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Optimum extraction equilibria of the systems (water + carboxylic acid + 1-hexanol/Alamine): Thermodynamic modeling

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ABSTRACT

Extraction equilibria of the systems (water + carboxylic acid + 1-hexanol/Alamine 300) have been investigated at $T = 298.2$ K. Among the studied C1–C3 carboxylic acids, propanoic acid gives the largest distribution ratio and separation factors, as compared to formic and acetic acids. The equilibrium data of monocarboxylic acids are used to establish the basis to an analytical structure for optimum extraction. Some aspects of selection of an appropriate criterion for designing optimum extraction are discussed. Solvation energy relation (SERLAS) with five parameters has been performed to estimate the properties of extraction systems containing a protic alcohol solvent. The tie-lines of the present systems have been predicted by the UNIFAC-original model. The reliability analysis of both models has been made statistically against the experimental extraction factors.

1. Introduction

The efficient separation of monocarboxylic acids from fermentation broth and wastewater including lower than 10% (w/w) acid concentrations has received increasing interest in the chemical fermentation industry [1–3]. Regarding the technical merits of high boiling solvents during the regeneration, many solvents have been tested to improve such recovery. Most heavy normal *n*-alkanol solvents used to extract a carboxylic acid show a distribution coefficient less than one [1]. In this regard, the extraction efficiency of a monocarboxylic acid can be improved through applying synergistic separation power of a solvent mixture of (alcohol + saturated aliphatic tertiary amines, e.g. Alamine 300), used as a commercial extractant for carboxylic acids [4–7]. Three major factors have been found to influence the equilibrium characteristics of amine extraction of a carboxylic acid from aqueous solutions, i.e., the nature of acid, the concentration of acid, and the type of organic solvent [6,7]. Process considerations dealing with the competition between chemical interaction and physical extraction of hydrophobic acids through hydrogen bonding or dipole–dipole interaction still remain a challenging problem since such systems show extremely nonideal behavior.

Study of numerous solvent/amine/acid extraction systems covering a large scale polar solvents by Senol [6–9] reveals that characterization of the simultaneous effect of physical extraction and chemical association of the acid is intimately connected to the solvation efficiency of the solvent overly dependent on its polarity and hydrogen bonding affinity. The effect of the solvent is mainly focused on its ability to solvate both polar acid–amine complexes and the acid alone that allows higher levels of the acid to stay in the organic phase. It has been found that the complementary solvation effect is more pronounced in the case of a polar alcohol solvent, affecting more readily both the solvent–complex aggregation and the amine-free solvent–acid association through hydrogen bonding and dipole–dipole interaction [6–9]. These findings are comprehensively supported by the liquid–liquid equilibrium (LLE) results for an oxo-carboxylic acid indicating that among the tested high boiling alcohols, the *n*-alcohol/amine system yields remarkably the largest synergistic extraction power [8,9].

However, it is essential that this phenomenon will have a significant impact on the implementation of a selected extraction method utilizing 1-hexanol/Alamine 300 system. It may be desirable to use a high-boiling solvent that does not have to be distilled so long as no azeotropes appear. Regarding the technical and economic merits of high boiling aliphatic alcohols during the regeneration by distillation, the selection of 1-hexanol of higher boiling temperature than water and C1–C3 monocarboxylic acids was made.

As continuation of the previous study [8,9], the present work aims to generate new LLE data for the extraction of formic, acetic and propanoic acids from water at $T = 298.2$ K using (1-hexanol + 3% by volume Alamine 300) solvent system of lower vapor pressure

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Nomenclature

a	coefficient of polynomial function
b	coefficient of polynomial function
C	coefficient defined in Eq. (4)
D	distribution coefficient
D_{M}	modified distribution ratio
D_{M_0}	the value of D_{M} at the extraction limit $x_2 = 0$
$\bar{e}$	mean relative error, $\bar{e}(\%) = (100/N)\sum_{i=1}^{N}(Y_{i,\mathrm{obs}} - Y_{i,\mathrm{mod}})/Y_{i,\mathrm{obs}}$
F	correction factor as defined in Eq. (4)
F_{E}	extraction factor
F_{E_0}	the value of F_{E} at the extraction limit $x_2 = 0$
G^{E}	excess Gibbs free energy function (J mol^{-1})
N	number of observations
O_{F}	optimization factor
O_{F_0}	the value of O_{F} at the extraction limit $x_2 = 0$
p	polynomial function
Pr	property as defined in Eq. (4)
Pr_0	property as defined in Eq. (4)
R	gas constant (J mol^{-1} K^{-1})
S	separation factor
S_{M}	modified separation factor
S_{M_0}	the value of S_{M} at the extraction limit $x_2 = 0$
SR	solvent-dependent composition ratio
SR_0	the value of SR at the extraction limit $x_2 = 0$
T	temperature (K)
V	the molar volume of a solute (dm^3 mol^{-1})
x_0	mole fraction of mutual solubility of a component
x_i'	mole fraction of a component in the aqueous phase
x_i''	mole fraction of a component in the solvent phase
x_{iv}	dimensionless independent variable ($x_{iv} = x_2''/x_3''$)
x_{pp}	mole fraction of a solute at the plait point
Y	independent variable

Greek letters

α; α^*	solvatochromic parameters
β; β^*	solvatochromic parameters
Γ_{L}	thermodynamic factor
γ	activity coefficient of a component in the organic phase
δ	solvatochromic parameter
δ_H; δ_{H}^*	Hildebrand solubility parameters (MPa$^{0.5}$)
π; π^*	solvatochromic parameters
σ	root-mean-square deviation, $\sigma = \sqrt{\sum_{i=1}^{N}(Y_{i,\mathrm{obs}} - Y_{i,\mathrm{mod}})}$

Subscripts

max	maximum
mod	modeled property
obs	observed property

(higher boiling temperature) than water and C1–C3 monocarboxylic acids. Experimental data for the present mixtures are not available in the open literature. The distribution data have been used to develop an optimization structure for the acid extraction. Due to the synergistic effect of physical and chemical interactions, the 1-hexanol/Alamine solvent can improve the extraction efficiency of the considered acids. The analysis is limited with 1-hexanol/Alamine (3% by volume) solvent system being regarded as a coupled solvent. LLE data for the extraction of monocarboxylic acids by a high boiling alcohol/Alamine solvent are scarce in the literature [8,9].

While various models, based on group-contribution theory and dipole–dipole interaction concepts exist for LLE systems, yet only few works have dealt with optimizing analytically the extraction efficiency of an equilibrium system [8]. However, this study deals with a new conceptual definition for optimum extraction as the locus of the proposed separation factors being used as the optimization criteria. Along with a consideration of these factors, this article will discuss the optimum condition for an efficiently extraction in terms of the derivative variation of separation factors. It is expected that the proposed analytical structure could be applicable to numerous liquid–liquid extraction systems while still being general with regard to the solubility properties. The analysis is limited with a ternary liquid system.

1.1. Survey of thermodynamic models for associating systems

Modeling the thermodynamic properties and phase equilibria of a system involving components, such as acids and alcohols capable of association through hydrogen bonding or dipole–dipole interaction, still remains a challenging problem because such systems show complex aggregation behavior. Many attempts have been made to describe vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) of alcohol-containing associated mixtures using the concept of multiscale association [10], as well as applying a generalized solvatochromic approach with linear solvation energy relationship (LSER) [11,12]. Traditionally, theoretically based approaches such as NRTL and UNIQUAC activity coefficient models, ASOG and UNIFAC group-contribution methods, and Redlich–Kwong–Soave cubic equation of state (EOS) derived from molecular-statistical theory, have been applied widely to these systems [13–15]. Group contribution methods are extensively used in the chemical industry, especially during the development of chemical processes [16], and the UNIFAC-original model [17–19] stands out because its parameter matrix is the most comprehensive one being obtained from extensive series of revisions and extensions of the VLE parameters or special LLE data-fitted parameters. To improve its predictive capability several modified UNIFAC models have been proposed, such as UNIFAC-Dortmund [20], UNIFAC-Lyngby [21] and A-UNIFAC [22–24]. Especially, the A-UNIFAC model adds an association term, based on the Wertheim theory, to the original UNIFAC residual and combinatorial contributions to the activity coefficients [22,23]. Despite a high flexibility of A-UNIFAC, taking into account association effects between groups, a rigorous validation of the formulated association framework requires an extension of the parameter matrix applicable to different kinds of LLE systems and their further analysis. However, most of the regressed association and residual group interaction parameters have been derived from the limited VLE data [22–24].

Recently, various versions of EOS including the family of so-called “chemical interaction” equations are widely used for calculating phase equilibria of systems with multiple associating sites, i.e. the associated perturbed anisotropic chain theory (APACT), the statistical associating fluid theory (SAFT), the lattice quasi-chemical hole model (HM), cubic-plus-association equation of state (CPA-EOS), and COSMO-RS method [14,15,25–34]. For the phase equilibrium of associating systems, an analysis of the predicted capabilities of these approaches was performed by many researches [25,26,32]. In spite of the difference in the physical interaction terms of the EOS, it was found reasonable results in the description of association equilibria, being in agreement with the experimental data.

During the last years, numerous EOS models suitable for associating fluids have been developed using the concepts of three theories categorized as: (a) perturbation theory of Wertheim (SAFT, CPA-EOS models); (b) chemical theory which accounts for the formation of various oligomers through a chemical interaction (AEOS