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Phase equilibria of ternary systems (water + pyruvic acid + high boiling alcohol). Thermodynamic modeling and optimization of extraction

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ABSTRACT

Phase equilibria of the systems (water + pyruvic acid + high boiling alcohol) have been determined at $T = 298.2$ K. Among the heavy alcohol solvents studied, 1-decanol gives the largest distribution ratio and separation factors for extraction of pyruvic acid. The distribution data of pyruvic acid are used to establish the basis for an analytical structure to provide optimum extraction. Some aspects of selection of an appropriate criterion for designing optimum extraction of acid are discussed. The solvation energy relation (SERLAS) with 5- and 10-parameters has been performed to correlate the (liquid + liquid) equilibria (LLE) of associated systems containing a protic alcohol solvent capable of hydrogen bonding. The extraction equilibria were also predicted through the UNIFAC-original model. The reliability of both models has been analyzed against the LLE data with respect to the distribution ratio and separation factor.

1. Introduction

In the chemical industry, various selective solvent systems have been tested to improve the efficient separation of carboxylic acids from aqueous fermentation solutions [1,2]. Especially, extractive recovery of acetic acid by selective solvent systems from aqueous solutions, such as fermentation broth, has received increasing interest [3,4]. Three major factors have been found to influence the equilibrium characteristics of solvent extraction of a carboxylic acid from aqueous solutions, *i.e.*, the nature of acid, the concentration of acid, and the type of organic solvent [5]. Simultaneously, the impact of additional controlling factors, such as the swing effect of a mixed solvent and the third phase formation can also modify the equilibrium. However, it may be desirable to use a high boiling solvent that presumably does not give an azeotrope with acid. The physical extraction of hydrophilic acids through hydrogen bonding or dipole–dipole interaction is still challenging because such systems show extremely non-ideal behavior.

In this study, the extraction equilibrium of the systems (water + pyruvic acid + cyclohexanol or 1-decanol or 1-phenylethanol) at $T = 298.2$ K has been investigated, along with using a proton-donating alcohol solvent of lower vapor pressure than water and pyruvic acid. The distribution data have been used to develop an optimization structure for the acid extraction.

Regarding the technical and economic merits of high boiling solvents during the regeneration by distillation, the selection of protic alcohol extracting agents from various classes of aliphatic, aromatic or cyclic type was made. They all have higher boiling temperatures than water and pyruvic (2-oxopropanoic) acid. (Liquid + liquid) equilibrium (LLE) data for extraction of an oxo-carboxylic acid from water through a protic high boiling alcohol are scarce in the literature [6–8]. Most heavy normal *n*-alkanol solvents used to extract a carboxylic acid show a distribution coefficient less than one [6]. Nevertheless, such studies, besides other purposes, are indispensable in calibration and verification of analytical models. It has not been found dependable LLE results for the present ternaries in the literature.

Pyruvic acid occurs naturally as an intermediate product in carbohydrate and protein metabolism in the body, where a six-carbon glucose molecule is broken down to two molecules of pyruvic acid in aerobic condition. On an industrial scale, pyruvic acid mainly serves as an effective starting material for the synthesis of many drugs and agrochemicals, pharmaceuticals (*i.e.*, L-tryptophan, L-DOPA), crop protection agents, polymers, cosmetics and food additives [9].

Recently, it has been reported in the literature that some processes for recovery of pyruvic acid from fermentation broth such as ion exchange, reverse osmosis membrane and amine complex extraction have applied pyruvic acid separation from a biotransformation solution or cell-free fermentation broth [8,9].

In this study, attempts have been made to correlate the properties and (liquid + liquid) equilibria of associated ternary mixtures through a solvation approach SERLAS (solvation energy relation

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for liquid associated systems) using the principles of linear solvation energy relation, LSER [7]. The model incorporates the modified solvatochromic parameters of LSER [10,11] with the thermodynamic factors (of activity coefficients) derived from the UNIFAC-Dortmund model [12] in a relation including expansion terms and two correction factors for the limiting conditions of extraction. The reliability analysis has been conducted on the performance of SERLAS model with 5- and 10-parameters. The tie-lines were also predicted by the UNIFAC-original model [13,14], and compared with the distribution data evaluated through SERLAS.

This study also deals with a new conceptual definition for optimum extraction as the locus of the proposed separation factors being used as the optimization criteria. It is expected that the proposed analytical structure could be applicable to numerous (liquid + liquid) extraction systems being general with regard to the solubility properties. The analysis is limited with a ternary liquid system.

2. Theoretical

2.1. Basic principles of LSER

Marcus and co-workers [10,11] have revealed that the properties, such as the solubility or distribution of non-electrolyte solutes between water and an immiscible organic solvent, can be well correlated by linear solvation energy relationship (LSER). It is a linear combination of dependences on up to five physical parameters. Accordingly, the general LSER form measures the property *XYZ* (*i.e.*, distribution coefficient) in terms of five physical solute–solvent interaction parameters and is given by equation (1).

$$XYZ = XYZ_0 + mV/100 + s(\pi + d\delta) + b\beta + a\alpha, \tag{1}$$

where XYZ_0 is an adjustable parameter for the distributed solute. LSER includes a cavity term, depending on the intrinsic molar volume of the solute ($mV/100$), a polarity/polarizability term [$s(\pi + \mathrm{d}\delta)$] measuring the endoergic effects of dipole–dipole and dipole–induced dipole interactions, and hydrogen-bonding terms ($b\beta$ and $a\alpha$) pertaining to the hydrogen bond donation (HBD) and acceptance (HBA) properties of the solute and solvent. The solvatochromic parameter π is an index of polarity/polarizability and δ is a polarizability correction parameter reflecting differences in the component polarizability. The β scale is the HBA (hydrogen-bond acceptor) ability of the solute to accept a proton in a solute-to-solvent hydrogen bond and α is the HBD (hydrogen-bond donor) ability of the solute to donate a proton in a solvent-to-solute hydrogen bond. Marcus [11] has proposed the use of the $\delta_{\mathrm{H}}/(\mathrm{MPa}^{0.5})$ (Hildebrand solubility parameter) in equation (1) as the cohesive energy density term (square of δ_{H}) instead of the cavity term, when dealing with free energies of solution.

In this study, the extraction equilibrium of 2-oxopropanoic acid has been estimated through SERLAS model based on the principles of LSER.

2.2. Correlation of LLE by SERLAS

Study of numerous LLE systems has revealed that the properties of ternary liquid systems, such as the separation factor (S) and the modified distribution ratio (D_{M}), can be correlated due to a solvation energy relation, SERLAS [7]. The assumption inherent in this approach is attributed to an additional effect of several physical parameters. The separation factor given by equation (2) and the modified distribution ratio (D_{M}) (*i.e.*, the ratio of the two-phases composition quantities including the mole fraction of overall components in the mixture), equation (3), all defined as *Pr* (log mean), can be expressed through a generalized log-basis equation (4). The quantity D_{M} was selected instead of distribution coefficient of acid D_2 ($D_2 = x''_2/x'_2$) to eliminate dealing with zero log value for $D = 1$

$$S = \frac{D_2}{D_1} = \frac{(x''_2/x'_2)}{(x''_1/x'_1)}, \tag{2}$$

$$D_{\mathrm{M}} = \frac{(x''_2 + x''_3)/(1 - x''_3)}{(x'_2 + x'_3)/(1 - x'_3)}, \tag{3}$$

$$Pr = F_1 Pr_0 + F_2 \cdot \sum_k \lfloor C_{\Gamma,k}(\Gamma_{\mathrm{L}})^k + C_{\mathrm{H},k}(\delta^*_{\mathrm{H}})^k + C_{\pi,k}(\pi^*)^k + C_{\beta,k}(\beta^*)^k + C_{\alpha,k}(\alpha^*)^k \rfloor, \tag{4}$$

where x'' and x' designate solvent-rich and water-rich compositions of water (1), acid (2), and solvent (3), respectively. D denotes the distribution coefficient of component. The model includes a part accounting for the properties at the composition limit of acid $x_2 = 0$ (Pr_0), and an expansion term with respect to the thermodynamic factor ($_{\mathrm{L}}$), the Hildebrand solubility parameter (δ_{H}), and the modified solvatochromic parameters $*$, α^*, and β^*. The corresponding Pr_0 properties attributed to the mutual solubility region ($x_2 = 0$) are defined as, $S_0 = (x''_{03}/x''_{01})/(x'_{03}/x'_{01})$ and $D_{\mathrm{M0}} = [x''_{03}/(1 - x''_{03})]/[x'_{03}/(1 - x'_{03})]$, where x_{03} and x_{01} denote the mole fractions of mutual solubility of solvent and water, respectively. Clearly, it has been selected the proposed quantity S_0 to be equal to the property D_{M0} at the limiting condition $x_2 = 0$ by reason of reducing a complex model structure.

Two composition dependent correction factors F_1 and F_2 are incorporated into Pr_0 and the expansion term to account for limiting conditions when either the physical interaction is zero for $x_2 = 0$ (*i.e.*, the end points of binodal curve reflecting the mutual solubility of both water and solvent in the absence of solute for which $Pr = Pr_0$) and the plait point of binodal curve at which the water-rich side composition is equal to the solvent-rich one, $x' = x''$, and extraction factors $S = 1$ and $D_{\mathrm{M}} = 1$. Estimates were performed assuming the composition dependent correction factors (F) to represent a solvent-basis composition ratio (F_1) and a water free correction factor (F_2), respectively. x_3 designates the mole fraction of organic solvent.

$$F_1 = \frac{\Delta x_3}{\Delta x_{3,max}} = \frac{x''_3 - x'_3}{x''_{03} - x'_{03}}; \quad F_2 = \frac{x''_3}{x''_2 + x''_3} - \frac{x'_3}{x'_2 + x'_3}. \tag{5}$$

Accordingly, for the plait point both F_1 and F_2 are equal to 0, and S and D_{M} are equal to 1. However, for the solute free region ($x_2 = 0$) $F_1 = 1$ and $F_2 = 0$ and the properties $Pr = Pr_0$, *i.e.* $S = S_0$ and $D_{\mathrm{M}} = D_{\mathrm{M0}}$. For a *n*-component system, thermodynamic factor ($_{\mathrm{L}}$) in terms of the transferring solute (acid) composition (x_2) relative to the organic phase is obtained by equation (6) due to Taylor and Kooijman [15]

$$\Gamma_{\mathrm{L}} = 1 + x_2 \cdot \partial(\ln \gamma_2)/\partial x_2|_{\Sigma}, \tag{6}$$

where, the symbol Σ (constrained condition) means that the differentiation with respect to the acid composition (x_2) is to be carried out while keeping all other mole fractions x_k ($k \neq j$, $k = 1, \ldots, n - 1$) constant except the *n*th. In this study, $_{\mathrm{L}}$ values were predicted from UNIFAC-Dortmund model using the derivative approaches for the activity coefficient (γ_i) of Mori et al. [16].

Modified solvatochromic parameters are evaluated as follows [8]:

$$\delta^*_{\mathrm{H}} = \delta_{\mathrm{H},2}\delta_{\mathrm{H,m}}1000; \quad \pi^* = (\pi_2 - 0.35\delta_2)\pi_{\mathrm{m}}; \quad \beta^* = \beta_2\beta_{\mathrm{m}}; \quad \alpha^* = \alpha_2\alpha_{\mathrm{m}}. \tag{7}$$

Index “2” designates the properties of the distributed (extracted) solute component. The subscript “m” denotes the parameters related to the mixture in terms of x composition in the organic phase, assuming the additional parameter estimation rule, *i.e.*, $\delta_{\mathrm{H,m}} = \sum_i x_i\delta_{\mathrm{H},i}$; $\pi_{\mathrm{m}} = \sum_i x_i(\pi_i - 0.35\delta_i)$; $\beta_{\mathrm{m}} = \sum_i x_i\beta_i$; $\alpha_{\mathrm{m}} = \sum_i x_i\alpha_i$,