $\bar{e} = 5.40\%$)	0.11087E+01	-0.47692E-05	-0.56467E+01	0.18830E+00	0.22534E+01	0.39359E+01
PA + TBA/Oleyl alcohol ($\sigma = 0.21$; $\bar{e} = 6.82\%$)	-0.20671E+01	-0.70940E-05	0.10412E+01	0.81059E+00	-0.12407E+02	0.56946E+00
PA + TBA/Octyl acetate ($\sigma = 0.23$; $\bar{e} = 7.39\%$)	0.20908E+00	-0.14568E-04	-0.68509E+00	-0.17251E+00	-0.20587E+00	-0.13071E+01
BA + TBA/Diisobutyl ketone ($\sigma = 0.39$; $\bar{e} = 13.15\%$)	0.19599E+02	0.77547E-04	-0.53831E+01	-0.61246E+01	0.14629E+02	0.15919E+02
BA + TBA/Oleyl alcohol ($\sigma = 0.30$; $\bar{e} = 9.47\%$)	-0.85052E+02	0.15402E-03	0.22241E+02	0.97619E+01	-0.52055E+02	-0.63960E+01
BA + TBA/Octyl acetate ($\sigma = 0.28$; $\bar{e} = 9.46\%$)	-0.10681E+02	0.44299E-04	-0.35833E+01	0.20343E+01	-0.25649E+02	0.23468E+02
	$Pr = \ln(SE)$; $Pr_0 = \ln(SE_{\max})^b$; $\sigma(SE)$; $\bar{e}(SE)$					
FA + TBA/Diisobutyl ketone ($\sigma = 0.89$; $\bar{e} = 15.44\%$)	-0.16706E+02	0.53556E-04	-0.13162E+00	0.22218E+01	0.11871E+02	-0.13745E+02
FA + TBA/Oleyl alcohol ($\sigma = 1.14$; $\bar{e} = 16.26\%$)	0.20157E+02	0.42935E-04	-0.14198E+01	-0.38635E+00	-0.12698E+02	-0.19614E+01
FA + TBA/Octyl acetate ($\sigma = 1.37$; $\bar{e} = 18.28\%$)	0.68063E+02	-0.39226E-03	-0.47135E+02	0.74265E+01	-0.34668E+02	-0.17247E+02
AA + TBA/Diisobutyl ketone ($\sigma = 0.85$; $\bar{e} = 14.84\%$)	0.65293E+01	-0.17617E-04	-0.24481E+01	0.15443E+01	-0.78211E+01	-0.77834E+01
AA + TBA/Oleyl alcohol ($\sigma = 0.54$; $\bar{e} = 9.88\%$)	0.39813E+00	-0.16167E-04	0.56344E+01	-0.13095E+00	-0.51040E+01	-0.26540E+01
AA + TBA/Octyl acetate ($\sigma = 0.57$; $\bar{e} = 10.89\%$)	-0.14630E+01	0.22702E-05	-0.38381E+01	0.10741E+01	0.10793E+02	-0.13156E+02
PA + TBA/Diisobutyl ketone ($\sigma = 0.17$; $\bar{e} = 2.82\%$)	0.70709E+01	-0.34552E-04	-0.78945E+01	-0.23996E+00	0.16647E+02	-0.98706E+01
PA + TBA/Oleyl alcohol ($\sigma = 0.15$; $\bar{e} = 2.55\%$)	0.12638E+01	-0.29090E-05	0.11561E+01	0.75743E-01	-0.14616E+01	-0.22475E+01
PA + TBA/Octyl acetate ($\sigma = 0.25$; $\bar{e} = 4.09\%$)	-0.12775E+01	0.75107E-04	-0.75903E+01	0.22847E+01	0.39726E+01	-0.97922E+01
BA + TBA/Diisobutyl ketone	0.10578E+02	0.38767E-04	-0.32541E+01	-0.24773E+01	0.11542E+02	-0.14825E+01

($\sigma = 0.36$; $\bar{e} = 5.65\%$)

BA + TBA/Oleyl alcohol 0.39454E+02 -0.20943E-04 -0.74948E+01 -0.30315E+01 -0.89848E+01 0.45539E+01

($\sigma = 0.67$; $\bar{e} = 7.84\%$)

BA + TBA/Octyl acetate -0.37324E+01 0.36202E-04 -0.12356E+01 0.24294E+01 -0.21918E+02 0.54354E+01

($\sigma = 0.49$; $\bar{e} = 6.75\%$)

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

^b D_0 , E_0 and s_{f0}^{chem} stand for the properties pertaining to the pure diluent alone.

^c FA formic acid, AA acetic acid, PA propionic acid, BA butyric acid, TBA tri-*n*-butyl amine.

^d $Z_{t,\text{max}}$ and SE_{max} represent the maximum values of extraction factors defined as follows, (a) for formic acid: $Z_{t,\text{max}} = 2.64$, $SE_{\text{max}} = 7.69$ (diisobutyl ketone); $Z_{t,\text{max}} = 2.67$, $SE_{\text{max}} = 9.34$ (oleyl alcohol); $Z_{t,\text{max}} = 2.68$, $SE_{\text{max}} = 11.73$ (octyl acetate), (b) for acetic acid: $Z_{t,\text{max}} = 2.32$, $SE_{\text{max}} = 8.04$ (diisobutyl ketone); $Z_{t,\text{max}} = 2.32$, $SE_{\text{max}} = 6.99$ (oleyl alcohol); $Z_{t,\text{max}} = 2.57$, $SE_{\text{max}} = 7.56$ (octyl acetate), (c) for propionic acid: $Z_{t,\text{max}} = 3.51$, $SE_{\text{max}} = 5.58$ (diisobutyl ketone); $Z_{t,\text{max}} = 3.50$, $SE_{\text{max}} = 5.36$ (oleyl alcohol); $Z_{t,\text{max}} = 3.53$, $SE_{\text{max}} = 5.94$ (octyl acetate), (d) for butyric acid: $Z_{t,\text{max}} = 4.23$, $SE_{\text{max}} = 7.12$ (diisobutyl ketone); $Z_{t,\text{max}} = 3.96$, $SE_{\text{max}} = 8.96$ (oleyl alcohol); $Z_{t,\text{max}} = 3.89$, $SE_{\text{max}} = 7.91$ (octyl acetate).

Table S5. Experimental mole fraction compositions of the conjugate solutions (x'_1, x'_2, x'_3, x'_4) and ($x''_1, x''_2, x''_3, x''_4$) for the quaternary LLE systems (water x_1 + acid x_2 + tributyl amine x_3 + diluent x_4)

Water-rich phase				Solvent-rich phase			
x'_1	x'_2	x'_3	x'_4	x''_1	x''_2	x''_3	x''_4
Water (1) + formic acid (2) + tributyl amine (3) + diisobutyl ketone (4)							
0.8813	0.1128	0.0003	0.0056	0.0984	0.0750	0.0392	0.7874
0.9294	0.0665	0.0004	0.0037	0.0953	0.1097	0.0725	0.7225
0.9584	0.0385	0.0005	0.0026	0.0913	0.1467	0.1083	0.6537
0.9732	0.0243	0.0006	0.0019	0.0881	0.1753	0.1428	0.5938
Water (1) + formic acid (2) + tributyl amine (3) + oleyl alcohol (4)							
0.9036	0.0936	0.0002	0.0026	0.1042	0.1397	0.0645	0.6916
0.9332	0.0646	0.0003	0.0018	0.0978	0.1726	0.1150	0.6145
0.9635	0.0350	0.0004	0.0013	0.0886	0.2245	0.1557	0.5312
0.9758	0.0229	0.0004	0.0010	0.0824	0.2518	0.2062	0.4595
Water (1) + formic acid (2) + tributyl amine (3) + octyl acetate (4)							
0.8946	0.1008	0.0002	0.0044	0.0909	0.0916	0.0421	0.7754
0.9372	0.0596	0.0004	0.0029	0.0876	0.1304	0.0824	0.6996
0.9589	0.0385	0.0005	0.0021	0.0833	0.1607	0.1132	0.6429
0.9790	0.0191	0.0006	0.0015	0.0786	0.2050	0.1520	0.5644
Water (1) + acetic acid (2) + tributyl amine (3) + diisobutyl ketone (4)							
0.9273	0.0677	0.0003	0.0048	0.0987	0.0717	0.0394	0.7902
0.9579	0.0386	0.0004	0.0032	0.0959	0.1021	0.0747	0.7273
0.9745	0.0228	0.0005	0.0022	0.0926	0.1300	0.1063	0.6711
0.9849	0.0129	0.0005	0.0016	0.0896	0.1556	0.1435	0.6113
Water (1) + acetic acid (2) + tributyl amine (3) + oleyl alcohol (4)							
0.9408	0.0568	0.0002	0.0022	0.1054	0.1309	0.0721	0.6916
0.9629	0.0353	0.0003	0.0015	0.0989	0.1666	0.1202	0.6143
0.9760	0.0225	0.0003	0.0011	0.0919	0.1945	0.1687	0.5448

0.9871	0.0118	0.0004	0.0009	0.0853	0.2284	0.2169	0.4694
Water (1) + acetic acid (2) + tributyl amine (3) + octyl acetate (4)							
0.9365	0.0596	0.0002	0.0037	0.0913	0.0876	0.0423	0.7788
0.9616	0.0355	0.0003	0.0026	0.0880	0.1182	0.0828	0.7110
0.9742	0.0235	0.0003	0.0020	0.0858	0.1426	0.1167	0.6549
0.9862	0.0120	0.0004	0.0015	0.0816	0.1742	0.1579	0.5863
Water (1) + propionic acid (2) + tributyl amine (3) + diisobutyl ketone (4)							
0.9811	0.0163	0.0001	0.0025	0.0943	0.1134	0.0377	0.7547
0.9884	0.0094	0.0001	0.0019	0.0925	0.1345	0.0719	0.7012
0.9924	0.0057	0.0003	0.0017	0.0905	0.1483	0.1051	0.6561
0.9941	0.0047	0.0004	0.0015	0.0902	0.1561	0.1453	0.6084
Water (1) + propionic acid (2) + tributyl amine (3) + oleyl alcohol (4)							
0.9828	0.0158	0.0001	0.0013	0.0986	0.1803	0.0600	0.6611
0.9897	0.0091	0.0002	0.0010	0.0928	0.2045	0.1129	0.5897
0.9938	0.0052	0.0002	0.0009	0.0884	0.2207	0.1543	0.5366
0.9962	0.0029	0.0003	0.0007	0.0847	0.2297	0.2077	0.4780
Water (1) + propionic acid (2) + tributyl amine (3) + octyl acetate (4)							
0.9813	0.0165	0.0001	0.0021	0.0874	0.1254	0.0415	0.7457
0.9872	0.0109	0.0002	0.0017	0.0856	0.1430	0.0793	0.6920
0.9920	0.0064	0.0002	0.0014	0.0830	0.1596	0.1163	0.6410
0.9946	0.0039	0.0003	0.0012	0.0818	0.1715	0.1588	0.5879
Water (1) + butyric acid (2) + tributyl amine (3) + diisobutyl ketone (4)							
0.9943	0.0039	0.0001	0.0018	0.0924	0.1322	0.0354	0.7400
0.9959	0.0024	0.0002	0.0016	0.0919	0.1402	0.0708	0.6971
0.9966	0.0017	0.0002	0.0015	0.0910	0.1428	0.1063	0.6598
0.9971	0.0012	0.0003	0.0013	0.0914	0.1469	0.1454	0.6163
Water (1) + butyric acid (2) + tributyl amine (3) + oleyl alcohol (4)							
0.9946	0.0043	0.0001	0.0010	0.0960	0.2019	0.0584	0.6436
0.9967	0.0024	0.0001	0.0008	0.0921	0.2104	0.1122	0.5852
0.9976	0.0015	0.0001	0.0008	0.0887	0.2110	0.1620	0.5384
0.9982	0.0009	0.0002	0.0007	0.0864	0.2112	0.2147	0.4877
Water (1) + butyric acid (2) + tributyl amine (3) + octyl acetate (4)							

0.9942	0.0042	0.0001	0.0015	0.0853	0.1442	0.0426	0.7279
0.9959	0.0026	0.0001	0.0013	0.0646	0.1534	0.0783	0.6837
0.9967	0.0018	0.0002	0.0012	0.0835	0.1565	0.1152	0.6449
0.9973	0.0013	0.0003	0.0011	0.0832	0.1595	0.1599	0.5974
