Extraction Equilibria of Nicotinic Acid Using Alamine 300/Diluent and Conventional Solvent Systems

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The distribution of nicotinic acid between water and Alamine 300 (tri-n-octylamine) dissolved in various (proton-donating and -accepting, polar and nonpolar) diluents, and a comparison with the extraction equilibria of pure diluent alone were studied at 298 K and a phase ratio of 1:1 (v/v). The cyclic alcohol/amine system yielded the highest synergistic extraction efficiency. The strength of the complex solvation was found to be reasonably high for halogenated aliphatic hydrocarbons and nitrobenzene, activating mainly the formation of the acid$_1$-amine$_1$ structure. The influence of the acid structure over distribution was evaluated through comparing the extractabilities of three acids containing different functional groups, i.e., nicotinic, benzoic and valeric acids. The results were correlated using versions of the mass action law, i.e., a modified Langmuir equilibrium model and a chemodel modelling approach comprising one or two acid-amine complex formation.

Key Words: Extraction equilibria, Nicotinic acid, Alamine 300, Modeling

Introduction

Long-chain, aliphatic tertiary amines (e.g., Alamine 336; 300) dissolved in suitable organic solvents are effective extractants for carboxylic acids$^{1-5}$. 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 the acid, concentrations of acid and amine, and the type of diluent$^{1-5}$. Simultaneously, the effect 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 the chemical interaction of hydrophobic acids remain a challenging problem since such systems show extremely nonideal behavior.

A project of extensive equilibrium studies with acid/amine systems was carried out by King and co-workers$^{1-3}$. The spectroscopic studies carried out by Yang et al.$^4$ revealed that Alamine binds the nondissociated part of acid in the organic phase through reversible complexation. The effect of diluent is mainly focused on its ability to solvate polar ion-pair organic species through dipole-dipole interaction or

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hydrogen bonding, favoring the formation of one or simultaneously two or more acid-amine complexes. The extraction results of Tamada et al.\textsuperscript{2} and Bizek et al.\textsuperscript{5} including diluents from different classes confirmed that the stoichiometry of acid-amine complexation is dependent on the strength of complex solvation by the diluent increasing in the following order: hydrocarbon $<$ halogenated aromatic $<$ ketone $<$ proton-donating halogenated aliphatic hydrocarbon $<$ nitrobenzene $\leq$ alcohols.

The distribution of nicotinic acid (3-pyridine carboxylic acid) between water and Alamine 300 dissolved in various diluents, and a comparison with the extraction capacity of pure diluent alone were studied at 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. Results were correlated in terms of a chemical modeling approach (chemodel) and modified Langmuir equilibrium model.

### Theoretical

Using the chemical modeling approach of Tamada et al.\textsuperscript{2}, the overall extraction equilibrium of the acid/amine/diluent system can be described by the set of reactions (1)

$$ pH_A + qNR_3 = (HA)_p(NR_3)_q \quad p = 1, k; q = 1, l $$

where $HA$ = the nondissociated acid in the aqueous phase and $NR_3$ = tertiary amine. The overbar denotes species in the organic phase. Supposing the ratio of activity coefficients of species to be constant for a given temperature, it can be incorporated into the “conditioned” extraction constant defined in molarity scale $[(\text{kmol/m}^3)^{1-p-q}]$ as

$$ \bar{\beta}_{pq} = \frac{C_{pq}}{C_{HA} C_{AM}} \quad p = 1, k; q = 1, l $$

where $C_{HA}$, $C_{AM}$ and $C_{pq}$ represent the equilibrium concentrations of undissociated acid in the aqueous phase, free amine and acid-amine $(p,q)$ complex (kmol/m\textsuperscript{3}), respectively. At a given temperature, $\bar{\beta}_{pq}$ is expected to depend on the properties of acid and the solvation efficiency of the diluent used. The total equilibrium content of complexed acid, $C_{HA}$, is the sum of contributions of the individual complexes:

$$ C_{HA} = \sum_{p=1}^{k} \sum_{q=1}^{l} p \cdot \bar{\beta}_{pq} \cdot C_{HA}^p \cdot C_{AM}^q $$

Incorporating Eq. (3) into the balance equation for acid, the equilibrium model is derived:

$$ C_{TA}^p = C_d + C_{HA}^p + C_{TA} $$

where $C_{TA}^p$, $C_{TA}$ and $C_d$ represent the initial and total aqueous phase acid concentrations and the concentration related to the acid portion physically extracted by the diluent in the solvent mixture, respectively. $C_{HA}$ is calculated from $C_{TA}$, pH and the dissociation equilibrium in the aqueous phase due to Eq. (5) ($pK_a = 4.75$ for nicotinic acid).

$$ C_{HA} = C_{TA} \cdot C_{H^+}/(C_{H^+} + K_a) $$
where $C_{H^+}$ and $K_a$ denote the molar concentration of protons in the aqueous phase and the dissociation constant of acid, respectively. The results of investigated amine systems revealed that all possible acid-amine $(p,q)$ combinations for $p = 1 \sim k$ and $q = 1 \sim l$ should not be explicitly evaluated. In the prediction of the equilibrium, different sets of appropriate structure combinations were 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 was assumed.

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

\[
\frac{C_{HA}}{(C_{HA})_{\text{max}}} = \frac{\beta_z \cdot (C_{HA})^z}{1 + \beta_z \cdot (C_{HA})}
\]

(6)

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

\[
zHA + NR_3 = (HA)_z (NR_3)
\]

(7)

\[
\beta_z = C_{(HA)_{\text{max}} (NR_3)}/(C_{HA}^z \cdot C_{\text{AM}})
\]

(8)

**Experimental**

**Materials:** Alamine 300 (Henkel Co.) is a tertiary amine mixture containing mainly tri-n-octylamine (> 93%). It is a light yellow liquid with an average molecular weight of 354 g/mol and a density of 0.80 g/cm$^3$. Nicotinic acid (pellagra preventive factor, 99.5% ), as well as the organic solvents of analytical grade (> 99.5%, GC) were obtained from Fluka. All the chemicals were used without further purification.

**Experiments:** The extraction experiments were performed using equilibrium glass cells, each equipped with a magnetic stirrer and thermostatted at (298 ± 0.1) K. Equal volumes (10 cm$^3$) 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 an Orion 601A pH-meter. Aqueous-phase acid concentration was determined by titration with aqueous NaOH (Titrosol A, Merck) and an UV-spectrophotometer (Waters, LambdaM Model 481, 263 nm). The acid content in the organic phase was determined with a mass balance.

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 (cyclopentanol), proton-accepting (methyl isobutyl ketone, MIBK) and inert (n-heptane) diluents. The initial amine concentrations ($C_{\text{AM}}$) in the range 0.0207-0.207 kmol/m$^3$, and the initial aqueous acid concentrations ($C_{T_A}$) of 0.01, 0.025, 0.050, and 0.102 kmol/m$^3$ were used. The physical extraction of nicotinic acid was also studied. The effect of the acid structure was evaluated for benzoic, valeric and nicotinic acids using both Alamine 300/1,2-DCE mixture and pure 1,2-dichloroethane alone.
Results and Discussion

Criterion of Extraction Degree

The results were interpreted in terms of distribution ratio ($D = C_{TA}^T/C_{TA}^A$, the ratio of the overall extracted acid to total aqueous-phase acid), degree of extraction ($E,\% = 100D/(1 + D)$), overall (total) loading factor ($Z_t$) and stoichiometric loading factor ($Z_s$). 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, $C_{TA}^T/C_{AM}^A$. 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, $(v \cdot C_{TA}^T)$, for the amount of acid extracted by the diluent in the solvent mixture.

$$Z_s = (C_{TA}^T - v \cdot C_{TA}^T)/C_{AM}^A$$  \hspace{1cm} (9)

where $v$ = the volume fraction of diluent in mixture, and $C_{TA}^T = $ concentration of acid extracted by the pure (amine-free) diluent alone. The relative proportion between physical interaction and chemical reaction was evaluated with respect to a modified separation factor ($s_f = C_{HA}/C_{TA}^T$, the ratio of the complexed acid to overall extracted acid).

Evaluation of results

Study of the extraction system in Table 1 containing 0.102 kmol/m$^3$ aqueous-phase acid solution and 0.0452 kmol/m$^3$ (Alamine 300/diluent) solvent mixture tested for 14 different diluents reveals that the physical solubility of nicotinic acid in pure diluent alone is remarkably small with a distribution ratio of about 1 for cyclopentanol ($D_o = 0.917$), and less than 1 for others, ranging from 0.01 for hydrocarbons to 0.8-0.9 for alcohols, but none suitable 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) yielding $D_o$ values of 0.016 and 0.011, respectively, may be attributed to the formation of intramolecular hydrogen bonding due to the second proton accepting group in the pyridine ring. Aprotic ketones, dibenzyl ether and benzyl acetate solvents as well as protic 1-octanol, containing an oxygenated functional group, yield different $D_o$ ranging from 0.04 to 0.35 regarding to the solvent polarity and hydrogen-bonding ability. Chlorinated hydrocarbons exhibit a low extraction ability related to $D_o < 0.03$. Conversely, the amine/diluent system favors the formation of not overloaded polar acid-amine structures ($p \leq q$) corresponding to the $Z_s$ factors restricted mainly between 0.45 and 0.92, except for hydrocarbons yielding $Z_s < 0.12$. The highest strength of the complex solvation was found for 1,2-dichloroethane ($Z_s = 0.804$) chloroform ($Z_s = 0.886$) and nitrobenzene ($Z_s = 0.914$) promoting probably (1,1) acid-amine complex formation related to the highest $s_f$ factors and at least 20 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 $s_f \geq 0.93$. The same holds for the solvents containing the benzene ring in the structure, i.e., benzyl acetate ($Z_s = 0.680; s_f = 0.813$) and dibenzyl ether ($Z_s = 0.599; s_f = 0.874$), except for protic benzyl alcohol ($Z_s = 0.463; s_f = 0.310$), which is indicative of the interaction between aromatic $\pi$ systems at the complexation stage leading to a high solvation degree. The synergistic extraction power of amine/alcohol and amine/ketone systems is noticeably larger yielding $D$ and $Z_s$ greater than 1, except for MIBK ($D = 0.606$), due to the simultaneous effect of the physical extraction and the diluent-complex
interaction through hydrogen bonding. But these solvents show a moderate solvation efficiency related to $Z_s$ of about 0.5-0.6 and a low $s_f < 0.50$ (except for MIBK), activating probably (1,2) or (2,3) acid-amine complex formation. Referring to Table 1, it can be concluded that the order of increased extraction efficiency of pure diluent alone and the most probable acid-amine $(p,q)$ complexation appear as follows:

Table 1. Summary of extraction equilibrium results for Alamine 300/diluent/nicotinic acid system at 298 K ($C_{TA} = 0.102$ kmol/m$^3$; $C_{AM} = 0.0452$ kmol/m$^3$)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>pH</th>
<th>$C_{TA}$ kmol/m$^3$</th>
<th>$D$</th>
<th>$E$</th>
<th>$Z_t$</th>
<th>$Z_s$</th>
<th>$s_f$</th>
<th>$(p,q)^a$</th>
<th>$(\beta_z)^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>3.47</td>
<td>0.1005</td>
<td>0.015</td>
<td>1.47</td>
<td>0.139</td>
<td>0.107</td>
<td>0.767</td>
<td>(1,9)</td>
<td></td>
</tr>
<tr>
<td>+ Alamine 300</td>
<td>3.49</td>
<td>0.0957</td>
<td>0.066</td>
<td>6.18</td>
<td>0.095</td>
<td>0.075</td>
<td>0.711</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>n-heptane</td>
<td>3.47</td>
<td>0.1008</td>
<td>0.012</td>
<td>1.18</td>
<td>0.133</td>
<td>0.107</td>
<td>0.804</td>
<td>(1,9)</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.49</td>
<td>0.0960</td>
<td>0.062</td>
<td>5.88</td>
<td>0.106</td>
<td>0.085</td>
<td>0.796</td>
<td>(1,11)</td>
<td></td>
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<tr>
<td>kerosene</td>
<td>3.47</td>
<td>0.1010</td>
<td>0.010</td>
<td>0.98</td>
<td>0.106</td>
<td>0.085</td>
<td>0.796</td>
<td>(1,11)</td>
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<td>0.0972</td>
<td>0.049</td>
<td>4.71</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1,2-DCB$^c$</td>
<td>3.47</td>
<td>0.1004</td>
<td>0.016</td>
<td>1.57</td>
<td>0.646</td>
<td>0.611</td>
<td>0.946</td>
<td>(2,3)</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.56</td>
<td>0.0728</td>
<td>0.401</td>
<td>28.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1,2-DCE$^c$</td>
<td>3.48</td>
<td>0.0995</td>
<td>0.025</td>
<td>2.45</td>
<td>0.858</td>
<td>0.804</td>
<td>0.937</td>
<td>(1,1)</td>
<td></td>
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<tr>
<td>+ Alamine 300</td>
<td>3.59</td>
<td>0.0632</td>
<td>0.614</td>
<td>38.04</td>
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<td></td>
<td></td>
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<tr>
<td>chloroform</td>
<td>3.48</td>
<td>0.1002</td>
<td>0.018</td>
<td>1.76</td>
<td>0.925</td>
<td>0.886</td>
<td>0.958</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.61</td>
<td>0.0602</td>
<td>0.694</td>
<td>40.98</td>
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<td></td>
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<tr>
<td>MIBK$^c$</td>
<td>3.52</td>
<td>0.0892</td>
<td>0.143</td>
<td>12.55</td>
<td>0.852</td>
<td>0.574</td>
<td>0.674</td>
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<tr>
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<td>0.0635</td>
<td>0.606</td>
<td>37.75</td>
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<td>cyclohexanone</td>
<td>3.59</td>
<td>0.0640</td>
<td>0.594</td>
<td>37.25</td>
<td>1.412</td>
<td>0.588</td>
<td>0.416</td>
<td>(2,3)</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.69</td>
<td>0.0382</td>
<td>1.670</td>
<td>62.55</td>
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<td></td>
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<td>nitrobenzene</td>
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<td>0.011</td>
<td>1.08</td>
<td>0.938</td>
<td>0.914</td>
<td>0.975</td>
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<td>3.61</td>
<td>0.0596</td>
<td>0.711</td>
<td>41.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dibenzyl ether</td>
<td>3.48</td>
<td>0.0980</td>
<td>0.041</td>
<td>3.92</td>
<td>0.686</td>
<td>0.599</td>
<td>0.874</td>
<td>(2,3)</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.57</td>
<td>0.0710</td>
<td>0.437</td>
<td>30.39</td>
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<td></td>
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<tr>
<td>benzy alcohol</td>
<td>3.50</td>
<td>0.0948</td>
<td>0.076</td>
<td>7.06</td>
<td>0.836</td>
<td>0.680</td>
<td>0.813</td>
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<tr>
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<td>3.59</td>
<td>0.0642</td>
<td>0.589</td>
<td>37.06</td>
<td></td>
<td></td>
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<tr>
<td>cyclopentanol</td>
<td>3.63</td>
<td>0.0532</td>
<td>0.917</td>
<td>47.84</td>
<td>1.527</td>
<td>0.468</td>
<td>0.307</td>
<td>(1,2)</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.72</td>
<td>0.0330</td>
<td>2.091</td>
<td>67.65</td>
<td></td>
<td></td>
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<td>1-octanol</td>
<td>3.55</td>
<td>0.0758</td>
<td>0.346</td>
<td>25.69</td>
<td>1.062</td>
<td>0.494</td>
<td>0.465</td>
<td>(1,2)</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.63</td>
<td>0.0540</td>
<td>0.889</td>
<td>47.06</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>benzyl alcohol</td>
<td>3.63</td>
<td>0.0545</td>
<td>0.872</td>
<td>46.57</td>
<td>1.493</td>
<td>0.463</td>
<td>0.310</td>
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<tr>
<td>+ Alamine 300</td>
<td>3.71</td>
<td>0.0345</td>
<td>1.957</td>
<td>66.18</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$ probable acid $(p)$/amine $(q)$ structure referred to Eq. (7); $^b$ equilibrium constant in (kmol/m$^3$)$^{-z}$ 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 = methyl isobutyl ketone

$kerosene (1,1,1) \cong n−heptane (1,9) \cong nitrobenzene (1,1) < cyclohexane (1,9) \cong 1,2-dichlorobenzene (2,3) < chloroform (1,1) < 1,2-dichloroethane (1,1) < dibenzyl ether (2,3) < benzyl acetate (3,4) < MIBK (2,3) < 1-octanol (1,2) < cyclohexanone (2,3) < benzyl alcohol (1,2) \cong cyclopentanol (1,2)$

No evidence of overloading of amine, i.e. $Z_s > 1$, was observed in any of the systems tested. The highest synergistic extraction efficiency yields amine mixtures of alcohols and cyclohexanone ($Z_t \approx 1.4$), as
compared to the hydrocarbons, aromatics, ethers and halogenated hydrocarbons varying less than 1 \((Z_t < 1)\). \((3,4)\) complex formation represents the aggregation of \((1,2)\) and \((1,4)\) structures.

The equilibrium data in Table 1 were interpreted in terms of a modified Langmuir model using the concepts of Poposka defined by Eqs. (7) and (8). It is supposed that the total concentration of complexed acid \((C_{HA})\) is evaluated from Eq. (8) and \(z = Z_{s,\text{max}}\).

\[
Z_t = \frac{C_d + C_{HA}}{C_{AM}} = \frac{vD_o C_{TA}^p}{(1 + D_o) C_{AM}} + \frac{\beta_z (C_{HA})^z C_{AM}}{C_{AM}^3}
\]

where \(C_d = vD_o C_{TA}^p / (1 + D_o)\) designates the concentration of the physically extracted acid part by the diluent in the mixture. \(D_o\) is the distribution ratio of acid related to the pure diluent alone. \(\beta_z\) was correlated by Eq. (10) supposing that the \(p/q\) ratio in Table 1 represents the associated number of the complex formation related to the maximum loading, \(z = Z_{s,\text{max}} = p/q\).

It is apparent from Figures 1 and 2 that the longer R-chain of valeric acid (VA) and the benzene ring of benzoic acid (BA) make these acids more hydrophobic and thus more easily extracted by a polar diluent alone, yielding \(D_o\) values about 100 times greater, as compared to those of less hydrophobic nicotinic acid capable of intramolecular hydrogen bonding. However, nicotinic acid (NA) is more sensitive to ion-pairing complexation with amine through dipole-dipole interaction or hydrogen bonding accompanying the multiple effects at the carboxyl group and electronegative pyridine ring (aromatic \(\pi\) system), which is indicated by the reasonably high loading factors (Figures 2 and 4) in contrast to the rather low \(D_o\) of distribution in polar 1,2-DCE and protic cyclopentanol diluents alone (Figure 1), as compared to the same quantities of valeric and benzoic acids. These concepts are verified by the results in Figure 1 and Table 1 manifesting that the controlling factor for physical extraction is the hydrophobicity of acid, which is indicated by the change in the extraction degree in pure 1,2-DCE alone as \(\text{NA} \ll \text{BA} \approx \text{VA}\), whereas the polarity of the formed structures at complexation stage are more strongly affected by both the polarity and ionizing strength of acid \((\mu_{VA} = 2.1 \times 10^{-12} \text{ C.m}, \varepsilon_{VA} = 2.66, pK_{a,VA} = 4.842)^{10}\). This is in accordance with the rather low \(Z_s\) factors for valeric acid estimated from Figures 1 and 2, as compared to the nicotinic acid ones, indicating that weaker interactive forces appear during valeric acid-amine complexation.

Consequently, it is expected that the polarity and the ionizing strength of acid 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 the acids studied. These findings are supported by the results for the relative proportion of physical interaction and chemical reaction \((s_f)\) from Figure 3, presuming that different mechanisms control one or simultaneously two or more acid-amine complex formation, depending on the solvation efficiency of diluent.
Figure 1. Physical extraction of nicotinic acid (NA) by conventional solvents. Comparison of extraction isotherms with valeric (VA) and benzoic (BA) acids.

Figure 2. Variation of overall loading of monocarboxylic acids vs. amine concentration for amine/1,2-DCE system ($C_{TA} = 0.01 \text{ kmol/m}^3$)

Figure 3. Variation of separation factor with aqueous-phase nicotinic acid concentration ($C_{AM} = 0.0452 \text{ kmol/m}^3$)

To estimate the strength of the complex solvation, as well as the effect of the acid and amine concentrations, runs were performed using MIBK, cyclopentanol, 1,2-DCE, and $n$-heptane diluents in the amine mixture. The equilibrium results for diluent alone and the amine/diluent mixture are presented in Figures 1 and 3-5. Referring to Figure 5, it is observed that the maximum stoichiometric loading ($Z_{s,max}$) corresponding to the plateau in the loading curve appears at $Z_{s,max} \leq 1$, reflecting a tendency toward the formation of two types of nicotinic acid-amine structures, i.e., an equimolar structure ($p = q$), or an aggregation related to the acid per multiple amines ($p < q$) structure. This effect is more pronounced in the
Extraction Equilibria of Nicotinic Acid Using Alamine ..., A. ŞENOL

case of polar 1,2-DCE diluent, affecting more readily the diluent-complex interaction than the diluent-acid association, which is indicated by the remarkably high $Z_s$ (Figure 5) with a maximum of about 1 ($Z_{s,max} \approx 0.95$) in contrast to the rather low $D_o$ (Figure 1), as compared to the same quantities of the other diluents. The same holds for the interactive effects of cyclopentanol, MIBK, and n-heptane diluents regarding $Z_{s,max}$ values estimated from Figures 4 and 5 as 0.50 0.67 and 0.12, respectively.

Table 2. Extraction constants of Eq. (3) and Eq. (11), root-mean-square deviation ($\sigma$) and relative error ($\bar{e}$)$^a$ of model estimates for nicotinic acid-amine complexation

<table>
<thead>
<tr>
<th>Diluent</th>
<th>complex I</th>
<th>complex II</th>
<th>$\sigma(Z_t)$</th>
<th>$\bar{e}(Z_t)^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-heptane</td>
<td>$T^b$</td>
<td>$S^b$</td>
<td>1.4465$ \times 10^2$ (1.2)</td>
<td>2.2182$ \times 10^1$ (1.9)</td>
</tr>
<tr>
<td>($\beta_z; z$)$^c$</td>
<td></td>
<td></td>
<td>1.2045$ \times 10^3$ (1.4)</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>(2.654; $z = 0.12$)</td>
<td></td>
<td></td>
<td>0.016</td>
</tr>
<tr>
<td>1,2-DCE</td>
<td>$S$</td>
<td></td>
<td>8.4592$ \times 10^4$ (1.1)</td>
<td></td>
</tr>
<tr>
<td>($\beta_z; z$)</td>
<td></td>
<td></td>
<td>(84.553; $z = 0.95$)</td>
<td></td>
</tr>
<tr>
<td>MIBK</td>
<td>$T$</td>
<td>$S$</td>
<td>4.4954$ \times 10^4$ (1.1)</td>
<td>1.3609$ \times 10^3$ (2.3)</td>
</tr>
<tr>
<td>($\beta_z; z$)</td>
<td></td>
<td>(33.174; $z = 0.67$)</td>
<td></td>
<td>0.038</td>
</tr>
<tr>
<td>cyclopentanol</td>
<td>$T$</td>
<td>$S$</td>
<td>1.2064$ \times 10^4$ (1.2)</td>
<td>1.8103$ \times 10^3$ (2.3)</td>
</tr>
<tr>
<td>($\beta_z; z$)</td>
<td></td>
<td>(46.238; $z = 0.50$)</td>
<td></td>
<td>0.232</td>
</tr>
</tbody>
</table>

$^a \bar{e} = (100/N)\sum_{N=1}^N|(Z_{t,obs} - Z_{t,cat})/Z_{t,obs}|$; $^b$ one (S) or two (T) complex formation (T in fig.4); $^c$ extraction constant ($\beta_z$) in (kmol/m$^3$)$^{-z}$ and associated number ($z$) due to Eq. (11)

Figure 4. Variation of overall loading with aqueous-phase nicotinic acid concentration ($C_{AM} = 0.0452$ kmol/m$^3$). Comparison with estimates through chemodel, Eq. (3)
The results, presented in Figures 3-5, were correlated in terms of a chemodel approach and an overall apparent extraction constant due to Eqs. (3) and (4). Figure 4 illustrates the increased solvation efficiency of diluent with increasing acid concentration, related to the extraction power of diluent alone and a probable single acid-amine (p,q) aggregation as cyclopentanol (1,2) > MIBK (2,3) > 1,2-DCE (1,1) > n-heptane (1,4). However, the chemodel presumes the formation of at least two complexes. Estimates were performed using the multivariable procedures of the LINPACK algorithm\textsuperscript{11} for one (S) and two (T) 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 cyclopentanol, (1,1) and (2,3) for MIBK, (1,1) for 1,2-DCE, and (1,2) and (1,9) for n-heptane. Table 2 presents a quantitative assessment of the predicted equilibrium constants ($\beta_{pq}$) of selected individual complexes (S and T) with respect to the mean relative error ($\bar{e}$, %) and root-mean-square deviation ($\sigma$) of the $Z_s$ factor. The model consistency was also studied through a plot of the modeled values (for two selected combinations) against observed performance (Figure 4).

Figure 5 illustrates the influence of the amine concentration on stoichiometric loading ($Z_s$). Since the nonpolar Alamine 300 by itself is a relatively poor solvating medium for the polar complexes, loading decreases with increasing amine concentration as the active solvent becomes a less favorable solvating agent. For the nonpolar mixture of inert diluent and amine, increasing the amine concentration, however, has little effect upon loading (Figure 5).

The equilibrium data in Figures 3-5 were also interpreted in terms of the modified approach of Poposka for $\beta_z$ defined by Eq. (6), assuming that $z = Z_{s,max} = (C_{HA})_{max} / C_{AM}$. The model was rearranged through incorporating $C_{HA}$ from Eq. (6) into Eq. (11) to give a sentence structure including both physical and
Extraction Equilibria of Nicotinic Acid Using Alamine ... A. ŞENOL

chemical interaction terms.

\[ Z_z = \frac{C_d + C_{HA}}{C_{AM}} = \frac{vD_o C_{TA}}{(1 + D_o) C_{AM}} + \frac{z\beta_z (C_{HA})^2}{1 + \beta_z (C_{HA})^2} \]  

(11)

The estimated $\beta_z$ values in (kmol/m$^3$)$^{-z}$ by Eq. (11), depending on the acid and amine concentrations, are given in Table 2. The maximum loading values ($z = Z_{s,\text{max}}$) of 0.12, 1.0, 0.67 and 0.50 for nicotinic acid related to $n$-heptane, 1,2-DCE, MIBK and cyclopentanol, respectively, were used. Figure 5 illustrates the consistency of the predictions for the modified Langmuir approach, Eq. (11).

Consequently, both approaches proved to be reasonably accurate, yielding $\bar{e}(\%)$ and $\sigma$(kmol/m$^3$) with regard to $C_{TA}$ variable of 13.74% and 0.0062 for Eq. (3) and 9.81% and 0.0018 for Eq. (11), considering all the systems studied.

Conclusion

The equilibrium distribution of nicotinic acid onto a aqueous/organic two-phase system containing Alamine 300 as a reactive extractant was elucidated by simultaneous effects of chemical and physical interactions closely related to the nature of the diluent used. Conventional solvents are not suitable separation agents for nicotinic acid, yielding $D_o < 1$. The highest synergistic extraction efficiency was found for the amine/cyclic alcohol system. Halogenated aliphatic hydrocarbons and nitrobenzene yield the largest strength of the complex solvation, promoting probably (1,1) acid-amine complex formation with $Z_{s,\text{max}} \approx 1$. Chemodel presumes mainly the formation of two acid-amine aggregated structures of type (1,2) and (2,3) for cyclopentanol, (1,1) and (2,3) for MIBK, (1,1) for 1,2-DCE, and (1,2) and (1,9) for $n$-heptane. Much research on these phenomena remains to be done, in particular at different isothermal conditions with mixed diluents to estimate the factors modifying the regeneration stage.

Acknowledgments

The author thanks Henkel Co. for providing Alamine 300. The author is also grateful to Dr. G. Şenol and Guven Co. for the technical support of this study.

Nomenclature

- $C_{AM}$ = concentration of free (uncomplexed) amine, (kmol/m$^3$)
- $C_{AM0}$ = initial concentration of amine in solvent mixture, (kmol/m$^3$)
- $C_d$ = concentration of acid extracted by the diluent, (kmol/m$^3$)
- $C_{HA}$ = proton concentration of acid in the aqueous phase, (kmol/m$^3$)
- $C_{HA0}$ = concentration of undissociated acid in aqueous phase, (kmol/m$^3$)
- $C_{HA}$ = overall concentration of complexed acid, (kmol/m$^3$)
- $C_{pq}$ = concentration of acid-amine complex, (kmol/m$^3$)
- $C_{TA}$ = the overall concentrations of acid in aqueous-phase, (kmol/m$^3$)
- $C_{TA}$ = the overall concentrations of acid in organic-phase, (kmol/m$^3$)
Extraction Equilibria of Nicotinic Acid Using Alamine ..., A. ŞENOL

\( C_{TA}^{a} \) = initial concentration of acid, (kmol/m³)
\( C_{TA}^{e} \) = concentration of acid extracted by the diluent alone, (kmol/m³)
\( D \) = distribution ratio of acid related to the amine mixture
\( D_{o} \) = distribution ratio of acid related to 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 observation
NR₃ = 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
\( \overline{\text{overbar}} \) = species in the organic phase

Greek letters
\( \varepsilon \) = dielectric constant
\( \beta_{pq}^{e} \) = apparent equilibrium extraction constant, Eq. (3), (kmol/m³)\( ^{1-p-q} \)
\( \beta_{z}^{e} \) = equilibrium extraction constant, Eqs. (10) and (11), (kmol/m³)\( ^{-z} \)
\( \mu \) = dipole moment, (C·m)
\( \sigma \) = root-mean-square deviation

Subscripts
AM = amine
cal = calculated
HA = undissociated acid
max = maximum
obs = observed
TA = total acid

References