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# Concentration Retention and Enrichment of Ammonia Bicarbonate Draw Solution in Forward Osmosis Desalination

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**Abstract:** Following the presentation of the novel ammonia-carbon dioxide forward osmosis (FO) desalination method in 2005, ammonium bicarbonate has been used frequently for the preparation of draw solution. However, the ammonium bicarbonate ($NH_4HCO_3$) salt decomposes at higher temperatures and retains less concentration than the solute added for desired concentration. In this study, the concentration retention properties of $NH_4HCO_3$ draw solution, in relation to temperature, time and desired concentration have been investigated. In order to achieve the desired concentration, the solution was enriched either with additional amount of $NH_4HCO_3$ or ammonium hydroxide ($NH_4OH$) solution. The results revealed that $NH_4OH$ is the good candidate to be added to the solution to get the targeted concentration.

**Key words:** desalination, forward osmosis, draw solution, ammonium bicarbonate, concentration retention, enrichment

## 1. Introduction

The growing global shortage of water and increasing demands for freshwater have led to a rising interest in desalination to produce water for both industrial and domestic usage. Currently, desalination plants based on thermal distillation and reverse osmosis, consume huge amounts energy. As a result, there has been always an interest in less-energy intensive approaches.

In recent times, forward osmosis (FO) process has been developed as a possible option for desalination, with the prospective for much lower energy consumption. In FO desalination method, an osmotic pressure gradient is created by a highly concentrated solution (Draw Solution) to pull water across a semi-permeable membrane from a feed water of lower salt concentration. As an osmotic pressure generator, draw solution plays the key role on the realization of forward osmosis.

Selection of draw solution has been an important aspect of past researchers. There are several reports on FO desalination which have mainly focused on attaining appropriate draw solutions using different type of chemicals that are either easily removable or consumable. An overview of these previous efforts is presented in Table 1 [1-16]. As per observation, ammonium bicarbonate ($NH_4HCO_3$) has been used frequently as draw solute after presentation of ammonia-carbon dioxide FO desalination method by McCutcheon et al. [9] in 2005. They have discussed ideal draw solution characteristics as well as have demonstrated that these criteria are satisfied by using ammonium bicarbonate draw solution. The concentrated draw solution was made by dissolving $NH_4HCO_3$ in deionized water. One main reason for

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using $NH_4HCO_3$ was the ease of separation of the fresh water from the draw solution. They performed FO experiments using 6M $NH_4HCO_3$ draw solution at 50°C for one hour. However, Gokel [17] reported that $NH_4HCO_3$ starts to decompose into ammonia, carbon dioxide, and water at 35°C, while complete decomposition is achieved above 60°C. The decomposition process causes ammonia and carbon dioxide gases to escape from the solution. As a result, the salt solution retains lesser solution concentration than what is intended. Also, Trypuc and Kielkowska [18] stated that $NH_4HCO_3$ salt is chemically unstable and decomposes at higher temperatures under atmospheric pressure. Considering that fact, they carried out investigations under required pressure conditions to prevent decomposition process. According to Speight [19], solubility of $NH_4HCO_3$ per 100 gram of water is 36.6 and 59.2 g at 40 and 60°C, respectively. On the other hand, Ng. et al. [11] found that $NH_4HCO_3$ was fully insoluble, when 36.6 g (4.064 M) of $NH_4HCO_3$ was dissolved in 100 gram of water even at 50°C. In addition, they observed gas bubbles releasing from the solution, which was an indication of $NH_4HCO_3$ decomposition. Due to these constraints, they conducted most of the experiments at 30 or 50°C with a draw solution concentration of 3M. No observed decomposition was found, in experiments conducted at 30°C. It was not possible for them, to produce 6 M of NH4HCO$_3$ draw solution at 50°C due to decomposition trouble. McCutcheon et al. [12] have made draw solution of desired concentration by mixing ammonium bicarbonate ($NH_4HCO_3$) and ammonium hydroxide ($NH_4OH$) with deionized water at proper proportions. They used higher ammonia to carbon dioxide molar ratios ranging from 1.2 for 1.1 M draw solution to 1.4 for 6M draw solution. During the FO tests, the draw solution temperature was held at 50°C. Asemsro [15] reported that additional amount of NH4HCO$_3$ salts above the calculated amount were needed to retain the solution concentration at 6 M. The experiments were conducted in FO mode at 50°C for one hour. Sarpong [16] found that lesser molar concentration of ammonium salt was retained than the desired molar amount that was mixed at the start of preparing the draw solution. In the investigation for recapture of ammonia carbon dioxide gases, molar concentration of 1 to 3 M of NH4HCO$_3$ solution were tested at 50 to 70°C for 1 hour to 2 hours.

**Table 1 Overview of draw solutions used by past investigators with separation strategy.**

| Year | Ref. | Draw solution | Separation strategy adopted or assumed |
|---|---|---|---|
| 1965 | 01 | $SO_2$ | Heating or stripping |
| 1965 | 02 | Alcohols, $SO_2$ | Standard means |
| 1972 | 03 | $Al_2SO_4$ | Add $Ca(OH)_2$ |
| 1975 | 04 | Glucose | Ingestion purpose |
| 1976 | 05 | Glucose & Fructose | Ingestion purpose |
| 1989 | 06 | Fructose | Ingestion purpose |
| 1992 | 07 | Glucose | Low pressure RO |
| 2002 | 08 | $KNO_3/SO_2$ | Precip. by cooling |
| 2005 | 09 | $NH_4HCO_3$ | Moderate heating |
| 2005 | 10 | NaCl | Osmotic distillation |
| 2006 | 11 | $NH_4HCO_3$ ,Glucose, Fructose | Distillation/ingestion |
| 2006 | 12 | $NH_4HCO_3$, $NH_4OH$ | Moderate heating |
| 2008 | 13 | Glucose Sucrose | Ingestion purpose |
| 2009 | 14 | NaCl, $MgCl_2$, $NH_4HCO_3$ | RO or distillation |
| 2009 | 15 | $NH_4HCO_3$ | Distillation |
| 2010 | 16 | $NH_4HCO_3$ | Distillation |

While many of these efforts contribute to the use of ammonium bicarbonate draw solution in FO experiments and share discussions on the observed solubility and decomposition problems, no work was found addressing in detail the concentration retention ability of the solution at different temperatures and its enrichment aspects to achieve the desired concentration. The purpose of this paper is to examine and disseminate the issues involved in preparing $NH4HCO_3$ draw solution. The solubility temperature and the temperature at the beginning of decomposition were reported over a wide range of molarities (1 M to 6 M). Concentrations of solution that were retained at solubility temperature sand at specific higher temperatures were presented. Also, loss of concentration in relation to time was investigated. Enrichment schemes like addition of excess $NH4HCO_3$ salt or $NH_4OH$ solution were tested to achieve desired concentration level.

## 2. Experimental Investigation

### *2.1 Materials& Instruments*

The following chemicals were used:

- Ammonium Bicarbonate: Fisher Scientific certified powder, M.W. 79.06.
- Sodium Chloride: Fisher Scientific certified crystalline, M.W. 58.44.
- Ammonium Hydroxide: Fisher Scientific certified, 14.8N, M.W. 35.05.
- Deionized (DI) Water (produced in a Millipore deionizing unit)

The following apparatuses and instruments were used for preparation of the required solutions and for measuring the required properties.

1) Kimax Kimble laboratory glassware assortment.
2) Biomega Hot Plate Magnetic Stirrer with stir bars.
3) Ohaus PA3102 Pioneer Precision Balance.
4) Fisher Scientific Thermocouple.
5) Oakton CON 610 waterproof TDS meter.
6) Precision System Inc. 5002 OSMETTE A™ Automatic High Sensitivity Osmometer.

### *2.2 Test Procedure*

A total of seven batches of experiments were conducted for the investigation. First batch of $NH4HCO_3$ solution, staring from 1M to 6M desired concentrations were prepared to study the concentration retention abilities at solubility temperature and at 45, 50, 55 and 60°C respectively. The second batch of solution was prepared in terms of molalities, so as to observe the variability if any with that prepared in terms of molarities. The next three batches were devoted to examine the concentration retention abilities after keeping the solution for 30, 60, 90 and 120 minutes under constant temperature. The remaining two batches were assigned for concentration enrichment studies. The existing room temperature as well as the DI water temperature was measured previous to preparing any solution. Instruments like TDS meter and Osmometer were calibrated with standard solutions (supplied with kit). Sodium Chloride (NaCl) solution, which is more stable, was prepared in specific concentrations to validate these instruments. It was to make sure that these instruments were confirming the specific concentration of NaCl within ±99.9%, for the amount of solute that was added. To prepare the $NH4HCO_3$ solution of particular molarity (M) or molality (m), calculated quantity of salt was weighed according to the molecular weight. Ammonia bicarbonate solutions were prepared from 1M through 6M for concentration retention evaluation. The salt was kept inside the 2000 ml flask and the flask was placed on the hot plate magnetic stirrer. Magnetic stir bar was put inside the flask. If the concentration of solution was to be measured in terms of molarity, then DI water was poured in to the flask until total volume of solution became one liter. Otherwise, one kilogram of DI water was added for measuring concentration of solution in terms of molality. The hot plate magnetic stirrer was switched on to prepare the solution. Time was noted as zero at this instant. Endothermic down temperature was noted three minutes after mixing the salt with DI water. Temperature and the time were noted down following the observation of gas bubbles releasing continuously from the solution. That instant was interpreted as the beginning of decomposition. The solution was said to be prepared, when it was appeared clear and transparent without any visible particles. Time and temperature were noted at the point of solution formation and samples were collected for concentration measurements. The prepared solutions were further heated and samples were collected each at 45, 50, 55 and 60°C for determining the concentration retention. Solutions were prepared separately to collect samples each at 50, 55 and 60°C after keeping it under constant temperature for 30, 60, 90 and 120 minutes. These data were useful to evaluate loss of concentration with time. For evaluation of the enriching efforts to achieve the desired concentration, two schemes were tried. In first scheme, additional amount by 0.5M of $NH4HCO_3$ salt was mixed to each solution of desired concentration from 1M through 6M. Ammonium hydroxide ($NH_4OH$) was added to $NH4HCO_3$ salt to make a composite solution in the second scheme. For composite salt solutions, samples were prepared from 1m through 6mand were collected only for Osmette, i.e., molality measurements.

### 2.4 Test Measurements

The temperature was measured using thermocouples to an accuracy of ±0.1°C. Temperature was controlled within ±1°C, when it was required to keep the solution at constant temperature for specific time. Oakton CON 610 TDS meter was used to measure total dissolve solids (TDS) of the solution in terms of ppm. Previous to any measurement, the instrument was calibrated daily with standard solution available with the meter kit. The osmolality of each solution was measured using a 5002OSMETTE A™ Automatic High Sensitivity Osmometer (Precision System Inc). The Osmometer determines the total osmolality of an aqueous solution by performing a comparative measurement of the freezing point of pure water and that of the solution being tested. A solution containing 1 Osmole (1000 m Osm) of dissolved solute per kg of water lowers the freezing point of water by 1.858°C [20]. In practice, however, the osmometer reads directly in mosm/kg $H_2O$ by converting the thermistor readings by direct comparison with readings obtained using standard aqueous salt solutions of known osmolality. For example, 0.5 molality i.e., 0.5 gram mole of NaCl (osmotic coefficient of 0.93) salt in 1 kg of DI water will show a reading of 930 m Osm/kg $H_2O$ in the Osmometer [20]. Similarly, 1 molality of $NH4HCO_3$ with a osmotic coefficient of 0.98 [21] will show a reading of 1960 m Osm/kg $H_2O$. The instrument was calibrated with standard solution, prior to any measurements. The Osmometer has a reading range of 0-3000 m Osm/kg $H_2O$. In view of the fact, each solution was diluted to same dilution factor, i.e., 10 so as to keep uniformity of test results.

## 3. Results and Discussions

### 3.1 Solubility of $NH4HCO_3$

$NH4HCO_3$ solutions with molarities starting from 1M to 6M were prepared. Immediately after mixing the salt with DI water, the temperature went down in the process, indicating an endothermic reaction. Only magnetic stirrer was switched on to prepare clear solution up to 2M without use of hot plate. The solution preparation process inventory for each molar concentration is presented in Table 2. The solubility temperature increases with increase in desired molar concentration. For 6M solution, solubility temperature was more than 50°C. The difference between existing DI water temperature and that of endothermic down temperature are reported inside bracket in Table 2. As the desired solution concentration increased, the temperature difference also increased from 5.2°C for 1M to 9.9°C for 6M. The endothermic effect was more as more quantities of solutes were mixed to make same volume of solution. Gas bubbles, i.e., decomposition of $NH4HCO_3$ was not observed for solutions of desired concentration up to 3 M. Decomposition started around 35°C for solutions of 4 M and above.

### *3.2 Concentration Retention of NH4HCO$_3$ at Solubility Temperature*

$NH_4HCO_3$ solutions prepared in provisions of molarities (1 M to 6 M) and molalities (1 m to 6 m) were tested for concentration retention measurements using TDS meter as well as Osmometer respectively. The measurements were taken immediately after the solution formation. The readings were multiplied with the dilution factor to evaluate real concentration of solution. The real TDS values in ppm were divided by the molecular weight (expressed in milligram) 79060 of NH4HCO$_3$ to convert to the molar values. Similarly, Osmometer values in mOsm are divided by 1960 to convert to the molal values. The concentration retention ability of $NH_4HCO_3$ are presented in Table 3 and Fig. 1. It was observed that desired solution concentration was never achieved for any molarity or molality values. Even if there was no visual decomposition for 3 M (3 m) or less, the retained concentration was less than the target. The percentage of retained concentration decreased with increase in desired solution concentration. Also, the percentage of retained concentration was nearly same for solutions, whether prepared in terms of molalities or molarities.

**Table 2 One liter NH4HCO$_3$ solutions preparation inventory.**

| Desired solution conc. in Molarity | Existing Room Temp. in °C | Existing DI Water Temp. in °C | Endothermic down Temp. in °C | Bubble Point Temp. in °C | Solution Temp. in °C |
|---|---|---|---|---|---|
| 1 M | 17.3 | 14.9 | 9.7 (5.2) | Not observed | 12.1 |
| 2 M | 18.8 | 16.7 | 11.3 (5.4) | Not observed | 16.3 |
| 3 M | 16.6 | 13.7 | 6.4 (7.3) | Not observed | 30.2 |
| 4 M | 17.1 | 14.9 | 6.5 (8.4) | 35.6 | 41.6 |
| 5 M | 16.2 | 14.4 | 5.3 (9.1) | 35.3 | 47.1 |
| 6 M | 18.9 | 18.2 | 8.3 (9.9) | 34.6 | 52.8 |

**Table 3 Concentration retention ability of $NH_4HCO_3$ solution at solubility temperature.**

| Desired solution concentration in molarity (molality) | Concentration retained in molarity | Concentration retained in molality | % of desired molarity retained | % of desired molality retained |
|---|---|---|---|---|
| 1 M (1 m) | 0.938 | 0.952 | 93.80 | 95.20 |
| 2 M (2 m) | 1.803 | 1.828 | 90.15 | 91.40 |
| 3 M (3 m) | 2.592 | 2.604 | 86.40 | 86.83 |
| 4 M (4 m) | 3.232 | 3.230 | 80.82 | 80.75 |
| 5 M (5 m) | 3.720 | 3.797 | 74.40 | 75.94 |
| 6 M (6 m) | 4.164 | 4.197 | 69.41 | 69.95 |

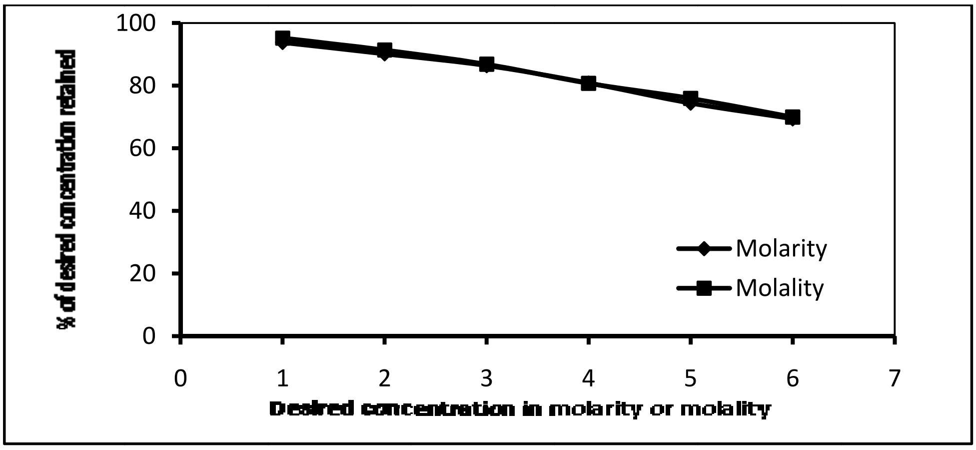

**Fig. 1 Concentration retention ability of $NH_4HCO_3$ at solubility temperature.**

### *3.3 Concentration Retention of $NH_4HCO_3$ at Higher Temperatures*

The solutions prepared in terms of molarities were further heated to collect samples for determining the concentration retention with variation of temperature. Samples were collected at 45, 50, 55 and 60°C for solutions up to 4 M. For 5 M and 6 M solution, samples were obtained at 50, 55 and 60°C, and at 55 and 60°C respectively. The results are illustrated in Fig. 2. As per observation, for any molar value, the retention of concentration decreased with increase in temperature of solution due to decomposition. Another interesting finding was that at a particular temperature, the percentage of retention was nearly constant for each concentration and was independent of molarity of solution.

### *3.4 Concentration Retention of NH4HCO$_3$ with Time*

As discussed in introduction section, FO tests are usually conducted at 50 to 55°C and for one to two hours. So, it was desired to test concentration retention with varying times from 30 minutes through 120 minutes at constant temperature. These solutions were prepared separately in terms of molarities. The results are presented in Fig. 3 through Fig. 5. At a particular temperature and for any molar value, the concentration retention decreased with increase in retention time of solution due to release of volatile gases to atmosphere. Also, the percentage of retention was nearly constant for each concentration of solution.

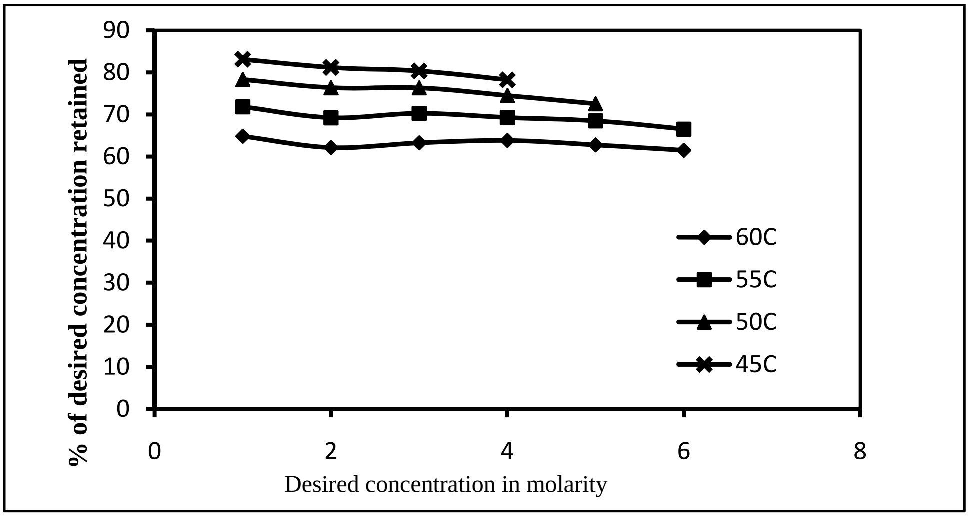

**Fig. 2 Concentration retention ability of $NH_4HCO_3$ at higher temperatures.**

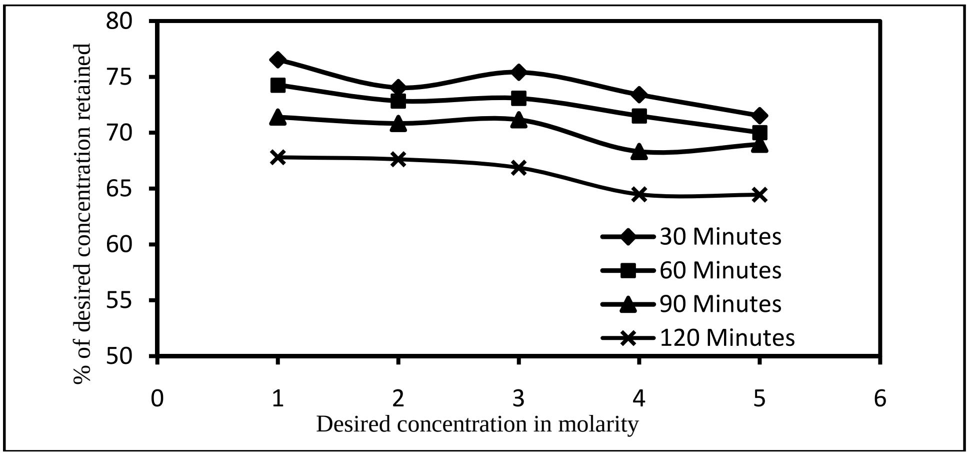

**Fig. 3 Concentration retention ability of $NH_4HCO_3$ with time at 50°C.**

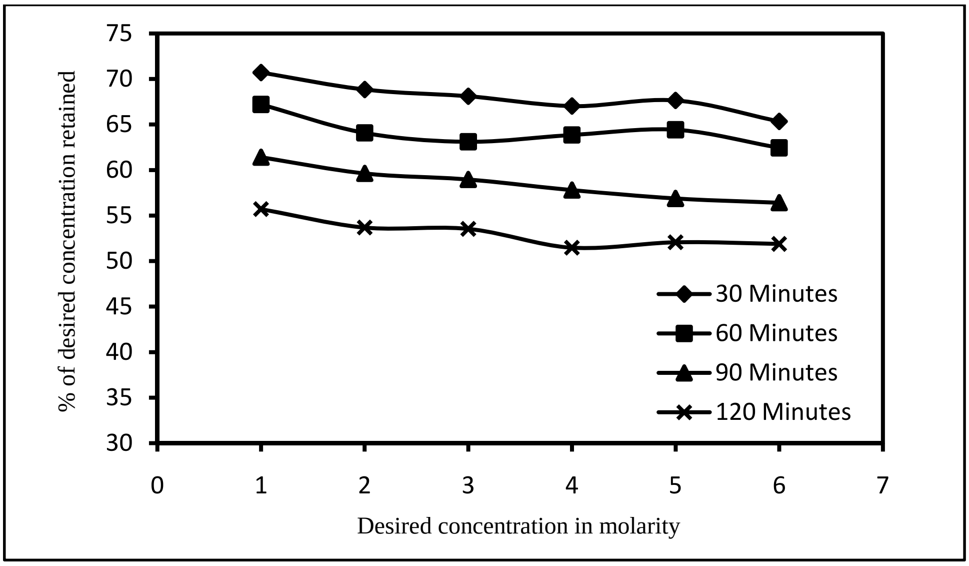

**Fig. 4 Concentration retention ability of $NH_4HCO_3$ with time at 55°C.**

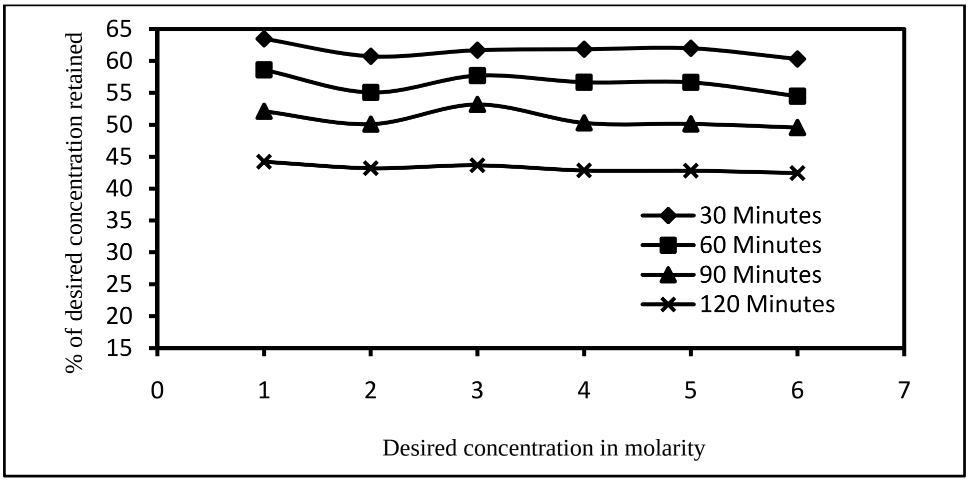

**Fig. 5 Concentration retention ability of $NH_4HCO_3$ with time at 60°C.**

### *3.5 Concentration Enrichment with Additional Amount of NH4HCO$_3$*

To get the desired solution concentration, trial was made to add extra amount of solute to the solution. For each desired molar concentrations up to 5 M, in addition to the calculated quantities, extra amount of solute by 0.5 M was added to DI water. Often, FO tests are conducted using a 6 M draw solution. To achieve the target concentration of 6 M, additional amount of solute by 0.5 M was added incrementally up to 8 M for each solution preparation. The results obtained are presented in Table 4. The samples were collected at solubility temperature. Target concentrations have been achieved up to 2 M solution. The desired solution concentration was never achieved for 6 M even after adding the solute in increments by 0.5 M up to 8 M.

### *3.6 Concentration Enrichment of NH4HCO$_3$ Solution with Addition of $NH_4OH$.*

To achieve the target molar concentration, ammonium hydroxide ($NH_4OH$) was added at the start of solution preparation. To keep the track of the amount of ammonium hydroxide, the molar ratio between ammonia and carbon dioxide was recorded for each solution preparation. Solutions were prepared in terms of molality and measurements were taken in the Osmometer. $NH_4OH$ was added with incremental molar ratio, until and when the desired concentration was achieved or exceeded. The results obtained are presented in Table 5. Unlike $NH_4HCO_3$, addition of $NH_4OH$ caused exothermic reaction. The endothermic down from DI water temperature was almost regained by addition of $NH_4OH$ solution. Almost in every case desired solution concentration was achieved for any molality values up to 6m. The ammonia to carbon dioxide molar ratios used in preparing the solution were ranged from 1.120 for 1m desired concentration to 1.884 for 6m.

**Table 4 Concentration enrichment efforts with additional amount of $NH_4HCO_3$ by 0.5 M.**

| Desired solution concentration in molarity | Equivalent total concentration after solute addition by 0.5 M in molarity | Concentration retained in molarity | % of desired molarity retained |
|---|---|---|---|
| 1 M | 1.5 | 1.312 | 131.20 |
| 2 M | 2.5 | 2.139 | 106.95 |
| 3 M | 3.5 | 2.913 | 97.10 |
| 4 M | 4.5 | 3.586 | 89.65 |
| 5 M | 5.5 | 4.092 | 81.84 |
| 6 M | 6.5 | 4.647 | 77.45 |
| 6 M | 7.0 | 4.824 | 80.40 |
| 6 M | 7.5 | 4.966 | 82.78 |
| 6 M | 8.0 | 5.202 | 86.70 |

**Table 5 Concentration enrichment of $NH_4HCO_3$ solution with addition of $NH_4OH$**

| Desired solution concentration in molality | Ammonia to carbon dioxide molar ratio kept during preparation | Concentration retained in molality at solubility | % of desired molality retained |
|---|---|---|---|
| 1 m | 1.120 | 1.102 | 110.200 |
| 2 m | 1.203 | 2.068 | 103.400 |
| 3 m | 1.326 | 3.046 | 101.533 |
| 4 m | 1.479 | 4.132 | 103.300 |
| 5 m | 1.652 | 5.024 | 100.480 |
| 6 m | 1.884 | 6.102 | 101.700 |

## 4. Conclusion

The data presented in this study demonstrate that ammonium bicarbonate draw solution is unstable and decomposes with increasing delay time and temperature. The desired concentration of solution cannot be achieved by mixing only ammonium bicarbonate solute with DI water. Ammonia bicarbonate and ammonium hydroxide shall be mixed at proper proportions to produce a solution of desired concentration.

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