

Equilibrium studies on butane-1,4-diamine extraction with 4-nonylphenol

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Abstract

BACKGROUND: The extraction of butane-1,4-diamine (BDA) from aqueous solutions with undiluted 4-nonylphenol (4NP) has been studied at three temperatures (298 K, 310 K and 323 K) in a batch system. A reactive extraction model based on mass action law was applied to describe the experimental data.

RESULTS: The model developed describes the distribution of BDA between the 4NP phase and the aqueous phase, and the average stoichiometry of the complexation due to interactions between the two amine groups of BDA and 4NP, as well as the complexation constant were fitted to experimental data with good accuracy for each of the three temperatures, the largest error at the confidence limit of the estimated parameters being 6%. Using a Van't Hoff plot, the thermodynamic parameters of the equilibrium constant were determined and used to estimate that in a single stage with only $S/F = 0.5$, over 99% of the BDA can be extracted from a 1.146 wt% aqueous solution. High distribution ratios at low BDA concentrations hampered the effective recovery by back-extraction in a single stage, therefore multistage processing was considered and short-cut calculations revealed a maximum concentration factor of 3.6.

CONCLUSION: Good agreement between single stage equilibrium data and the model was obtained and the model developed was used in short-cut calculation of a coupled multistage forward and back-extraction process showing a maximum concentration factor of only 3.6, therefore an alternative, more effective recovery strategy, e.g. through anti-solvent addition is suggested.

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Keywords: butane-1,4-diamine; putrescine; single stage extraction; 4-nonylphenol

NOTATION

ΔH	enthalpy (J mol^{-1})
ΔS	entropy ($\text{J mol}^{-1} \text{K}^{-1}$)
ΔG	Gibbs energy (J mol^{-1})
D	distribution (wt% / wt%)
E	extraction factor
E	extract flow (in forward extraction)
F	feed flow
I	ionic strength
K	equilibrium constants, various dimensions
M	molality (mol kg^{-1})
R	gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
S	solvent flow
T	temperature (K)
V	volume (L)
W	wash flow (in back-extraction)
x	concentration in aqueous phases
y	concentration in organic phase
z	ion charge

c	complexation
corr	corrected
e	extract phase
ini	inlet concentration
k	index for ionic species in ionic strength equation
n	stoichiometry of BDA in BDA_nNP complexes
org	organic phase
out	outlet concentration
tot	total (concentration)

Greek letters

α	activity
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Subscripts and superscripts

aq	aqueous phase
b	basicity
be	back-extract phase (wash)

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γ	activity coefficient
ϵ	dielectric constant
ρ	density, (kg m^{-3})
ξ	concentration factor [-]

INTRODUCTION

The demand for bio-based materials, both in industry and everyday life, is growing rapidly.^{1–4} The production of bio-based plastics such as polylactic acid (PLA) is relatively mature, although research on broader aspects of polymers is ongoing.^{5–8} One of the issues that need to be addressed is improvement of the mechanical properties of bio-based products to improve their potential applicability. PLA has the potential to replace some of the traditionally produced plastics, yet it lacks advanced material properties, such as high mechanical and thermal stability.⁹ Materials displaying such properties (i.e. polyamides) are still obtained through chemical synthesis of monomers and subsequent polymerization, leading to the production of toxic by-products.^{10–12} If the chemical process could be replaced by industrial fermentation, the production of toxic by-products may be significantly reduced. One example of a polymer that could be obtained from fermented monomers is Stanyl (also known as Nylon 4,6), which is widely used in the electronic and automotive industry.¹² The current process is based on the reaction between butane-1,4-diamine (BDA) and adipic acid.¹³ BDA is obtained through a series of chemical reactions involving some toxic additives and intermediates, but the potential to produce it via a fermentative route has already been identified.^{10–13} Adipic acid can be obtained as a derivative of succinic acid, which is already a bio-based platform chemical.^{14,15}

Economically viable bioprocesses require high yields in both upstream and downstream parts of the processes, and downstream processing to separate compounds from fermentation broths using the current state-of-the-art technology is costly.^{16–18} Among the available technologies, liquid–liquid reactive extraction has recently gained more and more support, as it does not require high energy inputs, can be operated in mild conditions, and is capable of selective recovery of the desired compound.^{19–22}

To the best of our knowledge, no fermentative process has been established for commercial scale production of diamines, nor has the applicability of liquid–liquid extraction for downstream processing been considered until we recently published a study on recovery of diamines (putrescine, cadaverine) from aqueous solutions using liquid–liquid extraction.²³ The study identified 4-nonylphenol (4NP, Fig. 1) as the most effective extractant.

In this paper, a more detailed study on the extraction of BDA by 4NP is described, including the development of a single stage equilibrium model that was applied in simulations of the extraction processes. The structures of BDA and 4NP (Fig. 1(A)), also the mechanism of complexation in 1:1 and 1:2 stoichiometric ratios between BDA and 4NP is displayed in Fig. 1(B). The aim of this study was to identify the requirements of equilibrium based extraction processes for the extraction of BDA with 4NP from fermentation broths in terms of the minimum solvent/feed ratio $(S/F)_{\text{min}}$ required for removal of 99% of BDA, and the required wash/extract ratio $(W/E)_{\text{min}}$ to recover the BDA from the extraction solvent as function of temperature.

EXPERIMENTAL SECTION

Chemicals

4-nonylphenol (99%) was obtained from TCI Europe (Germany) and 1,4-diaminobutane (99%) was obtained from Sigma Aldrich (The Netherlands).

Procedures

Determination of BDA basicity constants

BDA protonation was studied by measuring the pH of aqueous BDA solutions with concentrations ranging from 5–100 mmol L^{-1} at temperatures from 298 to 323 K under an inert (N_2) atmosphere. The solutions were purged with nitrogen gas and kept under a slight excess pressure of N_2 (~ 0.05 barg) while being heated to 323 K (± 0.5 K). During cooling to 298 K, pH measurements were collected every minute using an Inolab 730 pH meter connected with Multilab[®] Pilot software on a personal computer. The accuracy of the pH measurement was ± 0.005 .

Reactive liquid–liquid extraction of BDA

In reactive liquid–liquid extraction experiments, 130 mmol L^{-1} solutions of BDA were contacted with 4NP in stoppered flasks. Experiments were performed at 298, 310 and 323 K and at different S/F ratios ranging from 0.07 to 0.62 (v/v) for 17 h under continuous shaking (185 rpm), and the phases were then allowed to settle for 2 h. Samples of the aqueous phase were taken and the BDA concentration in the raffinate was determined with gas chromatography. The concentration of BDA in the 4NP phase was determined by mass balance.

Analytical procedures

The concentration of BDA in aqueous solutions was measured with gas chromatography using a Varian-430 GC apparatus equipped with an Agilent CP Volamine column and FID detector. The detection limit of the applied method was 1 mmol L^{-1} and the relative standard deviation was below 3%. A detailed description of the method has previously been reported.²⁴

Modeling and optimization software and procedures

Fitting of all parameters was carried out using a nonlinear-least squares approach (lsqnonlin) provided by the software package Matlab (Mathworks). The reported confidence intervals of the parameter values are 95% confidence limits.

Extraction theory and reactive extraction modeling

A temperature dependent single stage equilibrium model was developed to describe the single stage extraction and back-extraction equilibria. The single stage extraction model is based on the extraction mechanism, which can be either homogenous or heterogeneous,²⁵ depending on the location of the complexation reaction. When the solute to be extracted has negligible solubility in the extract phase (i.e. extraction of metals), the complexation reaction will take place only at the interface,²⁶ and the extraction mechanism is classified as heterogeneous. For polar compounds that are to some extent soluble in organic phase, the complexation reaction is not only limited to the interface, but is rather considered as a homogenous organic phase reaction. These models are typically applied in systems with diluted extractants, because the physical solubility is to a large extent determined by the solubility in the diluent. However, since in this work pure 4NP is used, it is not

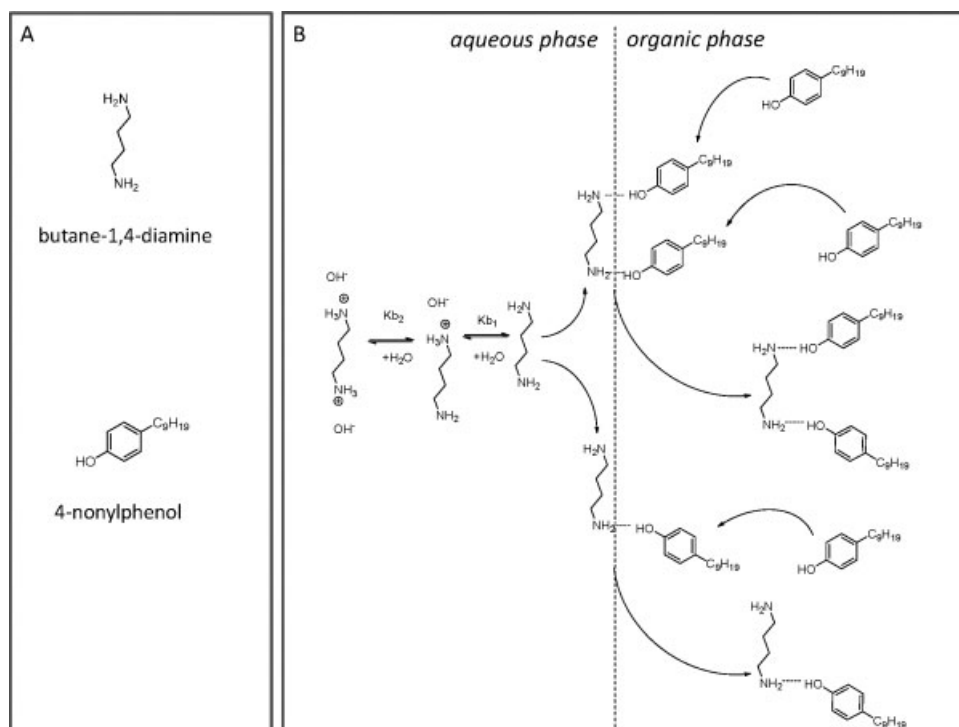


Figure 1. Chemical structures of solute (butane-1,4-diamine, BDA) and 4-nonylphenol extractant (A), and the two extraction mechanisms, showing 1:2 (BDA:4NP) complexation, and 1:1(BDA:4NP) complexation (B).

possible to measure the physical solubility of BDA in the solvent phase. Therefore, the approach of considering the heterogeneous equilibrium between 4NP and BDA has been chosen, an approach commonly used in extraction of metals²⁶ and for carboxylic acid extractions.²⁷

The extraction system can be described by the coupled protonation equilibrium relationships, the heterogeneous complexation equilibrium, and the mass balances of BDA and 4NP. Because of the electroneutrality constraint, it is assumed that only BDA in the non-protonated form is transferred to the organic phase. The aqueous phase protonation equilibria are described by Equations 1 and 2, where K_{b1} and K_{b2} are the protonation constants.

Because the applied solutions in the experimental study were of relatively high concentrations (5–100 mmol L⁻¹), the non-ideality of the system was taken into account:

$$K_{b1} = \left(\frac{\alpha_{BDAH^+} \alpha_{OH^-}}{\alpha_{BDA}} \right)_{aq} = \left(\frac{\gamma_{BDAH^+} \gamma_{OH^-} [BDAH^+] [OH^-]}{\gamma_{BDA} [BDA]} \right)_{aq} \quad (1)$$

$$K_{b2} = \left(\frac{\alpha_{BDAH_2^{2+}} \alpha_{OH^-}}{\alpha_{BDAH^+}} \right)_{aq} = \left(\frac{\gamma_{BDAH_2^{2+}} \gamma_{OH^-} [BDAH_2^{2+}] [OH^-]}{\gamma_{BDAH^+} [BDAH^+]} \right)_{aq} \quad (2)$$

where α_i is the activity and γ_i the activity coefficient for species i . For neutral BDA, it was assumed that the activity did not vary significantly over the concentration range, and any deviation from unity is included in the fitted basicity constant. For calculation of the activity coefficients of the ionic species, the Davies' equation was used:²⁸

$$\log \gamma_i = -z_i^2 \left(\frac{A\sqrt{I}}{1 + \sqrt{I}} - b.I \right) \quad (3)$$

where I is the ionic strength and b is the distance of the closest approach of two ions which for Davies model is 1.5;²⁸ A is the Debye–Hückel constant and z_i is the ion charge. The ionic strength can be expressed by:²⁸

$$I = 0.5 \sum_k m_k z_k^2 \quad (4)$$

where m is the molality (mol kg⁻¹) of ion k ; A is a constant that depends on the solvent and for BDA in water, it can be estimated from Equation 5:²⁹

$$A = 1.8252 * 10^6 \left(\frac{\rho_w}{\epsilon^3 T^3} \right)^{0.5} \quad (5)$$

where ρ and ϵ correspond to the density (g cm⁻³) and dielectric constant of water.³⁰

$$\epsilon = \frac{5321}{T} + 233.76 - 0.9297T + 1.417 * 10^{-3} T^2 - 8.292 * 10^{-7} T^3 \quad (6)$$

and

$$\rho_w = -4 * 10^{-6} T^2 - 5 * 10^{-5} T + 1,0009 \quad (7)$$

With these non-idealities taken into account, the activity of OH⁻ and the ionic strength can be found by simultaneously solving the ionic strength equation (Equation 4) and the electroneutrality relationship (Equation 8).

$$2 [BDAH_2^{2+}] + [BDAH^+] + [H^+] = [OH^-] \quad (8)$$

The experimentally observed activity of OH⁻ at various temperatures and overall concentrations of BDA in the aqueous solution can be used to fit ΔH_{Kb1} , ΔH_{Kb2} , ΔS_{Kb1} and ΔS_{Kb2} , that

are related to the basicity constants (and hence, to the modeled $[\text{OH}^-]$) through the well known Van't Hoff equation:

$$-RT \ln(K) = \Delta G = \Delta H - T\Delta S \quad (9)$$

For the heterogeneous complexation equilibrium, it was considered that the solute has two amine functional groups, and that stoichiometries deviating from unity are possible, and that complexes with 1 BDA:1 4NP and 1 BDA:2 4NP stoichiometries can be expected through hydrogen bonding between the amine and phenolic functional groups. 4NP in high concentrations is known to oligomerize, and in addition to the 1:1 and 1:2 complexes, due to this oligomerization complexes with higher stoichiometric ratios of 1:3 and 1:4 are also possible, as recently described by Bokhove *et al.*³¹ in a study on 4-cyanopyridine extraction with 4-nonylphenol. In this study, the average stoichiometry is taken into account, and the complexation equilibrium is described by Equation 10.

$$K_c = \frac{[\text{BDA}_n\text{NP}]_{org}}{[\text{BDA}]_{aq}^n [\text{NP}]_{org}} \quad (10)$$

In this equation, K_c is the complexation constant; NP the extractant; BDA_nNP the BDA-4NP complex with stoichiometry BDA: 4NP of $n = 1$.

The component balance for butane-1,4-diamine is given in Equation 11 and the component balance for the extractant in Equation 12.

$$V_{aq} [\text{BDA}]_{aq,0} = V_{aq} \left([\text{BDA}]_{aq} + [\text{BDAH}^+]_{aq} + [\text{BDAHH}^{2+}]_{aq} \right) + V_{org} n [\text{BDA}_n\text{NP}]_{org} \quad (11)$$

$$V_{org} [\text{NP}]_{org,0} = V_{org} \left([\text{NP}]_{org} + [\text{BDA}_n\text{NP}]_{org} \right) \quad (12)$$

Using the thermodynamic constants for the aqueous phase protonation equilibria, the total concentration of BDA in the aqueous phase can be related to the concentration of neutral BDA which is in equilibrium with the organic phase complex. By fitting the total aqueous phase BDA concentration to experimentally determined values at three temperatures (298, 310 and 323 K), the values for K_c and n were determined at these temperatures.

The temperature dependency of the equilibrium constant K_c was converted to the thermodynamic properties enthalpy and entropy using the well-known Van't Hoff relation:

$$-RT \ln(K_c) = \Delta G_c = \Delta H_c - T\Delta S_c \quad (13)$$

For multistage calculations, the distribution used is described by Equation 14, where the subscript *tot*

$$D = \frac{[\text{BDA}]_{org,tot}}{[\text{BDA}]_{aq,tot}} \quad (14)$$

indicates that all forms (including protonated and non-protonated in the aqueous phase and complexed in the organic phase) are included.

In multistage processes, the minimum S/F-ratio can be calculated based on the mass balance and the assumption of equilibrium between incoming feed and outgoing extract ($y_{out} = Dx_{in}$), this relation is given in Equation 15:³⁵

$$\left(\frac{S}{F}\right)_{min} = \frac{x_{in} - x_{out}}{Dx_{in} - y_{in}} \quad (15)$$

where x_{in} and x_{out} are the concentrations in the feed and the raffinate, and y_{in} is the initial BDA concentration in the extract phase.

For the back extraction, the minimum W/E ratio can be calculated:

$$\left(\frac{W}{E}\right)_{min} = \frac{y_{in} - y_{out}}{\frac{1}{D}y_{in}} \quad (16)$$

where $y_{in} = \text{BDA}_e$ concentration in the extract phase from extraction, $y_{out} =$ concentration BDA left in the extract flow. Over the combined extraction and back-extraction process, the concentration factor is defined as:

$$\zeta = \text{BDA}_{out,be} / \text{BDA}_{in} \quad (17)$$

Because in real extraction processes, the actual flow ratios S/F and W/E are typically about 1.5 times the minimum required flow ratios,³⁵ the actual concentration factor is the ideal concentration factor divided by $(1.5)^2$, as defined in Equation (18).

$$\zeta_{corr} = \zeta (1.5)^{-2} \quad (18)$$

RESULTS AND DISCUSSION

BDA basicity constants

To study the protonation equilibria as a function of temperature, the pH of unbuffered solutions of BDA was measured as described in the experimental section. The temperature dependency of the pH is displayed for four overall BDA concentrations in Fig. 2(A). It can be seen that with increasing temperature, the pH decreases as the concentration of $[\text{OH}^-]$ decreases, indicating that the protonation reactions are exothermic. Using the fitting procedure as described in the theory section, the enthalpy and entropy of BDA protonation were estimated to be $\Delta H_{Kb1} = -1.02 \times 10^4 \text{ J mol}^{-1}$ and $\Delta S_{Kb1} = -9.78 \times 10^1 \text{ J mol}^{-1} \text{ K}^{-1}$ for the first protonation, and $\Delta H_{Kb2} = -1.09 \times 10^4 \text{ J mol}^{-1}$ and $\Delta S_{Kb2} = -1.84 \times 10^2 \text{ J mol}^{-1} \text{ K}^{-1}$ for the second. Figure 2(A) shows that the modeled pH ($[\text{OH}^-]$) agrees well with the experimental observations. In Fig. 2(B) and 2(C), the effect of temperature on the protonation constants K_{b1} and K_{b2} is depicted.

From the observed K_{b1} and K_{b2} values, both of which are rather small, it follows that at typical extraction concentrations of up to 130 mmol L^{-1} , the concentration of BDAHH^{2+} is almost negligible, and also the concentration of BDAH^+ is low. It can thus be concluded, that in solutions of up to 130 mmol L^{-1} butane-1,4-diamine, the neutral form of DAB is mainly present, which is favorable for the extraction process.

Complexation constant K_c and complexation stoichiometry n

Experiments to estimate the equilibrium constant K_c and the stoichiometry parameter n were carried out with aqueous solutions of BDA, and 100% 4-nonylphenol under varying S/F-ratio at 298, 310 and 323 K as described in the experimental section. In Fig. 3, the total organic concentration of BDA (which is n times the concentration of the complex BDA_nNP) is plotted versus the total aqueous concentration ($[\text{BDA}]_{aq} + [\text{BDAH}^+]_{aq} + [\text{BDAHH}^{2+}]$) at equilibrium.

From Fig. 3 it can be seen that at very low concentrations, the increase in BDA concentration in organic phase with increasing aqueous BDA concentration is strong, reflected by the steepness of the curve. With increasing organic phase concentration of BDA the steepness of the curve reduces rapidly, although it does not

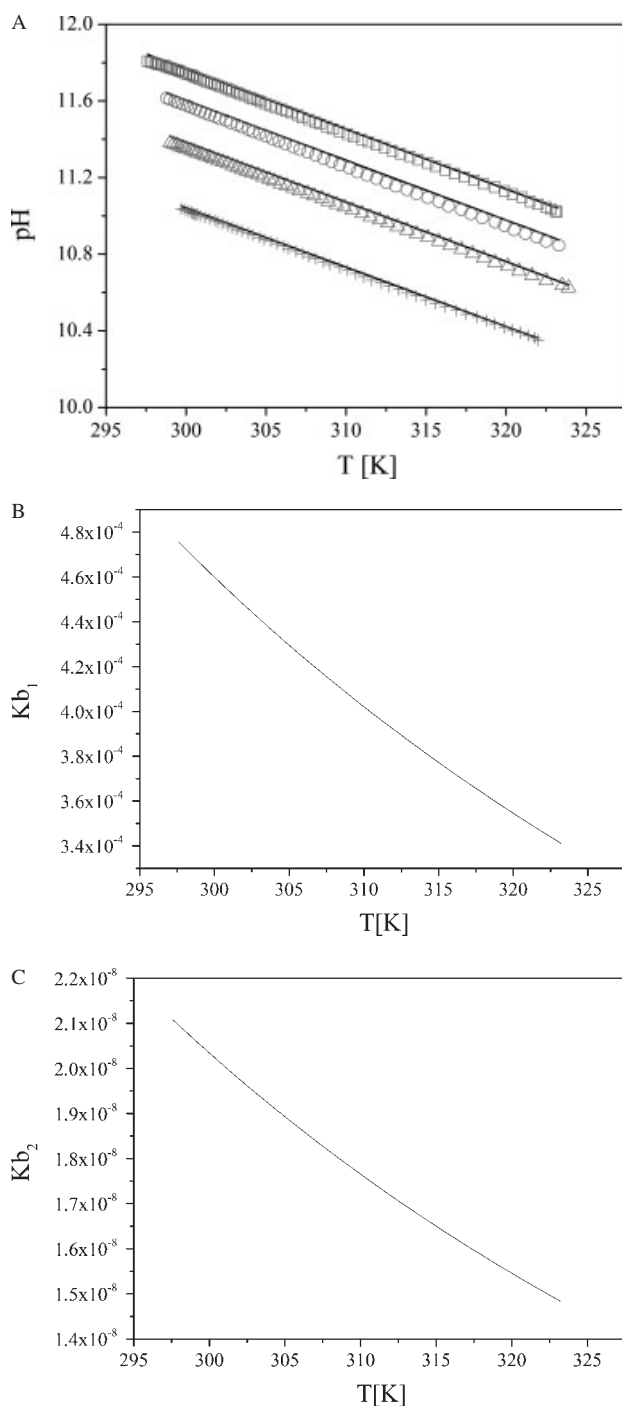


Figure 2. Dependency of pH on the temperature (A) and dependency of pK_{b1} and pK_{b2} on the temperature (Fig. 2(B) and 2(C), respectively). Symbols: experimental data: \square = BDA 100 mmol L⁻¹, \circ = BDA 50 mmol L⁻¹, Δ = BDA 20 mmol L⁻¹, $+$ = BDA 5 mmol L⁻¹. Line: calculated with $\Delta H_{kb1} = -1.02 \times 10^4$ J mol⁻¹ and $\Delta S_{kb1} = -9.78 \times 10^1$ J mol⁻¹ K⁻¹ and $\Delta H_{kb2} = -1.09 \times 10^4$ J mol⁻¹ and $\Delta S_{kb2} = -1.84 \times 10^2$ J mol⁻¹ K⁻¹.

approach an asymptotic organic BDA concentration. This means that even at the highest measured concentrations, the solvent NP is not saturated with BDA. The trend indicates that multiple NP molecules may be involved in the complex formation in the organic phase, which is in logical agreement with the presence of two amine functional groups. At very low BDA concentrations both groups may be bound to a phenol functionality, while due

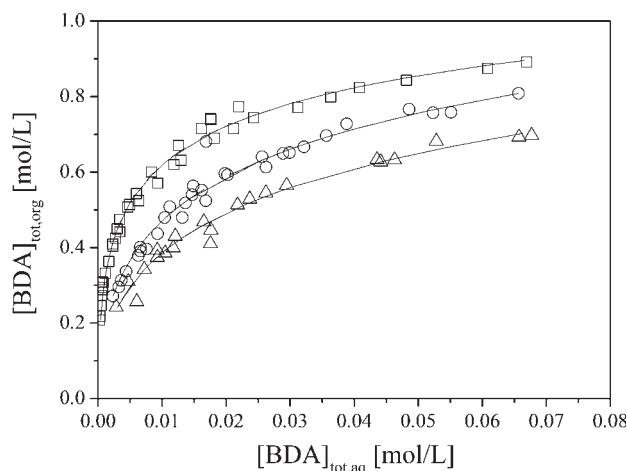


Figure 3. Extraction of butane-1,4-diamine with 4-nonylphenol, symbols = experimental: \square : T = 298 K, \circ : T = 310 K, Δ : T = 323 K, lines represent modeled concentrations.

to this stoichiometry, the availability of free NP for complexation reduces strongly, so that it becomes less favorable to take up even more BDA, hence the steepness of the curve reduces at higher BDA concentrations.

Another observation from Fig. 3 is the increasing steepness of the curves with reducing temperature. This is due to the complexation constant, K_c , decreasing with increasing temperature, thus reducing the effectiveness of extraction. Reduced complexation with increasing temperature is commonly observed in reactions between acids and bases.^{19,32,33}

Figure 3 also shows that the modeled curves fit the experimental data very well. The modeled curves were obtained with the fitted parameters K_c and n (Table 1), which were independently fitted for each temperature. The goodness of the fit is also represented by the 95% confidence limits, at which the uncertainty for each temperature in K_c was less than 3% and for n it was less than 6%.

From Table 1 it can also be seen, that the average stoichiometry of complexes between BDA and NP is about 1:2.5, and although there is a slight increase of n with temperature, this effect is rather small. This result is comparable with the findings of Bokhove *et al.*³¹

By plotting the estimated complexation constants in a Van't Hoff plot the enthalpy and entropy of complexation could be determined from the intercept with y-axis ($\Delta S_c/R$) and the slope ($-\Delta H_c/R$). Values of the enthalpy and entropy have been estimated as $\Delta H_c = -1.96 \times 10^4$ J mol⁻¹ and $\Delta S_c = -0.55 \times 10^2$ J mol⁻¹ K⁻¹. The determined ΔH_c of -19.6 kJ mol⁻¹ for the amine functionality is higher than the values of -15.3 kJ mol⁻¹ and -8.1 kJ mol⁻¹ found by Bokhove *et al.* for the complexation of pyridine and cyano functional groups, a trend in agreement with the trend in Lewis basicity of the functional groups.³⁴

Table 1. Complexation constants and number of BDA molecules per complex fitted for reaction between BDA and NP

Temperature [K]	K_c [L mol ⁻¹] ⁿ	95% confidence limits	n	95% confidence limits
298	3.79	+/- 0.1	0.36	+/- 0.013
310	2.64	+/- 0.06	0.42	+/- 0.025
323	2.05	+/- 0.37	0.42	+/- 0.02

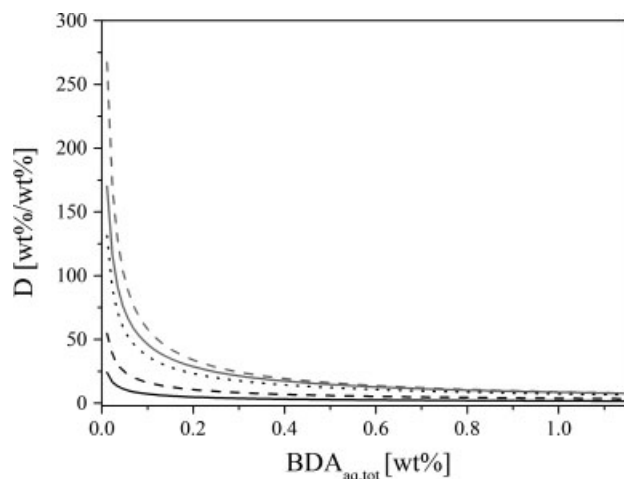


Figure 4. Calculated distribution ratio (D) versus raffinate concentration. Lines: - - - 298 K, — 310 K, 323 K, - · - · 373 K, — — — 433 K.

Modeling of distribution ratio

In multistage liquid–liquid extraction processes, the distribution ratio is an important parameter characterizing the extraction performance. The distribution ratio of BDA on mole basis is defined in Equation (14) and with the single stage equilibrium model developed in this study, the distribution of BDA as a function of the raffinate concentration was calculated for different temperatures (Fig. 4).

Figure 4 shows that the maximum achievable distribution ratio decreases with increasing temperature, which follows logically from the temperature dependency of the determined complexation constants. Another observation is the very strong dependency of the distribution ratio on the raffinate concentration. The strong increase of the distribution at very low BDA raffinate concentrations is beneficial for the efficiency of the extraction close to the raffinate outlet in the multistage processes. Due to the high distribution at low BDA raffinate concentration, it should be possible to effectively remove over 99% of the BDA.

Extraction and back-extraction simulations

Single stage simulations

Because of the very high distributions at low raffinate concentrations, for effective BDA extraction from aqueous solutions, a single stage may be economically favorable. In Fig. 5 the raffinate concentrations at varying volume ratios are displayed, with the horizontal line indicating a raffinate concentration of 1% of the feed concentration, i.e. 99% extraction efficiency. It can be seen from Fig. 5 that at 298 K already at a S/F ratio below 0.5 the desired extraction efficiency is reached.

Increasing the temperature results in decreasing distribution, hence single stage back-extractions were simulated using temperatures of 323 K (the highest experimentally validated temperature for the equilibrium constants) and an extrapolated temperature of 373 K, the atmospheric boiling point of water. The fraction of BDA that is recovered from the extract phase into the aqueous wash phase is plotted in Fig. 6 as a function of the Wash to Feed ratio, that equals twice the Wash to Extract ratio at an S/F of 0.5, which was used as starting condition for the back-extraction simulations.

Figure 6 clearly shows that even if the back-extraction is performed at the atmospheric boiling point of water, the fraction BDA that is recovered is rather low, only 0.15 at a W/F ratio of 1. This

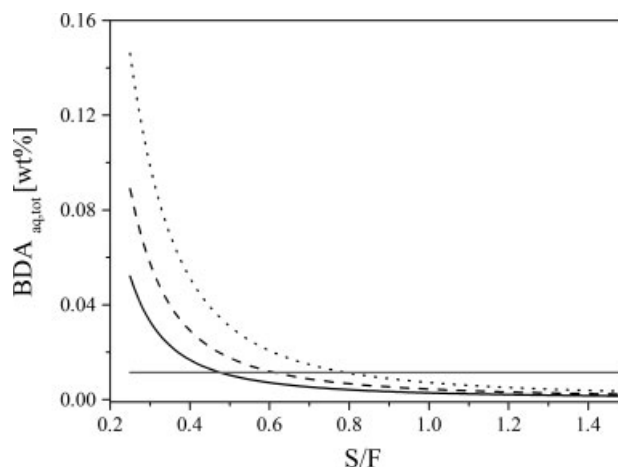


Figure 5. Effect of S/F ratio on the raffinate concentration in single stage equilibrium extraction from 1 wt% BDA aqueous solutions at different temperatures: 323 K, - · - · 310 K, — 298 K, ——— 0.01[BDA]_{in} (objective concentration).

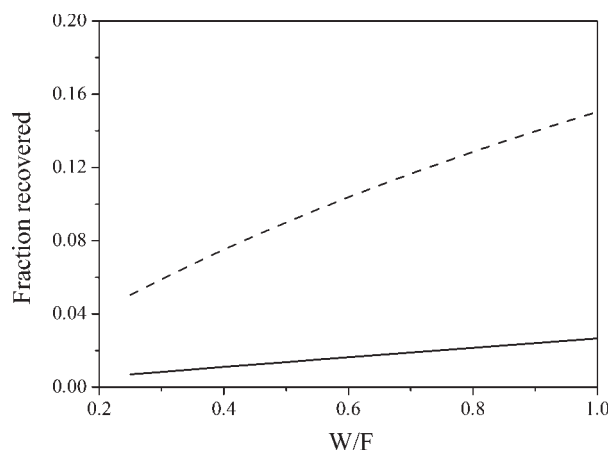


Figure 6. Recovery of BDA in a single stage equilibrium back-extraction, after initial extraction from 1 wt% aqueous solution at 298 K and $S/F = 0.5$, back-extraction temperatures: — 298 K, - - - 373 K.

means that with the maximum temperature swing at atmospheric pressure, it is not possible to recover BDA efficiently from an aqueous solution by coupled extraction and back-extraction at elevated temperature. Therefore, it is concluded that at least the back-extraction should be performed in a multi-stage mode, and perhaps also the forward extraction.

Single stage extraction with multistage back-extraction

The effectiveness of a single stage forward extraction at $S/F = 0.5$ and $T = 298$ K coupled with multistage back extraction has been examined. For this purpose, the desired fraction of BDA to be recovered from the organic extract phase was 0.99, and for this situation the minimum W/E and required number of theoretical stages N for the back-extraction were calculated using Equation 16, assuming the ingoing BDA concentration in the wash stream is zero.

Because the distribution of BDA is relatively low over a large part of the concentration range (Fig. 5), for a first optimistic estimation of the feasibility of this operational mode, the $(W/F)_{\min}$ required for recovery of 99% of BDA was calculated, which for this case with $(S/F) = 0.5$ equals twice $(W/E)_{\min}$ with the minimum values of D for each temperature. The $(W/F)_{\min}$ is displayed in Fig. 7 over the

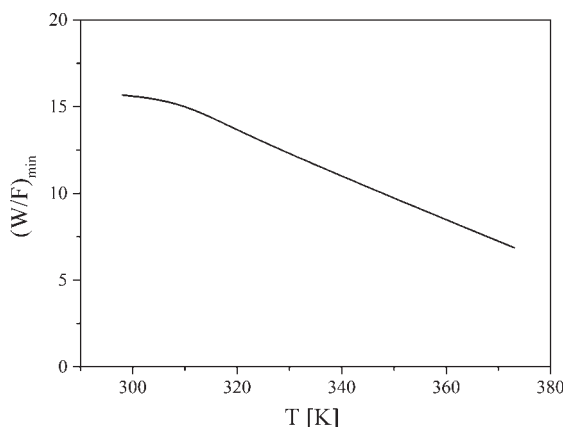


Figure 7. Influence of temperature on the minimum wash/feed ratio $(W/F)_{\min}$ required for the recovery of 99% BDA.

temperature range $298\text{ K} < T < 373\text{ K}$ and shows that over this temperature range the $(W/F)_{\min}$ drops from 15.6 at 298 K to 6.9 at 373 K.

It can thus be concluded that employing a single stage extraction and multistage back-extraction inevitably leads to very diluted wash streams, even if the back-extraction is operated at the atmospheric boiling point of water.

Multistage processing in both forward extraction and back-extraction

To maximize the concentration in the forward extraction, multistage processing was also simulated for a combination of an extraction process operated at minimum S/F-ratio and back-extraction process at minimum W/E-ratio given the requirements of extracting 99% of the feed BDA, recovering 99% of the extracted BDA in the back-extraction, and furthermore assuming the wash stream entering the back-extraction is free of BDA. Equations (15) and (16) were used to calculate minimum S/F and W/E ratios.

Because distribution is a function of the aqueous phase concentration, as an estimate the arithmetic mean value of distributions over the range $0.01\text{ BDA}_{\text{ini}}\text{--BDA}_{\text{ini}}$ was used (the range was calculated with increments of $0.01\text{ BDA}_{\text{ini}}$) in Equation 15, and because the aim was to make a concentration factor, for back-extraction the range over which the distributions were calculated was extended to $0.01\text{ BDA}_{\text{ini}}\text{--}5\text{ BDA}_{\text{ini}}$. The attainable concentration factors, both the ideal concentration factor and the concentration factor with real flow ratios, as defined in Equations 17 and 18 are depicted in Fig. 8.

Based on the concentration factors in Fig. 8, it can be concluded that for processes operated at about 1.5 times the minimum flow ratios, the maximum concentration factor at atmospheric pressure (i.e. at $T = 373\text{ K}$) is $\zeta_{\text{corr}} = 3.6$. This means that starting with a concentration of 1 wt% in the broth, the obtainable concentration in the wash is not higher than 3.6 wt%, hence, applying multistage extractions and back-extractions for the concentration of BDA is not very effective. Therefore it is concluded that another approach, providing higher concentration factors is required. One such option could be the application of an anti-solvent, which has previously been shown to provide promising results.²³

CONCLUSIONS

In this study the extraction of butane-1,4-diamine (BDA) from aqueous solutions using pure 4-nonylphenol (NP) has been studied both experimentally and by modeling. Using experimental data

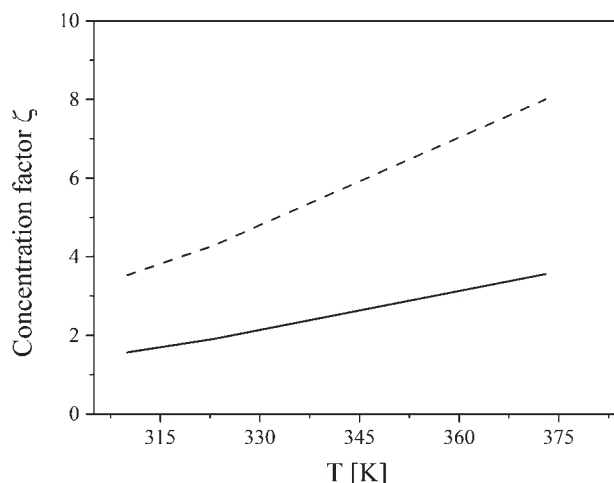


Figure 8. Maximum attainable concentration factors and corrected attainable concentration factors, - - - minimum S/F and W/E (ζ), — for $1.5(S/F)_{\min}$ and $1.5(W/E)_{\min}$ (ζ_{corr}).

of the aqueous phase protonation of BDA and the complexation of BDA with NP over a temperature range of 298–323 K, a single stage extraction model was developed and it was found that the complexation stoichiometry, n , between BDA and NP was only slightly dependent on temperature and the value about 0.4, meant that on average 2.5 molecules of NP complex with BDA. This stoichiometry was explained by oligomerisation of NP and the double amine functional groups of BDA. With the developed single stage model, BDA distribution was simulated for varying conditions and it was found that in a single stage with $S/F = 0.5$, over 99% of the BDA from a 1 wt% aqueous solution can be extracted. However, due to the very high distribution coefficient at low BDA concentrations, it could not effectively be recovered by back-extraction, even when the back-extraction temperature was increased to 373 K, the atmospheric boiling point of water. Thus a coupled multistage forward and back-extraction process appeared the most effective. A maximum concentration factor of 3.6 was achieved by coupling extraction at 298 K to back-extraction at 373 K. However, obtaining pure BDA from the resulting 3.6 wt% aqueous solution still requires evaporation of large amounts of water, and hence alternative recovery options, like using an anti-solvent in the back-extraction, need to be considered.

ACKNOWLEDGEMENTS

This has been an ISPT project. ISPT is Institute for Sustainable Process Technology, headquartered in Amersfoort, the Netherlands.

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