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1 **Solvent-mediated modification of thermodynamics and kinetics of monoethanolamine**
2 **regeneration reaction in amine-stripping carbon capture: computational chemistry**
3 **study**

N.D. Afify^{1,a} and M.B. Sweatman¹

¹ *Institute for Materials and Processes, School of Engineering, The University of Edinburgh,
Edinburgh EH9 3FB, UK*

¹Corresponding author: N.Afify@ed.ac.uk

4 A major limitation of amine-based post-combustion carbon capture technology is the necessity to regenerate amines
5 at high temperatures, which dramatically increases the operating costs. This paper concludes the effect of solvent
6 choice as a possible route to modify the thermodynamics and kinetics characterizing the involved amine
7 regeneration reactions, and discusses whether these modifications can be economically beneficial. We report
8 experimentally-benchmarked computational chemistry calculations of monoethanolamine (MEA) regeneration
9 reactions employing aqueous and non-aqueous solvents with a wide range of dielectric constants. Unlike previous
10 studies, our improved computational chemistry framework could accurately reproduce the right experimental
11 activation energy of zwitterion formation. From the predicted reactions thermodynamics and kinetics, the use of
12 non-aqueous solvents with small dielectric constants led to reductions in regeneration Gibbs free energies, activation
13 barriers and enthalpy changes. This can reduce energy consumption, and gives an opportunity to run desorption
14 columns at relatively lower temperatures, thus offering the possibility of relying on low-grade waste heat as an
15 energy input.

16 **I. INTRODUCTION**

17 Amine-based post-combustion carbon capture (PCCC) technology is currently one of the most mature routes in the
18 world fight against Climate Change.¹ This technology involves a continuous cyclic process of CO₂ molecules
19 absorption and desorption by an amine.²⁻³ An exhaust gas containing CO₂ passes through the bottom of an absorption
20 column, where it comes into contact with an amine solution. The CO₂ molecules then react with amine molecules,
21 forming carbamate at temperatures ranging from 40°C to 60°C at atmospheric pressure.²⁻³ The CO₂-rich amine
22 solution then flows to a stripping column, where it undergoes an endothermic regeneration reaction to reproduce
23 the spent amine and a purified CO₂ stream for storage. The remaining amine-rich solution then exits the bottom of
24 the stripping column and recirculates back to the absorption column for the next cycle.

25 The above amine-based PCCC technology suffers from high operating energy costs, since it requires regenerating
26 the spent amine at high temperatures, typically between 120°C and 140°C at 1-2 bar.^{2,4-7} Reduction of these energy

27 costs has become an important research area.²⁻⁸ In the past few years, researchers followed several approaches to
28 reduce such large energy costs. One approach was to replace conventional steam heating by microwave heating^{2,9-}
29 ¹¹ or frequency-tuned infrared preferential heating¹² of amine solutions. Another research approach used different
30 amine types¹³⁻¹⁸, including monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA),
31 diisopropanolamine (DIPA), 2-amino-2-methyl-1-propanol (AMP), and methyldiethanolamine (MDEA). A third
32 research direction to reduce amine regeneration energy consumption focused on evaluation of several aqueous¹⁹⁻²²
33 and non-aqueous solvents.²³⁻³⁰

34 In the present computational work, we are interested in understanding if the use of non-aqueous solvents with small
35 dielectric constants can lead to amine regeneration processes with less energy consumption or lower regeneration
36 temperatures requirements, when compared to the use of water as a solvent. Our study selected monoethanolamine
37 (MEA) as it is the most industrially used amine.¹¹ To obtain a clear picture on the role of solvent we studied several
38 solvents with a wide range of static dielectric constants, ranging from 7.43 up to 108.94 at room temperature. Our
39 solvents included tetrahydrofuran (THF), t-butanol, 1-pentanol, acetone, ethanol, methanol, dimethyl sulfoxide
40 (DMSO), water, and formamide.

41 **II. COMPUTATIONAL DETAILS**

42 Although our initial testing simulations were carried out using the GAUSSIAN 16³³ and General Atomic and
43 Molecular Electronic Structure System GAMESS³⁴ codes, for performance reasons, our production calculations
44 were fully carried out using the ORCA 5.0.3 code.³⁵ Our computational work was carried out on the Cirrus and
45 Eddie high performance computing clusters available at the University of Edinburgh. Before looking into the effect
46 of solvent choice on the thermodynamics and kinetics of involved amine regeneration reactions, it was very
47 important to benchmark the accuracy of our computational chemistry calculations against experimental data. This
48 was carried out through a comprehensive testing of the mechanisms and kinetics characterizing the CO₂ reaction
49 with MEA in presence of water as a solvent.

50 While geometry optimization, intrinsic reaction coordinate (IRC)³⁵, and frequency calculations were carried out
51 using density function theory (DFT), final single-point electronic energies were computed using the domain-based

52 local pair natural orbital coupled-cluster method DLPNO-CCSD(T)^{35,51} implemented in the ORCA code. In all
53 calculations, implicit solvent effects were included using the polarizable continuum model (PCM)³¹ in conjunction
54 with the Pauling atomic radii.³² The Def2-TZVP basis set³⁵ was employed in both DFT and DLPNO-CCSD(T)
55 calculations. To reach the most accurate computational framework we evaluated several DFT functionals. Although
56 most of previous computational studies³⁶⁻⁴⁶ were carried out using the most commonly used B3LYP hybrid
57 functional, the B3LYP functional has recently turned out to be of average performance when it comes to
58 thermochemistry calculations.⁵³ In addition to B3LYP, we tested several meta-GGA and hybrid meta-GGA
59 functionals, including TPSS, TPSSh, TPSS0, M06, M062X, M06L, rM06L, and SCANfunc, and range-separated
60 hybrid functionals, including wB97, wB97X, wB97X-D3, wB97X-D4, wB97X-D3BJ, and CAM-B3LYP.³⁵ Gibbs
61 free energies, activation barriers and enthalpy changes were calculated by combining the DLPNO-CCSD(T)
62 electronic energies and DFT vibrational analysis results.

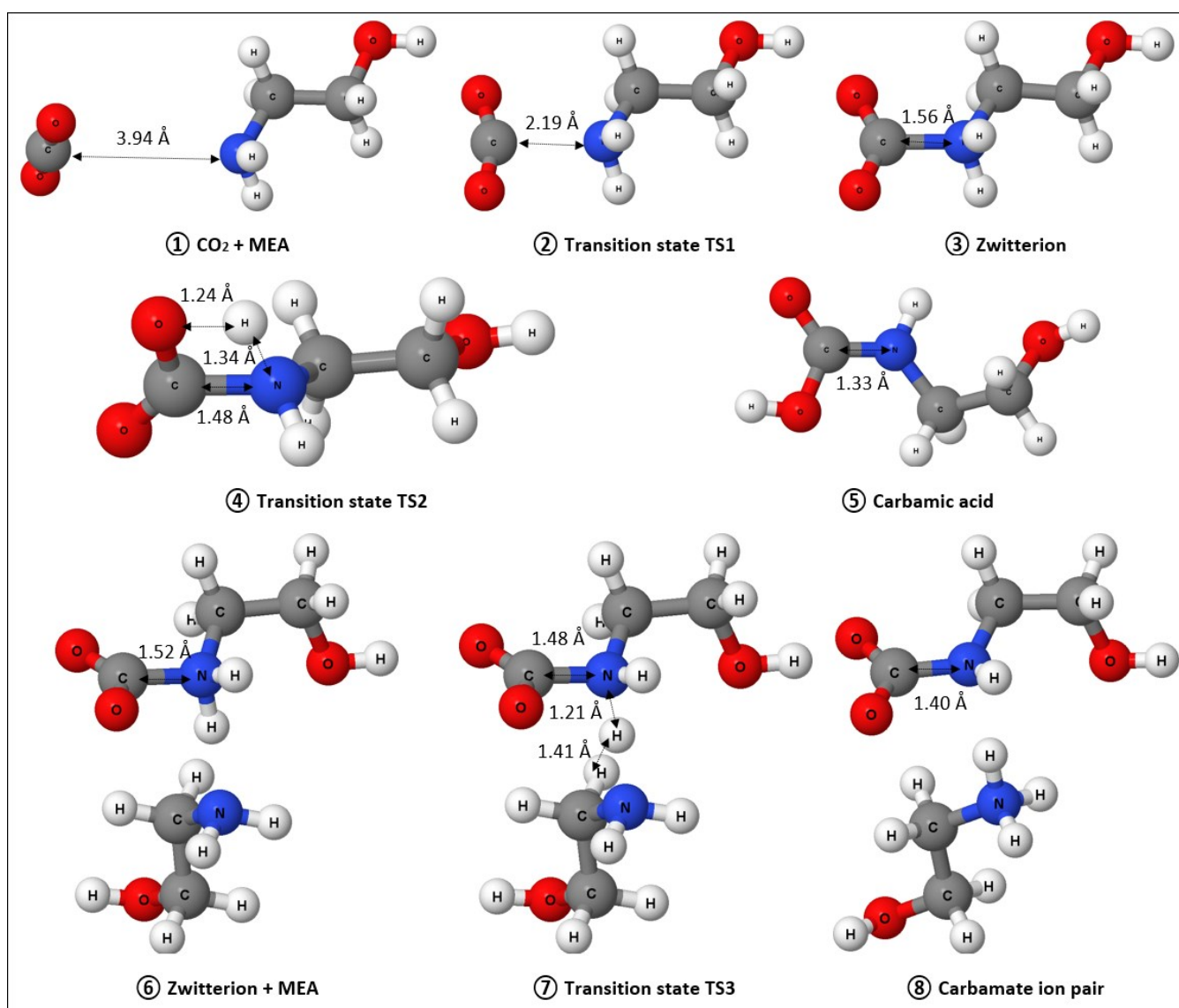
63 Our DFT calculations included the zero-point energy and geometrical counterpoise corrections.⁵⁴ We have also
64 evaluated the effect of including the Grimme's dispersion correction (D3BJ version)⁵⁵. As it will be discussed later,
65 for the current chemical reactions including the dispersion correction caused more deviation from experimental
66 activation energies. Therefore, we have decided to proceed only with the geometrical counterpoise correction, since
67 it produces the best agreement with experimental activation energies.

68 **III. RESULTS AND DISCUSSION**

69 **A. Accuracy of thermochemistry predictions**

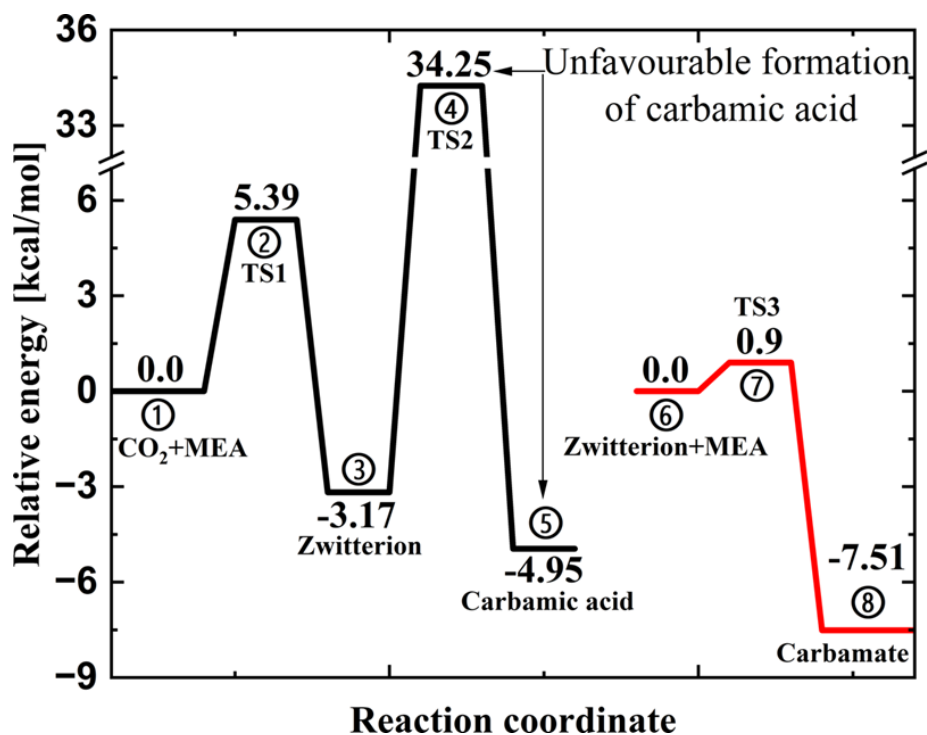
70 In this section we evaluate the accuracy of our computational framework in reproducing the correct reaction
71 mechanisms and experimental activation energy in the case of water as a solvent. In agreement with all previous
72 computational studies³⁶⁻⁴⁶, all evaluated DFT functionals have predicted the same reaction mechanisms. In Fig. 1
73 we report the DFT optimized molecular geometries in the major reaction steps in the case of the TPSS0 functional.
74 Relative electronic energies corresponding to these geometries are shown in the potential energy surface reported
75 in Fig. 2.

76 We first discuss the possible reactions mechanisms. From steps 1, 2 and 3 in Fig. 1, we can see that one CO₂
 77 molecule reacts with one MEA molecule to form zwitterion. This zwitterion can then enter one of the following
 78 two routes. The first possibility is the formation of carbamic acid (steps 3, 4 and 5). The second possibility is the
 79 reaction of zwitterion with a nearby MEA molecule to form carbamate ion pairs (steps 6, 7 and 8). From the potential
 80 energy surface reported in Fig. 2 we can confirm that the formation of carbamic acid is energetically unfavourable,
 81 in agreement with previous studies. In summary, the main reactions steps involved in amine-based carbon capture
 82 are the formation of zwitterion and the subsequent formation of carbamate ion pairs. This mechanism agrees well
 83 with several computational studies.³⁶⁻⁴⁶



84

85 **Fig. 1.** DFT optimized molecular geometries of reactants, products, and transition states involved in reaction of CO₂ with MEA
 86 in presence of water as solvent. Reported geometries correspond to the TPSS0/ Def2-TZVP level of theory.

88
89
90

91 **Fig. 2.** Relative potential energy surface corresponding to the molecular geometries reported in Fig. 1. Reported values
92 correspond to single-point electronic energies computed at the DLPNO-CCSD(T)/Def2-TZVP level of theory.

93 In Table 1 we report the activation energies for zwitterion and carbamate formation (i.e. forward reactions) and
94 regeneration (i.e. backward reactions). These activation energies were obtained by combining the DLPNO-
95 CCSD(T) electronic energies and DFT frequency calculations at 298.15 K and 1 bar. In Table S1 (Supplementary
96 Material) we compare these values to activation energies calculated purely from DFT electronic energies and
97 frequency calculations. Table S1 also contains the activation energies for the unfavourable carbamic acid reaction
98 route. At this point, it is important to decide which DFT functional produces the most accurate results. Experimental
99 activation energies for zwitterion formation were reported by Ali et al.⁴⁷ (11.14 kcal/mol) and Alper et al.⁴⁸ (11.16
100 kcal/mol) using the direct stopped-flow technique. From Table 1, it is clear that the TPSS0 was the best DFT
101 functional able to accurately predict the experimental activation energy of zwitterion formation.

102 In the following, we give an additional reason why the above result is indeed important. Some previous
103 computational chemistry studies compared their predicted activation energies for zwitterion formation to the above
104 experimental studies.³⁶⁻³⁹ Unfortunately, authors in these studies compared their predicted activation energies to the

105 wrong experimental value, namely 12.4 kcal/mol. The used experimental activation energy in fact corresponds to
 106 the case of the AMP amine, not MEA.^{47,49} This point was very important to comment on in order to avoid potential
 107 confusion in future studies.

108 **Table 1.** Activation energies (kcal/mol) obtained by combining the DFT frequency calculations at 298.15 K and DLPNO-
 109 CCSD(T) electronic energies. All calculation used water as a solvent and employed the Def2-TZVP basis set.

	Zwitterion		Carbamate	
	Forward	Backward	Forward	Backward
B3LYP	9.97	5.09	0.13	6.71
TPSS	8.19	4.20	0.10	6.39
TPSSh	10.80	4.56	-0.04	6.67
TPSS0	11.13	4.74	-0.22	6.96
M06	8.10	5.61	0.81	5.35
M062X	7.14	4.86	0.08	4.87
M06L	7.79	5.37	-0.97	5.86
rM06L	8.86	5.36	-0.72	6.96
SCANfunc	6.36	3.65	-1.27	5.30
wB97	8.17	5.00	0.79	5.47
wB97X	8.57	4.93	0.07	5.77
wB97X-D3	9.71	4.93	0.06	5.50
wB97X-D4	8.83	4.87	-0.08	5.57
wB97X-D3BJ	8.86	4.81	-0.20	5.61
CAM-B3LYP	9.48	4.84	-0.19	5.70

110 As mentioned above in the Computational Details section, our DFT calculations evaluated the effects of including
 111 the geometrical counterpoise⁵⁴ and Grimme's dispersion⁵⁵ corrections. In the following, we justify our decision to
 112 consider results obtained by incorporating only the geometrical counterpoise correction. In Table S3
 113 (Supplementary Material) we report the effect of including these two corrections on the zwitterion formation
 114 activation energy. Results are reported for the case of water as solvent, and B3LYP, TPSS, TPSSh and TPSS0 DFT
 115 functionals. In this table, ΔE_{exp} represents the deviation of the calculated activation energy from experimental value
 116 (11.15 kcal/mol). Inspection of the results reported in Table S3 reveals the following four cases.

117 Let us first discard both the counterpoise and dispersion corrections. In this case, the TPSS0 functional produces
 118 the best agreement with the experimental activation energy ($\Delta E_{\text{exp}} = 0.46$ kcal/mol), followed by TPSSh ($\Delta E_{\text{exp}} = 0.76$
 119 kcal/mol) and B3LYP ($\Delta E_{\text{exp}} = 1.61$ kcal/mol). In the second case, we included both the counterpoise and dispersion
 120 corrections. This makes B3LYP the most accurate functional ($\Delta E_{\text{exp}} = 1.68$ kcal/mol), followed by TPSSh ($\Delta E_{\text{exp}} =$
 121 2.24 kcal/mol) and TPSS ($\Delta E_{\text{exp}} = 2.76$ kcal/mol). In the third case, we included only the dispersion correction. In
 122 this case, again the B3LYP functional comes best ($\Delta E_{\text{exp}} = 1.68$ kcal/mol), followed by TPSS ($\Delta E_{\text{exp}} = 2.03$ kcal/mol)
 123 and TPSS0 ($\Delta E_{\text{exp}} = 2.54$ kcal/mol). In the fourth case, we included only the counterpoise correction. This puts the

124 TPSS0 functional as the absolute best ($\Delta E_{\text{exp}} = 0.02$ kcal/mol) functional, followed by the TPSSh ($\Delta E_{\text{exp}} = 0.35$
125 kcal/mol) and B3LYP ($\Delta E_{\text{exp}} = 1.18$ kcal/mol) functionals.

126 The above analysis reveals the sensitivity of the obtained activation energies to the employed DFT functional and
127 inclusion of dispersion and counterpoise corrections. In this study, we were looking for the best computational
128 framework able to produce best agreement with experimental data. Given results of the above analysis, we believe
129 the use of the TPSS0 functional in conjunction with the counterpoise corrections is effectively the best choice for
130 studying the current chemical reactions. This is consistent with a recent computational chemistry study⁵⁶, which
131 showed that the hybrid B3LYP functional, having 20% HF exchange, presented a poor performance compared to
132 hybrid meta-GGA functionals having 25% HF exchange.

133 **B. Effect of solvent choice on regeneration thermodynamics and kinetics**

134 In this section we comment on the effect of solvent choice on thermodynamics and kinetics of amine regeneration
135 reactions. As discussed above, the regeneration reaction consists of two main steps. The first step involves two
136 amine molecules, where carbamate anion abstracts one proton from another protonated amine molecule, resulting
137 in zwitterion and neutral amine molecules. The second step is the liberation of CO₂ molecule from zwitterion,
138 resulting in unreacted CO₂ and amine molecules. In Table 2 we report the Gibbs free energies and activation energy
139 barriers corresponding to these two steps, in addition to the total regeneration enthalpy change. In Table 2 we also
140 report experimental specific heat capacities of the different solvents, taken from the Springer Materials database.

141 First, we discuss the dependence of reactions thermodynamics on the solvent type. From the computed Gibbs free
142 energies, we can see that the regeneration of zwitterion from carbamate (first step) is an endothermic reaction. On
143 contrary, the regeneration of amine from zwitterion (second step) is spontaneous reaction, as evidenced from the
144 negative Gibbs free energy. From the enthalpy changes reported in Table 2, it is very clear that using non-aqueous
145 solutions with small dielectric constants can reduce the amount of input energy required to achieve the amine
146 regeneration reaction. It is important to point out that the reduction in the required energy input cannot be explained
147 only by the differences in specific heat capacities reported in Table 2. For example, the use of formamide would
148 require more energy input than water, although formamide has almost half of the heat capacity of water.

149 **Table 2.** Effect of solvent choice on thermodynamics and kinetics of amine regeneration reactions. These results were obtained
 150 by combining the DFT frequency calculations at 298.15 K and DLPNO-CCSD(T) electronic energies. DFT calculations were
 151 carried out at the TPSS0/Def2-TZVP level of theory.

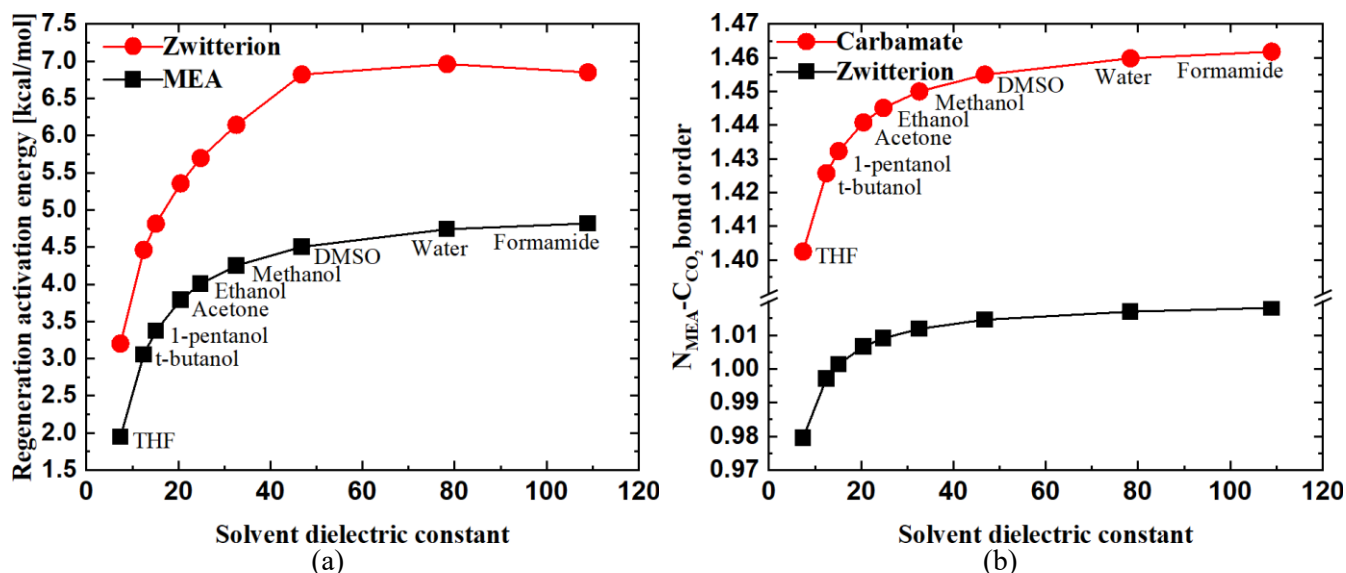
Solvent	Dielectric constant	Step 1: carbamate to zwitterion		Step 2: zwitterion to MEA		Enthalpy change [kcal/mol]	Specific heat capacity [J/gK]
		Gibbs free energy [kcal/mol]	Activation energy [kcal/mol]	Gibbs free energy [kcal/mol]	Activation energy [kcal/mol]		
THF	7.43	2.38	3.20	-7.77	1.95	0.43	1.770
t-butanol	12.47	4.18	4.46	-5.94	3.05	3.47	2.359
1-pentanol	15.13	4.67	4.81	-7.98	3.38	4.90	2.336
Acetone	20.49	5.35	5.36	-7.70	3.79	5.96	2.131
Ethanol	24.85	5.75	5.70	-7.19	4.01	6.49	2.512
Methanol	32.61	6.26	6.14	-4.76	4.25	6.48	2.508
DMSO	46.83	7.00	6.82	-6.62	4.50	7.68	1.960
Water	78.36	7.18	6.96	-6.39	4.74	8.22	4.188
Formamide	108.94	7.09	6.85	-6.20	4.82	8.45	2.388

152 This finding agrees well with recent experimental study.⁸ In this study, Bougie et al. studies several solvents
 153 including a mixture of ethylene glycol and 1-propanol, diethylene glycol monoethyl ether (DEGMEE), and N-
 154 methylformamide (NMF). They found that energy consumption reduces from 3630 kJ/mol in the case of water
 155 (dielectric constants of 78.355) to 929 kJ/mol in the case of DEGMEE (dielectric constant of 12.6). The findings in
 156 this experimental study fully support our computational results.

157 Now we focus on the effect of solvent choice on the kinetics of regeneration reaction. Activation energies for the
 158 two regeneration steps are reported in Table 2. In Fig. 3a we show the dependence of these activation energies on
 159 the solvent dielectric constant. As we can see, regeneration of zwitterion from carbamate exhibits higher activation
 160 energies compared to the regeneration of MEA from zwitterion. This indicates that the regeneration of zwitterion
 161 from carbamate is the rate-determining regeneration step regardless of the employed solvent. Going from
 162 formamide to THF we can see that the activation energy decreases as a function of the solvent dielectric constant.

163 To confirm the dependence of activation energy on the solvent, in Fig. 3b we report bond order analysis of the
 164 $N_{\text{MEA}}\text{-C}_{\text{CO}_2}$ bonds in zwitterion and carbamate. This bond order analysis gives us an idea about the relative chemical
 165 stabilities of zwitterion and carbamate. Bond order analysis was carried out using the Löwdin population analysis⁵⁰
 166 implemented in the ORCA code.³⁵ From Fig. 3b it can be understood that the $N_{\text{MEA}}\text{-C}_{\text{CO}_2}$ bond in zwitterion is
 167 covalent in nature, and becomes relatively weaker when we use solvents with small dielectric constant. The $N_{\text{MEA}}\text{-}$
 168 C_{CO_2} bond in carbamate have values between 1.4 and 1.46, depending on the employed solvent, which suggests it

169 is partially ionic bond. Thus, the $N_{\text{MEA}}\text{-C}_{\text{CO}_2}$ bond in carbamate is much stronger than that in zwitterion, which
 170 explains why zwitterion regeneration is the rate-determining step, which is indeed documented in Fig. 3a.



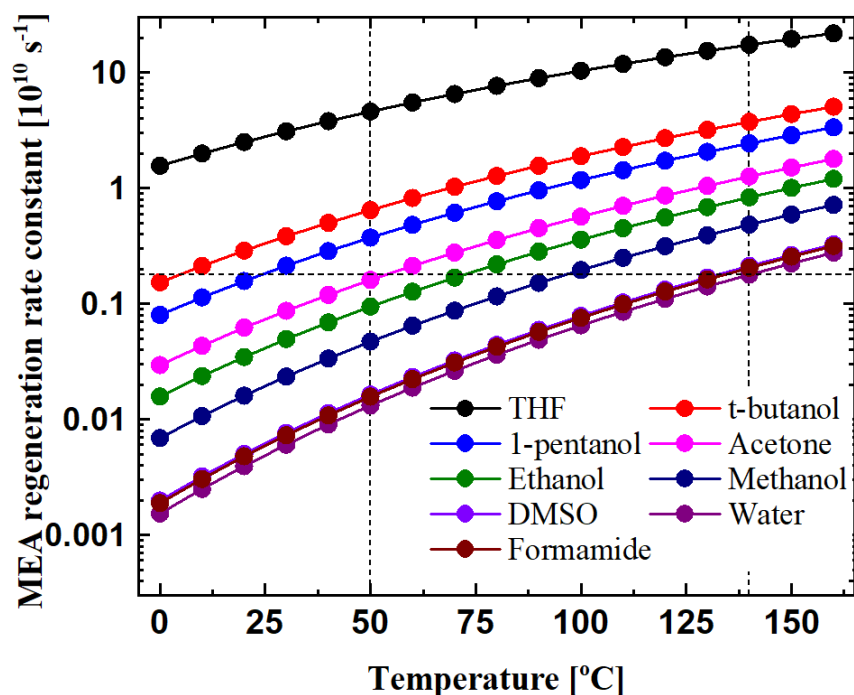
171 **Fig. 3.** (a) Effect of the solvent dielectric properties on the activation energies of the two regeneration reaction steps. Red circles
 172 and black squares correspond to converting carbamate to zwitterion and zwitterion to MEA. (b) Relative chemical stabilities
 173 of zwitterion and carbamate as calculated from bond order analysis of the $N_{\text{MEA}}\text{-C}_{\text{CO}_2}$ bond.
 174

175 In the following we seek to understand how the reduction in regeneration activation energy reported in Table 2 and
 176 Fig. 3a will play out in terms of heat input requirements. Higher activation energy implies that solution should be
 177 heated at higher temperature, thus molecules will have sufficient energy to cross energy barrier. Lowering this
 178 temperature will lower the rate at which carbamate decomposed into amine and CO_2 . The fact that non-aqueous
 179 solutions with low dielectric constants exhibit lower activation energies means that amines can be regenerated in
 180 these solutions at lower temperatures compared to aqueous solutions, assuming the same amine regeneration rate.

181 In Fig. 4 we report amine regeneration rate constant as a function of temperature for the different solvents. The
 182 MEA regeneration reaction rate constants were calculated using the Eyring equation.⁵¹ From this figure, the
 183 regeneration reaction rate at any regeneration temperature increases by decreasing the solvent dielectric constant.
 184 This agrees well with the recent experimental results obtained by Bougie et al.⁸ In this experimental study it was
 185 found that the amount of desorbed CO_2 in the case of the DEGMEE solvent (dielectric constant of 12.6) was much
 186 higher than the case of water (dielectric constant of 78.4). Similarly, the amount of desorbed CO_2 in the case of

187 water was much higher than the case of the NMF solvent (dielectric constant of 182.0). Thus, our computational
188 regeneration kinetics results are in line with those obtained experimentally.⁸

189 Taking into account that typical regeneration temperature in the case of water is about 140°C^{2,4-7}, we can now
190 estimate from Fig. 4 what regeneration temperatures are required for other solvents, keeping the same regeneration
191 rate constant. From this figure (see dashed lines) it is possible to achieve MEA regeneration reaction at much lower
192 temperatures if we use solvents with low dielectric constants. For example, in the case of acetone as a solvent the
193 regeneration temperature would be as low as 50°C, which is much less than the 140°C required in the case of water.



194
195
196
197

Fig. 4. MEA regeneration reaction rate constant as a function of temperature and solvent dielectric constant.

198 The solvent vapour pressure is a very important factor to consider when judging the suitability of a certain solvent
199 for carbon capture applications. Acetone for example has a vapour pressure of 30.6 kPa at 25 °C, which is much
200 higher than the vapour pressure of water (3.2 kPa at 25 °C). From this point of view, acetone might not be a suitable
201 solvent. Our results show that the required amine regeneration temperatures can be significantly reduced by using
202 non-aqueous solutions with small dielectric constants. However, it is important to look for a solvent with small
203 dielectric constant as well as low vapour pressure. One interesting solvent could be diethylene glycol monoethyl

204 ether (DEGMEE), which has dielectric constant of 15.6, which is very close to t-butanol included in our study.
205 DEGMEE has vapour pressure of 0.02 kPa which makes it a very good candidate. This explains why DEGMEE
206 was ranked as the best solvent in the recent experimental study conducted by Bougie et al.⁸

207 **III. CONCLUSION**

208 In this computational study we investigated the possibility of using non-aqueous solutions to reduce energy penalty
209 of amine regeneration in amine-based post-combustion carbon capture (PCCC) technology. We demonstrated the
210 ability of our computational framework to reproduce very well experimental activation energy of zwitterion
211 formation. We have shown that non-aqueous solutions with small dielectric constants are beneficial for more energy
212 efficient amine regeneration. From thermodynamics point of view, the change in regeneration enthalpy decreased
213 in the case of these non-aqueous solutions, suggesting less energy consumption in this case. Also in this case, the
214 reduction in activation energies will allow for running the desorption column at much lower temperatures. This
215 could enable us to completely rely on waste thermal energy instead of using expensive high-grade electrical heat
216 energy. Although these results are very promising, other factors such as the solvent volatility should be also
217 considered.

SUPPLEMENTARY MATERIAL

218 The Supplementary Material is available and contain activation energies (Table S1) and Gibbs free energies (Table
219 S2) of the different forward and backward reactions. These tables compare the values obtained purely from DFT
220 calculations to these obtained by combining coupled-cluster electronic energies and DFT vibrational frequency
221 calculations. Table S3 reports the evaluation of including the dispersion and geometrical counterpoise corrections.

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CONFLICTS OF INTEREST

The authors declare that there are no any conflicts of interest regarding the publication of this paper.

DATA AVAILABILITY

The data used to support the findings of this study are included within the article. Should further data or information be required, these are available from the corresponding author upon request.

REFERENCES

- ¹Z. (Henry) Liang, W. Rongwong, H. Liu, K. Fu, H. Gao, F. Cao, R. Zhang, T. Sema, A. Henni, K. Sumon, D. Nath, D. Gelowitz, W. Srisang, C. Saiwan, A. Benamor, M. Al-Marri, H. Shi, T. Supap, C. Chan, Q. Zhou, M. Abu-Zahra, M. Wilson, W. Olson, R. Idem and P. (PT) Tontiwachwuthikul, *Int. J. Greenh. Gas Control*, 2015, 40, 26–54.
- ²S. J. McGurk, C. F. Martín, S. Brandani, M. B. Sweatman and X. Fan, *Appl. Energy*, 2017, 192, 126–133.
- ³G. T. Rochelle, *Science (80-.)*, 2009, 325, 1652–1654.
- ⁴K. Z. House, C. F. Harvey, M. J. Aziz and D. P. Schrag, *Energy Environ. Sci.*, 2009, 2, 193.
- ⁵J. Husebye, A. L. Brunsvold, S. Roussanaly and X. Zhang, *Energy Procedia*, 2012, 23, 381–390.
- ⁶B. Dutcher, M. Fan and A. G. Russell, *ACS Appl. Mater. Interfaces*, 2015, 7, 2137–2148.
- ⁷C.-H. Yu, C.-H. Huang and C.-S. Tan, *Aerosol Air Qual. Res.*, 2012, 12, 745–769.
- ⁸F. Bougie, D. Pokras and X. Fan, *Int. J. Greenh. Gas Control*, 2019, 86, 34–42.
- ⁹N. D. Afify and M. B. Sweatman, *J. Chem. Phys.*, 2018, 148, 204513.
- ¹⁰N. D. Afify and M. B. Sweatman, *J. Chem. Phys.*, 2018, 148, 024508.
- ¹¹F. Bougie and X. Fan, *Int. J. Greenh. Gas Control*, 2018, 79, 165–172.
- ¹²N. D. Afify and M. B. Sweatman, *J. Chem. Phys.*, 2019, 151, 024503.
- ¹³G. Rochelle, E. Chen, S. Freeman, D. Van Wagener, Q. Xu and A. Voice, *Chem. Eng. J.*, 2011, 171, 725–733.
- ¹⁴S. Martin, H. Lepaumier, D. Picq, J. Kittel, T. de Bruin, A. Faraj and P.-L. Carrette, *Ind. Eng. Chem. Res.*, 2012, 51, 6283–6289.
- ¹⁵A. Hartono, A. F. Ciftja, P. Brúder and H. F. Svendsen, *Energy Procedia*, 2014, 63, 2138–2143.
- ¹⁶E. Gjernes, L. I. Helgesen and Y. Maree, *Energy Procedia*, 2013, 37, 735–742.
- ¹⁷F. Closmann, T. Nguyen and G. T. Rochelle, *Energy Procedia*, 2009, 1, 1351–1357.
- ¹⁸F. Bougie and M. C. Iliuta, *Ind. Eng. Chem. Res.*, 2010, 49, 1150–1159.

- ¹⁹B. Zhao, Y. Sun, Y. Yuan, J. Gao, S. Wang, Y. Zhuo and C. Chen, *Energy Procedia*, 2011, 4, 93–100.
- ²⁰S.-W. Park, J.-W. Lee, B.-S. Choi and J.-W. Lee, *Korean J. Chem. Eng.*, 2006, 23, 806–811.
- ²¹N. El Hadri, D. V. Quang, E. L. V. Goetheer and M. R. M. Abu Zahra, *Appl. Energy*, 2017, 185, 1433–1449.
- ²²M. Lail, J. Tanthana and L. Coleman, *Energy Procedia*, 2014, 63, 580–594.
- ²³M. Tao, J. Gao, P. Zhang, W. Zhang, Q. Liu, Y. He and Y. Shi, *Energy & Fuels*, 2017, 31, 6298–6304.
- ²⁴F. J. Tamajón, E. Álvarez, F. Cerdeira and D. Gómez-Díaz, *Chem. Eng. J.*, 2016, 283, 1069–1080.
- ²⁵P. M. Mathias, F. Zheng, D. J. Heldebrant, A. Zwoster, G. Whyatt, C. M. Freeman, M. D. Bearden and P. Koech, *ChemSusChem*, 2015, 8, 3617–3625.
- ²⁶M. Hasib-ur-Rahman and F. Larachi, *Environ. Sci. Technol.*, 2012, 46, 11443–11450.
- ²⁷R. Hart, P. Pollet, D. J. Hahne, E. John, V. Llopis-Mestre, V. Blasucci, H. Huttenhower, W. Leitner, C. A. Eckert and C. L. Liotta, *Tetrahedron*, 2010, 66, 1082–1090.
- ²⁸M. Cui, S. Chen, T. Qi and Y. Zhang, *J. Chem. Eng. Data*, 2018, 63, 1198–1205.
- ²⁹F. Barzagli, S. Lai and F. Mani, *Energy Procedia*, 2014, 63, 1795–1804.
- ³⁰F. Barzagli, F. Mani and M. Peruzzini, *Int. J. Greenh. Gas Control*, 2013, 16, 217–223.
- ³¹V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, 102, 1995–2001.
- ³²V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, 102, 1995–2001.
- ³³M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, et al., *Gaussian 16*, Rev. C. 01, 2016.
- ³⁴G. M. J. Barca, C. Bertoni, L. Carrington, D. Datta, N. De Silva, J. E. Deustua, D. G. Fedorov, J. R. Gour, et al., *J. Chem. Phys.*, 2020, 152, 154102.
- ³⁵F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, 152, 224108.
- ³⁶T. Davran-Candan, *J. Phys. Chem. A*, 2014, 118, 4582–4590.
- ³⁷S. Gangarapu, A. T. M. Marcelis, Y. A. Alhamed and H. Zuilhof, *ChemPhysChem*, 2015, 16, 3000–3006.
- ³⁸E. Orestes, C. Machado Ronconi and J. W. de M. Carneiro, *Phys. Chem. Chem. Phys.*, 2014, 16, 17213–17219.
- ³⁹H.-B. Xie, Y. Zhou, Y. Zhang and J. K. Johnson, *J. Phys. Chem. A*, 2010, 114, 11844–11852.
- ⁴⁰K. Z. Sumon, C. H. Bains, D. J. Markewich, A. Henni and A. L. L. East, *J. Phys. Chem. B*, 2015, 119, 12256–12264.

- ⁴¹H. M. Stowe and G. S. Hwang, *Ind. Eng. Chem. Res.*, 2017, 56, 6887–6899.
- ⁴²T. Zhang, Y. Yu and Z. Zhang, *Mol. Simul.*, 2018, 44, 815–825.
- ⁴³S. Kim, H. Shi and J. Y. Lee, *Int. J. Greenh. Gas Control*, 2016, 45, 181–188.
- ⁴⁴B. Han, C. Zhou, J. Wu, D. J. Tempel and H. Cheng, *J. Phys. Chem. Lett.*, 2011, 2, 522–526.
- ⁴⁵Y. Matsuzaki, H. Yamada, F. A. Chowdhury, T. Higashii, S. Kazama and M. Onoda, *Energy Procedia*, 2013, 37, 400–406.
- ⁴⁶Y. Matsuzaki, H. Yamada, F. A. Chowdhury, T. Higashii and M. Onoda, *J. Phys. Chem. A*, 2013, 117, 9274–9281.
- ⁴⁷S. H. Ali, *Int. J. Chem. Kinet.*, 2005, 37, 391–405.
- ⁴⁸E. Alper, *Ind. Eng. Chem. Res.*, 1990, 29, 1725–1728.
- ⁴⁹S. Xu, Y.-W. Wang, F. D. Otto and A. E. Mather, *Chem. Eng. Sci.*, 1996, 51, 841–850.
- ⁵⁰G. Bruhn, E.R. Davidson, I. Mayer and A.E. Clark, *Int. J. Quantum Chem.*, 2006, 106, 2065–2072.
- ⁵¹M.G. Evans, M. Polanyi, *Trans. Faraday Soc.*, 1935, 31, 875–894.; H. Eyring, *J. Chem. Phys.*, 1935, 3, 107–115.
- ⁵²I. Sandler, J. Chen, M. Taylor, S. Sharma, and J. Ho, “Accuracy of DLPNO-CCSD(T): Effect of Basis Set and System Size,” *J. Phys. Chem. A* 125(7), 1553–1563 (2021).
- ⁵³L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, and S. Grimme, “A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions,” *Phys. Chem. Chem. Phys.* 19(48), 32184–32215 (2017).
- ⁵⁴H. Kruse, and S. Grimme, “A geometrical correction for the inter- and intra-molecular basis set superposition error in Hartree-Fock and density functional theory calculations for large systems,” *J. Chem. Phys.* 136(15), 154101- 154101 (2012).
- ⁵⁵S. Grimme, S. Ehrlich, and L. Goerigk, “Effect of the damping function in dispersion corrected density functional theory,” *J. Comput. Chem.* 32(7), 1456–1465 (2011).
- ⁵⁶S. Grimme, S. Ehrlich, and L. Goerigk, “Effect of the damping function in dispersion corrected density functional theory,” *J. Comput. Chem.* 32(7), 1456–1465 (2011).