

Extraction equilibria of nicotinic acid using Alamine 336 and conventional solvents: effect of diluent

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Received 30 June 1999; received in revised form 31 July 2000; accepted 2 August 2000

Abstract

Distribution of nicotinic acid between water and Alamine 336, a mixture of tertiary aliphatic amines, dissolved in various (proton-donating and -accepting, polar and nonpolar) diluents, as well as a comparison with the extraction equilibria of pure diluent alone 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 and nitrobenzene promoting mainly the formation of acid₁–amine₁ structure. The influence of the acid structure over distribution has been evaluated through comparing the extractabilities of six acids containing different functional groups, i.e., benzoic, valeric, formic, levulinic, acetic and nicotinic acids. The results were correlated using various versions of the mass action law, i.e., a modified Langmuir equilibrium model and a chemodel approach comprising the formation of one or two acid–amine aggregated structures. © 2001 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Long-chain aliphatic tertiary amines (e.g., Alamine 336; 308) dissolved in suitable organic diluents are effective extractants for carboxylic acids. 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]. The implementation of amine extraction method argues an uncoupling of the behaviors relative to the diluent/complex interaction from the physical extraction of acid to formulate explicitly the dominating factors of complexation. 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 presented evidence of dependently varying the strength of acid/amine complexation with the solvation ef-

iciency of diluent being overly sensitive to its polarity and hydrogen bonding ability. However, the liquid–liquid equilibrium distribution of C₁–C₄ 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 coupled extractant of a tertiary amine and a water-immiscible alkylphosphoric (or alkylphosphonic) acid has been thoroughly discussed [10,11]. The spectroscopic studies of Yang et al. [4] revealed that Alamine 336 binds the nondissociated part of acid in the organic phase through reversible complexation. The extraction power of Alamine 336 has been found to decrease in order, butyric acid > propionic acid > lactic acid > acetic acid.

The effect of diluent is mainly focussed 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]. Commonly suggested (*p*, *q*) acid–amine complex formation of (1, 1), overloaded (*p*, 1) with *p* = 2–3, and not overloaded (1, *q*) with *q* = 2–3 structures depending on the nature of diluents have been theoretically treated to fit the data [2–6,10–12]. Interpretation of data including diluents from different classes 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

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Nomenclature

$\overline{C_{AM}}$	concentration of free (uncomplexed) amine (kmol/m ³)
$\overline{C_{AM}^0}$	initial concentration of amine in solvent mixture (kmol/m ³)
$\overline{C_d}$	concentration of acid extracted by the diluent (kmol/m ³)
C_{H^+}	proton concentration of acid in the aqueous phase (kmol/m ³)
C_{HA}	concentration of undissociated acid in aqueous phase (kmol/m ³)
$\overline{C_{HA}}$	overall concentration of complexed acid (kmol/m ³)
C_{TA}	the overall concentrations of acid in the aqueous phase (kmol/m ³)
$\overline{C_{TA}}$	the overall concentrations of acid in the organic phase (kmol/m ³)
$\overline{C_{TA}^0}$	initial concentration of acid (kmol/m ³)
C_{TA}^s	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 by the diluent alone
E	degree of extraction, extracted acid/initial acid (%)
\bar{e}	relative mean error (%)
HA	monocarboxylic acid
K_a	dissociation constant of acid
N	number of observations
NR ₃	tertiary amine
p	number of acid molecules involved in complex
q	number of amine molecules involved in complex
s_f	modified separation factor for amine/diluent mixture
v	volume fraction of diluent in solvent mixture
Z_s	stoichiometric loading factor of amine
Z_t	overall loading factor of amine
z	associated number

Greek letters

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

Subscripts

AM	amine
cal	calculated

HA	undissociated acid
max	maximum
obs	observed
TA	total acid

Superscripts

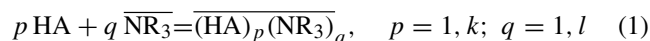
s	related to diluent
(overbar)	species in the organic phase

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 through theoretically based models of the mass action law including the physical interaction terms [5,10,12].

Distribution of nicotinic acid (3-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 at isothermal conditions. This article will also discuss 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. Results were correlated in terms of a chemodel approach and modified Langmuir equilibrium model.

2. Theoretical

Traditionally, characterization of the overall extraction equilibrium of acid/amine/diluent system is evaluated due to Eq. (1) using a chemical modeling approach of King and co-workers [1–3,5,10],



where HA and $\overline{\text{NR}_3}$ represent the undissociated acid in the aqueous phase and tertiary amine, respectively. Overbar denotes species in the organic phase. The activity coefficients of species in reaction (1) can be incorporated into the “conditioned” extraction constant defined in molarity scale, (kmol/m³)^{1-p-q}, as

$$\beta'_{pq} = \frac{\overline{C_{pq}}}{C_{HA}^p \overline{C_{AM}}^q}, \quad p = 1, k; q = 1, l \quad (2)$$

where C_{HA} , $\overline{C_{AM}}$ and $\overline{C_{pq}}$ denote the equilibrium concentrations of undissociated acid in the aqueous phase, free amine and acid–amine (p, q) complex, respectively. At a given temperature, β'_{pq} is expected to depend on the properties of acid and the solvation efficiency of diluent used. The total equilibrium content of complexed acid, $\overline{C_{HA}}$, is the sum of contributions of the individual complexes,

$$\overline{C_{HA}} = \sum_{p=1}^k \sum_{q=1}^l p \beta'_{pq} C_{HA}^p \overline{C_{AM}}^q \quad (3)$$

Using Eq. (3) in the balance equation for acid, the equilibrium model is derived,

$$C_{TA}^0 = \overline{C}_d + \overline{C}_{HA} + C_{TA} \quad (4)$$

where C_{TA}^0 , C_{TA} and \overline{C}_d represent the initial and total aqueous phase acid concentrations, and the concentration related to the acid portion physically extracted by the diluent, respectively. C_{HA} is calculated from C_{TA} , pH and the dissociation equilibrium in the aqueous phase due to Eq. (5) using pK_a values from Table 3,

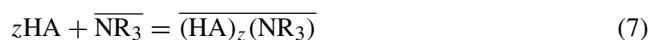
$$C_{HA} = \frac{C_{TA} C_{H^+}}{C_{H^+} + K_a} \quad (5)$$

where C_{H^+} and K_a designate the molar concentration of proton in the aqueous phase and the dissociation constant of acid, respectively. Interpretation of the extraction equilibrium results by many authors [2,5,10,12] revealed that all possible acid–amine (p, q) combinations for $p = 1-k$ and $q = 1-l$ should not be explicitly evaluated. In the prediction of equilibrium, different sets of the appropriate structure combinations have been selected for nicotinic acid, regarding the overall loading region and the maximum loading values, i.e., the plateau of the loading curve. Accordingly, aggregation of simple complexes into larger adducts has been assumed.

Poposka et al. [6] modified the Langmuir equilibrium model of Bauer et al. [13] assuming an overall acid–amine complexation with an associated number (z) related to maximum loading of amine, $z \equiv Z_{max}$, where the nondissociated acid molecules are regarded as “adsorbat”,

$$\frac{\overline{C}_{HA}}{(\overline{C}_{HA})_{max}} = \frac{\beta_z (C_{HA})^z}{1 + \beta_z (C_{HA})^z} \quad (6)$$

The extraction constant (β_z) in $(\text{kmol}/\text{m}^3)^{-z}$ is attributed to the overall reaction in terms of Eq. (7), assuming the formation of only one type of aggregated structure,



$$\beta_z = \frac{\overline{C}_{(\text{HA})_z(\text{NR}_3)}}{C_{HA}^z C_{AM}} \quad (8)$$

3. Experimental

3.1. Materials

Alamine 336 (Henkel), a C_8 – C_{10} saturated straight-chain tertiary amine mixture, is a pale yellow liquid practically insoluble in water (<5 ppm) with an average molecular weight of 392 g/mol and a density of 0.81 g/cm³. Nicotinic acid (pellagra preventive factor, 99.5%), as well as the organic solvents of analytical grade purity ($\geq 99.5\%$, GC) were furnished from Fluka. All the chemicals were used without further purification.

3.2. Experimental procedure

The extraction experiments were performed using equilibrium glass cells, each equipped with a magnetic stirrer and thermostated at 298 ± 0.1 K. The equal volumes (10 cm³) of initial aqueous and organic phases were agitated for 2 h and then left to settle for about 18–20 h at a fixed temperature (298 K) and pressure (101.2 kPa). The effective separation of the phases was ensured by centrifugation. Aqueous-phase pH was measured by Orion 601A pH-meter. Aqueous-phase acid concentration was determined by titration with aqueous NaOH (Titrosol A, Merck) and phenolphthalein indicator, as well as using an UV-spectrophotometer (Waters, Lambda M, Model 481, 263 nm). The acid content in the organic phase was determined by mass balance. Because the third phase formation was observed in preliminary experiments with amine/cyclic alcohol/acid system for aqueous acid concentrations varying above 0.125 kmol/m³, the initial acid concentrations were restricted in the range 0.01–0.101 kmol/m³. Tests covering the influence of diluents and the acid and amine concentrations on the extraction degree of nicotinic acid were performed using polar (1,2-dichloroethane, 1,2-DCE), protic (methylcyclohexanol), proton-accepting (cyclohexanone) and inert (xylene) diluents. The initial amine concentrations (C_{AM}^0) in the range 0.0207–0.207 kmol/m³, and the initial aqueous acid concentrations (C_{TA}^0) of 0.01, 0.025, 0.050, 0.076 and 0.101 kmol/m³ were used. The physical extraction of nicotinic acid was also studied. The effect of the acid structure was evaluated for benzoic, formic, acetic, valeric, levulinic and nicotinic acids using both Alamine 336/1-hexanol mixture, and pure diluents alone, 1,2-DCE and 1-hexanol.

4. Results and discussion

4.1. Criterion of extraction degree

The results were interpreted in terms of distribution ratio ($D = \overline{C}_{TA}/C_{TA}$, the ratio of the overall extracted acid to total aqueous-phase acid), degree of extraction (E (%) = $100D/(1 + D)$), overall (total) loading factor (Z_t), stoichiometric loading factor (Z_s), and modified separation factor (s_f). The overall loading factor of amine (Z_t) is the ratio of total amount of acid extracted to total amount of amine in the organic phase, $\overline{C}_{TA}/C_{AM}^0$. The stoichiometric loading factor, Z_s , is the ratio of the overall complexed acid to total amine in the organic phase. This factor includes a correction term, ($v C_{TA}^s$), for the amount of acid extracted by the diluent in mixture,

$$Z_s = \frac{\overline{C}_{TA} - v C_{TA}^s}{C_{AM}^0} \quad (9)$$

where v and C_{TA}^s denote the volume fraction of diluent in mixture, and amount of acid extracted by the pure

(amine-free) diluent alone, respectively. The relative proportion between physical interaction and chemical reaction was evaluated with respect to a modified separation factor, $s_f = \overline{C_{HA}}/\overline{C_{TA}}$, i.e., the ratio of the complexed acid to overall extracted acid.

4.2. Evaluation of results: factors influencing extraction degree

4.2.1. Effect of diluent

Study of the extraction system in Table 1 containing 0.101 kmol/m³ aqueous-phase acid solution and 0.0413 kmol/m³ (Alamine 336/diluent) mixture, tested for 18 different diluents, reveals that the physical extraction of nicotinic acid in pure diluent alone is remarkably small with a distribution ratio of about 1 for methylcyclohexanol ($D_0 = 0.924$), and less than 1 for others ranging

from 0.005 for hydrocarbons and dipropyl ether to 0.8–0.9 for some cyclic alcohols, but all disapprovingly not convenient as separation agents. The noticeably low extraction degree of nicotinic acid in polar diluents, e.g., 1,2-dichlorobenzene ($\mu = 7.54 \times 10^{-12}$ C m) and nitrobenzene ($\mu = 13.3 \times 10^{-12}$ C m) [14] yielding D_0 values of 0.01 and 0.004, respectively, may be attributed to the formation of intramolecular hydrogen bonding due to the second proton accepting group in pyridine ring. Accordingly, chlorinated hydrocarbons and ethers exhibit a low extraction ability related to $D_0 < 0.05$. Aprotic ketones and benzyl acetate solvents as well as protic 1-hexanol, containing oxygenated hydrogen bonding functional groups, yield different D_0 ranging from 0.07 to 0.67 regarding the diluent polarity and hydrogen-bonding ability. Conversely, the amine/diluent system favors the formation of not overloaded polar acid–amine structures ($p \leq q$) corresponding

Table 1

Liquid–liquid equilibrium results for Alamine 336/diluent/nicotinic acid system at 298 K ($C_{TA}^0 = 0.101$ kmol/m³; $\overline{C_{AM}^0} = 0.0413$ kmol/m³)

Solvent	pH	C_{TA} (kmol/m ³)	D	E (%)	Z_t	Z_s	s_f	(p, q) ^a , β_z ^b
<i>n</i> -heptane	3.48	0.1004	0.006	0.59				(1, 15), 8.28
+Alamine 336	3.50	0.0980	0.031	2.97	0.073	0.058	0.804	
Xylene	3.48	0.1002	0.008	0.79				(1, 5), 53.51
+Alamine 336	3.51	0.0922	0.095	8.71	0.213	0.194	0.911	
Cyclohexane	3.48	0.0996	0.014	1.39				(1, 10), 6.21
+Alamine 336	3.50	0.0962	0.050	4.75	0.116	0.083	0.714	
Chlorobenzene	3.48	0.0998	0.012	1.19				(2, 3), 141.93
+Alamine 336	3.58	0.0734	0.376	27.33	0.668	0.640	0.957	
1,2-DCB ^c	3.48	0.1000	0.010	0.99				(2, 3), 141.01
+Alamine 336	3.57	0.0736	0.372	27.13	0.663	0.640	0.964	
Chloroform	3.48	0.0997	0.013	1.29				(1, 1), 264.51
+Alamine 336	3.61	0.0610	0.656	39.60	0.969	0.938	0.968	
1,2-DCE ^c	3.48	0.0990	0.020	1.98				(1, 1), 131.52
+Alamine 336	3.60	0.0625	0.616	38.12	0.932	0.885	0.949	
Cyclohexanone	3.59	0.0635	0.591	37.13				(2, 3), 56.21
+Alamine 336	3.68	0.0405	1.494	59.90	1.465	0.575	0.393	
MIBK ^c	3.52	0.0890	0.135	11.88				(2, 3), 133.99
+Alamine 336	3.59	0.0630	0.603	37.62	0.920	0.635	0.691	
MEK ^c	3.61	0.0605	0.669	40.10				(2, 3), 33.14
+Alamine 336	3.69	0.0397	1.544	60.69	1.484	0.523	0.353	
Nitrobenzene	3.48	0.1006	0.004	0.40				(1, 1), 248.08
+Alamine 336	3.61	0.0620	0.629	38.61	0.944	0.935	0.990	
Dipropyl ether	3.47	0.1006	0.004	0.40				(1, 9), 72.73
+Alamine 336	3.50	0.0961	0.051	4.85	0.119	0.109	0.920	
Dibenzyl ether	3.50	0.0977	0.034	3.27				(2, 3), 167.16
+Alamine 336	3.59	0.0712	0.419	29.50	0.722	0.643	0.891	
Benzyl acetate	3.51	0.0943	0.071	6.63				(3, 4), 464.85
+Alamine 336	3.59	0.0640	0.578	36.63	0.896	0.737	0.823	
MCHol ^c	3.63	0.0525	0.924	48.02				(1, 2), 78.87
+Alamine 336	3.71	0.0342	1.953	66.14	1.617	0.467	0.288	
Cyclopentanol	3.63	0.0530	0.906	47.52				(1, 2), 614.58
+Alamine 336	3.71	0.0335	2.015	66.83	1.634	0.495	0.303	
Cyclohexanol ^d	3.60	0.0630	0.603	37.62				(1, 2), 143.98
+Alamine 336	3.68	0.0438	1.306	56.63	1.385	0.483	0.349	
Benzyl alcohol	3.63	0.0540	0.870	46.53				(1, 2), 156.81
+Alamine 336	3.71	0.0350	1.886	65.35	1.598	0.483	0.302	

^a Probable acid (p)/amine (q) structure referred to Eq. (7).

^b Equilibrium constant in (kmol/m³)^{-z} due to Eq. (10) assuming $z = Z_{s,max} = p/q$.

^c 1,2-DCB: 1,2-dichlorobenzene, 1,2-DCE: 1,2-dichloroethane, MIBK: methylisobutyl ketone, MEK: methylethyl ketone, MCHol: methylcyclohexanol.

^d Values obtained at 303 K.

Table 2

Extractability of monocarboxylic acids for Alamine 336/acid/1-hexanol system at 298 K ($C_{TA}^0 = 0.101 \text{ kmol/m}^3$; $\overline{C_{AM}^0} = 0.0413 \text{ kmol/m}^3$)^a

		pH	C_{TA} (kmol/m ³)	D	E (%)	Z_t	Z_s	s_f	$(p, q)^b, \beta_z^b$
d	N	3.55	0.0768	0.315	23.96				(3, 4), 98.48
m		3.65	0.0492	1.053	51.29	1.254	0.680	0.542	
d	F	2.67	0.0752	0.343	25.54				(3, 4), 438.34
m		2.81	0.0455	1.220	54.95	1.344	0.732	0.544	
d	L	3.23	0.0742	0.361	26.53				(2, 3), 40.45
m		3.32	0.0515	0.961	49.01	1.199	0.563	0.469	
d	A	3.26	0.0690	0.464	31.68				(1, 2), 180.87
m		3.34	0.0495	1.040	50.99	1.247	0.488	0.391	
d	V	3.86	0.0058	16.414	94.26				(1, 8), 17.34
m		4.12	0.0031	31.581	96.93	2.370	0.111	0.047	

^a N: nicotinic acid, F: formic acid, L: levulinic acid, A: acetic acid, V: valeric acid, d: referred to properties of pure 1-hexanol alone, m: referred to Alamine 336/1-hexanol mixture.

^b As defined in Table 1.

to the Z_s factors restricted mainly between 0.45 and 0.95, except for xylene, dipropyl ether and hydrocarbons yielding $Z_s < 0.2$. The highest strength of the complex solvation has been found for 1,2-dichloroethane ($Z_s = 0.885$, $s_f = 0.949$), chloroform ($Z_s = 0.938$, $s_f = 0.968$) and nitrobenzene ($Z_s = 0.935$, $s_f = 0.990$) promoting probably (1, 1) acid–amine complex formation related to at least 20–25 times larger D as compared to the pure diluent one. In fact, all the tested halogenated compounds and nitrobenzene are good solvating agents for nicotinic acid–amine complexation giving $s_f \geq 0.95$. The same remark holds for the diluents containing benzene ring in the structure, i.e., benzyl acetate ($Z_s = 0.737$, $s_f = 0.823$), dibenzyl ether ($Z_s = 0.643$, $s_f = 0.891$), and xylene ($Z_s = 0.194$, $s_f = 0.911$), except for protic benzyl alcohol ($s_f = 0.302$) that is indicative for the complementary interaction between aromatic π systems at the complexation stage leading to a high solvation degree.

It can be argued that the synergistic extraction power of amine/alcohol and amine/ketone systems is remarkably larger yielding $D > 1$, except for methyl isobutyl ketone, MIBK ($D = 0.603$) due to the simultaneous effect of the physical extraction and the diluent–complex interaction through hydrogen bonding. In spite, these diluents exhibit a moderate solvation efficiency related to Z_s of about 0.5 and $s_f < 0.40$ (except for 1-hexanol, $Z_s = 0.680$), activating probably a (1, 2) acid–amine complexation. Referring to Tables 1 and 2, the order of increased extraction efficiency of pure diluent alone, as well as the most probable nicotinic acid–amine (p, q) complexation appear as follows:

n -heptane (1, 15) \cong nitrobenzene (1, 1)
 \cong dipropyl ether (1, 9) < cyclohexane (1, 10)
 < 1, 2-dichlorobenzene (2, 3)
 < chlorobenzene (2, 3) \cong chloroform (1, 1)
 < xylene (1, 5) < 1, 2-dichloroethane (1, 1)

< dibenzyl ether (2, 3) < benzyl acetate (3, 4)
 < MIBK (2, 3) < 1-hexanol (3, 4)
 < cyclohexanone (2, 3)

< cyclohexanol (1, 2) < methylethyl ketone (2, 3)
 < benzyl alcohol (1, 2) < cyclopentanol (1, 2)
 < methylcyclohexanol (1, 2).

Correspondingly, the extraction power of amine/diluent system in terms of Z_t or D increases as follows:

n -heptane < cyclohexane < dipropyl ether < xylene
 < 1, 2-dichlorobenzene < chlorobenzene
 < dibenzyl ether < benzyl acetate

< MIBK < 1, 2-dichloroethane < nitrobenzene
 < chloroform < 1-hexanol < cyclohexanol
 < cyclohexanone < methyl ethyl ketone

< benzyl alcohol < methylcyclohexanol < cyclopentanol.

It is recognized that no evidence of overloading of amine ($Z_s > 1$) has been observed in any of the systems tested. The highest synergistic extraction efficiency yields amine mixtures of alcohols and cyclohexanone ($Z_t \approx 1.5$). This fact can be elucidated by assuming the simultaneous formation of at least two acid–amine complexes or a more complicate aggregation which are affected by the diluent in different ways regarding its polarity and hydrogen-bonding ability. (3, 4) complex formation represents the aggregation of (1, 2) and (1, 4) structures.

The equilibrium data from Tables 1 and 2 were interpreted in terms of a modified Langmuir model using the concepts of Poposka defined by Eqs. (7) and (8). The assumption

inherent in this approach is attributed to a total concentration of complexed acid ($\overline{C_{HA}} = z \overline{C_{(HA)_z(NR_3)}}$) evaluated from Eq. (8) and $z = Z_{s,max}$,

$$Z_t = \frac{\overline{C_d} + \overline{C_{HA}}}{C_{AM}^0} = \frac{vD_0 C_{TA}^0}{(1 + D_0) C_{AM}^0} + \frac{z\beta_z (C_{HA})^z \overline{C_{AM}}}{C_{AM}^0} \quad (10)$$

where $\overline{C_d} = vD_0 C_{TA}^0 / (1 + D_0)$ represents the concentration of the physically extracted acid part by the diluent. D_0 is the distribution ratio of acid referred to the diluent alone. β_z was correlated by Eq. (10) supposing the p/q ratio in Tables 1 and 2 to represent the associated number of the complex formation related to the maximum loading, $z = Z_{s,max} = p/q$.

4.2.2. Effect of acid: synergistic extraction power of amine/diluent system

Besides the diluent solvation power, an inherent concern is the group contribution effect of the acid structure that is a prerequisite for proceeding with the extraction method. It turns out from Fig. 1 and Table 2 that the longer R-chain of valeric (1-pentanoic) acid (V) and benzene ring of benzoic acid (B) make these acids more hydrophobic and thus more easily to extract by polar (1,2-DCE) and protic (1-hexanol) diluents alone, yielding D_0 values about 50 times larger, as compared to those of less hydrophobic formic acid (F) having no R-chain structure, and nicotinic (N) and levulinic (4-oxovaleric) acids both capable of intramolecular hydrogen bonding due to the second proton accepting group. Also, the existence of only 1 methyl group on acetic acid (A) and the carbonyl group (CO) on levulinic acid (L) categorize

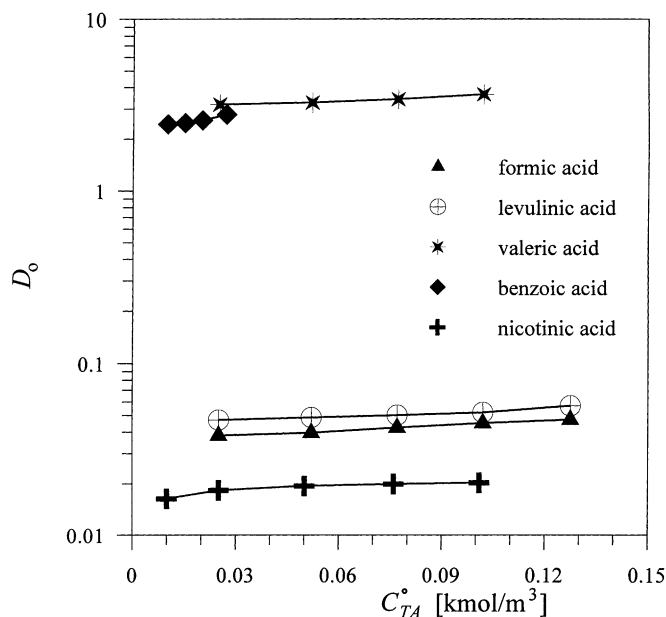


Fig. 1. Physical extraction of monocarboxylic acids by 1,2-dichloroethane. Comparison of extraction isotherms in terms of distribution ratio (D_0).

Table 3

Dipole moments, dielectric constants and pK_a values of acids [14–16]

Acid	pK_a (298 K) [14,15]	ϵ^a	$(\mu \times 10^{12})^a$ (C m)
Nicotinic acid	4.750		
Formic acid	3.751	58.50	4.70
Acetic acid	4.756	6.15	2.80
Valeric acid	4.842	2.66	2.10 ^b
Levulinic acid	4.590		
Benzoic acid	4.204		5.67 ^c

^a Values at 293 K.

^b Value obtained for isovaleric acid (3-methyl butanoic acid).

^c Value at 403 K.

both acid structures as more hydrophilic and less capable to association with diluent. These concepts can be confirmed by the results from Table 2 for Alamine 336/1-hexanol system manifesting that the controlling factor for physical extraction is hydrophobicity of acid related to the extraction degree of acid in pure 1-hexanol alone ranging as, $N < F < L < A \ll V$. Referring to the acid properties from Table 3, it is reasonable to conclude that the polarity and solvation ability of the formed structures at complexation stage are more strongly affected by both the polarity and the ionizing strength of acid distinguishing the divergent behaviors relative to the hydrophilic (e.g., $\mu_F = 4.7 \times 10^{-12}$ C m, $\epsilon_F = 58.5$ and $pK_{a,F} = 3.751$ for formic acid) and hydrophobic (e.g., $\mu_V = 2.1 \times 10^{-12}$ C m, $\epsilon_V = 2.66$ and $pK_{a,V} = 4.842$ for valeric acid) acid structures [14–16]. This is in accordance with lower factors of $Z_{s,V} = 0.111$ and $s_{f,V} = 0.047$ for valeric acid clarifying that weaker interactive forces appear during valeric acid–amine complexation. Formic and nicotinic acids are more sensitive to acid–base type complexation with amine ($Z_{s,F} = 0.732$, $s_{f,F} = 0.544$; $Z_{s,N} = 0.680$, $s_{f,N} = 0.542$) than valeric and levulinic acids, due to the high polarity ($\epsilon_F = 58.5$) and ionizing strength of formic acid, and the influence of electronegative aromatic π system in nicotinic acid reflecting probably dipole–dipole interaction through hydrogen-bonding accompanying the multiple effects at carboxyl group and pyridine ring (aromatic π system). Consequently, it is expected the polarity and the ionizing strength of acid to control the complex formation of acid–base type of structures with different polarity that may influence the solvation degree. Nevertheless, the large differences among D and Z_s values for nicotinic acid in different diluents (Table 1) indicate that the complex solvation by the diluent is a critical factor in amine extraction of acids studied. These findings, among other factors, are comprehensively supported by the results for the relative proportion of physical interaction and chemical reaction (s_f) from Figs. 2 and 3 presuming that different mechanisms control one or simultaneously at least two acid–amine complex formation depending on the solvation degree of diluent. However, it is essential that this phenomenon will have a significant impact on the implementation of a selected extraction method.

To estimate the strength of the complex solvation depending on the acid and amine concentrations runs were

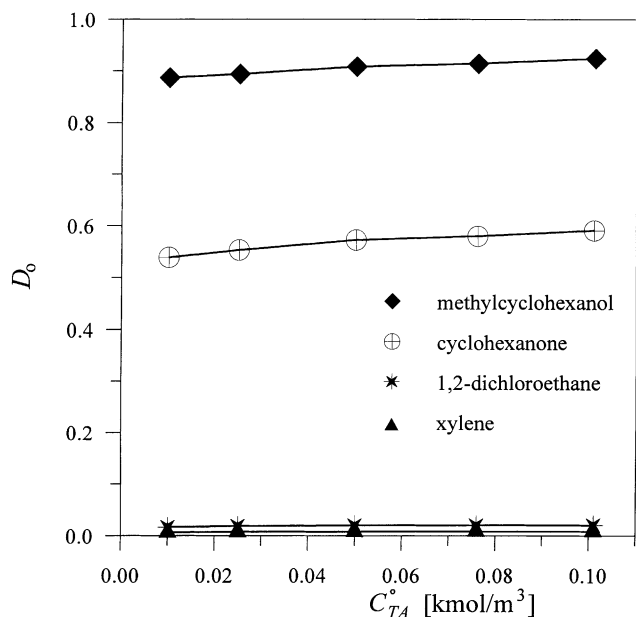


Fig. 2. Physical extraction of nicotinic acid by conventional solvents. Variation of distribution ratio (D_0) with aqueous-phase acid concentration.

performed using methylcyclohexanol, cyclohexanone, 1,2-DCE, and xylene diluents in amine mixture. The equilibrium results for diluent alone and amine/diluent mixture are presented in Figs. 2–5. It is apparent from Fig. 4 that the maximum stoichiometric loading ($Z_{s,max}$) corresponding to the plateau in the loading curve appears at $Z_{s,max} \leq 1$, contemplating a tendency towards the formation of two types of nicotinic acid–amine structures, i.e., an equimolar structure ($p = q$), and an aggregation related to the acid per multiple amines ($p < q$) structure. This fact seems to

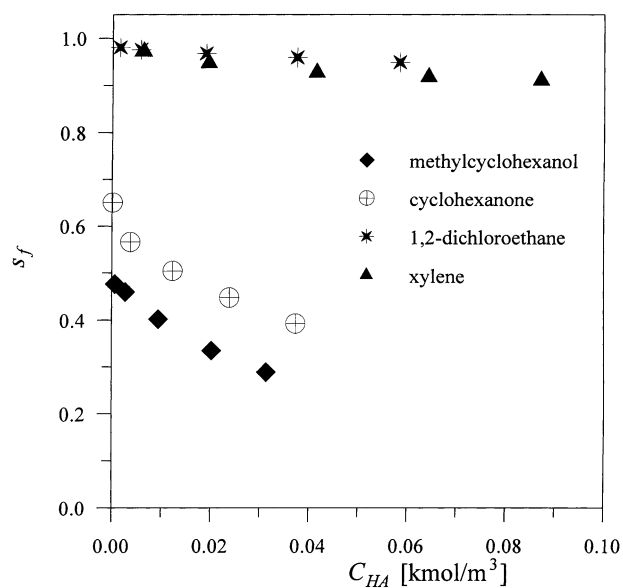


Fig. 3. Variation of separation factor with aqueous-phase nicotinic acid concentration ($C_{AM}^0 = 0.0413 \text{ kmol/m}^3$).

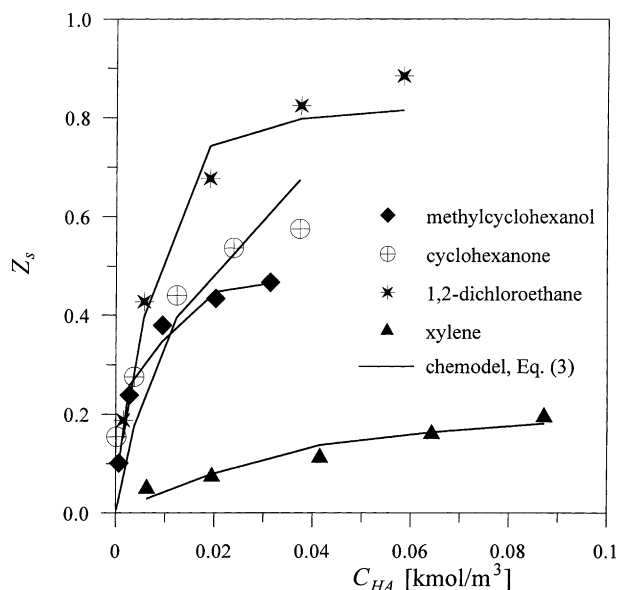


Fig. 4. Variation of loading with aqueous-phase nicotinic acid concentration ($C_{AM}^0 = 0.0413 \text{ kmol/m}^3$). Comparison with estimates through chemodel, Eq. (3).

be a common strategy for designing the amine extraction of nicotinic acid. The effect is more pronounced in the case of polar 1,2-DCE diluent, affecting more readily the diluent–complex interaction than the diluent–acid association, that is indicative from the remarkably high Z_s (Fig. 4) with a maximum about 1 ($Z_{s,max} \approx 1$) in contrast to the rather low D_0 (Fig. 2), as compared to the same quantities of the other diluents. The same remark holds for the $Z_{s,max}$ values estimated from Figs. 4 and 5 as, 0.50, 0.67, 0.20 and

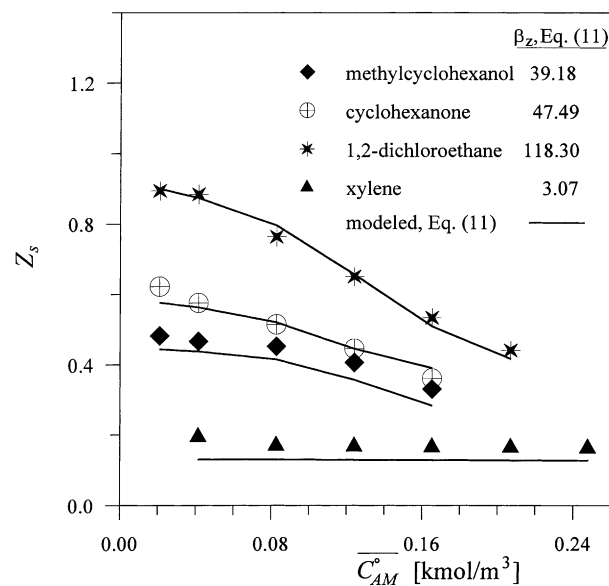


Fig. 5. Variation of loading with amine concentration (nicotinic acid concentration, $C_{TA}^0 = 0.101 \text{ kmol/m}^3$). Comparison with estimates through Eq. (11).

Table 4

Extraction constants of Eq. (3), and root-mean-square deviation (σ) and mean relative error (\bar{e}^a) of chemodel estimates for nicotinic acid–amine complexation

Diluent		Complex I: $\beta'_{pq}; (p, q)$ (kmol/m^3) $^{1-p-q}$	Complex II: $\beta'_{pq}; (p, q)$ (kmol/m^3) $^{1-p-q}$	$\sigma(Z_t)$	$\bar{e}(Z_t)$ (%)
Xylene	T ^b	$0.19350 \times 10^1; (1, 1)$	$0.22745 \times 10^4; (1, 3)$	0.0155	13.77
	S ^b	$0.13382 \times 10^3; (1, 2)$		0.0159	14.06
1,2-DCE ^c	S	$0.12111 \times 10^3; (1, 1)$		0.0730	9.33
Cyclohexanone	T	$0.71762 \times 10^2; (1, 1)$	$0.82047 \times 10^6; (2, 3)$	0.0809	12.23
	S	$0.28848 \times 10^8; (2, 3)$		0.1470	21.72
Methylcyclohexanol	T	$0.59678 \times 10^4; (1, 2)$	$0.22310 \times 10^7; (2, 3)$	0.0179	2.04
	S	$0.88586 \times 10^4; (1, 2)$		0.2450	17.85

^a $\bar{e} = (100/N) \sum_{N=1}^N |(Z_{t,\text{obs}} - Z_{t,\text{cal}})/Z_{t,\text{obs}}|$.

^b One (S) or two (T) complex formation (T used in figures).

^c 1, 2-DCE = 1, 2-dichloroethane.

1.0, for methylcyclohexanol, cyclohexanone, xylene and 1,2-DCE, respectively.

4.3. Model estimates and reliability analysis

The results, presented in Figs. 2–5, were interpreted in terms of the chemodel approach and an overall apparent extraction constant due to Eqs. (3) and (4). Fig. 4 illustrates the increased solvation efficiency of diluent with increasing the acid concentration, related to the extraction power of diluent alone and a probable single acid–amine (p, q) aggregation as, methylcyclohexanol (1, 2) > cyclohexanone (2, 3) > 1, 2-DCE (1, 1) \cong xylene (1, 2). However, the chemodel presumes the formation of at least two complexes. Estimates were performed using the multivariable procedures of lin-pack algorithm [17] for 1, 2 and 3 selected appropriate complex combinations regarding Z_s . The best fits display the approach comprising the simultaneous formation of two associated acid–amine (p, q) structures of different stoichiometry (except for 1,2-DCE) depending on the diluent used, i.e., (1, 2) and (2, 3) for methylcyclohexanol, (1, 1) and (2, 3) for cyclohexanone, (1, 1) for 1,2-dichloroethane, and (1, 1) and (1, 3) for xylene. Table 4 presents a quantitative assessment of the predicted equilibrium constants (β'_{pq}) for one (S) and two (T) selected individual complexes in terms of the mean relative error (\bar{e} , %) and root-mean-square deviation (σ) of Z_t factor. The model reliability was also studied through a plot of modeled values (for two selected combinations) against observed performance (Fig. 4). Referring to the β'_{pq} definition and concerned complex formation from Table 4, the chemodel matches the overall experimental Z_t and Z_s data with an average error $\bar{e} = 11\%$ ($\bar{e}(Z_t) = 9.3\%$ and $\bar{e}(Z_s) = 12.7\%$).

Fig. 5 illustrates the influence of the amine concentration on stoichiometric loading (Z_s). Since the nonpolar Alamine 366 by itself is a relatively poor solvating medium for the polar complexes, loading decreases with increasing amine concentration as the active (methylcyclohexanol, 1,2-DCE, cyclohexanone) solvent becomes a less favorable solvating agent. For the nonpolar mixture of inert diluent (xylene)

and amine, increasing the amine concentration, however, has little effect upon loading. The equilibrium data from Figs. 2–5 were also correlated with respect to the modified approach of Paposka for β_z defined by Eq. (6) assuming that $z = Z_{s,\text{max}} = (\overline{C_{\text{HA}}})_{\text{max}}/C_{\text{AM}}^0$. The model was rearranged through incorporating $\overline{C_{\text{HA}}}$ from Eq. (6) into Eq. (11) to give a sentence structure including both physical and chemical interaction terms,

$$Z_t = \frac{\overline{C_d} + \overline{C_{\text{HA}}}}{C_{\text{AM}}^0} = \frac{vD_0C_{\text{TA}}^0}{(1 + D_0)C_{\text{AM}}^0} + \frac{z\beta_z(C_{\text{HA}})^z}{1 + \beta_z(C_{\text{HA}})^z} \quad (11)$$

The estimated β_z values in (kmol/m^3) $^{-z}$ by Eq. (11) depending on the acid and amine concentrations are given in Fig. 5. The maximum loading values ($z = Z_{s,\text{max}}$) of 0.20, 1.0, 0.67 and 0.50 for nicotinic acid related to xylene, 1,2-DCE, cyclohexanone and methylcyclohexanol, respectively, were performed. The reliability analysis of Eq. (11) results in a root-mean-square deviation of 0.042 for Z_s (Fig. 5). The model is expected to be an improvement in data fit for the associated acid–amine systems, reproducing the Z_t and Z_s data for active diluents with an average error of 10.25% ($\bar{e}(Z_t) = 7.2\%$ and $\bar{e}(Z_s) = 13.3\%$). The reliability of Eq. (11) proved to be disappointingly less accurate for inert diluent (xylene) yielding $\bar{e}(Z_t) = 32.95\%$ ($\sigma = 0.0439$).

Figs. 4 and 5 and Table 4 illustrate the consistency of predictions achieved for both the chemodel and the modified Langmuir approach, defined by Eqs. (3) and (11), respectively. Consequently, both approaches proved to be reasonably accurate, yielding $\bar{e}(\%)$ and σ (kmol/m^3) with regard to $\overline{C_{\text{TA}}}$ variable of 9.34% and 0.0029 for Eq. (3) and 13.65% and 0.0033 for Eq. (11) considering all the systems studied.

5. Conclusions

The isothermal equilibrium distribution of nicotinic acid onto aqueous/organic two-phase system containing Alamine 336 as a reactive extractant has been elucidated by simultaneous effects of chemical and physical interactions closely

related to the nature of diluent used. The distribution degree of nicotinic acid in conventional solvents is rather low ranging less than 1, or about 1 for some cyclic alcohols ($D_0 \leq 1$). The highest synergistic extraction efficiency was found for the amine/cyclic alcohol system.

Characterization of acid/amine complexation is intimately connected to the solvation efficiency of diluent sensitively depending on its polarity and hydrogen bonding affinity. The way to formulate a design strategy for nicotinic acid–amine complexation including both physical and chemical interaction variables along with contribution of not overloaded ($p \leq q$) structures has been discussed. Halogenated aliphatic hydrocarbons and nitrobenzene yield the largest strength of the complex solvation, promoting probably (1, 1) acid–amine complex formation referred to $Z_{s,max} \approx 1$. Chemodel presumes the formation of two aggregated acid–amine structures of type: (1, 2) and (2, 3) for methylcyclohexanol, (1, 1) and (2, 3) for cyclohexanone, (1,1) for 1,2-DCE, and (1, 1) and (1, 3) for xylene. Much research in these phenomena remains to be done, above all at different isothermal conditions with mixed diluents to estimate the factors modifying the regeneration stage.

Acknowledgements

The author thanks Henkel Co. for providing Alamine 336. The author is also grateful to Dr. Gulceray Senol for the technical support of this study.

References

- [1] A.S. Kertes, C.J. King, J. Biotechnol. Bioeng. 28 (1986) 269–282.
- [2] J.A. Tamada, A.S. Kertes, C.J. King, Ind. Eng. Chem. Res. 29 (1990) 1319–1326.
- [3] J.A. Tamada, C.J. King, Ind. Eng. Chem. Res. 29 (1990) 1327–1333.
- [4] S.T. Yang, S.A. White, S.T. Hsu, Ind. Eng. Chem. Res. 30 (1991) 1335–1342.
- [5] V. Bízek, J. Horáček, M. Koušová, Chem. Eng. Sci. 48 (1993) 1447–1457.
- [6] F.A. Poposka, K. Nikolovski, R. Tomovska, J. Chem. Eng. Jpn. 30 (1997) 777–785.
- [7] A. Heyberger, J. Procházka, E. Volaufova, Chem. Eng. Sci. 53 (1998) 515–521.
- [8] G. Malmay, M. Faizal, J. Albet, J. Molinier, J. Chem. Eng. Data 42 (1997) 985–987.
- [9] M.A. Reinsel, J.J. Borkowski, J.T. Sears, J. Chem. Eng. Data 39 (1994) 513–516.
- [10] R.S. Juang, R.H. Huang, Chem. Eng. J. 65 (1997) 47–53.
- [11] R.S. Juang, W.T. Huang, J. Chem. Eng. Jpn. 27 (1994) 498–504.
- [12] T. Kirsch, G. Maurer, Ind. Eng. Chem. Res. 35 (1996) 1722–1735.
- [13] U. Bauer, R. Marr, W. Ruckl, M. Siebenhofer, Ber. Bunsen-Ges. Phys. Chem. 93 (1989) 980–984.
- [14] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents. Physical Properties and Methods of Purification, 4th Edition, Wiley/Interscience, New York, 1986.
- [15] J.A. Dean, Lange's Handbook of Chemistry, 30th Edition, McGraw-Hill, New York, 1985.
- [16] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th Edition, McGraw-Hill, New York, 1987.
- [17] D.M. Himmelblau, Basic Principles and Calculations in Chemical Engineering, 5th Edition, Prentice-Hall, Englewood Cliffs, NJ, 1989.