

Liquid-Liquid Equilibria for Aqueous Systems Containing *N,N*-Diethylmethanamine and Sodium Chloride or Sodium Sulfate

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Liquid-liquid equilibria were measured to study the feasibility of using *N,N*-diethylmethanamine (DEMA) for extractive crystallization of sodium chloride or sodium sulfate. The experimental results show that DEMA selectively extracts water from saturated sodium chloride solution at low temperatures (5–10 °C), causing sodium chloride crystals to precipitate. DEMA also selectively extracts water from saturated sodium sulfate solution at moderate temperatures (21–25 °C), precipitating sodium sulfate decahydrate.

Introduction

In numerous chemical processes, inorganic salts are produced either as primary products or as secondary byproducts. In general, they are produced from aqueous solutions. If the salt is to be recovered in solid form, the last step of the process requires crystallization. If the solubility of the salt is sensitive to temperature, crystallization can be achieved by a change in temperature, but if solubility is relatively insensitive to temperature, crystallization is commonly achieved by evaporation of water. Although evaporation can be achieved easily by boiling, the high heat of vaporization of water makes evaporation energy-intensive. To reduce the energy cost, multieffect evaporators are widely employed in industry. Although multieffect evaporators reduce energy consumption by a factor of 2–3, installation and capital costs of such evaporators are appreciable. To reduce energy costs drastically, it is desirable to precipitate salt without vaporization of water.

It is well known that electrolytes can be used to remove organic compounds from water by "salting out", which can be explained by noting that water molecules that surround ions are unavailable for the solvation of organic-solute molecules. Similarly, polar organic molecules in aqueous salt solutions "capture" some of the water molecules, thereby reducing the solubility of the salt (1). If such an organic solvent is brought into contact with a saturated salt solution, water is extracted and salt precipitates. This process is known as extractive crystallization. Weingaertner et al. (2) showed that sodium chloride can be produced economically by extractive crystallization with diisopropylamine (DIPA) at a subambient temperature (e.g., –5 °C). DIPA has a lower critical solution temperature with water of 27 °C, and exhibits a lower critical solution temperature of –7.5 °C with saturated sodium chloride solution. To reduce the energy cost of refrigeration, an alternative solvent is desired that exhibits hydrophilic and hydrophobic characteristics similar to DIPA but has a critical solution temperature with water higher than that for DIPA. *N,N*-Diethylmethanamine (DEMA), a tertiary amine that has a lower critical solution temperature with water of 51 °C, was chosen.

The goal of this study was to determine experimentally whether DEMA is a suitable organic solvent for the extractive crystallization of sodium chloride or sodium sulfate. Therefore, measurements were made to determine liquid-liquid equilibria for the systems DEMA/water/sodium chloride and DEMA/

water/sodium sulfate as a function of temperature.

Experimental Section

1. DEMA/Water/Sodium Chloride. Figure 1 shows a sketch of the experimental apparatus. A 3-gal insulated glass tank contained the water bath. A 32-cm-long by 3.8-cm-diameter flat-bottomed test tube immersed in the water bath was used as the equilibrium vessel. A magnetic stirrer and stir bar provided agitation in the test tube. To ensure that the experiment was conducted at atmospheric pressure, a three-way glass valve was installed at the stopper, which was open to the atmosphere. The temperature inside the test tube was monitored by an OMEGA 2176A digital thermometer.

The temperature of the water bath was governed by a Hart Scientific 3002 PID temperature controller with a 500-W immersion heater. Below 25 °C, a cooling coil submerged in the water bath provided cooling. It was connected to a Forma Scientific 2160 refrigerated bath and circulator. The temperature of the water bath was monitored by a Hewlett-Packard 2804A quartz thermometer.

The test tube was initially charged with approximately 130 g of saturated sodium chloride solution and 28 g of DEMA. The DEMA was from Aldrich Chemical Co. The sodium chloride was from Fisher Scientific Co.; distilled water was used. Excess sodium chloride was added to ensure saturation. The weight ratio of water to DEMA was maintained at approximately 7:3 because this is the composition at the lower critical solution temperature for salt-free DEMA and water. After thermal equilibrium was reached, agitation was continued for 3 h to ensure complete equilibrium. Then, agitation was halted and sodium chloride crystals settled to the bottom. Two 0.16-cm-o.d. glass tubes, one immersed in the organic phase and the other in the aqueous phase, were used to collect samples. The three-way valve was closed to the atmosphere and opened to a nitrogen tank. Nitrogen was introduced into the test tube at 1.3 atm. When the opening of the organic-phase sampling tube was covered with a stopper, the sample from the aqueous phase was forced out by the nitrogen into a sample container. The organic-phase sample was obtained in a similar fashion. In both cases, the first 4 mL of sample was discarded.

After the samples were obtained, the three-way valve was closed to the nitrogen tank and opened to the atmosphere. DEMA and saturated sodium chloride solution were added to replenish the equilibrium vessel. They were added to the vessel by pasteur pipets through the three-way valve.

For the system subsaturated with sodium chloride, the equilibrium vessel was charged with pure DEMA and with aqueous solution of known concentration of sodium chloride. The experimental procedures were the same as those for the saturated case. After each run, the entire contents in the equilibrium vessel were discharged. For the next run, the vessel was charged with pure DEMA and with aqueous solution of sodium chloride at a known but different concentration of sodium chloride.

2. DEMA/Water/Sodium Sulfate. The experiments were divided into three parts. The first part was to determine liquid-liquid equilibria when the system is saturated with sodium sulfate (two liquid phases and a solid phase). The second part

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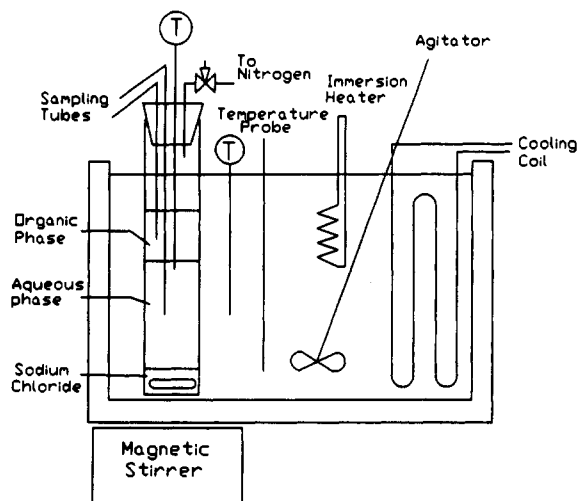


Figure 1. Sketch of experimental apparatus for measuring liquid-liquid equilibria for the system DEMA/water/sodium chloride.

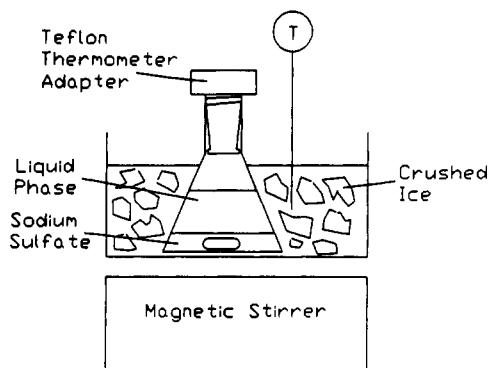


Figure 2. Sketch of experimental apparatus for the system DEMA/water/sodium sulfate with large concentration of DEMA.

was to determine whether the anhydrous form of sodium sulfate can be precipitated from aqueous solution when the crystallization is induced by a large amount of organic solvent below 32.4 °C, which is the transition temperature of anhydrous sodium sulfate crystals to the decahydrate form. The third part was for the systems that are subsaturated with sodium sulfate (two liquid phases and no solid phase).

2.1. DEMA/Water/Sodium Sulfate System Saturated with Sodium Sulfate. The experimental apparatus and procedures were the same as those for the DEMA/water/sodium chloride system discussed in section 1.

2.2. DEMA/Water/Sodium Sulfate System with Large Concentration of DEMA. Figure 2 shows a diagram of the experimental apparatus for the system where crystallization was induced by a large amount of organic solvent below the transition temperature of sodium sulfate. A 100- × 50-mm crystallization dish containing a mixture of crushed ice and water served as the temperature-controlled bath. A 25-mL Erlenmeyer flask was used as the equilibrium vessel. A magnetic stirrer and stir bar provided agitation in the Erlenmeyer flask. A 14/20 tapered Teflon thermometer adapter, with a septum sealing the thermometer port, was used as the stopper. It minimized the evaporation of DEMA and provided a sampling port for gas-chromatographic analysis. The stopper was lifted periodically to ensure that the experiment was conducted at atmospheric pressure.

The 25-mL Erlenmeyer flask was initially charged with approximately 13 g of DEMA. The Erlenmeyer flask was then immersed in an ice bath to lower the DEMA temperature to 0 °C. Once the DEMA reached 0 °C, 1 mL of 28.8-wt % sodium sulfate solution was slowly added to the Erlenmeyer flask. The sample was agitated for 2 h. A 1- μ L syringe was then used

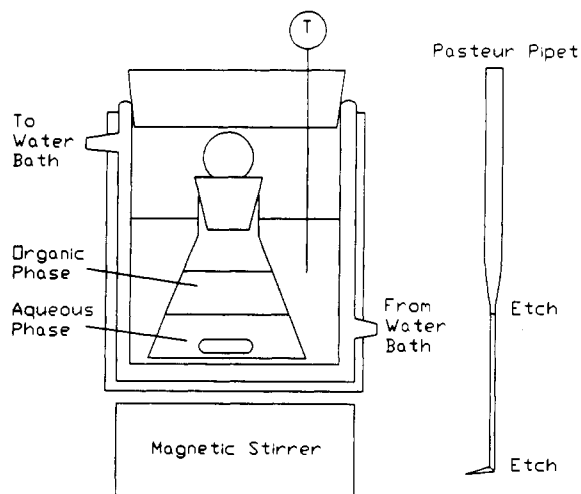


Figure 3. Sketch of experimental apparatus for measuring liquid-liquid equilibria for the system DEMA/water/sodium sulfate subsaturated with sodium sulfate.

to obtain a 0.08- μ L sample for gas-chromatographic analysis. Five samples were analyzed to ensure that the results were representative. After the analysis, another 1 mL of sodium sulfate solution was added, and the above procedures were repeated.

2.3. DEMA/Water/Sodium Sulfate System Subsaturated with Sodium Sulfate. For the system subsaturated with sodium sulfate, Figure 3 shows a diagram of the experimental apparatus. An insulated 250-mL jacketed reaction beaker contained the water bath. Water from the temperature-controlled water bath described in section 1, was circulated in the jacket to maintain constant temperature within the beaker. A 25-mL Erlenmeyer flask placed within the jacketed reaction beaker was used as the equilibrium vessel.

A magnetic stirrer and stir bar provided agitation within the Erlenmeyer flask. The temperature in the jacketed reaction beaker was monitored by an OMEGA 2176A digital thermometer. It was determined experimentally that the temperature of the contents within the Erlenmeyer flask was within 0.2 °C of the temperature of the water bath inside the jacketed reaction beaker within 1 h. The Erlenmeyer flask was capped loosely to ensure atmospheric pressure within the Erlenmeyer flask.

The Erlenmeyer flask was initially charged with 13 mL of sodium sulfate solution of known concentration and with 8 mL of DEMA. Once thermal equilibrium was reached, agitation was continued for an additional 1 h. The temperature of the contents within the Erlenmeyer flask was measured with an OMEGA 2176A digital thermometer. Disposable pasteur pipets were used to extract samples from the organic phase. Sealed disposable pasteur pipets shown in Figure 3 were used to obtain samples from the aqueous phase. To avoid contamination from the organic phase, the pipets were sealed by flame. After the sealed pipet passed through the organic phase and reached the aqueous phase, it was tapped against the bottom of the Erlenmeyer flask to break off the tip. An etch mark was previously made near the tip to help the breakage. An aqueous-phase sample was drawn into the pipet. The pipet was removed from the Erlenmeyer flask, and the exterior of the pipet was wiped with Kimwip. The bottom half of the pipet was then removed by breaking the pipet at a second etch mark near the center. The sample in the top half of the pipet was charged into a sample vial. Since the second etch mark was higher than the liquid level within the Erlenmeyer flask, the outside wall of the top half of the pipet did not touch the organic phase. This procedure eliminated contamination of the aqueous-phase sample by the organic sample adhering to the pipet's wall while

it was being discharged from the pipet.

Analytical Techniques

1. DEMA/Water/Sodium Chloride System. One 1-g and two 3-g samples of each phase were collected in 4-mL pre-weighed screw-top vials and then weighed again. To each 1-g sample, approximately 1 g of anhydrous ethylene glycol (Aldrich) was added, and the vial was weighed again to determine the amount of ethylene glycol added. The ethylene glycol prevented the sample, which was obtained below ambient temperature, from splitting into two phases as the sample reached room temperature. It also served as the internal standard for gas-chromatographic analysis.

Chromatographic Measurements. A Hewlett-Packard 5890A gas chromatograph equipped with a thermal conductivity detector (TCD) and a 10-m HP-5 capillary column was used to determine the water concentration in each sample. When the DEMA concentration was above 5 wt % of the entire sample, its concentration could also be determined accurately by gas chromatography. The chromatograph's signal was integrated by a Hewlett-Packard 3392A integrator. Five consecutive injections were made from each sample to ensure that the results were representative. The results for each sample were then averaged. The injection size was approximately 0.08 μ L.

The concentrations of water and DEMA in each sample were calculated by using calibration factors. The calibration factor (CF) between ethylene glycol (EG) and water is defined in eq 1, and the calibration factor between water and DEMA is defined similarly.

$$CF = \left(\frac{\text{wt of water}}{\text{wt of EG}} \right) \left(\frac{\text{area of EG}}{\text{area of water}} \right) \quad (1)$$

The calibration factor correlates the relative area percents of two components from gas-chromatographic analysis to their weight ratio. The values of the calibration factors are determined from gas-chromatographic analysis of standard solutions with known water, DEMA, and ethylene glycol concentrations. If the absolute weight of one component (i.e., the internal standard) and the corresponding calibration factor are known, the weight of the second component can be calculated. The relative concentrations of two components can be determined if the calibration factor is known. Experiments had shown that the calibration factor between water and ethylene glycol was a function of the area percent of the water peak. Since the area percent of the water peak changes with the water concentration within a sample, the calibration factor is a function of water concentration. The calibration factor between ethylene glycol and water varied linearly from 0.651 to 0.840 when the relative area percent of water to ethylene glycol increased from 14.4% to 54.7%. The calibration factor between water and DEMA varied linearly from 1.286 to 1.048 when the relative area percent of water to DEMA increased from 12.7% to 93.2%. This change of calibration factor is the result of a nonlinear response from the (TCD) detector and the loss of sample on the column or in the injection port; both are common in gas-chromatographic analysis.

Ultraviolet Spectroscopic Measurements. When the DEMA concentration was below 5 wt % of the entire sample, especially in the aqueous phase, a Hewlett-Packard 8452 diode array ultraviolet (UV) spectrophotometer was used to determine the DEMA concentration. UV spectroscopy utilizes Beer's law, which states that, at low concentrations, the absorbance of a substance is proportional to its concentration. The absorbance of a substance, which is a dimensionless quantity, is defined as

$$A = -\log F \quad (2)$$

where A is absorbance and F is the fraction of original incident light passed through the sample.

Experiments had shown that DEMA absorbs UV light between 190 and 240 nm while sodium chloride solution absorbs between 190 and 220 nm. To minimize the effect of sodium chloride on the analysis, an analytical wavelength of 222 nm was chosen. Absorbance is proportional to concentration over the range of 0–0.5 g of DEMA/L of solution.

For calibration, the presence of sodium chloride in the samples was taken into account. Each 100-mL standard solution of DEMA used to calibrate the UV spectrophotometer contained 3 g of saturated sodium chloride solution. In general, the presence of sodium chloride lowers the absorbance reading of DEMA by 9 % at 222 nm. All aqueous-phase samples with low DEMA concentrations were diluted with distilled water so that they fell within the linear range for analysis.

Atomic Absorption Spectroscopic Measurements. Sodium chloride concentrations in the organic-phase and aqueous-phase samples were determined by a Perkin-Elmer 2280 atomic absorption (AA) spectrophotometer equipped with a Perkin-Elmer Intensitron Sodium Lamp. The linear concentration range for analysis was 0–0.007 g of sodium chloride/L of solution, and the samples were diluted with distilled water to this range. Experiments had shown that the presence of DEMA in the diluted sample did not affect the AA analysis, provided that the DEMA was less than 10 wt % of the diluted sample.

2.1. DEMA/Water/Saturated Sodium Sulfate and DEMA/Water/Subsaturated Sodium Sulfate. The analytical techniques for analyzing the organic-phase samples are the same as those for the DEMA/water/sodium chloride system. However, anhydrous ethylene glycol was not needed to homogenize the samples for GC analysis because the samples were obtained above room temperature (21.4–59.4 °C) and did not split into two phases as they reached room temperature.

For the aqueous-phase samples, UV spectroscopy was used to determine DEMA concentrations. AA spectroscopy was used to determine sodium sulfate concentrations. By knowing the weights of the aqueous-phase samples, water concentrations were determined by mass balances. The water concentrations were not determined by gas chromatography because the samples were obtained above room temperature (21.4–59.4 °C), and sodium sulfate decahydrate crystals precipitated within the samples as they reached room temperature.

2.2. DEMA/Water/Sodium Sulfate with Large Concentrations of DEMA. For this set of experiments, there was only one liquid phase and a solid phase. The goal of this study is to determine the relative amounts of anhydrous sodium sulfate and decahydrate crystals present in the solid phase. It is assumed that complete precipitation occurred. This is a reasonable assumption because the DEMA/water/saturated sodium sulfate data (presented later) show that sodium sulfate is virtually insoluble in DEMA when the water concentration is small (<20 wt %). It is also assumed that solid sodium sulfate has no affinity for DEMA; therefore, all the DEMA must be present in the liquid phase. When the total amounts of DEMA, water, and sodium sulfate present in the Erlenmeyer flask, and the ratio of DEMA to water in the liquid phase, are known, the amount of water that stays in the liquid phase can be determined (gas-chromatographic analysis gives the ratio of DEMA to water in the liquid phase). All the water that is not in the liquid phase must be associated with sodium sulfate crystals in the form of sodium sulfate decahydrate.

Experimental Results

The results are divided into two sections. The first section reports data for the DEMA/water/sodium chloride system. The second section reports data for the DEMA/water/sodium sulfate system.

1. DEMA/Water/Sodium Chloride. The experimental data for the DEMA/water/sodium chloride system are divided into

Table I. Equilibrium Data for the System *N,N*-Diethylmethylamine/Water/Sodium Chloride (Saturated with Sodium Chloride)

temp/ °C	aqueous-phase composition/(wt %)			organic-phase composition/(wt %)		
	NaCl	DEMA	water	NaCl	DEMA	water
-0.5	21.8	7.8	70.4	13.9	30.5	55.6
-0.1	22.1	5.6	72.3	12.1	38.0	49.9
1.0	22.3	3.9	73.8	9.4	48.5	42.1
2.0	22.8	3.2	74.0	7.3	58.1	34.6
3.4	23.6	2.4	74.0	4.7	68.0	27.3
6.3	24.2	2.1	73.7	1.6	78.2	20.2
8.2	24.4	1.9	73.7	0.59	80.8	18.6
10.0	24.5	1.7	73.8	0.39	83.2	16.4
15.1	24.6	1.3	74.1	0.12	87.6	12.3
20.2	24.8	1.1	74.1	0.055	89.8	10.1
25.1	25.2	1.0	73.8	0.019	91.8	8.2
30.1	25.2	0.90	73.9	0.008	93.4	6.6
40.0	25.8	0.69	73.5	0.005	95.0	5.0
50.0	26.0	0.57	73.4	0.005	95.9	4.1
60.0	26.7	0.46	72.8	0.005	96.2	3.8

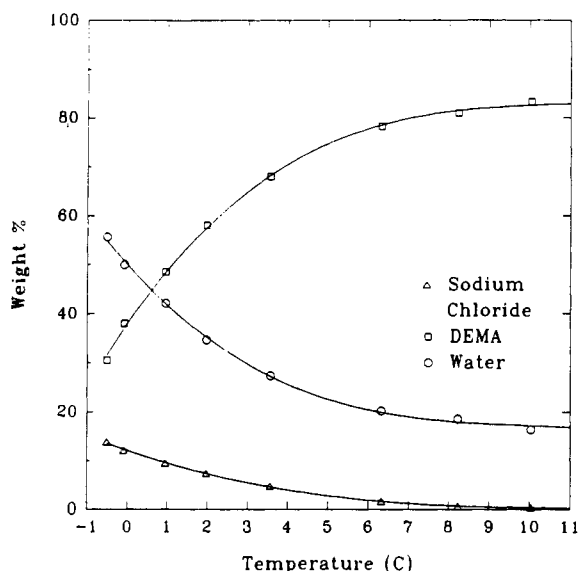


Figure 4. Organic-phase equilibrium composition for the system DEMA/water/saturated sodium chloride at low temperatures.

two parts. The first part is for the temperature range where two liquid phases and a solid phase exist. The two liquid phases are an aqueous phase and an organic phase. The solid phase is sodium chloride. Both liquid phases are saturated with sodium chloride.

Table I shows how the equilibrium compositions of the two liquid phases change with temperature. Above 15 °C, sodium chloride is virtually insoluble in the organic phase, and the solubility of DEMA in the aqueous phase is small. As temperature decreases, the mutual solubilities of DEMA and water increase and the solubility of sodium chloride in the organic phase also rises. The concentrations of water, DEMA, and sodium chloride in the organic phase are plotted as a function of temperature in Figure 4 for the temperature range -0.5 to +10.0 °C. The lower critical solution temperature is estimated at -0.6 °C. Below -0.6 °C, only one liquid phase was observed.

The data show that from +10.0 to -0.5 °C, the weight percent water in the organic phase increases from 16% to more than 55%. Such an increase indicates that water can be extracted from a saturated sodium chloride solution by contacting the solution with DEMA at a low temperature. However, the weight percent sodium chloride in the organic phase also increases from 0.39% to 13.9% in this temperature range. Table II shows the sodium chloride concentration

Table II. Sodium Chloride Concentration (Amine-Free Basis) in the Organic Phase of the System *N,N*-Diethylmethylamine/Water/Saturated Sodium Chloride as a Function of Temperature

temp/ °C	NaCl/ (wt %)	temp/ °C	NaCl/ (wt %)	temp/ °C	NaCl/ (wt %)
-0.5	20.0	6.3	7.3	25.1	0.2
-0.1	19.5	8.2	3.1	30.1	0.1
1.0	18.3	10.0	2.3	40.0	0.1
2.0	17.4	15.1	1.0	50.0	0.1
3.4	14.7	20.2	0.5	60.0	0.1

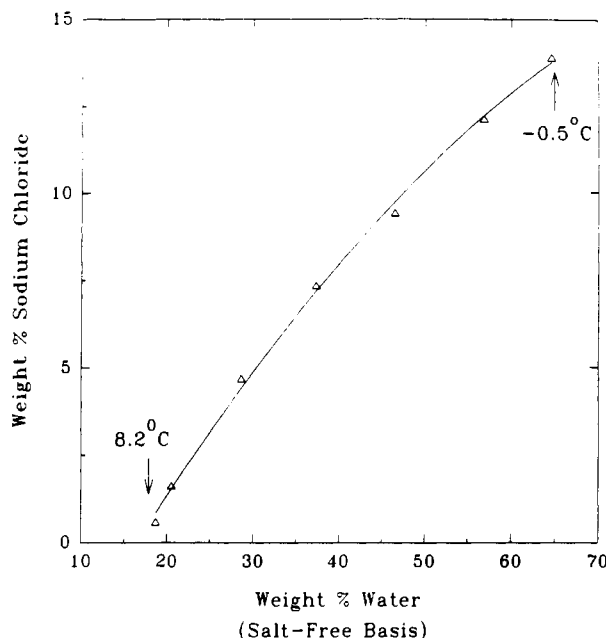


Figure 5. Solubility of sodium chloride in the organic phase of the system DEMA/water/saturated sodium chloride.

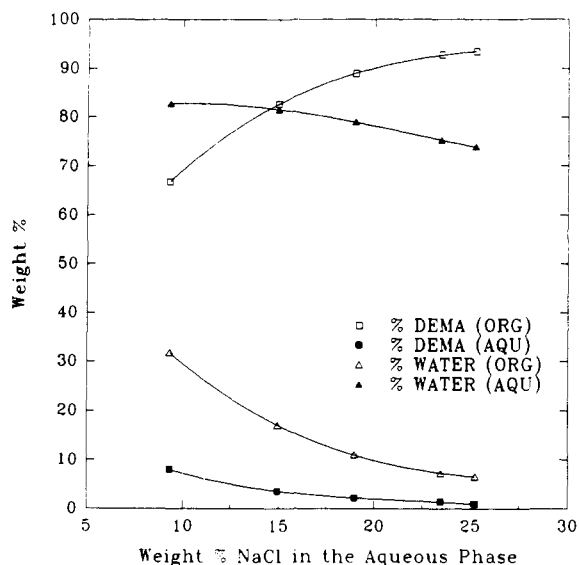
(amine-free basis) in the organic phase as a function of temperature. The data show that the sodium chloride concentration (amine-free basis) in the organic phase approaches the saturation composition of sodium chloride in water (approximately 26 wt %) as the temperature decreases from +10.0 to -0.5 °C. A high sodium chloride concentration (amine-free basis) in the organic phase is undesirable for extractive crystallization of sodium chloride because it indicates that salt is only circulated in the extractive crystallization process rather than precipitated from the aqueous solution. Therefore, the optimal temperature range for extractive crystallization of sodium chloride is about 5 °C. Near this temperature, water can be extracted from a saturated sodium chloride solution while the sodium chloride concentration in the organic phase remains small (less than 3 wt %).

In Figure 5, the solubility of sodium chloride in the organic phase is plotted as a function of water concentration (amine-free basis) in the organic phase for all data points containing at least 0.5 wt % sodium chloride. The data were obtained at different temperatures (+8.2 to -0.5 °C), with the highest water content corresponding to the lowest temperature. The solubility of sodium chloride increases greatly as the temperature drops, in sharp contrast to its behavior in pure water. This indicates that the solubility of sodium chloride in the organic phase is a strong function of the water-to-DEMA ratio and is relatively insensitive to temperature.

When the system is subsaturated with sodium chloride at a specified temperature, the equilibrium compositions of the two liquid phases change with sodium chloride concentration in the aqueous phase. The second set of data shows how the DEMA/water equilibrium compositions change with sodium chloride concentration. Experiments were performed at 30 °C;

Table III. Equilibrium Data for the System *N,N*-Diethylmethylamine/Water/Sodium Chloride Subsatrated with Sodium Chloride at 30 °C

aqueous-phase composition/(wt %)			organic-phase composition/(wt %)		
NaCl	DEMA	water	NaCl	DEMA	water
9.3	8.0	82.7	1.4	66.8	31.8
14.9	3.6	81.5	0.24	82.7	17.1
19.0	2.1	78.9	0.06	88.9	11.0
23.4	1.4	75.2	0.023	92.8	7.2

**Figure 6.** Equilibrium data for the system DEMA/water/sodium chloride subsaturated with sodium chloride at 30 °C.

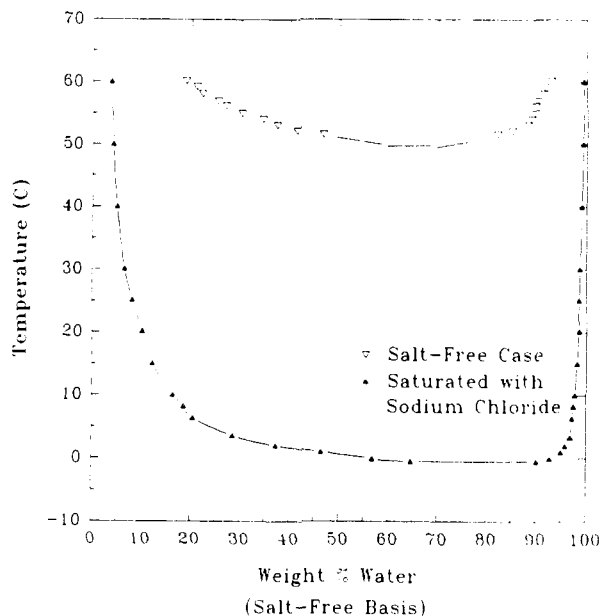
the data are presented in Table III.

As the sodium chloride concentration in the aqueous phase decreases from saturation, the water concentration in the aqueous phase must rise. An increase of water concentration must be accompanied by a corresponding increase of water activity. At equilibrium, the water activity in the organic phase must equal the water activity in the aqueous phase. Therefore, an increase of water activity in the aqueous phase increases water solubility in the organic phase. Since the sodium chloride concentration in the organic phase is a function of water concentration, the sodium chloride concentration in the organic phase also increases as the sodium chloride concentration in the aqueous phase falls. Figure 6 shows equilibrium compositions of DEMA and water as a function of sodium chloride concentration in the aqueous phase.

When the sodium chloride concentration in the aqueous phase is below 30% of saturation at 30 °C, only one liquid phase is observed.

To demonstrate the effect of sodium chloride on the equilibrium behavior of the DEMA/water system, Figure 7 shows the liquid-liquid equilibrium data for the DEMA/water/sodium chloride system (salt-free basis) together with the liquid-liquid equilibrium data for the DEMA/water system. The data show that the presence of sodium chloride widens the two-phase envelope, and decreases the lower critical temperature from +51 to -0.6 °C. This widening follows because the attractive interaction between water and sodium chloride is stronger than that between DEMA and water. Therefore, the concentration of DEMA in the aqueous phase is reduced by salt. The activity of water in the aqueous phase is also reduced by sodium chloride. Since the activity of water must be the same in both phases, the decrease of water activity reduces its solubility in the organic phase.

2. DEMA/Water/Sodium Sulfate. The results are divided into three parts. The first part is for the temperature range

**Figure 7.** Liquid-liquid equilibrium data for the system DEMA/water/saturated sodium chloride.**Table IV. Equilibrium Data for the System *N,N*-Diethylmethylamine/Water/Sodium Sulfate (Saturated with Sodium Sulfate)**

temp/ °C	aqueous-phase composition/(wt %)			organic-phase composition/(wt %)		
	Na ₂ SO ₄	DEMA	water	Na ₂ SO ₄	DEMA	water
21.4	11.7	2.85	85.4	0.89	43.6	55.5
23.0	17.7	1.67	80.7	0.37	51.7	47.9
25.1	19.3	0.80	79.9	0.12	61.4	38.5
27.2	23.1	0.41	76.5	0.029	69.9	30.1
29.8	26.8	0.22	73.0	0.012	77.5	22.5
37.7	32.9	0.10	67.0	0.006	85.0	15.0
44.1	30.9	0.10	69.0	0.004	87.4	12.6
54.6	30.0	0.10	69.9			

where a solid phase and two liquid phases exist. The two liquid phases are an aqueous phase and an organic phase. The solid phase is sodium sulfate decahydrate. Both liquid phases are saturated with sodium sulfate.

Table IV shows how the equilibrium compositions of the two liquid phases change with temperature. Above 29.8 °C, sodium sulfate is virtually insoluble in the organic phase, and the solubility of DEMA in the aqueous phase is small. As the temperature decreases, the mutual solubilities of DEMA and water increase and the solubility of sodium sulfate in the organic phase also rises. The solubilities of all three components in the organic phase and in the aqueous phase are plotted as a function of temperature in Figures 8 and 9, respectively. The lower critical solution temperature is estimated at 20 °C. Below 20 °C, only one liquid phase was observed.

The data show that from 29.8 to 21.4 °C, the weight percent water in the organic phase increases from 22.5% to 55.5%, indicating that water can be extracted from a saturated sodium sulfate solution by contacting the solution with DEMA within this temperature range. The weight percent sodium sulfate in the organic phase only increases from 0.0012% to 0.89% within this temperature range. This is desirable because it indicates that water (but not sodium sulfate) is selectively extracted from the saturated sodium sulfate solution. Moreover, the weight percent DEMA in the aqueous phase remains small (from 0.22% to 2.85%) within this temperature range. The small solubility of DEMA in the saturated solution minimizes the effort of removing organic solvent from aqueous streams in an extractive-crystallization process. Therefore, 21–25 °C is the optimal temperature range for extractive crystallization of so-

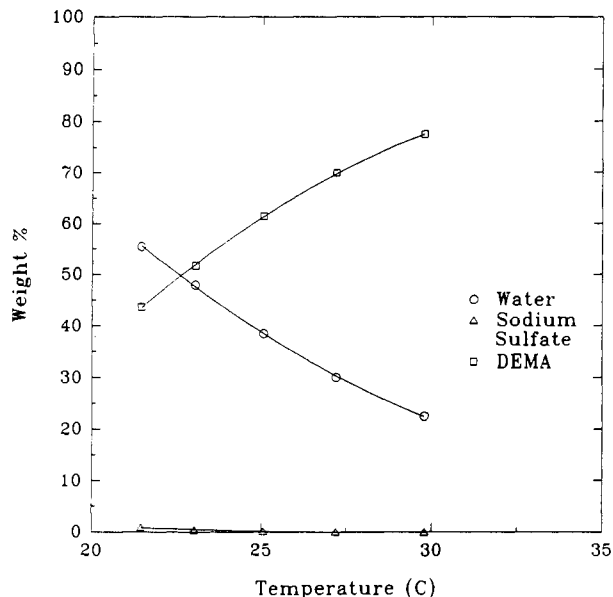


Figure 8. Organic-phase equilibrium composition for the system DEMA/water/saturated sodium sulfate.

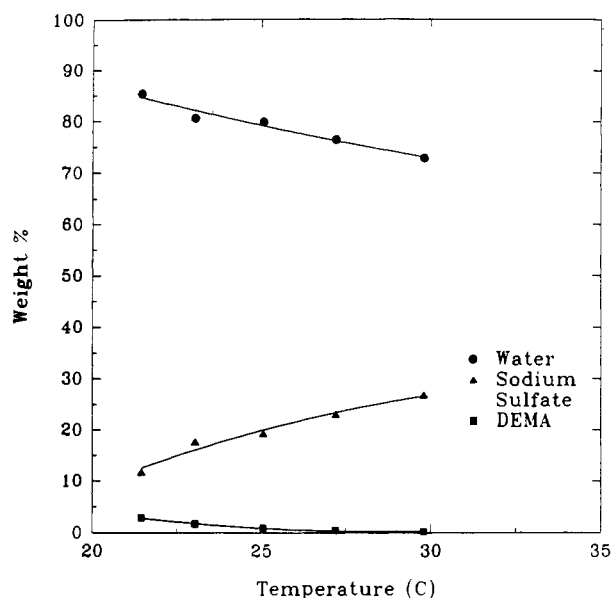


Figure 9. Aqueous-phase equilibrium composition for the system DEMA/water/saturated sodium sulfate.

dium sulfate. Figure 10 shows liquid-liquid equilibrium data for the DEMA/water/sodium sulfate system (salt-free basis) within the optimal temperature range.

In Figure 11, the solubility of sodium sulfate in the organic phase is plotted as a function of water concentration (salt-free basis) in the organic phase. As was the case with sodium chloride, the solubility of sodium sulfate in the organic phase is a strong function of the water-to-DEMA ratio. The solubility is much less sensitive to temperature within the range (21.4–54.6 °C) of these experiments.

The experiments above showed that DEMA can extract water from a saturated sodium sulfate solution, causing sodium sulfate decahydrate crystals to precipitate. To determine whether a high concentration of DEMA would cause anhydrous sodium sulfate crystals (rather than decahydrate) to precipitate, water was extracted from a saturated sodium sulfate solution below 20 °C (the lower critical solution temperature for the system DEMA/water/saturated sodium sulfate). If, at low temperatures, the attractive interaction between DEMA and water is stronger than that between water and sodium sulfate

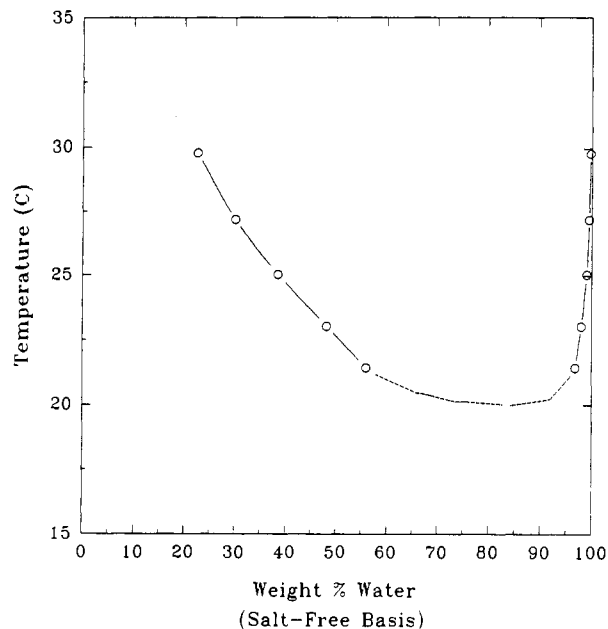


Figure 10. Liquid-liquid equilibrium data for the system DEMA/water/saturated sodium sulfate.

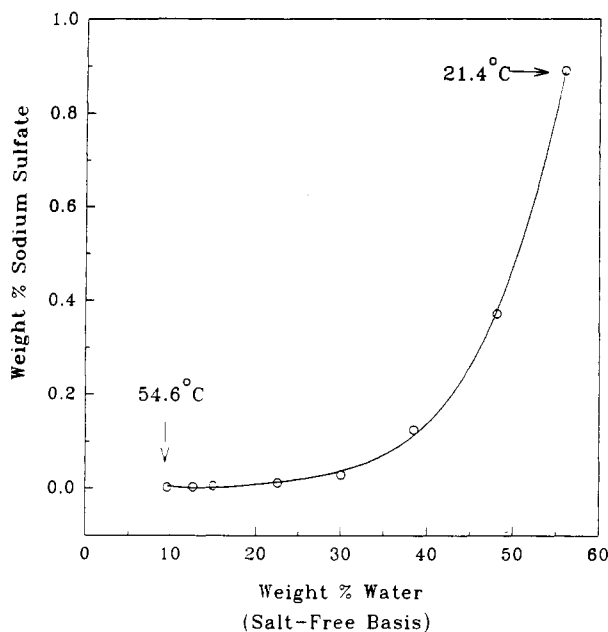


Figure 11. Solubility of sodium sulfate in the organic phase of the system DEMA/water/saturated sodium sulfate.

Table V. Equilibrium Data for the System *N,N*-Diethylmethylamine/Water/Sodium Sulfate (Saturated with Sodium Sulfate with One Liquid Phase at 0 °C)

liquid-phase composition/(wt %)		solid-phase composition/(wt %)	
DEMA	water	Na ₂ SO ₄	Na ₂ SO ₄ ·10H ₂ O
94.0	6.0	80.1	19.9
91.4	8.6	35.0	65.0
89.9	10.1	3.2	96.8
87.5	12.5	0.0	100.0

in the sodium sulfate decahydrate crystals, water would be extracted from the decahydrate crystals and anhydrous sodium sulfate crystals (rather than decahydrate) could be obtained below the transition temperature of sodium sulfate. The data for crystallization induced by a large amount of organic solvent are presented in Table V. The experiment was conducted at

Table VI. Equilibrium Data for the System *N,N*-Diethylmethylamine/Water/Sodium Sulfate Subsaturated with Sodium Sulfate at 54.6 °C

aqueous-phase composition/(wt %)			organic-phase composition/(wt %)		
Na ₂ SO ₄	DEMA	water	Na ₂ SO ₄	DEMA	water
1.08	6.2	92.7	0.004	77.2	22.8
4.42	4.3	91.3	0.003	82.2	17.8
10.2	1.8	88.0	0.003	84.9	15.1
14.9	1.0	84.1	0.003	87.0	13.0
20.3	0.45	79.3	0.003	88.6	11.4
24.2	0.25	75.6	0.003	90.2	9.8
30.0	0.10	69.9	0.002	90.4	5.6

Table VII. Equilibrium Data for the System *N,N*-Diethylmethylamine/Water/Sodium Sulfate Subsaturated with Sodium Sulfate at 59.4 °C

aqueous-phase composition/(wt %)			organic-phase composition/(wt %)		
Na ₂ SO ₄	DEMA	water	Na ₂ SO ₄	DEMA	water
0.00	8.3	91.7	0.00	79.3	20.7
1.38	5.6	93.0	0.001	82.5	17.5
4.28	3.8	91.9	0.001	84.4	15.6
9.82	1.8	88.4	0.001	87.5	12.5
14.8	0.93	84.3	0.001	89.0	11.0
20.2	0.45	79.3	0.001	90.3	9.7
24.2	0.27	75.5	0.001	90.8	9.2
28.4	0.18	71.4	0.001	91.6	8.4

0 °C for convenient temperature control. Since the temperature is below the lower critical solution temperature for the system DEMA/water/sodium sulfate, only one liquid phase and a solid phase exist.

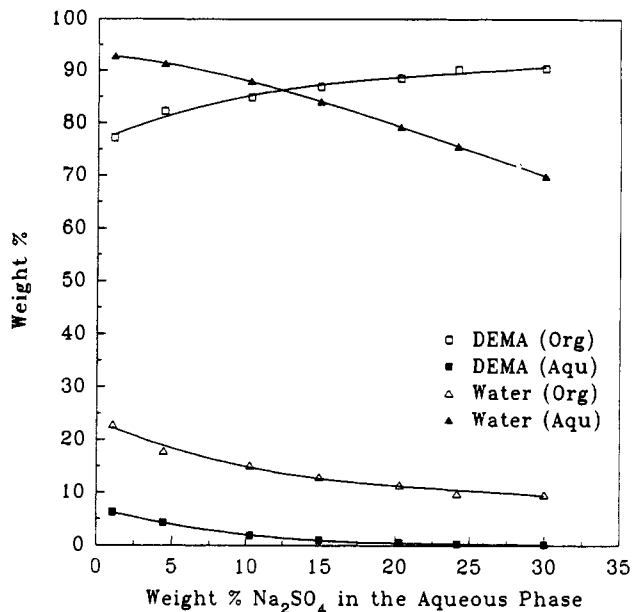
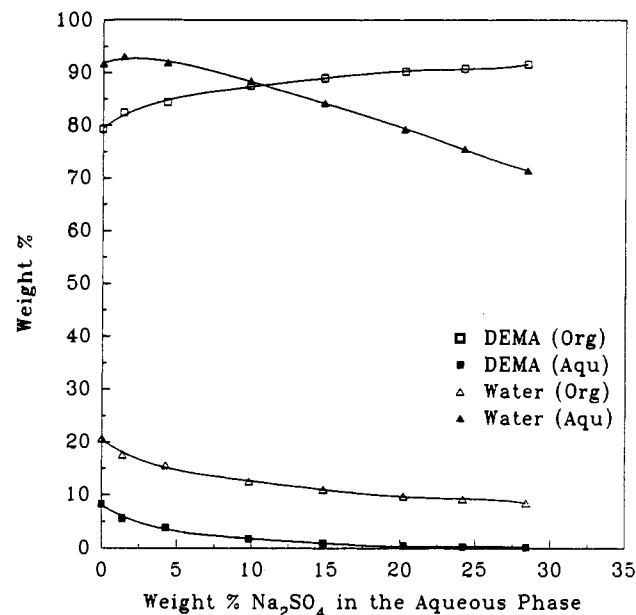
Table V shows how the weight percent of sodium sulfate decahydrate crystals in the solid phase changes with the water concentration in the liquid phase. The data show that pure anhydrous sodium sulfate crystals cannot be obtained at low temperatures, even when the DEMA concentration is about 94 wt %. The formation of sodium sulfate decahydrate increases rapidly with water concentration in the liquid phase. When the water concentration exceeds 10 wt %, virtually all the precipitated sodium sulfate is in the decahydrate form. Therefore, the precipitation of anhydrous sodium sulfate at low temperatures is not economically feasible. These data also indicate that sodium sulfate heptahydrate, which can form as a metastable phase from aqueous solutions, is unlikely to precipitate from DEMA-containing solutions.

When the system is subsaturated with sodium sulfate at a specified temperature, the equilibrium compositions of the two liquid phases change with the sodium sulfate concentration in the aqueous phase. The third set of data shows how these compositions change with sodium sulfate concentration. The experiments were performed at 54.6 and 59.4 °C. The data are given in Tables VI and VII, and shown in Figures 12 and 13.

As in the system DEMA/water/sodium chloride, the increase of water concentration in the aqueous phase increases the water activity. At equilibrium, the increase of water activity in the aqueous phase must be accompanied by an increase of water activity in the organic phase, thereby increasing the water solubility in the organic phase. Because of the favorable interaction between sodium sulfate and water, the DEMA concentration in the aqueous phase decreases rapidly (from 8.3% to 3.8%) with an increase in sodium sulfate concentration (from 0% to 4.28%).

Conclusions

DEMA can extract water from saturated sodium chloride solution at low temperatures (+10 to -0.5 °C), causing sodium chloride crystals to precipitate, but the weight percent sodium

**Figure 12. Equilibrium data for the system DEMA/water/sodium sulfate subsaturated with sodium sulfate at 54.6 °C.****Figure 13. Equilibrium data for the system DEMA/water/sodium sulfate subsaturated with sodium sulfate at 59.4 °C.**

chloride in the organic phase also increases from 0.39% to 13.9% in this temperature range. The optimal temperature for extractive crystallization of sodium chloride with DEMA is 5–10 °C. In this temperature range, water can be extracted from the brine solution while the sodium chloride concentration in the organic phase remains small (less than 3 wt %). When the sodium chloride concentration in the organic phase is above 0.5 wt %, sodium chloride solubility in wet DEMA is a strong function of the water-to-DEMA ratio and is relatively insensitive to temperature. The lower critical solution temperature for the salt-saturated DEMA/water/sodium chloride system is -0.6 °C.

DEMA can extract water from saturated sodium sulfate solution at moderate temperatures (21–25 °C). In this temperature range, water (but not sodium sulfate) can be selectively extracted from saturated sodium sulfate solution, causing sodium sulfate decahydrate crystals to precipitate. Moreover, in this temperature range, the solubility of sodium sulfate in the organic phase is a strong function of the water-to-DEMA ratio and is relatively insensitive to temperature. The lower critical

solution temperature for the salt-saturated DEMA/water/sodium sulfate system is 20 °C.

Registry No. DEMA, 124-40-3; H₂O, 7732-18-5; sodium chloride, 7647-14-5; sodium sulfate, 7757-82-6.

Literature Cited

- (1) Alfassi, Z. B. *Sep. Sci. Technol.* 1979, 14 (2), 155.

- (2) Weingaertner, D. A.; Lynn, S.; Hanson, D. N. *Ind. Eng. Chem. Res.* 1991, 30, 490.

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Effects of Regeneration Conditions on the Characteristics of Water Vapor Adsorption on Silica Gel

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Equilibrium adsorption and desorption isotherms of water vapor on a silica gel were measured at 288, 298, and 308 K. Isotherms were of type I according to Brunauer's classification and provided a single characteristic curve when correlated according to Polanyi's potential theory. Literature data on different samples of silica gel exhibited differences in uptake capacity from each other and from the present data. The uptake capacity at 298 K did not change significantly when regeneration temperatures were varied in the range of 373–442 K, nor when the regeneration time was increased from 4 to 16 h. The heats of adsorption suggest that silica gel has an energetically heterogeneous surface for water vapor adsorption.

Introduction

Silica gel has been employed widely as a dehumidifying material in the chemical and petroleum industries, food industries, and construction industries, as well as in solar desiccant cooling. Recently it has found a major application in desiccant-based air conditioning systems, in which silica gel is employed in a rotary dehumidification wheel to adsorb water vapor from moist air. After a predetermined period of time, silica gel is regenerated by an auxiliary heat source, such as by hot air or electrical heating. For applications in which silica gel undergoes repeated water adsorption/regeneration cycles, data on regeneration temperatures and times are needed to optimize the design of a desiccant system.

Although silica gel is one of the major solid desiccants employed in industry, limited equilibrium isotherm data for water vapor are reported in the open literature for commercially available silica gel. Pedram and Hines (1) obtained equilibrium adsorption data of water vapor on Mobil Sorbead R silica gel at three temperatures. Although Polanyi's potential theory (2) provided a good correlation of the data, the Brunauer–Emmett–Teller (BET) equation fitted the data only in the relative pressure range of 0.05–0.40. They also noted that adsorption capacities for water vapor obtained in their experiments were approximately 20% lower than Mobil's values. They attributed this discrepancy to differences in regeneration temperatures. Machin and Stuckless (3) used Davison Grade 03 silica gel in their study at 273.65 and 298.15 K, but work was mainly fo-

Table I. Physical Properties of Silica Gel

particle size ^b	6 × 12 mesh
surface area, S/(m ² /g) ^a	
micropores	663
meso- and macropores	9
total	672
pore volume, V/(cm ³ /g) ^a	
micropores	0.38
meso- and macropores	0.02
total	0.40
average pore diameter, 4V/S/Å ^a	23.6
bulk density/(g/cm ³) ^b	0.72

^a Analysis made by Porous Materials, Inc., Ithaca, NY.
^b Analysis provided by the manufacturer.

cused on understanding the pressure–volume behavior of condensed water in capillaries. Pesaran et al. (4) carried out a comprehensive literature survey on water vapor adsorption by silica gel, and also measured water adsorption capacities of three batches of silica gel (Davison Grade 40). They noted that adsorption capacities varied from batch to batch and found large differences between their observations and the manufacturer's data.

In this study, adsorption isotherms for water vapor on silica gel were measured at three temperatures, and the effects of regeneration temperatures and times on adsorption capacities at 298 K were studied. The equilibrium data were used to calculate heats of adsorption and thereby to determine the role of surface heterogeneity on the adsorption process. The data were correlated according to Polanyi's potential theory.

Experimental Section

The silica gel used in this study was grade 40, 6 × 12 mesh (lot no. MIL-D-3716 type II) and was supplied by Davison Chemical Co. The properties of the silica gel are presented in Table I. The adsorbate was double-distilled water that was further purified by passing through an ion-exchange column. The experimental adsorption and desorption studies were carried out gravimetrically in an all-glass apparatus using a Cahn C-2000 electrobalance. The description of the apparatus is given elsewhere (5). A vacuum of 10⁻⁴ mmHg can be attained in the system prior to initiating an adsorption run, with a leak rate of the complete system of approximately 10⁻³ mmHg/h. Pressures below 10⁻⁴ mmHg were measured by ionization gauges and pressures from 10⁻³ by using convectron gauges. The adsorption pressures during an experimental run were

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