DEHYDRATION OF HYDRAZINE BY AZEOTROPIC DISTILLATION

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A process was developed for dehydrating aqueous solutions of hydrazine by azeotropic distillation with aniline as an entrainer. The ternary system hydrazine-water-aniline, which contains the minimum-boiling aniline-water azeotrope and the maximum-boiling hydrazine-water azeotrope, was studied by fractionation analysis to determine the position of the ridge or distillation barrier in the vapor and liquid surface. The studies showed that the position and curvature of this ridge were favorable for the production, by rectification, of a solution richer in hydrazine than the azeotropic proportions. The process comprised three operations. Approximately 70% of the hydrazine charged to the system was dehydrated.

***Entrainers* that form binary minimum-boiling azeotropes with both hydrazine and water are discussed. Ternary systems with these entrainers have saddlepoint azeotropes that boil intermediate with respect to the other invariant components in the system.**

Hydrazine is currently being produced by modifications of the German Raschig process, in which it is obtained in a low-concentration (1 to 3%) aqueous solution (*1*). Because of the maximum-boiling hydrazine-water azeotrope, sometimes called hydrazine hydrate, conventional distillation methods cannot be used to concentrate this solution to more than about 70 wt. % hydrazine and 30% water. (*6*). In the past, anhydrous hydrazine has been produced chemically through the formation of inorganic or organic derivatives which must be subjected to further treatment to yield the dehydrated product (*2*). Since these methods are costly, exploratory work was undertaken to determine whether an aqueous hydrazine solution could be dehydrated by distilling the solution in the presence of a third component that formed a minimum-boiling azeotrope with water. Of the numerous materials tested initially, aniline was the first to show real promise as an effective entrainer, and the process described is based on its use.

THE HYDRAZINE-WATER-ANILINE SYSTEM

The ternary system hydrazine-water-aniline was studied by fractionation analysis to determine the principal features of the vapor-liquid equilibrium surfaces. The basic principle of this method is that when an invariant component, i.e., a pure compound or azeotrope, is distilled from a mixture, the composition of the remaining solution moves rectilinearly in the opposite direction from the invariant component. This method was used by Ewell and Welch (*3*) for studying ternary systems with binary azeotropes, and by Lecat (*4*) for determining the composition of azeotropes in binary systems. The Todd precise fractionation assembly was used for the present analysis.

The Todd fractionating column consisted of a 1/2-in. glass column packed 36-in. high with 1/16-in. glass helices. The pot had an opening for a standard-taper thermometer and one for the entrance of nitrogen. All the vapors were condensed in the column head and the reflux was varied by adjusting a valve on the take-off line. Rubber tubing connecting the receiver vent to a bubbler provided a nitrogen seal and assured operation under a slight positive pressure of nitrogen. Vapor temperatures were measured by a thermometer in the reflux head. The column was shielded with glass and was heated with resistance wires to minimize heat losses. Both the heat load to the pot and the column heaters were controlled by variable resistors.

Two-hundred-gram samples of various ternary mixtures were distilled at a reflux ratio of 4 to 1 (reflux to distillate). Samples of the overhead vapors were collected at each temperature change of more than 2°C. during the distillations, or more often where large amounts of material came over at one temperature. Each sample was weighed and analyzed. All analyses for hydrazine were made by the method of iodate titration described by Penneman and Audrieth (*5*). The composition of a ternary mixture was then established from the analysis for hydrazine and a measurement of the refractive index.

Two typical distillation curves for ternary mixtures which yielded initial overhead vapors of different compositions are shown in Figure 1 to illustrate the method of determining vapor-liquid–equilibrium surface features on a ternary temperature-composition diagram. One curve is for a ternary mixture containing 29.5% hydrazine, 20.5% water, and 50% aniline (run 1) and the other is for a mixture containing 72% hydrazine, 7% water, and 21% aniline (run 2).

The curve for run 1 shows that the first 7.5 g. to distill over was the aniline-water azeotrope at 98.5°C. The next 23.5 g. came over in a temperature range between 116 and 118°C. Analyses of three fractions in this range showed the presence of aniline and water with increasing amounts of hydrazine as the distillation proceeded. After this point (31 g. distilled) the distillate came over at 118.0° to 118.5°C., near boiling point of the hydrazine-water azeotrope, until all the hydrazine and water were distilled. The temperature then rose toward the boiling point of aniline. All cuts except one taken in this third temperature range analyzed more than 73% hydrazine and from 15 to 18% water. Thus complete dehydration did not occur, as is expected in usual azeotropic-distillation practice, an indication that there was some distillation barrier in the system.

The curve for run 2 shows that the first material to distill over was hydrazine, B.P. 113.5°C. About 40 g. came over at this temperature. The overhead temperature then rose to 116°C. and after about 58 g. had distilled, dropped to 114°C. After an additional 12 g. of vapor was collected, the temperature rose to 117°C. The fractions between 40 and 70 g. distilled contained between 86 and 90% hydrazine and the balance was water. These results also indicated the presence of a distillation barrier in the system.

Figure 2 is a plot of the ternary diagram of hydrazine-water-aniline showing the boiling temperatures of the pure compounds and the two azeotropic mixtures. An inspection of this diagram, together with the results of the distillations described above, suggested the presence of a ridge in the vapor-liquid surface of this ternary system between the hydrazine-water azeotrope and aniline, similar to those present in other ternary systems containing azeotropes, as described by Ewell and Welch (*3*). Additional distillation experiments, to be described later, confirmed this, and the position and curvature of the ridge were determined. These ridges are usually curved and form a distillation barrier, but they can be crossed from the concave side by rectification. They cannot be crossed, however, from the convex side. In the region of these ridges the vapor and liquid surfaces are rather flat and therefore cannot be represented by a sharp line as shown in the figure. Their effect as a distillation barrier occurs over a narrow area across the diagram depicted by the ridge boundaries in the figure.

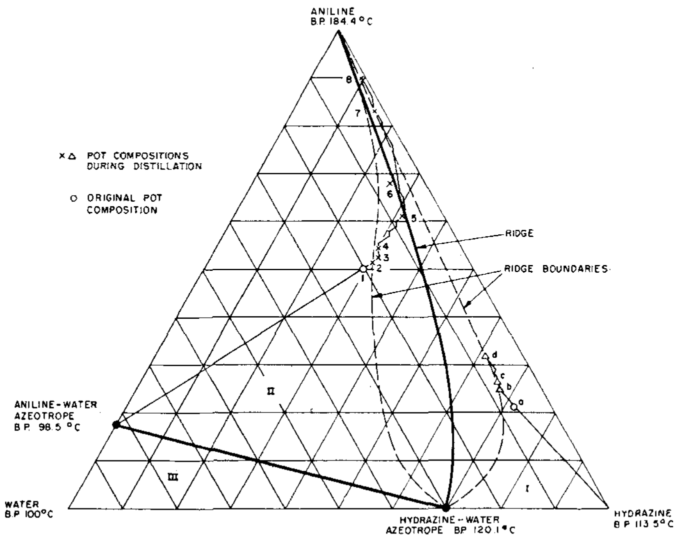

FIG. 2. HYDRAZINE-WATER-ANILINE SYSTEM.

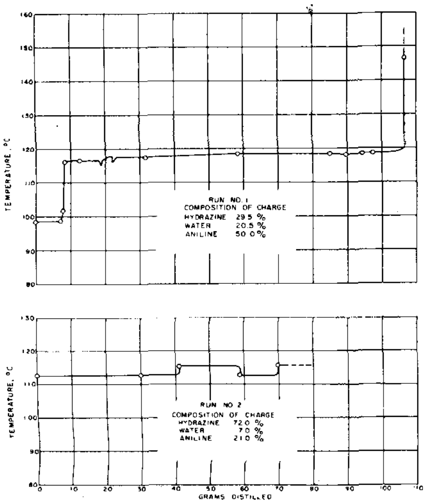

FIG. 1. DISTILLATION CURVES FOR SYSTEM HYDRAZINE - WATER - ANILINE; POINTS REPRESENT QUANTITATIVE DATA; THE SHAPES OF THE CURVES, QUALITATIVE OBSERVATIONS MADE DURING EXPERIMENTS.

In Figure 2 a line has been drawn connecting the invariant compositions of the azeotropes. This, together with the ridge area, divides the diagram into three fractionation areas. Any ternary mixture lying in area I will, when fractionated, give pure hydrazine in the first overhead vapors because it is the most volatile component in this particular region. A mixture with a composition falling in area II will give the low-boiling aniline-water azeotrope as the first fraction, and likewise a mixture with a composition lying in area III will give the aniline-water azeotrope in the first fraction. A mixture with a composition falling on or near the ridge, where aniline and the hydrazine-water azeotrope may be said to be in equilibrium, will, when fractionated, yield the hydrazine-water azeotrope first.

The mechanism of the two distillations described above can be followed on the diagram in Figure 2 by calculating and plotting the pot compositions throughout the experiments. In the first system (run 1) the original composition (point 1) lies in area II, where the first material to distill over should be the aniline-water azeotrope. Inspection of the distillation curve (Figure 1) shows that this was the case. As long as the pure aniline-water azeotrope came over, the composition of the pot shifted rectilinearly in the opposite direction. After a few grams of this material had distilled, the overhead vapor temperature started to rise rapidly, indicating a change in composition. The composition of the pot at this time is shown by point 2. There was no hydrazine present in the initial overhead fraction. The next three fractions showed increasing amounts of hydrazine by analysis and came over in a fluctuating temperature range close to the boiling point of the hydrazine-water azeotrope. The pot compositions at the end of these fractions (points 3, 4, and 5) were still in area II on the diagram with respect to the crown of the ridge, as indicated by the presence of aniline in the distillate. When the composition of the pot reached point 2, it approached the ridge area, where aniline and the hydrazine-water azeotrope were in equilibrium. Since the hydrazine-water azeotrope was the lower boiling, it appeared in the overhead vapors. While this material was distilling, the pot composition shifted rectilinearly in the opposite direction until its composition moved off the ridge into the area where again the aniline-water azeotrope was the lowest boiling component. After a small amount of the aniline-water azeotrope came over, the pot composition moved back upon the ridge, and the hydrazine-water azeotrope again appeared in the overhead vapors. This stepwise shifting of distillate composition continued until the crown of the ridge was crossed, shortly after the end of the fifth cut (point 5).

Once the crown of the ridge was crossed, the pot composition fell in area I, where it was under the influence of the convex side of the ridge and where pure hydrazine was the most volatile component. However, the material to distill over immediately after the crown of the ridge was crossed was the hydrazine-water azeotrope because the composition of the pot was

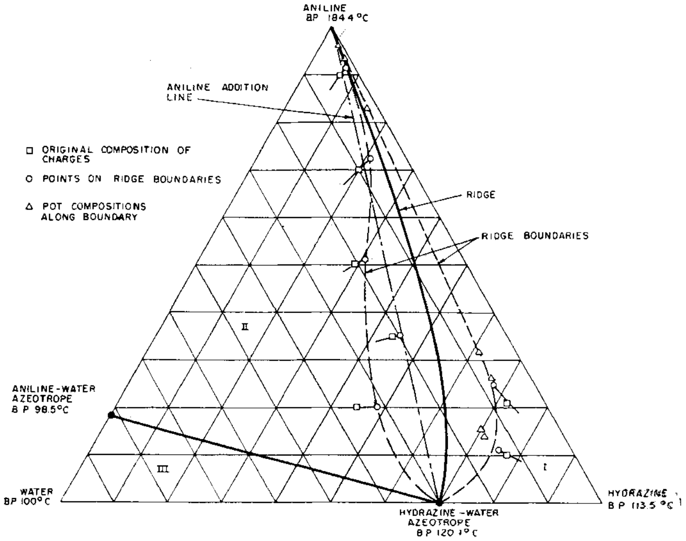

FIG. 3. HYDRAZINE-WATER-ANILINE SYSTEM.

within the ridge boundary. This shifted the pot composition further into area I, and soon pure hydrazine started to come overhead. Hydrazine continued to distill over until the pot composition shifted back to the ridge boundary, where the hydrazine-water azeotrope distilled over again. The distillation from this point on consisted of infinitesimal steps along the ridge boundary, owing to the shifting of the distillate composition, until all the hydrazine and water had been removed.

The temperature of the overhead vapors that came off after the crown of the ridge had been crossed was in the 118 to 118.5°C. range, showing that some of the hydrazine-water azeotrope was present. The composited distillate contained much more hydrazine than the azeotropic proportions. Therefore aniline could be used to increase the concentration of hydrazine in an aqueous solution beyond the azeotrope.

The original pot composition (point *a* in Figure 2) for run 2 was in area I, where hydrazine was the most volatile component, and the first fraction to distill overhead was nearly pure hydrazine. After about 40 g. of over 95% hydrazine had distilled over, the pot composition shifted to the area within the ridge boundary (point *b*) and material with the composition of the hydrazine-water azeotrope started to come overhead. After a few grams of this material came over, the pot shifted past the boundary back into area I. Since in this case the ridge was approached from the convex side, it could not be crossed and the remainder of the distillation was comprised of a continual shifting of the overhead composition between pure hydrazine and the hydrazine-water azeotrope. The pot composition moved along the ridge boundary (points *c* and *d*) toward the point represented by the composition of pure aniline.

LOCATION OF THE RIDGE

Optimum recoveries of high-purity hydrazine depend upon the location and curvature of the ridge and ridge boundaries. To find these quantitatively, several distillation experiments were made in the Todd column with varying amounts of hydrazine, water, and aniline. These are shown in Figure 3.

The straight line between the compositions of aniline and the hydrazine-water azeotrope, called the "aniline-addition line" in Figure 3, represents all possible ternary mixtures obtainable by adding aniline to the azeotrope. In the region of low aniline concentrations, the aniline-addition line was inside the ridge boundary, where very little water could be removed before the distillate became contaminated with hydrazine. Although this area could be narrowed by use of higher reflux ratios, at any reasonable reflux ratio there would be a wide area at low aniline concentrations that would act as an effective distillation barrier. At high aniline concentrations, both the ridge and the ridge boundary were some distance from the aniline-addition line. Since the primary objective was to remove water, the optimum recovery of anhydrous hydrazine would be obtained by distilling a charge farthest removed from the ridge boundary. This would be a charge that contained between 60 and 90% aniline. Additional experiments were made with aniline concentrations above this value, therefore, to determine more precisely the optimum conditions for maximum water removal.

A maximum of about 68% of the water was removed from the hydrazine-water azeotrope at an aniline concentration of 70%. This meant that when the enriched hydrazine solution was separated

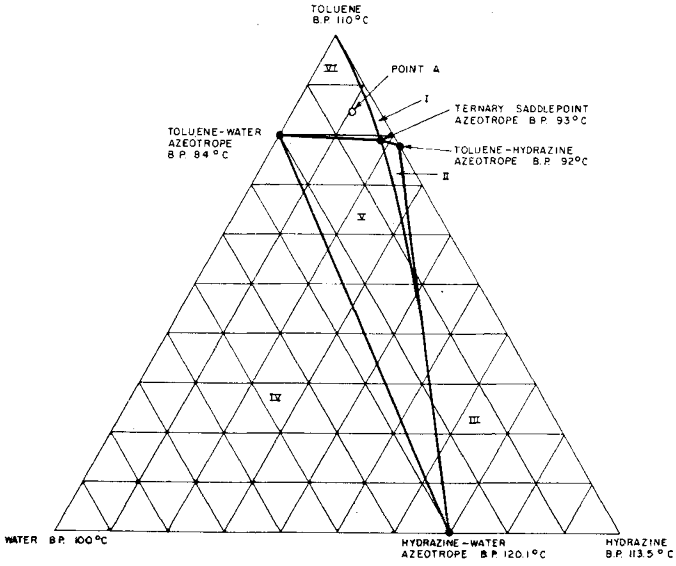

FIG. 4. HYDRAZINE-WATER-TOLUENE SYSTEM.

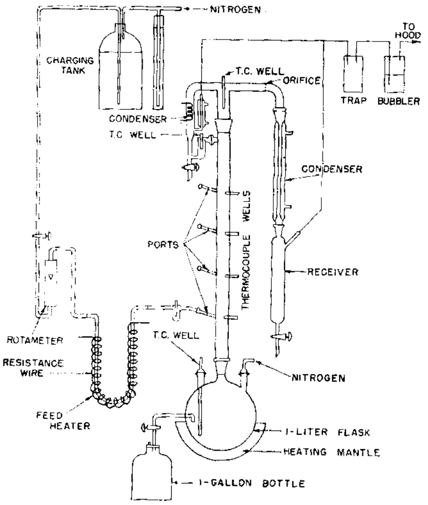

Fig. 5. Two-Inch Distilling Column.

from the entrainer and redistilled, approximately 68% of the original hydrazine could be recovered as anhydrous material. The balance would have to be recycled.

TERNARY SYSTEMS WITH THREE BINARY AZEOTROPES

In the search for a suitable entrainer, cursory experiments were made with materials that formed binary azeotropes with both water and hydrazine. Benzene, toluene, and xylene are representative of this group. These systems have ridges in their vapor and liquid surface similar to the one in the hydrazine-aniline-water system, but they also contain saddlepoint azeotropes, which are azeotropes that boil intermediate to the other invariant components in the system.

Figure 4 is a ternary diagram for the hydrazine - water - toluene system showing the location and boiling points of the binary and saddlepoint azeotropes. Lines connecting the invariant compositions with the ridge divide this system into six fractionation areas. Advantage can be taken of the position of the saddlepoint azeotrope to effect the dehydration of hydrazine if the charge is chosen within the ridge boundary (not shown in the figure), to ensure that the saddlepoint azeotrope is the first fraction to come overhead. For a reasonable recovery, it is also necessary that the composition of the charge be chosen so that when the pot composition shifts rectilinearly in the opposite direction from the ternary azeotrope, it remains within the ridge boundary for a maximum length of time.

A ternary mixture that satisfied these conditions was fractioned to yield a hydrazine solution richer in hydrazine than the azeotropic proportions. The starting ternary feed mixture contained 10.9% hydrazine, 4.7% water, and 84.4% toluene. Point *A* on the diagram represents this composition. About 33% of the hydrazine in the charge came over in a ternary mixture containing 18% hydrazine, 3% water, and 79% toluene. The phases were separated and the aqueous portion, which contained approximately 85% hydrazine, was redistilled to produce an anhydrous product.

DEVELOPMENT OF THE PROCESS

A 2-in. column (*see* Figure 5) that could be operated continuously was built to study the process on a larger scale. This column was packed 37 in. with 1/4-in. glass Raschig rings. There were thermocouple wells equally spaced in the packed section. Opposite each thermocouple well was an opening which could be used either for the entrance of feed or as a sampling port. The reflux head was designed to split the overhead vapors into reflux and product in the vapor phase. An orifice in the product line maintained an 8 to 1 reflux ratio (reflux to distillate), which was very nearly independent of the boil-up rate. The insulation on the column was heated with resistance windings to reduce the heat losses. The still pot was a 5-liter three-necked flask fitted with a thermocouple well and a nitrogen inlet. For continuous operations, an opening in the side of the flask provided for gravity flow out of the pot. The feed flowed to the column from a storage tank through a rotameter and a heater which was made of stainless steel tubing wrapped with resistance wire. A 10-point Micromax (Leeds and Northrup) recorder measured and recorded temperatures throughout the system.

One possible arrangement of distillation equipment for the process comprised three columns in series for the following steps:

1. Removal of about 70% of the water as the aniline-water azeotrope.
2. Separation of the resulting enriched hydrazine solution from the entrainer.
3. Distillation of anhydrous hydrazine from the enriched hydrazine solution.

Each of these steps was performed both batchwise and continuously in the 2-in. column. In continuous distillations made on the first, or water-removal step, and average of 69% of the water charged to the column was removed as the aniline-water azeotrope. The bottoms from step 1 were then fed continuously to the same column to separate the enriched hydrazine solution from the entrainer (step 2). The overhead product from this step averaged 87% hydrazine and the balance water. In step 3 the 87% hydrazine solution was fed continuously to the 2-in. column to produce anhydrous hydrazine. The overhead from this step analyzed 99.9% hydrazine.

PROCESS DESCRIPTION

Figure 6 is a line drawing of a three-column distillation for carrying out the process. The feed to column 1 contains 30% of the hydrazine-water azeotrope and 70% aniline. All the aniline charged is recycled, except a small quantity lost owing to its solubility in water. The first column removes about 70% of the water charged to the column as overhead in the form of the aniline-water azeotrope. The water is separated from the aniline in a phase separator and discarded. The aniline is recycled. The balance of the hydrazine, water, and aniline is taken off as bottoms

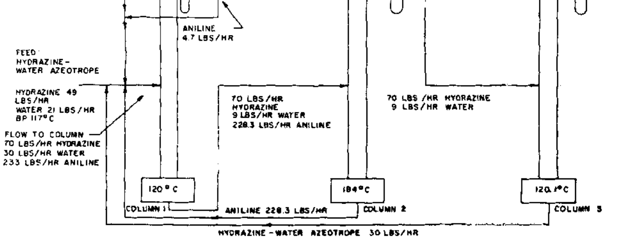

Fig. 6. Process for Dehydrating Hydrazine Hydrate by Azeotropic Distillation with Aniline as an Entrainer.

and charged to column 2. This column separates the entrainer (aniline) from the 88.6% aqueous hydrazine solution, which is taken overhead, the aniline bottoms being recycled to make up part of the feed to the first column. The enriched hydrazine solution from the second column is fed to column 3, where it is separated into anhydrous hydrazine as overhead and the hydrazine-water azeotrope as bottoms. The bottoms, which contain about 30% of the hydrazine feed to the first column, are recycled.

CONCLUSIONS

Aqueous solutions of hydrazine can be economically dehydrated by azeotropic distillation in a multicolumn distillation system with aniline as an entrainer. Although the ridge in the vapor-liquid surface of the ternary system necessitates some recycle of the hydrazine, under optimum operating conditions about 70% of the hydrazine charged to the system can be recovered in one pass through the columns as essentially anhydrous material. The process is patented (*7*).

ACKNOWLEDGMENT

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GAS ABSORPTION IN BEDS OF RINGS AND SADDLES

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New data are presented for the system carbon dioxide—sodium hydroxide. The effect of $CO_3^=$ build-up upon K_Ga values was investigated first and the data were then used to construct a curve by means of which all data were corrected to an arbitrarily chosen reference state of 25% $CO_3^=$ concentration. K_Ga values increased with increasing liquid rate but were not dependent on gas rate if the packings were operated below loading. For some packings examined in the loading range, however, K_Ga values increased with increasing gas rate.

K_Ga values examined in relation to specific surface area were found to be very irregular in connection with rings. The surface-area utilization pattern of the saddles was considerably more uniform. The ring and saddle data for the carbon dioxide–sodium hydroxide system were in good qualitative agreement with the ammonia absorption data of Fellinger and the water–water vapor data of Mehta and Parekh.

The object of this paper is to describe the behavior of rings and saddles in gas absorption. Capacity data have been observed for a wide range of conditions, and conclusions on surface-area utilization are presented. Another object of the paper is to ascertain the data level of capacity coefficients for the new Intalox saddle packing. The carbon dioxide–sodium hydroxide system was chosen for the comparison because equilibrium conditions are established quickly in the column, the analytical procedure is simple, and the *liquid film* seems to offer the controlling resistance. Since data sufficiently complete to permit a packing-behavior comparison are already available for the systems NH_3-H_2O (partly gas-film controlled and $(H_2O)_l - (H_2O)_g$ (wholly gas-film controlled), procurement of the present liquid-film–controlled data will permit a general packing-performance analysis.

LITERATURE

In a study of this kind, where the relative merits of packings are to be evaluated, careful attention must be given to the construction of the experimental tower, to the analytical procedure adopted, and to the range of variables explored. Above all, it must be shown that for the system considered, the broad findings of others and the corresponding new results are in substantial agreement. A summary of the principal experimental conditions and results of earlier reported work for the carbon dioxide–sodium hydroxide system is given in Table 1. The data of Blum, Stutzman and Dodds (*2*) are of only general interest, since the columns and packings were small. Of greater interest is the work of Stutzman and Dodds (*11*); although they reported cocurrent flow data, having worked with liquid and gas rates far in excess of the present flows, some of their quantitative effects of carbonate build-up upon the data level have been noted and incorporated. The tower of Greenwood and Pearce (*6*) was suitably large, but their operating pressure (5.4 atm.) was sub-

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