

Recovery of Nitrogen Bases with
Weak Acids

by

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Introduction

The recovery of nitrogen bases is of particular interest in chemical plants that operate in conjunction with coal-carbonization facilities. Traditionally, nitrogen bases such as ammonia, pyridine, and quinoline have been recovered by processes that involve acid extraction followed by neutralization with caustic soda or lime.^{1,2)} Such processes have inherent disadvantages with regard to excessive consumption of acids and bases as well as concomitant waste-disposal problems.

Recently, several processes have been developed for nitrogen-base recovery by regenerative cyclic techniques. For example, recovery of ammonia from coke-oven gas and pyridine from coke-oven light oil have been reported.^{3,4,5)} These processes for recovery of nitrogen bases are characterized by the use of an aqueous acid solution for the extraction step followed by a high-temperature stripping, or springing, operation that liberates the nitrogen bases and simultaneously regenerates the acid extractant. The selection of an appropriate acid extractant for a particular nitrogen-base system is an important factor in designing or developing a regenerative process. Previously reported studies^{3,4,5)} have demonstrated that monoammonium acid phosphate is a suitable extractant for ammonia recovery, whereas either phosphoric acid or monopyridinium sulfate is adequate for pyridine recovery. However, the theory for selection of appropriate reagents for regenerative nitrogen-base recovery has not been developed and, consequently, the general applicability of this recovery technique has not received significant attention. It is the object of this paper to demonstrate that readily available thermodynamic data can be used to determine the feasibility of a regenerative technique for recovery of particular nitrogen bases. The discussion is based on the behavior of particular acids during the extraction and springing operations. Data are also presented on the extraction and springing steps for recovery of pyridine and quinoline from coal-tar fractions.

Discussion of the Regenerative Technique

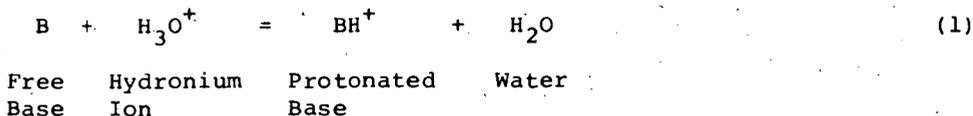
The general scheme for a regenerative recovery process for

* See References.

nitrogen bases involves three steps: a) extraction, b) separation, and c) regeneration. The system can be seen in Figure 1 as a generalized flow diagram. Usually, nitrogen bases are recovered from streams in which they are present in low concentrations (about 0.1 to 5%), such as coke-oven light-oil streams.

Selection of Reagents for Regenerative Systems

The selection of an appropriate acidic extractant for a particular nitrogen base is the initial problem encountered in developing a regenerative process. Although such factors as solubility, volatility, decomposition, and side reactions must be considered, the acid component essentially must be strong enough to effect efficient removal of the nitrogen base from the hydrocarbon stream during the extraction step and yet be sufficiently weak to allow decomposition of the resultant acid salt during the regeneration step. Therefore the values of the equilibrium constants at the springing and extraction temperatures (K_{T_2} and K_{T_1}) for the following reaction are of significance in determining whether the regenerative technique is feasible.



The temperature dependence of the equilibrium constant follows the expression

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

where

ΔH = the heat of reaction, and
 R = the gas constant.

It is desirable that the ratio (K_{T_2}/K_{T_1}) be less than unity for a regenerative system (ΔH , the heat of reaction, must be negative).

In an effort to develop suitable parameters for the selection of reagents for regenerative systems, the ionization equilibria of acids and bases have been examined.

In a discussion of acid-base systems, the following equations are applicable. Acid extraction of a nitrogen base (B) from a hydrocarbon stream involves the equilibrium reaction



which can be represented by an equilibrium constant

$$K_e = \frac{[\text{BH}^+]}{[\text{B}][\text{H}_3\text{O}^+]} \quad (4)$$

The ionization constant of the base involves the equilibrium



expressed by an ionization constant

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad (6)$$

By using the ionization constant for H_2O

$$K_w = [OH^-][H_3O^+] \quad (7)$$

and combining Equations 4, 6, and 7, the following expression is obtained to show the concentration of protonated base in an aqueous extract.

$$[BH^+] = \frac{K_b}{K_w} [B][H_3O^+] \quad (8)$$

The dependence of $[BH^+]$ on $[H_3O^+]$ can be represented in terms of the strength of any acid (HA) by using the equilibrium dissociation constant of the acid.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (10)$$

$$[H_3O^+] = \left([HA] K_a \right)^{1/2} \quad (11)$$

Combining (11) with (8) gives

$$[BH^+] = \frac{K_b}{K_w} K_a^{1/2} [HA]^{1/2} [B] \quad (12)$$

Equation 12 indicates that, for a given concentration $[B]$ and strength (K_b) of base, the concentration $[BH^+]$ can be increased by increasing the strength of acid (K_a).

$$[BH^+] \propto K_a^{1/2} \quad (13)$$

A similar discussion of the regeneration step is pertinent. The reaction involved is



The equilibrium constant for the reaction can be represented as

$$K_r = \frac{[B][H_3O^+]}{[BH^+]} \quad (15)$$

and can be expressed in terms of Equation 8 to give

$$K_r = \frac{K_w}{K_b} = \frac{[B][H_3O^+]}{[BH^+]} \quad (16)$$

Therefore

$$[B] = \left(\frac{K_w}{K_b}\right)^{1/2} [BH^+]^{1/2} \quad (17)$$

$$[B] \propto K_b^{-1/2} \quad (18)$$

Thus, for a given concentration $[BH^+]$ in the aqueous extract, the concentration $[B]$ of base is high for bases of low base strength (K_b).

From Equations 12 and 17, the following generalizations can be made concerning the selection of an acid and a base for recovery of nitrogen bases by a regenerative process. To get good extraction, maximize $[BH^+]$ by using an acid with as large a value for K_a as is possible, consistent with other requirements of the process. To get good regeneration, maximize $[B]$ (a base with a small K_b value should be involved).

Accordingly, suitable systems appear to involve an acid extractant with a large K_a value and a nitrogen base with a small K_b value. Consistent with the above, the ΔpK was examined as a useful guide in selecting components for regenerative systems,

where

$$pK = -\log K \quad (19)$$

$$\Delta pK = (pK_b - pK_a), \text{ and} \quad (20)$$

ΔpK is expressed as the absolute value of $(pK_b - pK_a)$. It is anticipated that the larger the ΔpK of a system, the better it will function in a regenerative recovery process. Therefore it appears that recovery of nitrogen bases is facilitated by combinations of relatively weak bases and relatively strong acids or relatively strong bases and weak acids.

Systems for Recovery of Ammonia and Pyridine Bases

As mentioned above, several processes have previously been reported for recovery of ammonia and pyridine bases from coke-oven product streams. The data on ammonia and pyridine are consistent with the discussion presented above, Tables I and II. Experimentally it has been demonstrated that, although ammonia can be recovered in a regenerative manner using monoammonium phosphate, neither phosphoric acid nor sulfuric acid can be used ($H_2PO_4^-$ is suitable for NH_3 recovery, whereas H_3PO_4 , HSO_4^- , and H_2SO_4 are not applicable).

It has also been shown that pyridine can be recovered successfully with either H_3PO_4 or HSO_4^- ; however, neither $H_2PO_4^-$ nor H_2SO_4 can be employed.

The use of the parameter ΔpK does not appear to fit the observed behavior of all the systems examined. However, the elementary ionization equilibrium theory explains certain inconsistencies with ΔpK values. For example, in general, (1) systems in which both components have pK values greater than about 6 are not useful since interaction is too weak to effect extraction, (2) systems in which both components have pK values less than about 6 are not useful since interaction is too strong for dissociation of the acid-base salt during regeneration, and (3) when either component is a strong acid or a strong base, the system is not applicable because interaction is too strong for regeneration of the reagent.

Recovery of Pyridine and Quinoline from Coal-Tar Fractions

A regenerative system for recovery of pyridine from coal-tar fractions has been examined on the basis of the above consideration of ΔpK . Values of ΔpK for the pyridine - HSO_4^- and pyridine - H_3PO_4 systems are 6.85 and 6.64, respectively, Table II. Each system was examined to determine the behavior of these acids in the extraction and regenerative steps. Data on the quinoline regenerative recovery system are presented for comparison. Ionization data on quinoline ($K_b = 6.3 \times 10^{-10}$, $pK = 9.87$) suggest that either HSO_4^- or H_3PO_4 could be used as the extractant. The respective values of ΔpK are 7.95 and 3.22. Since HSO_4^- gives a larger value of ΔpK , the recovery of quinoline with quinolinium acid sulfate solution as the extractant was examined for comparison.

Experimental

Data on the extraction of pyridine and quinoline bases were obtained by using conventional laboratory equipment consisting of a stirred 1-liter 3-neck flask equipped with a bottom outlet stopcock. Single-stage extraction tests were conducted over the temperature range 0 to 55 C. The data on the pyridine - sulfuric acid system are presented in Table III, and data on the pyridine - phosphoric acid and the quinoline - sulfuric acid systems appear in Tables IV and V, respectively. The extraction data indicate that the nitrogen bases can be concentrated in the aqueous phase by the extraction technique.

To examine the vapor-liquid equilibrium data for the pyridine - phosphoric acid system, the pyridine - sulfuric acid system, and the quinoline - sulfuric acid system, solutions were prepared of various strengths of acid and concentration of the respective nitrogen bases. Acid strengths covered the range 20 to 40 percent and base-to-acid mole ratios varied from 0.6 to 1.9.

An Othmer equilibrium still was used to determine concentrations of pyridine and quinoline in the vapor and liquid phases for the various sample solutions.

Discussion

The Othmer equilibrium data indicate that pyridine concentration

in the vapor increases with increasing concentration of acid (consistent with Equation 17) and, at a given level of acid strength, with increasing pyridine-to-acid mole ratio, see Figures 2 and 3, Tables VI and VII.

Although it was expected that quinoline should behave similar to pyridine, such was not the case. Quinoline was realized in the distillate of the Othmer still; however, the quinoline concentration is significantly lower than pyridine for a given mole ratio of base to acid. Two factors, low vapor pressure and low solubility, cause problems in the quinoline system. Because of the relatively poor solubility of quinoline in water (0.08 g/100 ml at 25 C), recovery of quinoline as a distillate product depends on the limitations of a steam distillation system. Accordingly, the distillate composition is a function of the vapor pressure of quinoline at the boiling point of the mixed liquid phase. Because of the low volatility of quinoline, only about 2 weight percent quinoline is realized in the distillate during the regeneration step. Thus, typical Othmer equilibrium data are not realized for quinoline.

Therefore, although quinoline can be recovered by a cyclic regenerative process, the system is not analogous to the pyridine system. The quinoline system appears suitable on the basis of ΔpK data, but other factors such as solubility and volatility must be considered for practical application.

Summary

A method for selecting reagents for recovery of weak bases from hydrocarbon streams has been developed, based on thermodynamic ionization equilibrium constants. An acid can be selected for recovery of a given base according to the value of ΔpK calculated for the system. Experimental data have been presented on the pyridine - sulfuric acid system, the pyridine - phosphoric acid system, and the quinoline - sulfuric acid system and demonstrate the utility and limitations of the method.

The technique should also be applicable to development of systems for recovery of acids from effluent streams by extraction with selected nitrogen base reagents. When it is required to effectively remove nitrogen impurities in conjunction with a subsequent refining operation on a hydrocarbon stream, a regenerative process may also be applicable; however, provision must be made for adequate removal of nitrogen bases by using a sufficient number of extraction stages.

References

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Table I

Data on Regenerative Recovery Systems
for Nitrogen Bases¹⁾

<u>Nitrogen Bases</u>	<u>Extractant</u>	<u>K_a</u>	<u>K_b</u>
NH ₃	(NH ₄)H ₂ PO ₄	6.23 x 10 ⁻⁸ ²⁾	1.79 x 10 ⁻⁵
NH ₃	H ₃ PO ₄	7.52 x 10 ⁻³³)	1.79 x 10 ⁻⁵
NH ₃	(NH ₄)HSO ₄	1.20 x 10 ⁻²²)	1.79 x 10 ⁻⁵
NH ₃	H ₂ SO ₄	-4)	1.79 x 10 ⁻⁵
Pyridine	(PyH)H ₂ PO ₄	6.23 x 10 ⁻⁸ ²⁾	1.71 x 10 ⁻⁹
Pyridine	H ₃ PO ₄	7.52 x 10 ⁻³³)	1.71 x 10 ⁻⁹
Pyridine	(PyH)HSO ₄	1.20 x 10 ⁻²²)	1.71 x 10 ⁻⁹
Pyridine	H ₂ SO ₄	-4)	1.71 x 10 ⁻⁹

- 1) Handbook of Chemistry and Physics, 44th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1963.
- 2) K_a for second hydronium-ion dissociation.
- 3) K_a for first hydronium-ion dissociation.
- 4) Completely dissociated.

Table II

ΔpK Values for Acid-Base Systems

<u>Systems</u>	<u>ΔpK</u>	<u>Suitability of System</u>
NH ₃ -(NH ₄)H ₂ PO ₄	2.46	Yes
NH ₃ -H ₃ PO ₄	2.63	No
NH ₃ -NH ₄ HSO ₄	2.83	No
NH ₃ -H ₂ SO ₄	*	No
Pyridine-(PyH)H ₂ PO ₄	1.55	No
Pyridine-H ₃ PO ₄	6.64	Yes
Pyridine-(PyH)HSO ₄	6.85	Yes
Pyridine-H ₂ SO ₄	*	No

* ΔpK Not applicable.

Table III

Extraction of Pyridine Bases from Light Oil
With Pyridinium Sulfate Solution*

<u>Test No.</u>	<u>Mole Ratio of Pyridine to H₂SO₄</u>	<u>Pyridine in Washed Light Oil, %</u>	<u>Pyridine in Extract, %</u>
1	1.68	0.15	29
2	1.67	0.12	29
3	1.63	0.08	28
4	1.54	0.05	27

* In each test, light oil containing 0.44 percent of P-bases was washed with a lean pyridinium sulfate solution (mole ratio 1.05) prepared by adding crude P-bases to a 30 weight percent sulfuric acid solution.

Table IV

Extraction of Pyridine Bases from Light Oil
(30 Percent Phosphoric Acid at 55 C)

<u>Test No.</u>	<u>Mole Ratio of Pyridine to H₃PO₄</u>	<u>Pyridine in Light Oil, %</u>	<u>Pyridine in Washed Light Oil, %</u>	<u>Pyridine in Extract, %</u>
1a)	1.0	5.67	0.44	19.5
2a)	1.0	2.10	0.40	19.2
3a)	0.70	4.60	0.24	14.5
4a)	0.92	4.60	0.59	18.1
5b)	0.95	4.60	0.58	18.6

- a) One-stage wash.
b) Two-stage wash.

Table V

Extraction of Quinoline from a Tar Fraction
With Sulfuric Acid^{1,2)}

<u>Test No.</u>	<u>Mole Ratio of Quinoline to H₂SO₄</u>	<u>Quinoline in Washed Oil, %</u>	<u>Quinoline in Acid Extract, %</u>
1	1.46	1.59	36.7
2	1.41	2.06	35.7

1) Tar fraction contained 12.1 weight percent quinoline bases.

2) Extractant contained 30 weight percent H₂SO₄.

Table VI

Pyridine Concentrations in Vapor at Equilibrium With
Refluxing H₂SO₄ Solutions - Othmer Still Data

<u>Initial H₂SO₄ Concentration, wt %</u>	<u>Mole Ratio of Pyridine to H₂SO₄</u>	<u>Pyridine Content of Vapor, wt %</u>
20.4	1.63	4.7
19.9	1.95	21.1
30.9	1.60	10.4
30.4	1.81	23.8
30.6	1.98	41.6
40.3	1.60	21.3

Table VIII

Pyridine Concentrations in Vapor at Equilibrium With
Refluxing H₃PO₄ Solutions - Othmer Still Data

Initial H ₃ PO ₄ Concentration, wt %	Equivalent Ratio of Pyridine to Acid	Pyridine Content of Vapor, wt %
10.45	0.60	0.54
10.44	0.80	2.08
10.41	0.98	6.86
19.88	0.40	0.0
20.42	0.60	0.87
20.40	0.81	4.72
20.34	0.97	13.84
31.20	0.60	1.11
30.38	0.80	6.52
31.08	0.98	21.46
30.98	0.99 ^{a)}	19.92
31.06	0.99 ^{b)}	21.65 ^{c)}

- a) Pyridine contained 23.4 percent picoline.
 b) Pyridine replaced with picoline.
 c) Analyzed as picoline.