

Effect of addition of weak acids on CO₂ desorption from rich amine solvents

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Abstract—Experiments were conducted to study the effect of addition of four weak acids (adipic, suberic, phthalic and sebacic acids) on the regeneration of three types of CO₂-loaded rich solvents (Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA)). It was found that CO₂ could be released faster and in a larger quantity when the amount of acid added to the solvent was increased while other desorption conditions were maintained unchanged. Adipic acid appeared to be more effective than phthalic, suberic and sebacic acids in enhancing solvent regeneration rate. Among the three amines investigated, MEA had the highest CO₂ desorption rate, while DEA saved the most energy. The effect of adipic acid residue in the MEA solvent on CO₂ absorption was also investigated. The residue acid reduced the absorption capacity of the MEA solvent significantly when the solvent concentration was low and slightly when the concentration was high.

Key words: CO₂ Absorption, pH Swing, Solvent, CO₂ Desorption

INTRODUCTION

Solvent absorption as a post-combustion capture method in power generation has been commercially used because of its high capture capacity and fast rate of absorption [1-3]. However, the high energy consumption in the process of solvent regeneration limits its widespread application [4,5], so efforts are being made to improve the energy efficiency of the regeneration process.

A new method, pH swing, has been proposed to reduce the energy consumption of solvent regeneration [6]. In the method, a weak acid is added into the rich solvent prior to regeneration to reduce the pH of the solvent. It is anticipated that at a lower pH the solvent would require lower regeneration energy [7]. After regeneration, the acid is recovered by an acid crystallization process. As a result, the pH of the solvent returns to its original value, ready for next absorption/desorption cycle.

Recently, Feng et al. [8] reported that the addition of some weak acids into a CO₂-loaded Monoethanolamine (MEA) could significantly increase the amount of CO₂ released as well as the desorption rate. The amount of CO₂ released was found to be proportional to the amount of acid added. Therefore, the theory of pH swing seems to be plausible and a significant energy saving could be possibly achieved in the regeneration process. However, the work did not test other solvents and did not show whether acid recovery could be achieved and how residue acid in the solvent would affect subsequent CO₂ absorption. Therefore, the present paper investigated the effect of acid addition on the regeneration of three types of solvent, the solubility of acids in the solvents, and the effect of acid on CO₂ absorption capacity of the solvents.

EXPERIMENTAL

The experimental procedure was similar to that reported in the previous work [8]. First, CO₂-loaded solvents were obtained in an absorption stage. Subsequently the CO₂-loaded solvents were divided into 20 mL samples and tested for CO₂ desorption with addition of various acids at various quantities. The absorption behaviors of the solvents with various quantities of acid were also obtained to investigate the effect of residue acid on absorption.

1. Acids and Solvents

Four weak organic acids were tested in this work, including adipic ((CH₂)₄(COOH)₂, Fluka Chemie GmbH, ≥99.5%), phthalic (C₆H₄(CO₂H)₂, SIGMA-ALDRICH; ≥99%), suberic (C₈H₁₂(COOH)₂, SIGMA-ALDRICH; ≥99%) and sebacic acids ((HOOC)(CH₂)₈

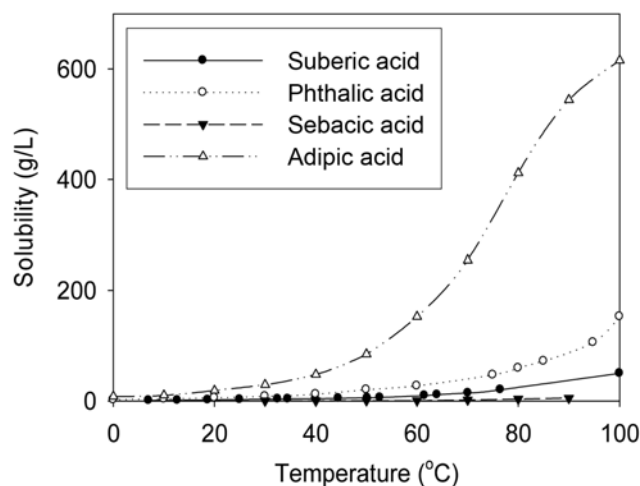


Fig. 1. Aqueous solubility curves of four acids in water.

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(COOH), SIGMA-ALDRICH; ≥99%). Solubility curves of some weak acids in water are available in the literature [9], and solubility curves of the four acids were obtained experimentally, as shown in Fig. 1. Among all four acids, adipic acid exhibits the steepest solubility curve.

The solubility curves of adipic acid in various solvents were also obtained experimentally. In a typical test, a certain amount of water (e.g., 100 mL) was measured and poured into a beaker. A solvent at a certain amount was then added into the beaker to produce the solvent sample with desired concentration. Adipic acid in solid form was gradually added in small quantities into the solvent solution (which was continuously stirred) until it was completely dissolved. Adipic acid was no longer added if acid solid was observed in the solution after 30 minute stirring. The total amount of acid added into the beaker divided by the total volume of water and solvent was then taken as the solubility. The solubility at different temperatures was obtained. The beaker was placed on top of a heating plate and the temperature of the solution was controlled by the heating plate.

The solvents tested were Monoethanolamine (MEA, SIGMA-ALDRICH, ≥99%), Diethanolamine (DEA, SIGMA-ALDRICH, ≥98%) and Methyldiethanolamine (MDEA, SIGMA-ALDRICH, ≥99%).

2. Absorption and Desorption Experiments

Six rich solvents (0.2 M and 0.4 M of three solvents, respectively) were obtained through absorption experiments, with the conditions and CO₂ absorption amounts listed in Table 1. In the absorption experiments, the solvent temperature was maintained at 21 °C while a flow of N₂ (at 500 mL/min) and CO₂ (at 72 mL/min) was introduced into the solvent container. The CO₂ concentration was monitored continuously using a Fourier transfer infrared spectrometer and the CO₂ concentration curve was integrated to obtain the amount of CO₂ absorbed. The solvents were then divided into 20 mL samples and used for regeneration tests.

The experimental conditions of desorption or regeneration are summarized in Table 2. In a typical desorption experiment, the solvent container was rapidly merged into an oil bath which was maintained at 95 °C while a N₂ flow of 500 mL/min was maintained during desorption. The temperature of the solvent and the CO₂ concentration were monitored continuously and used for the calculation of energy consumption and CO₂ desorption rate and amount. More details on the procedure are available in the previous work⁹.

3. CO₂ Absorption with Residue Acid

The effect of adipic acid addition (10, 20, and 30 g/L solvent) into the three types of solvent (200 mL and at 0.4 M) on their sub-

Table 2. Desorption experiments

Sample ID	Acid	Mass of acid (g)
1	No	0
	Adipic	0.1, 0.2, 0.3
	Suberic	0.3
	Phthalic	0.3
	Sebacic	0.3
2	No	0
	Adipic	0.1, 0.2, 0.3, 0.4, 0.5, 0.6
3	No	0
	Adipic	0.1, 0.2, 0.3
	Suberic	0.1, 0.2, 0.3
4, 5, 6	No	0
	Adipic	0.2, 0.4, 0.6

sequent absorption capacity was also investigated. The absorption experimental conditions were the same as before and the absorption time was fixed to be 1 hour. Two MEA solvents at relatively high concentrations (200 mL at 7.5 M and 11.4 M) were also tested for the absorption and desorption behaviors with the addition of different amounts of adipic acid.

4. Performance Indicators

Two performance indicators were defined for the analysis of results. One performance indicator is CO₂ desorption rate, which is defined as the ratio of regeneration efficiency to desorption time. Regeneration efficiency is obtained by dividing the amount of CO₂ desorbed by that absorbed. The other performance indicator is energy consumption, which is the total energy consumed for CO₂ desorption divided by the mole of CO₂ released. It indicates how effectively energy is utilized for CO₂ release during the regeneration process. The total energy is the same as previously defined [10,11], which is,

$$\text{Total energy} = \text{Heat of reaction} \\ + \text{Latent heat of vaporization of water} + \text{Sensible heat of solution}$$

Details of calculation of the energy terms are given in the previous work [8].

RESULTS AND DISCUSSION

1. Desorption Results

Desorption conditions and results for different solvents are tabu-

Table 1. Absorption experiments

Sample ID	Solvent	Concentration (M)	Total volume (mL)	Absorption time (s)	Volume of CO ₂ absorbed in solution (mL)	CO ₂ absorbed in solution (mol)
1	MEA	0.2	200	3067	813.792	0.03633
2	DEA	0.2	200	3118	1272.320	0.05680
3	MDEA	0.2	200	3432	456.960	0.02040
4	MEA	0.4	200	2723	1133.440	0.05060
5	DEA	0.4	200	5436	1637.440	0.07310
6	MDEA	0.4	200	5901	1642.368	0.07332

Table 3. Desorption conditions and results for sample1-0.2M MEA

Acid	Mass of acid (g)	Finish volume (mL)	Finish pH	pH after cooling	Desorption time (s)	CO ₂ desorbed (mol)	Latent heat (kJ)	Sensible heat (kJ)	Heat of reaction (kJ)	Total heat (kJ)	Energy consumption (kJ/mol CO ₂)
None	0	16.4	9.95	9.95	907	0.00260	8.136	5.04	0.169	13.345	5132.69
Adipic	0.1	16.6	9.74	9.82	897	0.00302	7.684	5.04	0.196	12.920	4278.25
Adipic	0.2	17.0	9.27	9.4	632	0.00314	6.780	5.04	0.204	12.024	3829.33
Adipic	0.3	18.6	6.24	6.43	364	0.00340	3.164	5.04	0.221	8.425	2477.94
Suberic	0.3	18.1	8.84	9.03	557	0.00320	4.294	5.04	0.208	9.542	2981.88
Phthalic	0.3	18.0	8.54	8.79	511	0.00309	4.52	5.04	0.201	9.761	3158.85
Sebeic	0.3	16.7	9.1	9.25	806	0.00325	7.458	5.04	0.211	12.709	3910.54

Table 4. Desorption conditions and results for sample 2-0.2 M DEA

Acid	Mass of acid (g)	Finish volume (mL)	Finish pH	pH after cooling	Desorption time (s)	CO ₂ desorbed (mol)	Latent heat (kJ)	Sensible heat (kJ)	Heat of reaction (kJ)	Total heat (kJ)	Energy consumption (kJ/mol CO ₂)
None	0	16.5	9.90	9.90	1554	0.00322	7.910	5.04	0.1953	13.145	4082.39
Adipic	0.1	15.5	8.53	9.46	1259	0.00440	10.170	5.04	0.2963	15.506	3174.26
Adipic	0.2	17.5	8.32	9.20	1216	0.00488	5.650	5.04	0.2669	10.957	2490.20
Adipic	0.3	18.5	7.64	8.82	768	0.00485	3.390	5.04	0.2942	8.724	1798.79
Adipic	0.4	18.8	6.59	7.08	500	0.00500	2.710	5.04	0.3033	8.053	1610.65
Adipic	0.5	19.6	5.35	5.48	445	0.00439	0.910	5.04	0.2663	6.216	1416.00
Adipic	0.6	19.7	5.38	5.01	401	0.00535	0.680	5.04	0.3245	6.045	1129.81

Table 5. Desorption conditions and results for sample 3-0.2 M MDEA

Acid	Mass of acid (g)	Finish volume (mL)	Finish pH	pH after cooling	Desorption time (s)	CO ₂ desorbed (mol)	Latent heat (kJ)	Sensible heat (kJ)	Heat of reaction (kJ)	Total heat (kJ)	Energy consumption (kJ/mol CO ₂)
None	0	16.4	9.10	9.10	1213	0.00179	8.14	5.04	0.089	13.265	7427.38
Adipic	0.1	17.5	8.63	8.95	1201	0.00184	5.65	5.04	0.092	10.782	5859.78
Adipic	0.2	18.0	8.48	8.58	1155	0.00213	4.52	5.04	0.107	9.667	4538.26
Adipic	0.3	18.2	6.10	6.20	413	0.00221	4.07	5.04	0.111	9.221	4172.17
Suberic	0.1	17.3	8.65	8.88	1204	0.00204	6.10	5.04	0.102	11.242	5510.78
Suberic	0.2	17.7	8.27	8.48	840	0.00208	5.20	5.04	0.104	10.344	4973.08
Suberic	0.3	18.0	7.72	7.90	687	0.00228	4.52	5.04	0.114	9.674	4242.98

Table 6. Desorption conditions and results for sample 4-0.4 M MEA

Acid	Mass of acid (g)	Finish volume (mL)	Finish pH	pH after cooling	Desorption time (s)	CO ₂ desorbed (mol)	Latent heat (kJ)	Sensible heat (kJ)	Heat of reaction (kJ)	Total heat (kJ)	Energy consumption (kJ/mol CO ₂)
None	0	16.4	10.07	10.07	1251	0.00333	8.136	5.04	0.216	13.393	4021.76
Adipic	0.2	16.9	9.72	9.75	850	0.00416	7.006	5.04	0.270	12.316	2960.67
Adipic	0.4	17.2	9.18	9.42	728	0.00460	6.328	5.04	0.299	11.667	2536.30
Adipic	0.6	19.5	5.18	5.28	372	0.00478	1.130	5.04	0.311	6.481	1355.80

lated in Tables 3-8. It was confirmed that acid addition affects the desorption of CO₂ significantly for MEA, DEA and MDEA. Instant release of CO₂ was observed when a weak acid was added to the solvents.

2. Effect of Different Acids

Four organic weak acids (suberic, phthalic, sebacic and adipic acids) were tested in the desorption experiments of samples 1 and

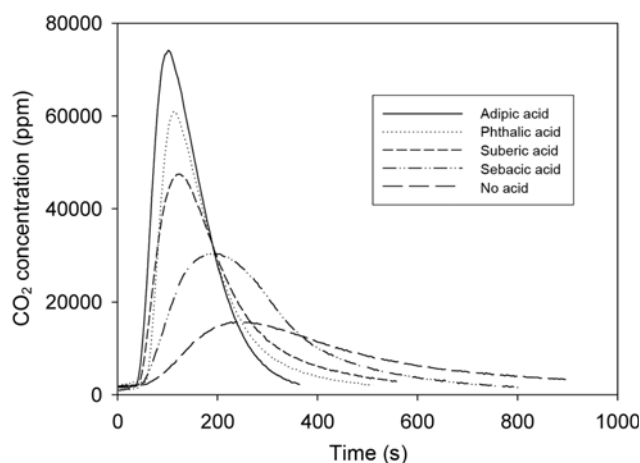
3. Fig. 2 shows CO₂ concentration curves during the regeneration of the 0.2 M MEA solvent after adding 0.3 g of different acids. It can be seen that different acids have different levels of impact. Adipic acid seems to have been the most effective in enhancing CO₂ desorption, demonstrated by the highest CO₂ peak concentration. Adipic and suberic acids were also tested for the regeneration of 0.2 M MDEA solvent, and the results are shown in Fig. 3. The CO₂ des-

Table 7. Desorption conditions and results for sample 5-0.4 M DEA

Acid	Mass of acid (g)	Finish volume (mL)	Finish pH	pH after cooling	Desorption time (s)	CO ₂ desorbed (mol)	Latent heat (kJ)	Sensible heat (kJ)	Heat of reaction (kJ)	Total heat (kJ)	Energy consumption (kJ/mol CO ₂)
None	0	15.1	9.91	9.91	1790	0.00700	11.074	5.04	0.425	16.537	2362.65
Adipic	0.2	16.3	9.05	9.33	939	0.00630	8.362	5.04	0.382	13.784	2187.95
Adipic	0.4	16.9	8.69	8.90	777	0.00630	7.006	5.04	0.382	12.428	1972.71
Adipic	0.6	18.6	7.78	8.17	520	0.00658	3.164	5.04	0.399	8.603	1307.46

Table 8. Desorption conditions and results for sample 6-0.4 M MDEA

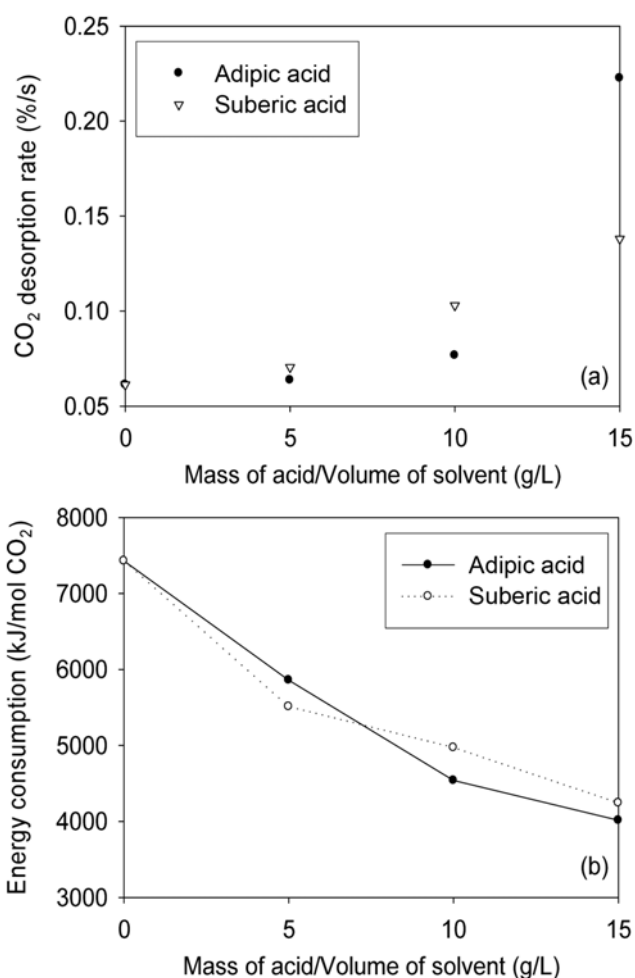
Acid	Mass of acid (g)	Finish volume (mL)	Finish pH	pH after cooling	Desorption time (s)	CO ₂ desorbed (mol)	Latent heat (kJ)	Sensible heat (kJ)	Heat of reaction (kJ)	Total heat (kJ)	Energy consumption (kJ/mol CO ₂)
None	0	14.0	9.41	9.41	1733	0.00484	13.56	5.04	0.242	18.842	3892.98
Adipic	0.2	15.8	9.02	9.24	1504	0.00407	9.492	5.04	0.330	14.862	2251.82
Adipic	0.4	16.5	8.70	9.02	1354	0.00583	7.910	5.04	0.346	13.296	1921.38
Adipic	0.6	18.5	8.20	8.75	1045	0.00609	3.390	5.04	0.349	8.779	1259.47

**Fig. 2. Effect of addition of 0.3 g different acids on the regeneration of 0.2 M MEA.**

orption rate was found to increase, while the energy consumption decreased, with the increase of the amount of acid added. The CO₂ desorption rate was increased by nearly 300% when 15 g/L adipic acid was added, and the energy consumption was reduced by about 45%. It also appeared that the addition of adipic acid resulted in a slightly lower energy consumption, compared with the addition of other acids (see Table 3 and Fig. 3). Therefore, more detailed work was conducted with the addition of adipic acid.

3. Effect of Different Solvents

Adipic acid was subsequently tested with different solvents at different concentrations. Fig. 4 presents the effect of adipic acid amount on the CO₂ desorption rate and energy consumption for three solvents, MEA, DEA and MDEA, at 0.2 M concentration, while Fig. 5 shows the results of the solvents at 0.4 M concentration. Again, it was observed that the CO₂ desorption rate increased, and the energy consumption decreased, with the increase of adipic acid amount. The MEA solvents had the highest CO₂ desorption rate and DEA had the lowest energy consumption. Although there was a big dif-

**Fig. 3. Effect of acid amount on (a) desorption rate of CO₂ and (b) energy consumption during regeneration of 0.2 M MDEA.**

ference between the 0.2 M solvents in energy consumption, the difference became much smaller between the 0.4 M solvents.

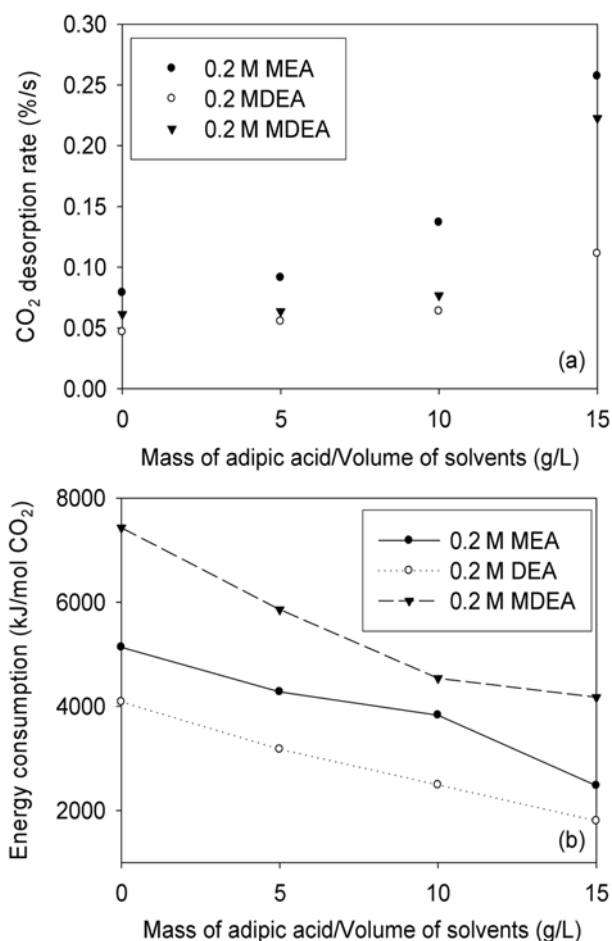


Fig. 4. Effect of adipic acid amount on (a) desorption rate of CO₂ and (b) energy consumption during regeneration of 0.2 M MEA, DEA and MDEA solvents.

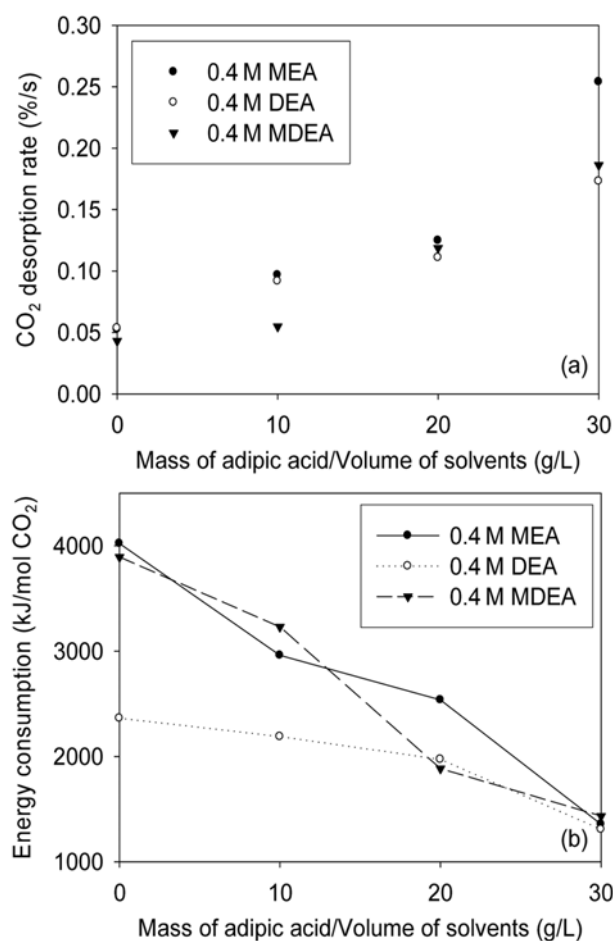


Fig. 5. Effect of adipic acid amount on (a) desorption rate and (b) energy consumption during regeneration of 0.4 M MEA, DEA, and MDEA solvents.

4. Solubility of Adipic Acid in Solvents

In the pH swing method, acid is supposed to be recovered, ideally through a crystallization process when the temperature of the solvent is reduced to below a certain value at which the solubility of acid is nearly zero. Practically complete acid recovery is not possible, so there will always be some residue acid remaining in the solvent. How much acid remains in the solvent and how it would affect the subsequent CO₂ absorption capacity were thus investigated in this work. The amount of residue acid in a solvent is determined by the solubility curve of the acid in the solvent; the solubility curves of adipic acid in various solvents were obtained as shown in Fig. 6. It appeared that the solubility of adipic acid was significantly higher in solvents than in water, and it increased with the increase of solvent concentration. The amount of acid added into the solvents in the experiments was well below the saturation point; thus no acid crystallization was observed at all even when the temperature of the solvent was reduced to 0°C. For high concentration solvents that are normally used in practical systems, it is perhaps not feasible to add an amount that is above the saturation point based on the data obtained in this work. As a result, it would not be possible to recover any acid once it is added in a practical process. Since the addition of small amount of acid (well below the saturation point) could still reduce the energy consumption during regeneration, it is

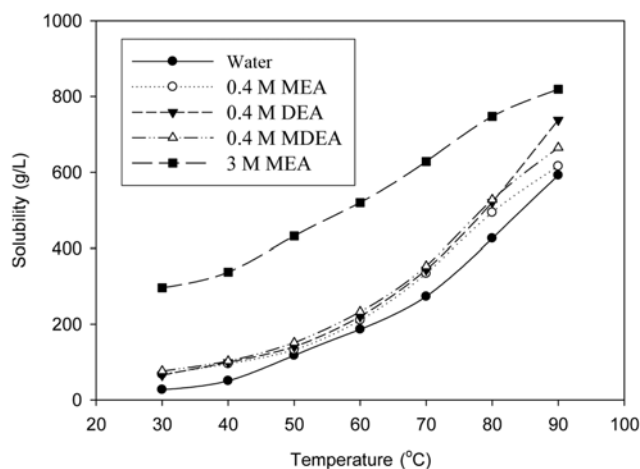


Fig. 6. Solubility curves of adipic acid in different solvents.

interesting to study how the residue acid affects the absorption performance of the solvents.

5. Effect of Residue Acid on CO₂ Absorption

Adipic acid at different masses was added to 200 mL solvents at 0.4 M concentration and the corresponding CO₂ absorption amount

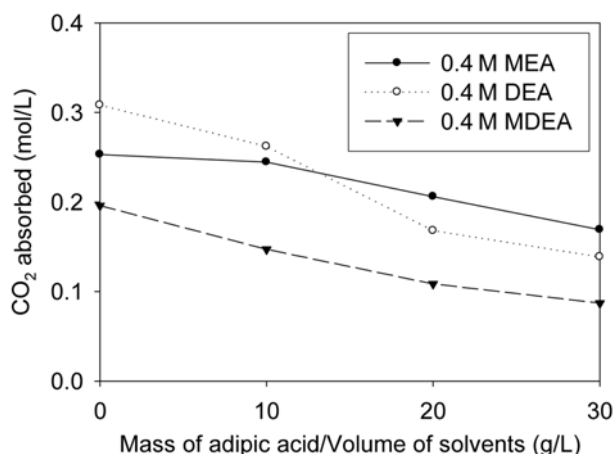


Fig. 7. Effect of acid amount in solvent on CO₂ absorption for 0.4 M MEA, DEA and MDEA solvents.

was obtained. The residue of adipic acid apparently reduced the CO₂ absorption capacity of the solvents significantly (see Fig. 7). This degradation in absorption capacity has been found for all three solvents, MEA, DEA and MDEA. Take MDEA for example: half of the CO₂ absorption capacity was lost when there was 30 g adipic acid in every liter solvent compared with that when no acid was added.

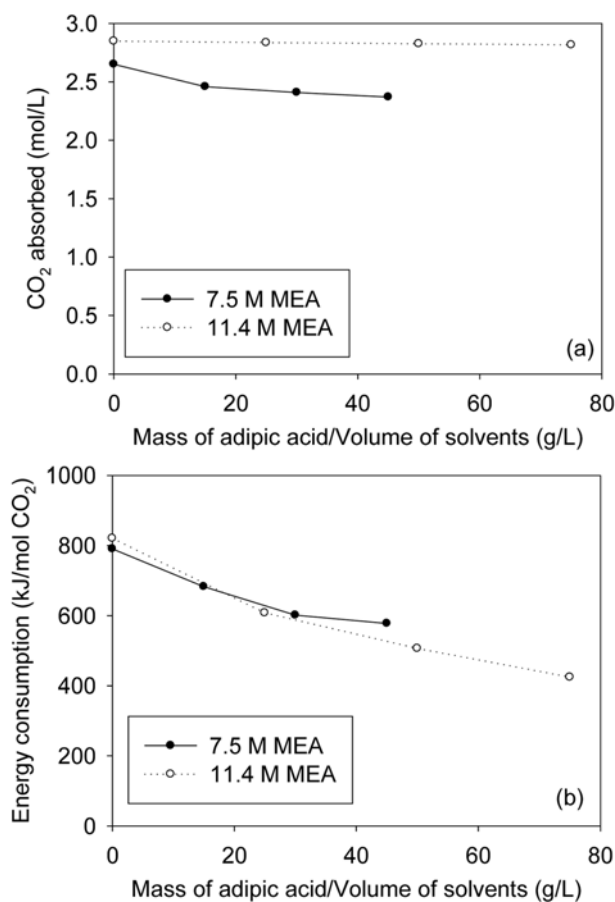


Fig. 8. Effect of acid amount on (a) CO₂ absorption capacity and (b) energy consumption during regeneration of 7.5 M and 11.4 M MEA solvents.

Two MEA solvents at high concentrations, at 7.5 M and 11.4 M, respectively, were also examined, because in practical systems a high concentration solvent is normally used. The results are shown in Fig. 8. It was interesting to observe that while the CO₂ absorption amount was reduced slightly for the two solvents, the energy consumption was reduced significantly. This suggests that acid addition would be effective in reducing energy consumption without negatively affecting CO₂ absorption significantly, at least for solvents at high concentrations. It was also noticed that high concentration solvents had much lower energy consumption than low concentration ones.

6. Discussion

It appears that the pH swing method would not work in the way as initially proposed. The major difficulty lies in the recovery of acid after regeneration. The solubility of acid in solvent was observed to be significantly higher than that in water, which makes it almost impractical to add acid by an amount above the saturation point. However, the observation that residue acid had little effect on CO₂ absorption for high concentration solvents while maintaining its effectiveness in reducing the energy consumption in regeneration makes acid addition still a potentially attractive option. In this case, acid would be used as an additive to the original solvent to reduce the overall energy consumption, and it will remain in the solvent once added. The impact of acid as additive on the operation of a solvent system thus needs to be evaluated. The pH value of the solvent could be as low as 5.01 (see Table 4), which could have negative effect on plant maintenance. Furthermore, since the acid is not to be recovered, it is interesting to see whether inorganic acid would work as effectively as organic acids. Further work should be conducted to evaluate the impact of acid addition on corrosion and to investigate the effect of inorganic acids on the performance of solvents. It would also be interesting to test different solvents commercially available in the market at concentrations employed in practical applications.

CONCLUSIONS

Four weak acids (adipic, suberic, phthalic and sebacic acids) were confirmed to be able to reduce the energy consumption of CO₂ desorption if added into three CO₂-loaded rich solvents (Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA)). The effectiveness was found to increase with the increase of the amount of acid. The solubility of acid in solvents was found to be significantly higher than that in water. The residue acid in solvent reduced the CO₂ absorption capacity significantly for low concentration solvents and slightly for high concentration solvents.

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