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Influence of conventional diluents on amine extraction of picolinic acid

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Abstract

Distribution of picolinic acid between water and Alamine 336, a mixture of tertiary aliphatic amines, dissolved in various diluents of proton-donating and -accepting, polar and inert types, as well as a comparison with the extraction equilibria of pure diluent alone (1-octanol and 1,2-dichlorobenzene) have been studied at 298 K and the phase ratio of 1:1 (v/v). Cyclic alcohol/amine system yields the largest synergistic extraction efficiency. The strength of the complex solvation has been found to be reasonably high for halogenated aliphatic hydrocarbons promoting mainly the formation of acid_1–amine_1 structure. The influence of the acid structure over distribution has been evaluated through comparison of the extractabilities of five acids containing different functional groups, i.e., formic, levulinic, acetic, valeric, and picolinic acids. The results were correlated using various versions of the mass action law, i.e., a modified Langmuir equilibrium model and a chemical modeling approach comprising the formation of one or two acid–amine aggregated structures.

Keywords: Extraction equilibria; Picolinic acid; Alamine 336; Diluent; Modeling

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1. Introduction

Long-chain (C_8–C_{10}) aliphatic tertiary amines (e.g., Alamine 336; 308) dissolved in suitable organic diluents are effective extractants for carboxylic acids. Recently, extractive recovery of carboxylic acids by amine systems from aqueous solutions, such as fermentation broth and wastewater including lower than 10% (w/w) acid concentrations has received increasing interest [1–3]. Three major factors have been found to influence the equilibrium characteristics of amine extraction of carboxylic acids from aqueous solutions, i.e., the nature of acid, concentrations of acid and amine, and the type of diluent [1–5]. Simultaneously, the influence of additional controlling factors, such as the swing effect of a mixed diluent and the third phase formation can also modify the reversible complexation stage [6,7]. Process considerations dealing with the competition between physical extraction and chemical interaction of hydrophobic acids still remain a challenging problem since such systems show extremely nonideal behavior.

A project of extensive equilibrium studies with acid/amine systems has been fulfilled by King and co-workers [1–3]. They have concluded that characterization of acid–amine complexation is intimately connected to the solvation efficiency of diluent overly dependent on its polarity and hydrogen bonding affinity. However, the liquid–liquid equilibrium distribution of C_1–C_4 monocarboxylic acids into conventional solvents have been studied recently [8,9]. Also, a complex problem of achieving a synergistic or antagonistic effect pertaining to the extraction of polycarboxylic acids (e.g. citric and lactic acids) by a mixed extractant of a tertiary amine and a water-immiscible alkylphosphoric (or alkylphosphonic) acid has been thoroughly discussed [10,11]. The experimental studies of King and co-workers [1–3], Yang et al. [4] and Bízek et al. [5] revealed that Alamine 336 binds the nondissociated part of acid in the organic phase through reversible complexation. Recently, it has been found that the acid–base couple (amine-based) solvents extract both the undissociated and dissociated parts of the carboxylic acid [12]. The extraction power of Alamine 336 has been found to decrease in order, butyric acid > propionic acid > lactic acid > acetic acid [4].

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Nomenclature

$\overline{C_{\mathrm{d}}}$	concentration of acid extracted by the diluent (kmol/m^3)
$C_{\mathrm{H^+}}$	proton concentration of acid in the aqueous phase (kmol/m^3)
C_{HA}	concentration of undissociated acid in the aqueous phase (kmol/m^3)
$\overline{C_{\mathrm{HA}}}$	overall concentration of complexed acid (kmol/m^3)
$\overline{C_{(\mathrm{HA})_z(\mathrm{NR}_3)}}$	concentration of acid–amine complex (kmol/m^3)
$\overline{C_{\mathrm{NR}_3}}$	concentration of noncomplexed amine (kmol/m^3)
$\overline{C^0_{\mathrm{NR}_3}}$	initial concentration of amine in the solvent mixture (kmol/m^3)
$\overline{C^0_s}$	initial concentration of diluent in the solvent mixture (kmol/m^3)
C_{TA}	overall concentration of acid in the aqueous phase (kmol/m^3)
$\overline{C_{\mathrm{TA}}}$	overall concentration of acid in the organic phase (kmol/m^3)
C^0_{TA}	initial concentration of acid (kmol/m^3)
$\overline{C^{\mathrm{s}}_{\mathrm{TA}}}$	concentration of acid extracted by the diluent alone (kmol/m^3)
D	distribution ratio of acid referred to the amine mixture
D_0	distribution ratio of acid referred to the diluent alone
E	degree of extraction, extracted acid/initial acid (%)
$\bar{e}$	relative mean error (%)
HA	monocarboxylic acid
$\overline{(\mathrm{HA})_p(\mathrm{NR}_3)_q}$	acid–amine complex
$\overline{(\mathrm{HA})_z(\mathrm{NR}_3)}$	acid–amine complex
K_{a}	dissociation constant of acid
N	number of observation
NR_3	tertiary amine
p	number of acid molecules involved in the complex
q	number of amine molecules involved in the complex
s_{f}	modified separation factor for amine/diluent mixture
v	volume fraction of diluent in the solvent mixture
Z_{s}	stoichiometric loading of amine
Z_{t}	overall loading factor of amine
z	associated number
$\overline{\quad}$ (overbar)	species in the organic phase

Greek letters

β_{pq}	apparent equilibrium extraction constant ((kmol/m^3)$^{1-p-d}$)
β_z	equilibrium extraction constant ((kmol/m^3)$^{-z}$)
ε	dielectric constant
μ	dipole moment (C m)
σ	root-mean-square deviation

Subscripts

HA	undissociated acid
mod	modeled
obs	observed
TA	total acid

The effect of diluent mainly depends on its ability to solvate polar ion-pair organic species through dipole–dipole interaction or hydrogen bonding, favoring the formation of one or simultaneously at least two acid–amine complexes [1–7,10,11]. Interpretation of data including diluents from different classes (protic, nonprotic and inert) by Tamada et al. [2] and Bízek et al. [5] elucidated that the stoichiometry of acid–amine complexes is intimately connected to the strength of the complex solvation increasing in the order: aliphatic hydrocarbon < alkyl aromatic < halogenated aromatic < ketone < proton-donating halogenated hydrocarbon ≤ nitrobenzene ≤ alcohols. Attempts were also made to estimate the extraction equilibria of an acid/amine/diluent system through theoretically-based models of the mass action law including the physical interaction terms [5,10,13–15].

As an isomer of nicotinic acid (3-pyridine carboxylic acid), picolinic acid is the body's prime natural chelator of the vital trace elements chromium, zinc, manganese, copper, iron, and molybdenum. Picolinic acid, a natural product of tryptophan catabolism synthesized in the liver and kidney, is endowed with a variety of effects on ion traffic, cell cycle, bacterial growth, and host immune responses. It has protective and therapeutic effects against tumor. Commercially, picolinic acid is used as an intermediate to produce pharmaceuticals, herbicides and metal salts for the application of nutritional supplements. Picolinic acid is also an effective catalyst in the chromic acid oxidation of primary and secondary alcohols. The main purpose of this study is to generate liquid–liquid equilibrium data for the extraction of picolinic acid from water.

Distribution of picolinic acid (2-pyridine carboxylic acid) between water and Alamine 336 dissolved in various diluents, as well as the extraction capacity of pure diluent alone have been studied under isothermal conditions. This article also discusses the effect of the acid structure on the extraction power of solvents, as well as the competition between physical interaction and chemical reaction regarding the diluent used, i.e., the behavior of both ring included diluent and pro-