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Cyanamide and Dicyandiamide Separation

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ABSTRACT

Solvent extraction of cyanamide and dicyandiamide (1-cyano-guanidine) from aqueous ammoniacal solution with Aliquat 336 dissolved in Shellsol T has been studied. Extraction isotherms with different ionic forms of the anion-exchanger are reported for the separation of the compounds of interest as well as for mixtures of the solutes. The optimum organic phase consists of a mixture of 10% (v/v) 2-ethylhexanol and 30% Aliquat in Shellsol T. With this phase the influence of temperature, extractant concentration, and the effect of changing ammonia concentration in the feed solution on the degree of extraction as well as the selectivity between the components have been investigated. In addition, experiments with different reextractants have been examined for the recovery of cyanamide and dicyandiamide. The evaluation of a physical chemical model for the extraction mechanism is done with the support of a computer program.

INTRODUCTION

Cyanamide, NH_2CN, and its dimer dicyandiamide (or 1-cyano-guanidine) have many applications in organic synthesis (1, 2) (Figs. 1 and 2) due to the reactivity of the cyano group, reactions with the amino group (or in the case of dicyandiamide, with the guanidine group), and reactions of both groups and splitting reactions. Solutions of these materials are not

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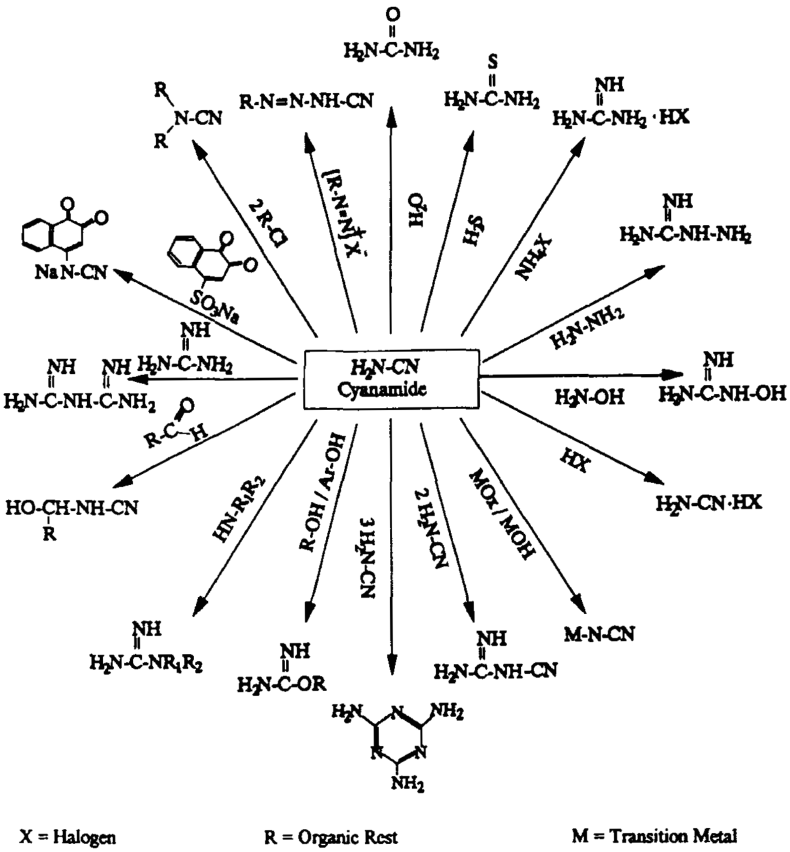

FIG. 1 Reactions of cyanamide.

stable in acidic or in basic media, and dimerization and hydrolysis can occur.

The present work describes a method for the separation of cyanamide and dicyandiamide by solvent extraction from aqueous (ammoniacal) solutions. In pH-neutral solutions the compounds can be separated with solvating extractants, whereas in alkaline solutions the compounds exist as anions, and anion-exchange extractants are necessary. For this purpose, quaternary amines are the only stable extractants in this medium that can be used (a survey of amine extraction is given in Ref. 3). These ion exchangers can be used with different negative charged counterions like SO_4^{2-}, Cl^-, OH^-, CO_3^{2-}, etc., which result in different degrees of extrac-

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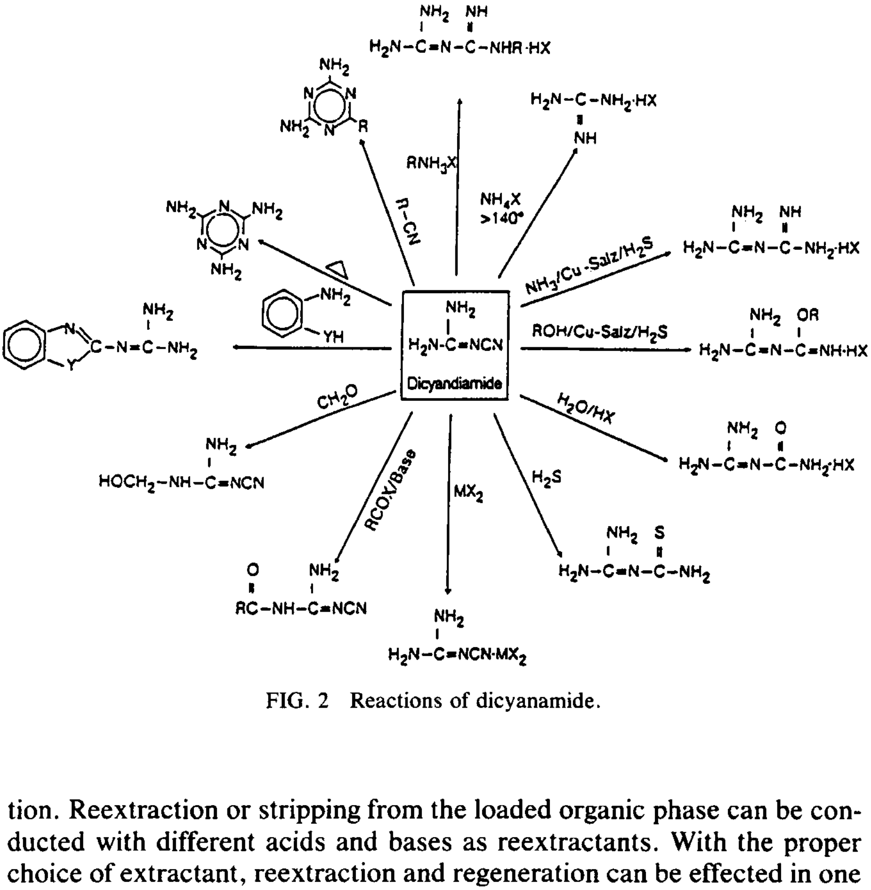

FIG. 2 Reactions of dicyanamide.

tion. Reextraction or stripping from the loaded organic phase can be conducted with different acids and bases as reextractants. With the proper choice of extractant, reextraction and regeneration can be effected in one step, which avoids secondary wastes.

EXPERIMENTAL

Materials

Cyanamide and dicyandiamide (1-cyano-guanidine) were obtained from Merck as analytical grade products of 98% purity. Ammonia was obtained as a 25% aqueous solution (technical product) and diluted to the desired concentrations. The solvating extractants (phosphine-oxides), Cyanex 923 from American Cyanamide Co. and Hostarex PX 320 from Hoechst AG, were used as received. The mixture of trialkyl-methyl-ammonium chlorides (trialkyl = C8–C10, mainly capryl), known as Aliquat 336, was received from Henkel Co. An alcohol-modified hydrocarbon diluent was employed to avoid third phase formation with the extractants. The hydro-

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carbon diluent used in all experiments was Shellsol T which was obtained from the Shell Chemical Co. In the initial comparison of the solvating extractants with the anionic extractant (Aliquat 336), isodecanol was employed as the modifier. For the detailed study of separations based on Aliquat 336 extraction, 2-ethyl-1-hexanol was employed as a modifier because it provided better organic phase stability. The various ionic forms of Aliquat 336 used in this work were converted from the commercially available chloride form using to the following steps: 1) dilution of Aliquat 336 to a 50% (vol% is used throughout this paper) solution with Shellsol T, 2) contact of the organic solution with an equal volume of a 1.5 M solution of H_2SO_4 (or 1.5 M Na_2CO_3 or 1.5 M NaOH) in a shaker for 2 minutes, and 3) settling of the aqueous phase. This procedure was repeated four times. After phase separation the organic solution was diluted further, and the modifier was added to obtain the desired composition of the solvent.

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Analytical Methods

Karl-Fischer titrations were performed on a Radiometer Copenhagen Titroprocessor for water determination. Cyanamide and dicyandiamide concentrations were determined by high performance liquid chromatography (HPLC). The NH_2CN in the aqueous ammoniacal solution was analyzed by a modified method described in the literature (4). To avoid the interference of ammonia the samples were extracted with ether after neutralization, the ether evaporated, the residue dissolved with water, and than derivatized as described. The quantitative determination was made with external calibration and fluorescence detection similar to the described method. Dicyandiamide solutions were diluted to a detectable concentration and analyzed by HPLC and external calibration with ultraviolet detection at 218 nm. The measurements were carried out with a Perkin-Elmer binary gradient pump, a RP-18 analytical column from Millipore Waters, an UV-VIS detector from Perkin-Elmer, and a fluorescence detector from Shimadzu.

Extraction Experiments

Temperature was controlled by a thermostated water bath equipped with an automatic shaker apparatus for effecting good contact and mixing of the organic and aqueous phases. Equal volume contacts of the aqueous and organic phases in glass vessels were employed. A contact time of 10 minutes was used to assure that phase equilibrium was reached in all experiments. The concentrations of solutes in the aqueous phase were determined as described above. Concentrations of the organic phase were calculated by mass balances.

Reextraction Experiments

Reextraction experiments using aqueous solutions of acids and bases as stripping agents were conducted in a manner identical to those described above for extraction. However, it was necessary to carry out the stripping experiments using CO_2 and water in a mechanically stirred, high-pressure autoclave. It was demonstrated that the stirring was adequate for reaching phase equilibrium. The concentrations of solutes in the aqueous phase were determined using HPLC after appropriate dilution. Concentrations of the organic phase were calculated by mass balances.

RESULTS AND DISCUSSION

Extraction of Cyanamide with Solvating Extractants

At pH 7, cyanamide exists in neutral form and can be extracted with solvating agents like phosphine oxides (Cyanex 923 and Hostarex PX 320, which carry different substituents on the central phosphorus atom). Figure 3 shows the results. Using these extractants the separation of cyanamide

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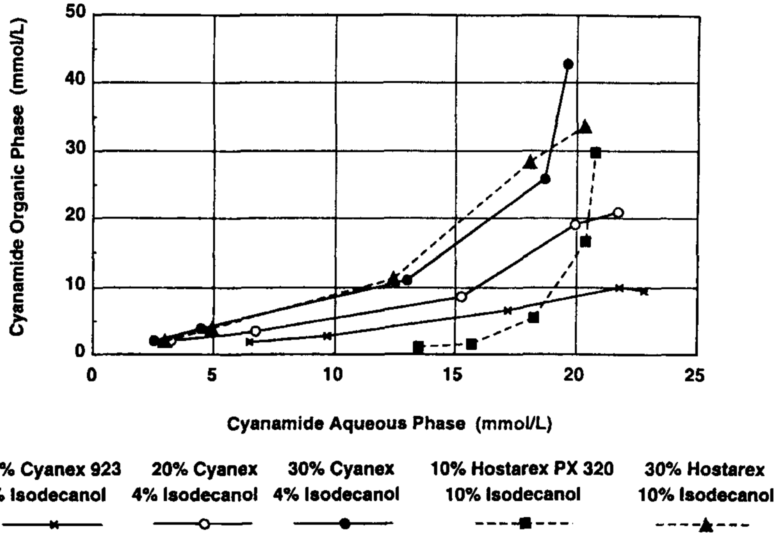

FIG. 3 Extraction of cyanamide with solvating extractants from aqueous solutions using isodecanol as modifier. (Cyanex with 4 vol%, Hostarex with 10 vol% Isodecanol).

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is possible but does not yield high selectivity because all other dissolved components are also coextracted.

Extraction of Cyanamide with Aliquat 336

In alkaline solution cyanamide exists according to its p*K* values (5) in its deprotonated form and can be separated from this unstable solutions by anion exchange:

$$\overline{R_4NX} + HNCN^- \rightleftarrows \overline{R_4NHNCN} + X^- \qquad (1)$$

Figure 4 shows the results using the commercially available chloride form of Aliquat 336 and isodecanol as modifier. Compared with the experiments with solvating extractants, higher degrees of separation and higher selectivity between cyanamide and dicyandiamide (discussed later) were obtained.

When other ionic forms of Aliquat 336 were used, phase disintegration and third-phase formation occurred during experiments because of nonideal solvation of the formed complex with the modifier isodecanol. There is only a small region between 1 and 4% of modifier concentration where

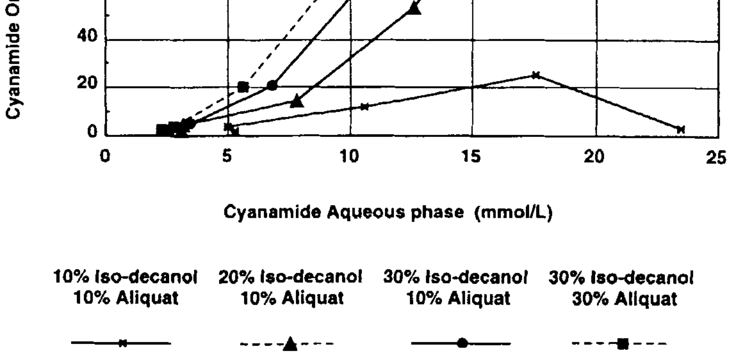

FIG. 4 Extraction of cyanamide from ammoniacal solution using Aliquat 336 and isodecanol.

this problem did not occur. Therefore experiments can only be conducted at well-defined laboratory conditions, and those are not likely to be practical for technical operations.

Among the tested modifiers, 2-ethylhexanol yielded the best results and was chosen as the appropriate modifier for all other experiments. The second reason is the good hydrodynamic properties of this modifier. A concentration of 30% Aliquat 336 showed optimum results whereas lower concentrations gave worse results. Higher concentrations had poorer hydrodynamic properties but similar degrees of extraction. Figure 5 shows the extraction of cyanamide at 40°C with the carbonate and hydroxide form of Aliquat 336. Improved results were observed using the latter ionic form. This can be explained by the higher dissociation constant (lower p*K* value) of this form:

$$\begin{gathered} R_4NX \rightleftarrows R_4N^+ X^- \\ X = OH^-,\ pK_2 = 3.15,\ T = 40^\circ C\ (6) \\ X = CO_3^{2-},\ pK_2 = 3.45,\ T = 40^\circ C\ (6) \end{gathered} \qquad (2)$$

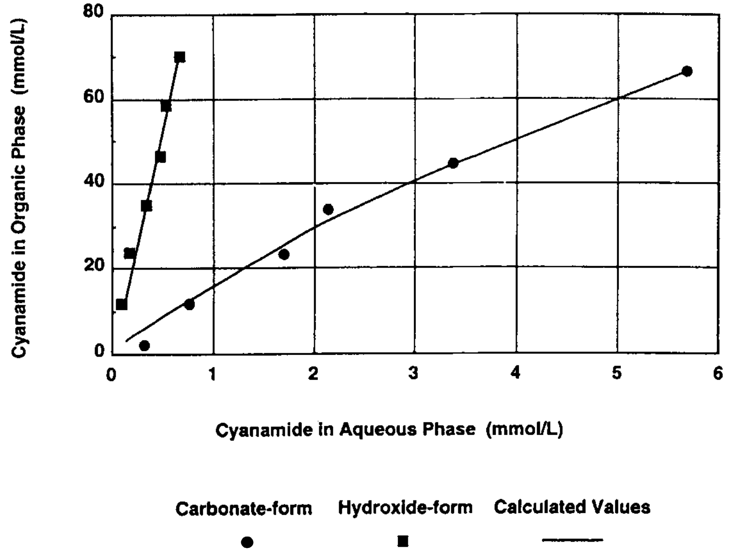

FIG. 5 Extraction of cyanamide with 30% Aliquat 336 and 10% 2-ethylhexanol from 25% ammoniacal solution at 40°C.

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The extraction mechanism can be described as follows:

$$2x\overline{\mathrm{NR}_4^+} + y\mathrm{HNCN}^{(2-)} \rightleftarrows \overline{(\mathrm{R}_4\mathrm{N})_{2x}(\mathrm{HNCN})_y} \qquad (3)$$

The evaluation of the stoichiometric coefficients and the p*K* values of all unknown reactions was made with the computer program QLEQUI (6), which accepted information on the extraction system and provided a comparison between experimental and calculated values. Table 1 shows the calculated values for the cyanamide extraction. The appearance of noninteger coefficients can be explained by the fact that cyanamide has two deprotonation steps. The second step is much more unrealistic under given conditions, but the possibility exists of cyanamide forming stabilized tautomeric forms.

Extraction of Dicyandiamide

Extraction of dicyandiamide was also examined with different ionic forms of Aliquat 336 which were dissolved in Shellsol T. 2-Ethylhexanol was used as a modifier for all described experiments. The results are shown in Fig. 6 and summarized in Table 2. In contrast to the cyanamide results, extraction calculations for dicyandiamide gave integer stoichiometric coefficients. The two p*K* values for the deprotonation of this component are similar, and dicyandiamide possesses the ability to form stabilized tautomers. Therefore, the extraction reaction can be characterized as follows:

$$\overline{\mathrm{R}_4\mathrm{N}^+} + (\mathrm{HNH_2N{-}C{=}N{-}CN})^- \rightleftarrows \overline{(\mathrm{R}_4\mathrm{N})(\mathrm{HNH_2N{-}C{=}N{-}CN})} \qquad (4)$$

$$2\overline{\mathrm{R}_4\mathrm{N}^+} + (\mathrm{HNHN{-}C{=}N{-}CN})^{2-} \rightleftarrows \overline{(\mathrm{R}_4\mathrm{N})_2(\mathrm{HNHN{-}C{=}N{-}CN})} \qquad (5)$$

It must be pointed out that the 1:1 complex (compare Table 2) is more likely to occur than the 2:1 complex.

TABLE 1
Extraction of Cyanamide at 40°C from 25% Ammoniacal Feed Solution with Aliquat 336, Calculated p*K* Values and Stoichiometry

Ionic form	$-\log K_2$	$-\log K_3$	$\mathrm{R_4N^+}$: HN-CN
$\mathrm{OH^-}$ form	3.15	3.79	1:1
$\mathrm{CO_3^{2-}}$ form	3.45	3.85	1.25:1

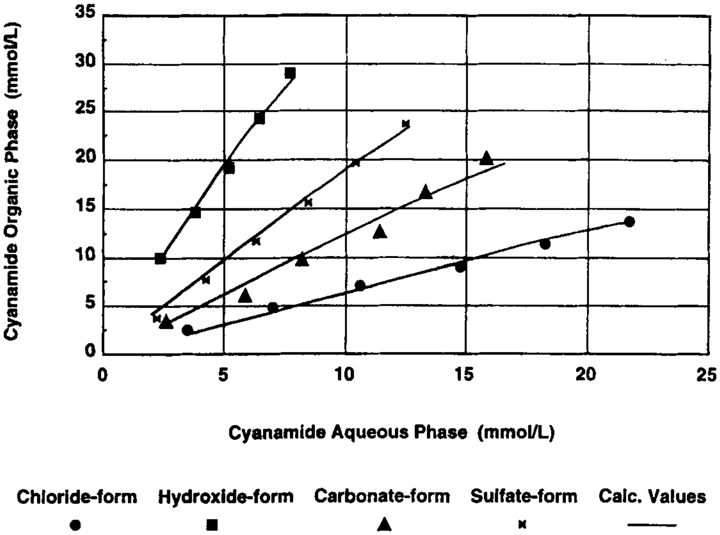

FIG. 6 Extraction of dicyandiamide with different ionic forms of Aliquat 336. Aqueous phase: 0.1% dicyandiamide in 10% NH_3. O/A = 1. Organic phase: 0.6 M Aliquat 336, 10% 2-ethylhexanol.

Influence of Ammonia

Since ammonia affects the deprotonation of the compounds under investigation, experiments with different ammonia concentrations in the aqueous feed solutions were conducted. As expected, the tendency of increasing extraction with increasing ammonia concentration was observed. Table 3 shows the extraction percentages for a single contact of phases. Extraction mixtures of cyanamide from a 1% ammoniacal solution as

TABLE 2

pK Values for the Extraction of Dicyandiamide with Various Ionic Forms of Aliquat 336. K_5 = Formation of 2:1 Complex; K_4 = 1:1 Complex

Ionic form	OH	SO_4^{2-}	CO_3^{2-}	Cl^-
$-\log K_2$	3.25	3.495	3.651	3.89
$-\log K_5$	8.4	8.4	8.4	8.4
$-\log K_4$	4.28	4.28	4.28	4.28
1:1 complex	60%	61.8%	73%	84%

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TABLE 3
Cyanamide and Dicyandiamide Extraction from Various Ammoniacal Solutions at 40°C

NH_3 concentration (%)	1	10	25
	Dicyandiamide Extraction		
Degree of extraction (%)	69.6	76.4	89.6
	Cyanamide Extraction		
Degree of extraction (%)	—	97.1	99

aqueous phase formed unstable emulsions, which is due to aggregation and a low interfacial tension of the organic phase. The increasing percentage of extraction with a higher NH_3 concentration is expected because of the increase in the fraction of the compounds in anionic form with increasing basicity.

Temperature Dependence of Extraction

As known from thermodynamics, changes in temperature affect changes of equilibrium constants. Therefore, experiments with constant modifier and extractant concentration were carried out at various temperatures. With increasing temperature the equilibrium constants for the dicyandiamide extraction decrease in the sequence 20°C > 40°C > 60°C. For the cyanamide extraction a different behavior was obtained (Table 4) due to aggregation phenomena and changing reaction stoichiometry. Included in Table 4 is the equilibrium constant for the deprotonation step of cyanamide, which is totally at the side of the extractable anionic species.

Selectivity between Cyanamide and Dicyandiamide

For separation and enrichment, the selectivity between the components must be studied. Because cyanamide tends to dimerize and polymerize

TABLE 4
Extraction of Cyanamide with the Carbonate Form of Aliquat 336 at Various Temperatures

	20°C	40°C	60°C
R_4N^+: $HN{-}CN^-$	1.41:1	1.24:1	1.53:1
Deprotonation of cyanamide	−3.606	−4.068	−4.387
$-\log K_3$	4.00	3.76	4.10

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at higher temperatures and in alkaline solution (7), the selectivity between cyanamide and dicyandiamide was studied with different ammonia concentrations in the aqueous feed solution at constant but moderate temperatures (Fig. 7). At an ammonia concentration of 10% in the aqueous feed solution, the degree of coextraction of dicyandiamide decreases linearly with increasing loading of the solvent with cyanamide. On the contrary, for aqueous solutions with an ammonia concentration of 25%, the degree of extraction of cyanamide is nearly constant, but the distribution coefficient of dicyandiamide rises until a certain loading of the solvent is reached, where selectivity changes and the extraction of dicyandiamide is suppressed.

Stripping of Cyanamide

For recovering an extracted compound from the organic phase, different methods are possible like thermal stripping, reextraction by change of pH, substitution of the anion, distillation, or combined procedures. However, for the stripping of cyanamide the following points must be kept in mind:

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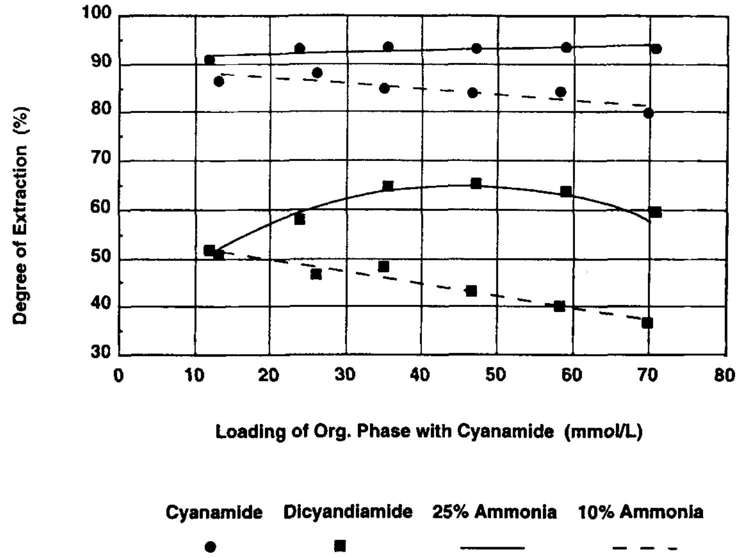

FIG. 7 Coextraction of cyanamide and dicyanamide as a function of loading with cyanamide; extraction with hydroxide form of Aliquat 336. Aqueous phase: 0.1% dicyanamide, 0.1% cyanamide. Organic phase: 0.6 M Aliquat 336, 10% 2-ethylhexanol. O/A = 1.

Cyanamide is thermally unstable
The highest stability lies between pH 4 and 5
During stripping, the cyanamide anion must be reconverted to H_2NCN

Because of the low thermal stability of cyanamide, thermal procedures are excluded a priori, which means that only a combination of substitution reaction and change in pH value can be applied.

Stripping of Cyanamide with Acids and Bases

For this series of experiments the organic phase was at first loaded with an equal amount of cyanamide. Afterward stripping experiments were carried out with different concentrations of acids and bases at constant phase ratio (A/O = 1). Using sodium hydroxide (0.5 to 5 M NaOH) as reextractant, 15 to 25% stripping of the cyanamide was obtained in an one-step stream operation. The recovered product solutions were not stable for a longer period, and cyanamide formed its sodium salt.

Another possibility studied was reextraction with sulfuric and hydrochloric acid; an excess of protons in the aqueous receiving phase should facilitate the stripping. Additionally, slightly higher temperatures were applied to lower the stability of the organic complex. The results are shown in Fig. 8. There is evidence that only at low acid concentrations were the reextraction degrees higher than 50%. In most cases, increased temperature affected the stripping degrees negatively. For HCl the effect was positive up to 0.5 M and negative at 1 to 2 M; for H_2SO_4 it was positive at 0.25 M and negative at 0.5 M.

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Stripping with CO_2 and Water

With an optimal choice of reextractant, both stripping and regeneration of the ion exchanger can be carried out simultaneously. Using the carbonate form of Aliquat 336 as the extractant, stripping of cyanamide can be effected according to the following equation:

$$2\overline{R_4NHNCN} + H_2O + CO_2 \rightleftarrows \overline{(R_4N)_2CO_3} + 2H_2NCN \qquad (6)$$

Besides, cyanamide is obtained in its neutral form and exists in a stable product solution. The results of the experiments which were conducted between 0.5 and 250 bar are shown in Fig. 9. It is evident that the results are relatively independent of the applied CO_2 pressure, and only a small excess of carbon dioxide is necessary. Reextraction degrees in the range of 60% could be reached even at a slight overpressure in a one-step cross-stream operation.

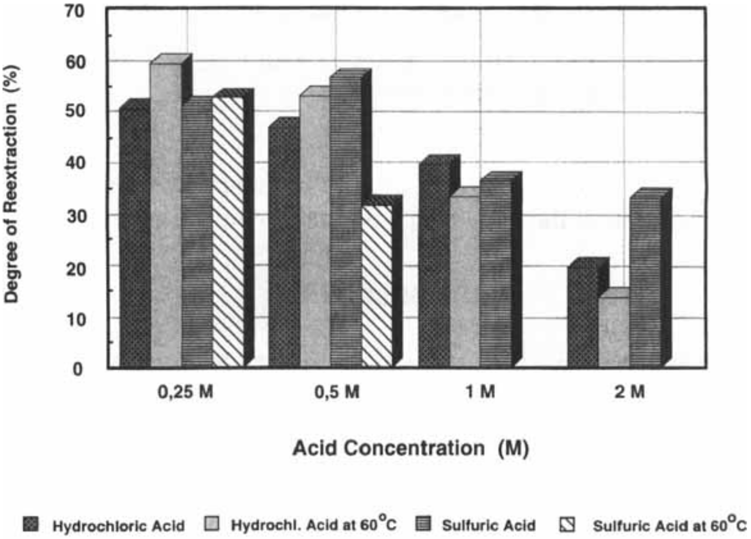

FIG. 8 Reextraction experiments at room temperature and 60°C.

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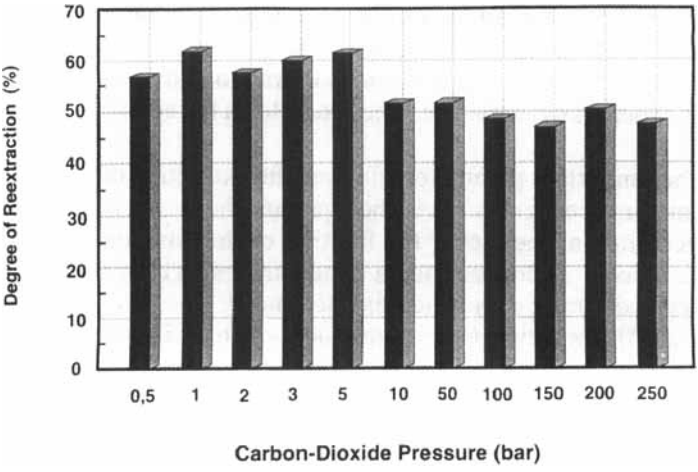

FIG. 9 Reextraction of cyanamide at various carbon dioxide pressures.

Stripping of Dicyandiamide

Likewise, dicyandiamide was stripped with CO_2 and water reextractants. Reextraction isotherms of the form

$$c_o/c_a = D$$

where c_o means concentration of dicyandiamide in the organic phase and c_a concentration in the aqueous phase were obtained with $D = 2/3$.

CONCLUSIONS

Solvent extraction with different liquid ion exchangers removes cyanamide and dicyandiamide from neutral as well as from ammoniacal aqueous solutions. Experiments with solvating agents have shown that extraction of cyanamide is possible. Various ionic forms of the quaternary ammonium compound Aliquat 336 were tested for their availability as ion exchangers for the deprotonated compounds of cyanamide and dicyandiamide from alkaline solution. The competitive effect of the exchange of the amine counterion by the solutes could thus be quantified. Increasing the concentration of amine in the solvent phase increased the degrees of extraction of both compounds. A concentration of 0.6 M Aliquat 336 and 10 vol% modifier gave the best hydrodynamic properties and extraction results.

Cyanamide extraction was best with the hydroxide form of Aliquat 336. Worse, but nevertheless acceptable, results were obtained using the carbonate form. Dicyandiamide separation degrees with different ionic forms of Aliquat 336 follow the order $OH^- > SO_4^{2-} > CO_3^{2-} > Cl^-$. Increasing temperature affects the dicyandiamide extraction adversely (20°C > 40°C > 60°C), whereas cyanamide extraction follows the sequence 40°C > 20°C > 60°C.

Another important parameter affecting the extraction of the compounds is the ammonia concentration in the aqueous phase; the higher the ammonia concentration, the higher the fraction of the compounds as their extractible anions. At low ammonia concentrations (1%), emulsion formation occurred during cyanamide extraction.

The selectivity between the components, which is an important factor for an adequate separation, depends on the loading of the organic phase. With 25% ammoniacal feed solution the degree of cyanamide extraction remains constant whereas the coextraction of dicyandiamide increases with organic loading and remains about constant at organic cyanamide concentrations higher than 40 mmol/L. The selectivity factor (the ratio of the distribution coefficient of cyanamide in relation to dicyandiamide) is

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about 12. Ten percent ammoniacal feed gives a slightly worse extraction of cyanamide in comparison to 25% ammonia. However, the selectivity is much better and is 30 at 40 mmol/L organic loading. According to the nonlinear dicyanamide coextracting at 25% ammonia, an influence of ammonia concentration on selectivity diminishes at low organic loading (e.g., 10 mmol/L cyandiamide). The striking difference in selectivity is at higher loading (higher than 40 mmol/L cyandiamide) which is favorable for industrial applications.

Stripping experiments showed that mild conditions give best results. Using carbon dioxide and water as reextractants at room temperature, stable product solutions are obtained. Acids and bases (even at high temperatures) yield similar results but the acidic or basic product solutions are unstable.

From the technical point of view it seems clear that only when using adequate ionic forms of Aliquat 336 and appropriate reextractants (for example, carbonate form and CO_2/H_2O) can secondary wastes be avoided. Finally, this extractant/reextractant system is highly selective for cyanamide/dicyandiamide separation. The product solution can be converted to crystalline products by further procedures like evaporation and/or crystallization, if desired.

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