

DISSOCIATION EXTRACTION PROCESS FOR THE SEPARATION OF ISOMERIC ORGANIC COMPOUNDS

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Separation of mixture of isomeric organic compound was achieved by exploiting the difference in their dissociation constants by employing dissociation extraction technique. Mixture of 3-picoline and 4-picoline was partially separated with sodium dihydrogen phosphate to demonstrate the phenomenon of dissociation extraction. A theoretical treatment of separation of isomers is given which can be utilized to predict the separation factor of dissociated and undissociated species of isomers. Increase in temperature had a positive influence on the separation of isomers and also on the phase disengagement between the aqueous and the organic phases. A process is described to develop a suitable chemical material bed in the column for gas-liquid chromatography that reduces the retention time and gives high resolution of picolines.

Key words: Dissociation extraction, Separation factor, Dissociation constants.

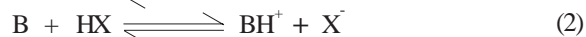
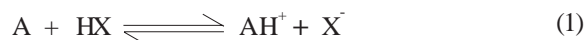
Introduction

Dissociation extraction is a unique technique, capable of achieving the separation of isomeric mixture of organic acids and bases. Its research and applications have spread into the fields of extraction and separation of chemical substances (Wadkar & Sharma 1981; Lo & Baarid 1996; Hulton *et al* 2000; Ahmed *et al* 2002) from coal-tar oils, polyphenols, substituted phenols, amines alkaloids, herbicides and pharmaceutical products.

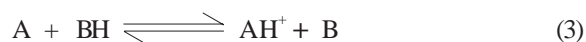
To achieve the separation, the dissociation extraction technique utilizes the difference in the strengths of the components as acids or bases, i.e. difference in their dissociation constants which are considerable due to different molecular arrangements in the isomers. Consider a mixture of components (e.g. two organic bases dissolved in an organic solvent) with a stoichiometric deficiency of an extracting agent in another phase (e.g. an aqueous acid). The term stoichiometric deficiency generally, implies that the amount of acid taken is just sufficient to neutralize the stronger base of the two. The organic bases enter the aqueous phase in their undissociated form and compete with each other to react with stoichiometrically deficient acid. The stronger base reacts preferentially with the acid. The aqueous phase becomes enriched with the stronger base while the organic phase is concentrated with the weaker base. The process is akin to the processes developed by authors (Ahmed *et al* 1989, Ahmed *et al* 1994) for solvent extraction of metals. According to the work of Anwar *et al* 1979 and Caira *et al* 1997 the picoline isomers possess different dissociation constants which

provide a satisfactory basis for their separation. However, their attention was concentrated primarily on the use of dissociation extraction to effect separation of particular complex mixture in the laboratory. In the present paper, theoretical analysis of the technique is described to bring about the separation. Moreover, a Gas-Liquid Chromatography column bed is developed which gives 28 min retention time for separation as compared to 3 h by commercially available columns.

Theory. Consider the extraction of two organic bases A and B, dissolved in a water-immiscible organic solvent by aqueous solution of weakly acid salt HX. The acid salt HX is taken in a stoichiometric deficiency as compared to base isomers, in order to have competition between the two isomers in the aqueous phase. The more strongly base A tends to react preferentially with hydrogen ions forming a dissociated salt in the aqueous phase. The base B does not react and remains in undissociated form increasing its concentration in the organic phase. The following reactions are expected in the aqueous phase:



Since, A is the stronger base; the overall reaction is an exchange reaction between bases A and B in the aqueous phases:



The dissociation constants of the organic bases are defined as:

$$K_A = [AH^+][X^-] / [A] \quad (4)$$

$$K_B = [BH^+][X^-] / [B] \quad (5)$$

The distribution coefficients of the undissociated bases are:

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$$D_A = [A]_o / [A]_a \quad (6)$$

$$D_B = [B]_o / [B]_a \quad (7)$$

Where subscripts 'o' and 'a' denote organic and aqueous phases, respectively.

Overall distribution coefficients are defined as:

$$D'_A = [A]_o / ([A]_a + [AH^+]) \quad (8)$$

$$D'_B = [B]_o / ([B]_a + [BH^+]) \quad (9)$$

The dissociation constants of the acidic reagent, K_x , and water, K_w , are defined as:

$$K_x = [H^+] / [X^-] / [HX] \quad (10)$$

$$K_w = [H^+] [OH^-] \quad (11)$$

The equilibrium constant for reaction (1), K_1 , is given by:

$$K_1 = K_A K_x / K_w \quad (12)$$

$$K_2 = K_B K_x / K_w \quad (13)$$

$$K_3 = K_A / K_B \quad (14)$$

Showing that the equilibrium of the key exchange reaction is related to the relative strength of the two bases.

The equations presented above, contribute to the overall state of the system, the following two equations are derived from stoichiometry assuming that reactions (1) and (2) do not completely consume the acidic reagent, HX, for which the feed concentration is Z moles per litre.

For every mole of HX, one mole of AH^+ or BH^+ is formed:

$$[HX]_{feed} = Z = [HX]_{eq} + [AH^+] + [BH^+] \quad (15)$$

Where $[HX]_{eq}$ is the concentration of unreacted reagent in the aqueous phase at equilibrium.

$$[X^-] = [AH] + [BH^+] \quad (16)$$

The separation factor α_{AB} for the organic bases is:

$$\alpha_{AB} = D'_B / D'_A \quad (17)$$

From equations (17), (8) and (9):

$$\alpha_{AB} = D'_B / D'_A = \frac{[B]_o ([A]_a + [AH^+])}{[A]_o ([B]_a + [BH^+])} \quad (18)$$

From equations (6), (12), (15) and (16):

$$\frac{K_B K_x}{K_w} = K_1 = \frac{[BH^+] [X^-]}{[B]_o [HX]} = \frac{([AH^+] + [BH^+]) [BH^+]}{([B]_o / D_B) [Z - ([AH^+] + [BH^+])]} \quad (19)$$

and similarly, from equation (7), (13) (15) and (16):

$$\frac{K_A K_x}{K_w} = \frac{([AH^+] + [BH^+]) [AH^+]}{([A]_o / D_A) [Z - ([AH^+] + [BH^+])]} \quad (20)$$

In equations (19) and (20), K_A , K_B , K_x and K_w are known as physical constants having literature values of 10.62×10^{-9} ,

4.59×10^{-9} , 6.23×10^{-8} and 10^{-14} , respectively; Z, $[A]_o$ and $[B]_o$ are system variables which may be assigned an experimental values at equilibrium. Therefore, if D_A and D_B are known at the actual values of the system concentration variables, then we have two equations, (19) and (20) containing only two unknown: $[AH^+]$ and $[BH^+]$. The equation may be solved simultaneously, in order to yield the unknowns. However, if the equations are not linear and simple then the analytical solutions are not possible, whereas, a computer programme is the most convenient method of obtaining the real and positive solution values of $[AH^+]$ and $[BH^+]$.

On obtaining $[AH^+]$ and $[BH^+]$, $[HX]_{eq}$ and $[X^-]$ may be derived from relations (15) and (16) and $[A]_a$ and $[B]_a$ from equations (6) and (7). All the terms in equation (18) are now known and the required value of α_{AB} may be calculated. If desired, the values of the overall distribution coefficients may be calculated from equations (8) and (9).

Experimental

The system chosen for detailed studies was the separation of 3-picoline and 4-picoline which caused a separation problem in coal-tar industry. The extractant employed was sodium dihydrogen phosphate.

Preparation of GLC column. It is extremely important to have suitable material bed in the column that is capable of providing sufficient retention time to give high resolution of picolines. In order to achieve this objective, Matexil (the stationary phase material) 1.2g and potassium hydroxide 0.45g was dissolved in 35ml of methanol in a 150 ml round bottom flask. The low solubility of potassium hydroxide in methanol was overcome by the addition of a few drops of distilled water. Chromosorb G AW DMCS (the support material) 15.0 g of 80-100 mesh was added to the methanol solution with continuous stirring.

The flask was placed in a constant temperature bath at $65^\circ\text{C} \pm 1^\circ\text{C}$ to evaporate methanol. The material was stirred with glass rod until the methanol was completely evaporated. The flask was then placed in an oven at $85^\circ\text{C} \pm 1^\circ\text{C}$ for 20 h to obtain dried material with same flow characteristics as it had initially.

This process caused the chromosorb G AW DMCS to be coated uniformly on the Matexil. It is filled in the clean and dry glass coil-shaped column of 5 ft. length and 3 mm internal diameter to fit in Gas-Liquid Chromatograph.

To obtain the distribution coefficients of the undissociated species under various conditions, known volumes of bases in organic solvents and aqueous solution of sodium dihydrogen phosphate were shaken for 15 min at room temperature. The phases were separated and the organic phase injected in the

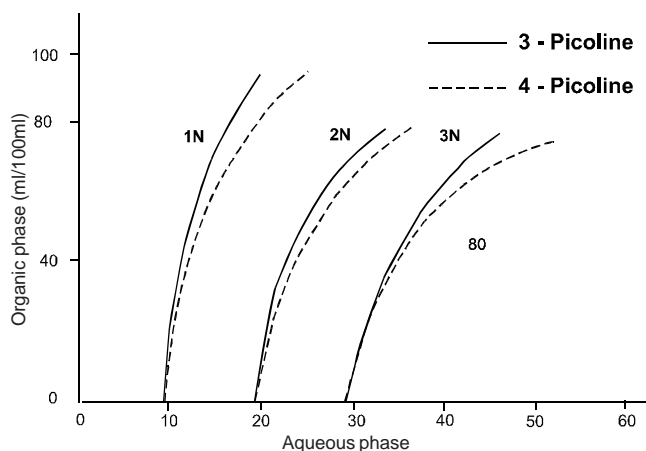


Fig 1. Distribution of bases between benzene and sodium dihydrogen phosphate.

Matexil bed for analysis by Gas-Liquid Chromatograph without any further treatment. The experimental and analytical procedure is the same as described in the previous paper (Ahmed *et al* 2002).

Experimental work was also carried out to study separation factors directly and determine the effects of total isomer concentrations, isomer ratio and sodium hydrogen phosphate concentration.

The chemicals used were of Analar grade and obtained from BDH.

Results and Discussion

The equilibrium constant, K_e , for reaction between picoline and dihydrogen phosphate is given below in concentrations, neglecting activity coefficients:

$$K_e = \frac{[C_6H_7NH^+][HPO_4^{2-}]}{[C_6H_7N][H_2PO_4^-]}$$

Now, the dissociation constants for picolines, acid and water can be calculated by equations (4), (5), (10) and (11):

$$\begin{aligned} K_A &= 10.62 \times 10^{-9} \text{ 4-Picoline} \\ K_B &= 4.59 \times 10^{-9} \text{ 3-Picoline} \\ K_X &= 6.23 \times 10^{-8} \text{ Sodium dihydrogen phosphate} \\ K_W &= 10^{-14} \text{ water} \end{aligned}$$

The dissociation constants for both picolines clearly show that a partial reaction takes place in the aqueous phase. Picoline is too weak a base to generate a high concentration of PO_3^{3-} ions, therefore, the presence of PO_4^{3-} ions in the aqueous phase is neglected. Furthermore, the dissociation constants are very small showing that any excess of base present in the aqueous phase after neutralization of the acid content will be almost entirely in the undissociated form. Analysis confirmed

Table 1
Distribution coefficients of undissociated 3- and 4-picoline between benzene and sodium dihydrogen phosphate

Concentration of base in organic phase (ml/100ml)	Distribution coefficient					
	1N		2N		3N	
	3-pic.	4-pic.	3-pic.	4-pic.	3-pic.	4-pic.
9.59	17.30	16.40	11.60	10.63	7.40	6.75
19.15	17.30	16.40	11.60	10.63	7.40	6.75
28.28	16.17	14.65	9.80	9.10	7.00	6.46
47.40	15.89	14.40	9.48	8.98	6.88	6.40
60.00	11.46	10.10	6.92	6.30	5.75	5.40
80.00	9.70	8.42	6.50	5.74	4.40	4.00

Table 2
Variation in separation factor of picolines at different temperatures

Temperature	Total conc. In the aqueous phase (ml/10ml)	Equilibrium concentration of the isomers in the conjugate phase				Separation factor
		Organic phase (Molar %)		Aqueous phase (Molar %)		
		3-pic.	4-pic.	3-pic.	4-pic.	
		3-pic.	4-pic.	3-pic.	4-pic.	
25°C	2.91	59.30	40.70	44.90	55.10	1.79
30°C	2.31	59.60	40.40	40.90	59.10	2.13
35°C	1.60	56.50	43.50	38.20	61.80	2.10

that the concentration of base in the organic phase is nearly zero, until sufficient base has been added to neutralize completely the aqueous acid. The rates of increase of base concentration in the organic and aqueous phases as shown in Fig. 1, virtually become constant representing distribution coefficients of the undissociated bases. The changes in gradient of the curves show that the distribution coefficients are inversely proportional to the increase in the base concentration. The effect of change of base concentration in the organic phase on the distribution coefficient is given in Table 1. It clearly shows that the presence of dissociated picoline affects the activity of undissociated picoline in the aqueous phase since the distribution coefficient decreases considerably with increase in the strength of acid in the aqueous phase. Similar observations were reported for the separation of phenolic derivatives (Hutton *et al* 2000), cresol isomers (Ahmed *et al* 2002) and picolines (Caira *et al* 1997).

The overall distribution coefficients of two isomers are determined individually, which usually donot give any guide whether the separation of a mixture of the two isomers is practicable by dissociation extraction. The isomers may have

identical distribution coefficients when measured in this way, however, the dissociation constants are sufficiently different to influence the separation of these isomers by dissociation extraction.

Table 2 confirms that the separation factor increases with temperature due to an increase in the concentration of the solutes in the aqueous phase. The latter observation is of importance for a practical separation process, especially, in a multistage separation (Wadekar & Sharma 1981, Arif *et al* 1995) of isomers. Moreover, there was an improved phase separation under higher temperature and no traces of emulsion were noticed appearing in either phases.

The low concentration of the required products on the output phase is a feature adversed to the commercial application of this process. When 20% by weight sodium dihydrogen phosphate was equilibrated with 6.0 g picoline isomers in benzene then the phases were separated. The aqueous phase loaded with picoline was equilibrated with fresh feed of 6.0 g picoline mixture and again phases were separated after equilibration. This process was repeated which showed emulsification at 30% loading (Caira *et al* 1997) of picoline, because the specific gravities of the output phases became closer to each other. Nevertheless, the separation of 4-picoline from 3-picoline was improved, tremendously.

Conclusion

Dissociation extraction is a useful technique for separation of isomeric organic compounds of organic bases (or acids) which are difficult to separate by more common methods of separation such as extraction, crystallization, distillation, etc.

It can be seen from the results that the extent of reaction between the picoline isomers and sodium dihydrogen phosphate is modest. Thus, the competition between the isomers is limited. It would be desirable to find another reagent which would react more strongly and preferably whilst still allowing reversal of the reaction by the other physical separation processes. However, the theory and result are presented to establish the basic feasibility of achieving the separation by not so well known process of dissociation extraction.

Although, no attempt was made for the selection of solvent, the result shown gives a reasonable separation in the benzene media. Authors (Ahmed *et al* 1979; Wadekar & Sharma 1981) stress on the feasible choice for the selection of proper solvents.

Nomenclature

A,B	= Organic bases
D	= Distribution coefficient of undissociated bases
D	= Overall distribution coefficient

H ⁺	= Concentration of cations
AH ⁺ , BH ⁺	= Concentration of dissociated base A and B, respectively
HX	= Weak acid in the aqueous phase
K	= Dissociation constants
K ₁	= Equilibrium constants
OH ⁻	= Activity coefficient of hydroxyl ions
X ⁻	= Concentration of anions
Z	= Total concentration of acid
∞	= Separation factor

Subscript

A	= Refers to base A
a	= Aqueous phase
B	= Refers to base B
eq	= Equilibrium
o	= Organic phase
W	= Refers to water
X	= Refers to acid reagent

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