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Investigation on solubility of hydroxy dibasic acids in alkanolamine solutions

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Abstract. Solubilities of three hydroxy dibasic (adipic, suberic, and sebacic) acids in alkanolamine solutions were measured within the 30-90°C temperature range. It is found that solubility of these acids sharply grows with temperature and concentration of alkanolamine solvent. In addition, the study substantiates the adjustment of pH to optimize the CO₂ absorption and desorption processes. The precipitation of added acids from alkanolamine solvents by cooling is found to be quite problematic, which makes the recovery of residual acids from lean alkanolamine solvents non-feasible and requires the application of alternative methods.

1. Introduction

The work is a continuation of the author's previous study [1], where the feasibility of adding hydroxy dibasic acids for reducing the energy consumption of CO₂ desorption from alkanolamine solutions was verified. The preliminary results obtained in [1] strongly suggested that addition of some hydroxy dibasic acids could decrease the energy consumption of CO₂ desorption from alkanolamine solvents, but residual acids may cause degradation of alkanolamine solvents. To check whether adipic acid could be recovered by the cooling method, the experimental study of the solubility of hydroxy dibasic acid/alkanolamine solution is required.

In this study, an attempt is made to reduce the solution pH by adding some acids to desorption solvents, to reduce the energy consumption, with the further recovery of these acids by cooling. This procedure is based on the steep solubility curves of some hydroxy dibasic acids in water. However, when the aqueous solutions are replaced by alkanolamine solvents, the situation may drastically change. Therefore, the determination of solubility in this study is instrumental to solving this problem.

2. Experimental

2.1. Experimental devices and reagents

The experimental device is shown in figure 1. The bottom is the heating agitator for heating and stirring the solution in a beaker. There are three holes on the top of the beaker. One is for measuring the pH and temperature of the solution, and the other two are for the solute addition. The intermediate interface is for placement of the condenser. An oil bath for heating the solvents is on the outside of the container. The oil heated to a certain preset temperature controlled by the oil bath flows from the upper inlet into the lower one.

Measuring devices are as follows: weight meter (accuracy ± 0.001 g), pH meter (accuracy ± 0.001), thermometer (accuracy ± 0.1 °C), measuring cylinder (accuracy ± 0.5 mL).



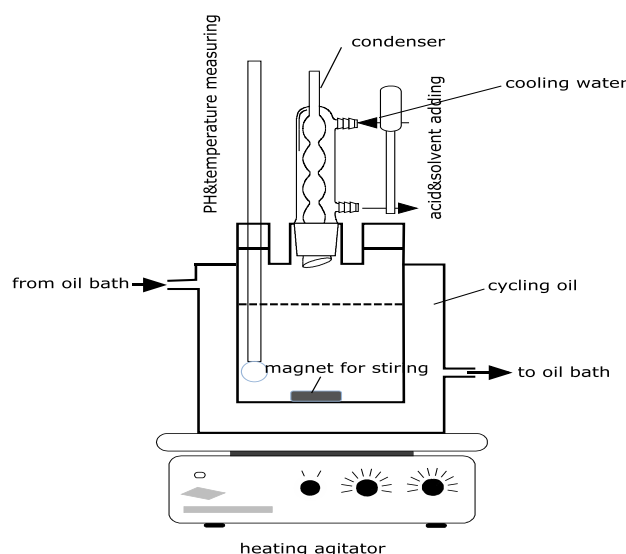


Figure 1. Schematic flow diagram of the solubility experimental apparatus.

Three hydroxy dibasic acids are used in experiments, including adipic ($(\text{CH}_2)_4(\text{COOH})_2$, Fluka Chemie GmbH, $\geq 99.5\%$), suberic ($\text{C}_6\text{H}_{12}(\text{COOH})_2$, Sigma-Aldrich (US); $\geq 99\%$) and sebacic acids ($(\text{HOOC})(\text{CH}_2)_8(\text{COOH})$, Sigma-Aldrich (US); $\geq 99\%$).

The solvents tested are Monoethanolamine (MEA, Sigma-Aldrich (US), $\geq 99\%$), Diethanolamine (DEA, Sigma-Aldrich (US), $\geq 98\%$) and Methyldiethanolamine (MDEA, Sigma-Aldrich (US), $\geq 99\%$).

2.2. Experimental process

Firstly, 20 mL water was measured and poured into a beaker with a volume of 50 mL, then the water was heated to 30°C with real-time monitoring of temperature. Alkanolamine solvents were prepared as 50 mL sample with concentrations of 0.2, 0.4 and 3 mol/L. Then, acids were added to the solution until a trace of crystal precipitation was observed, which indicated that the solution was saturated. The mass of the acids added to the solution was recorded as well. Besides, pH of the solution was recorded in real time. Another criterion for solution saturation is that the pH does not change anymore. The above steps were repeated to obtain the data of solubility for three acids in the alkanolamine solvents at $30\text{--}90^\circ\text{C}$, then solubility curves were plotted. The uncertainty of this test results directly from the minimal portion of a solute being added to the vessel and temperature control. The experimental contents are shown in table 1.

Table 1. Experimental contents.

Acids	Solvents	Concentration of solvents (mol/L)	Temperature ($^\circ\text{C}$)
Adipic acid	MEA	0, 0.2, 0.4, 3	30-90
	MDEA		
	DEA		
Suberic acid	MEA		
Sebacic acid	MEA		

3. Results and discussion

3.1. The solubility of adipic acid in three alkanolamine solvents

The solubility curves of adipic acid in MEA, DEA, and MDEA solvents are plotted in figures 2, 3, and 4, respectively, and the corresponding data are tabulated in tables 1-3.

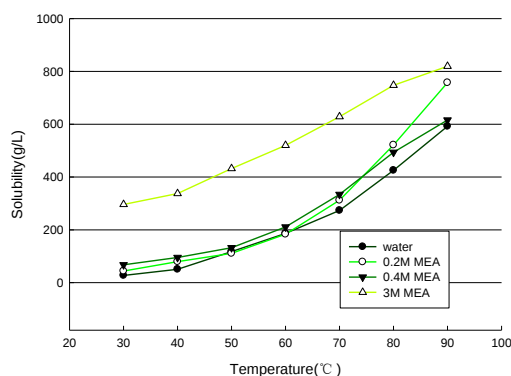


Figure 2. Solubility curves of adipic acid in water and MEA(0.2 , 0.4 , and 3 mol/L).

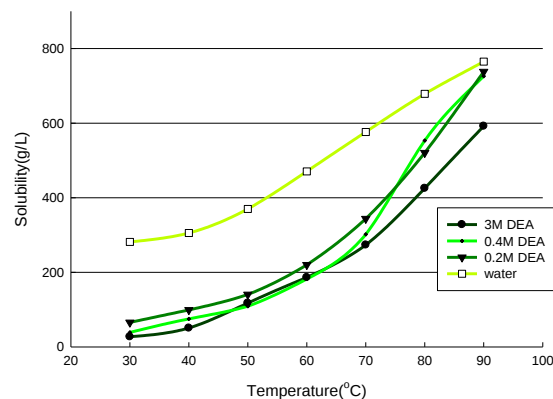


Figure 3. Solubility curves of adipic acid in water and DEA(0.2 , 0.4 , and 3 mol/L).

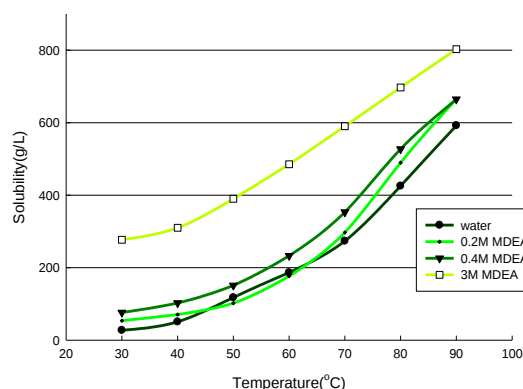


Figure 4. Solubility curves of adipic acid in water and MDEA (0.2 , 0.4 , and 3 mol/L).

Table 2. Solubility and pH of adipic acid in water and MEA (0.2 , 0.4 , and 3 mol/L).

Temperature (°C)	Water	0.2 mol/L solution		0.4 mol/L solution		3 mol/L solution	
	Solubility (g/L)	pH value	Solubility (g/L)	pH value	solubility (g/L)	pH value	Solubility (g/L)
30	27.23	4.408	44.12	4.613	67.66	5.360	296.15
40	50.65	4.153	79.52	4.436	95.20	5.139	337.31
50	117.48	3.980	110.96	4.232	132.11	4.872	431.88
60	186.41	3.730	183.54	3.969	210.70	4.641	519.87
70	273.38	3.390	311.96	3.62	334.08	4.418	628.49
80	425.37	3.120	521.09	3.327	493.73	4.197	747.54
90	592.07	2.941	757.36	3.125	615.82	4.092	819.24

The above results imply that the solubility of adipic acid in alkanolamine solvents is higher than that in aqueous solutions, and that solubility sharply increases with the alkanolamine concentration. The solubility curve of adipic acid in water is similar to that in alkanolamine solvents, i.e., the solubility increases steeply with temperature [2,3]. The pH of the saturated solution decreases with temperature, and the pH value is lower than 7.

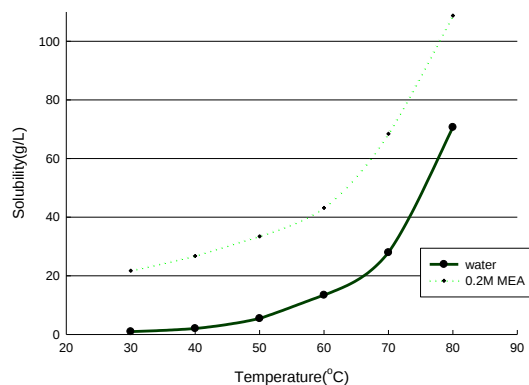
Table 3. Solubility and pH of adipic acid in water and DEA (0.2 , 0.4 , and 3 mol/L).

Temperature (°C)	Water	0.2mol/L solution		0.4mol/L solution		3mol/L solution	
	Solubility (g/L)	pH value	Solubility (g/L)	pH value	Solubility (g/L)	pH value	Solubility (g/L)
30	27.23	4.440	38.91	4.582	65.66	5.192	281.53
40	50.65	4.040	74.97	4.336	99.09	5.059	305.34
50	117.48	3.845	109.01	4.140	140.64	4.865	369.92
60	186.41	3.560	181.90	3.876	220.20	4.589	470.58
70	273.38	3.262	301.82	3.565	343.72	4.348	576.34
80	425.37	3.000	553.32	3.280	520.63	4.137	678.55
90	592.07	2.780	725.95	3.030	738.03	4.960	764.92

It was found that the solubility of each acid in the same concentration of three alkanolamine solvents is nearly identical. For the following two acids, only the solubility in MEA solution was measured.

3.2. The solubility of suberic acid in MEA solvents

The solubility curves of suberic acid in 0.2 mol/L MEA and water are shown in figure 5, and the corresponding data are presented in table 4. It is found that the solubility of suberic acid in 0.2 mol/L MEA solvent is quite different from that in water, exceeds it at 30°C by almost 20 times. When the temperature rises, the solubility difference is reduced. The solubility curve of suberic acid in 0.2 mol/L MEA solution also exhibits a sharp increase with the temperature. The pH values of the solutions after saturation exceed 7, which means that the solutions are acidic. When the solution temperature rises to 70°C, suberic acid starts to evaporate from the solution.

**Figure 5.** Solubility curves of suberic acid in water and 0.2 mol/L MEA.**Table 4.** Solubility and pH of adipic acid in water and MDEA (0.2 , 0.4 , and 3 mol/L).

Temperature (°C)	Water	0.2 mol/L solution		0.4 mol/L solution		3 mol/L solution	
	Solubility (g/L)	pH value	Solubility (g/L)	pH value	solubility (g/L)	pH value	Solubility (g/L)
30	27.23	4.278	53.84	4.558	76.31	5.217	277.07
40	50.65	4.079	70.75	4.361	102.55	5.104	309.97
50	117.48	3.879	101.94	4.140	151.10	4.846	390.07
60	186.41	3.584	176.72	3.865	232.90	4.595	485.37
70	273.38	3.287	297.04	3.615	353.15	4.350	590.21
80	425.37	2.981	489.55	3.373	527.32	4.122	697.27
90	592.07	2.790	665.30	3.080	664.72	3.968	802.86

3.3. The solubility of sebacic acid in MEA solvents

The solubility curves of sebacic acid in 0.2 mol/L MEA and water are shown in figure 6 and the corresponding data are given in table 5. It is found that the solubility of sebacic acid in MEA solvents is much higher than that in water, and increases steeply with temperature, which is similar to the first two acids. As shown in table 6, in contrast to the previous two acids, the solubility of sebacic acid in alkanolamine solvents is much lower at approaches zero at 0°C. Its dissolution and crystallization processes are much slower as well. It was also revealed that the pH value of saturated solutions exceeded 7 at 30°C, and dropped below 7 when the temperature rose to 40°C.

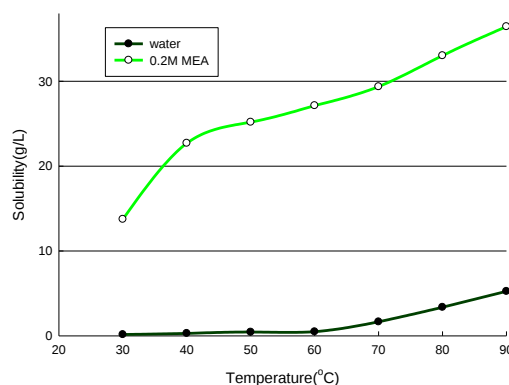


Figure 6. Solubility curves of sebacic acid in water and 0.2 mol/L MEA.

Table 5. Solubility and pH of suberic acid in water and 0.2 mol/L MEA.

Temperature (°C)	Water	0.2 mol/L solution	
	Solubility (g/L)	pH value	Solubility (g/L)
30	0.98	5.494	21.75
40	2.04	5.177	26.79
50	5.45	4.960	33.45
60	13.42	4.772	43.17
70	27.94	4.488	68.43
80	70.64	3.967	108.73

Table 6. Solubility and pH of sebacic acid in water and 0.2 mol/L MEA.

Temperature (°C)	Water	0.2 mol/L solution	
	Solubility (g/L)	pH value	Solubility (g/L)
30	0.16	9.144	13.74
40	0.29	5.779	22.71
50	0.45	5.565	25.19
60	0.49	5.413	27.14
70	1.66	5.263	29.37
80	3.37	5.140	33.03
90	5.25	4.977	36.45

3.4. Further elaboration of the findings

The results of solubilities of adipic acid in water are very close to the data from literature [4-6], which indicates that the devices and processes of this experiment are reliable. The purpose of this work is to determine the difference between the solubility of three acids in alkanolamine solvents and water, and whether the added acids can be precipitated from the desorption lean-solvents by cooling. This study allows one to optimize CO₂ absorption and desorption processes by the method of pH swing [1]. The

results show that the solubility curves of the three acids in alkanolamine solvents follow the trend of "increasing steeply with the rising temperature". The solubility observed in alkanolamine solvents was higher than in water. As the concentration of alkanolamine increases, the difference is further enlarged. These are mainly due to the following factors. First, the pH of alkanolamine solvents is alkaline, and the solubility of three acids in alkaline solutions should exceed that in water; Secondly, when hydroxy dibasic acids and alkanolamine coexist in aqueous solution, some reactions may occur, and additional products can be formed [7]. For MEA and adipic acid, the following reaction may occur [8,9]:



The occurrence of this reaction breaks the original adipic acid hydrolysis equilibrium, allowing more adipic acid to dissolve into the solution, which leads to degradation of alkanolamine solvents and reduction of CO₂ absorption capacity. Thus, the concept of recycling some weak organic acids from alkanolamine solvents by cooling is not yet feasible. New methods need to be further explored to deal with the residual acids in the alkanolamine solvents.

4. Conclusions

Through the experimental results of solubility of three hydroxy dibasic acids in MEA, DEA and MDEA solvents, the following conclusions can be drawn:

- The solubility curves of three acids in alkanolamine solvents still follow the trend of increasing with increasing temperature, as the case in aqueous solution.
- The solubility of three acids in alkanolamine solvents increases steeply with the concentration of alkanolamine solutions.
- The added acids cannot be mostly precipitated from alkanolamine solvents by cooling, which means that it is unreasonable to recovery the residual acids from lean alkanolamine solvents.

Acknowledgments

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