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Optimum solvent concentration to lower energy demands for CO2 capture in refinery cases

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Abstract

An open-access novel low-energy solvent HS-3 has been proposed and verified in the lab scale for post-combustion CO_2 capture. The HS-3 solvent consists of a tertiary amine with a strong bicarbonate former and a primary amine with high reactivity. Blends of these two solvents have been reported to be promising solvent candidate. In this work empirical density, viscosity, and thermal properties correlations together with the rigorous thermodynamic model were used to evaluate the energetic performance of individual solvent components and their blends. A simplified method mimicking the absorber and stripper conditions was used to evaluate performance of the solvents. Blends of these two amines at five different ratios were evaluated and the results show better energy performance than MEA 30 mass%. Based on the evaluation done, the blend of 40 mass% of Amine 1 and 15 mass% Amine gives the lowest energy requirement (2.5 MJ/kg CO2). In addition, the viscosity increases with solvent concentration but the changes were considered not to be so significant.

Keywords: Thermodynamic; eNRTL; Cyclic capacity; Energy penalty; CCS; Solvent;

1. Introduction

The refinery sector is categorized as third biggest stationary CO_2 producer after the power sector and the cement industry. It contributes about 4% of the total anthropogenic CO_2 emissions and shares about 1 billion metric tons per year. Since the 1990s, a significant reduction in energy usage has been achieved in this sector, but it was not followed by low CO_2 production. Direct CO_2 emission of up to 200 kg CO_2/ton crude oil remains to be reduced [1]. Carbon capture, utilization, and storage (CCUS) are one viable option technology to reduce these emissions. The absorption process with a chemical reactive absorbent is a mature and viable capture technology, but it still suffers from its high energy usage. Therefore, solvent selection remains a vital tool to lessen the energy demand. An open-access novel low-energy solvent HS-3 has been proposed and verified in the lab scale [2] for post-combustion CO_2 capture. The HS-3 solvent consists of a tertiary amine that has a strong bicarbonate former [3] and a primary amine that has high

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reactivity. Blends of these two solvents were reported to be a promising solvent candidate, however, limited equilibrium data and thermodynamic property [4, 5] were persisted and need to fully develop.

Energy requirement and environmental aspects are fundamental properties of the absorbent system and part of the design and operation [6]. The energy required is expressed in Eq. 1 and classified as three primary sources, i.e., heat for reversion of the heat of reaction (Q_{Des}), sensible heats (Q_{Sens}), i.e., to obtain lean amine loading condition and stripping heat (Q_{Strip}), i.e. steam needed to maintain the pressure in the stripper.

$$Q_{Req.}\left(\frac{kJ}{mol\ CO2}\right) = Q_{Sens} + Q_{Des} + Q_{Strip} \quad (1)$$

Where the individual contribution is expressed as:

$$Q_{Sens} = \frac{\rho \cdot Cp \cdot \Delta T}{(\alpha_{rich} - \alpha_{lean}) \cdot C_{Am}}$$

$$Q_{Des} = -\Delta H_{abs\ CO_2}$$

$$Q_{Strip} = \frac{P^{Sat}_{H_2O}(T_{Top,Des.}) \cdot x_{H_2O,freebasis}}{P^{*}_{CO_2}(T_{Top,Des.})} \cdot \Delta H^{vap}_{H_2O}$$

The individual reactions are influenced by the key characteristics of a solvent, i.e., higher cyclic capacity reduces the sensible heat, lower heat of absorption reduces the heat of desorption to reverse the reaction between CO_2 and amine and temperature sensitibility of equilibrium behaviour temperature is reflected by influences the CO_2 partial pressure and, thus, stripping steam requirement. Overall, the goal is to find solvents candidates with lower thermal energy requirement for regeneration [7].

To evaluate Eq. 1, tedious work needs to be performed to describe physical and transport (mass/ thermal) properties as well as varor-liquid equilibrium (VLE) behvaiour . VLE behaviour is one of the crucial properties to evaluate when identifying potential solvent candidates. The gathered experimental data are normally used for input in correlations and models describing the performance of the system. The VLE data can be fitted to empirical correlations [8, 9] or rigorous thermodynamic models [10, 11] as a function pressure, temperature, amine, and CO_2 concentrations. However, only rigorous thermodynamic models could be used to optimize solvent concentrations.

In this work, the developed thermodynamic model for the HSE-3 solvent using literature data for each amine component and the blend is presented. The final ternary/ quaternary models are used to find an optimum concentration of each compound for the lowest energy demand. Even though this paper focuses on the one specific amine blend, the aim of this work is investigate the opportunities to used thermodynamic models to optimize concentrations of amines in a blend.

Nomenclature

Cp	Heat capacity (J/K/kg)
C	Concentration (mol/ L)
H	Enthalpy (kJ/mol)
T	Temperature (K)
NRTL	Non-Randomness Two Liquid Theory (-)
eNRTL	Electrolyte NRTL (-)

Greek alphabet

ρ	Density of solvent (kg/m^3)
α	CO_2 loading (mol CO_2/ mol amine)

Superscript

Sat	Saturated
Vap	Vaporization (kJ/mol)
*	Equilibrium condition

Subscript

Abs	Absorption
Am	Amine
CO_2	Carbon dioxide
Des.	Desorber
H_2O	Water
Lean	Lean loading
Rich	rich loading
Req.	Requirement
Sens	Sensible
Strip	Stripper
Top	Top position

1.1. Solvent Selection

The selected solvent, HS-3, was originally identified in a project focusing on solvents combining a strong bicarbonate forming solvent[3] to increase absorption capacity and a fast reaction rate of the primary amine [2]. The HS3 solvent is a blend of 1-(2-Hydroxyethyl)pyrrolidine and 3-Amino-1-propanol. In this paper 1-(2-Hydroxyethyl)pyrrolidine referred as amine 1 and 3-Amino-1-propanol as amine 2. Existing density, viscosity, and heat capacity data was modelled using empirical correlations [12].

The reported vapor-liquid equilibria (VLE) data with and without CO_2 was modeled using the NRTL/ eNRTL thermodynamic framework for the liquid phase activities [13, 14]. Additionally, to vapor-liquid equilibrium data (partial pressure of CO_2 as a function of loading), the model can give information about the volatility of the amine components as well as estimation of heat of absorption.

1.2. Evaluation criteria for the optimum solvent concentration

The heat requirement in Eq. (1) is evaluated arbitrarily with two chosen conditions which reflect the absorber (40°C and pCO_2 = 5kPa) and stripper conditions (120°C and pCO_2 = 0.5 kPa) whereas the delta T approach is selected as 10K between the lean and rich solvent temperatures at the hot side of the cross-heat exchanger.

2. Results and discussion

2.1. Solvent property

The density and viscosity of individual and their blend are presented in Figures 1 and 2 as a function of temperature and concentration. Figures 1 and 2 suggest that each aqueous solvent experiences of having a maximum value. Solvent viscosity directly correlates to the mass transfer property. Viscous solvent hinders mass transfer and enhance the pump cost. A low viscosity solvent is preferable for the solvent candidate to enhance the mass transfer property. Figure 2 shows that the viscosity increases with the concentration of amine but decreases with increased temperature (Figures 2a and 2b). The same behavior is also seen for the blends at 40°C (Figure 2c). Amine 2 shows to be more viscous than Amine 1 and water, respectively. More concentrated Amine 2 could provide a better absorption rate, but it may not be significantly benefit as the solvent viscosity also increases. The selected concentrations of individual Amine are summarized in Tables 1 and 2 whereas the heat capacity of the solvents were estimated from literature [15].

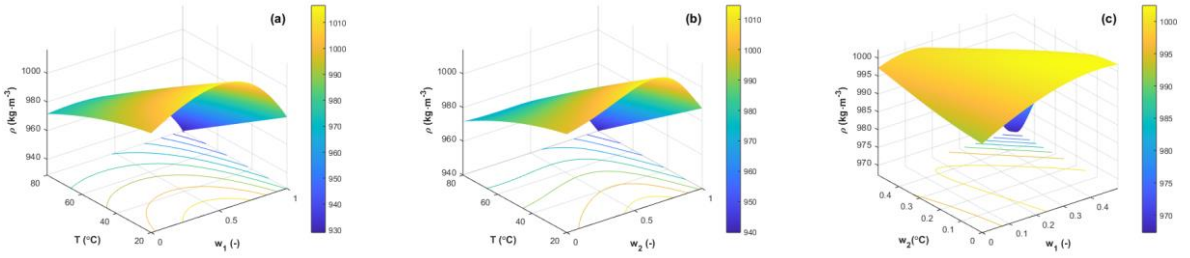

Figure 1. Density profile for each solvent (a) Amine 1; (b) Amine 2, and (c) Blends of amines at 40°C.

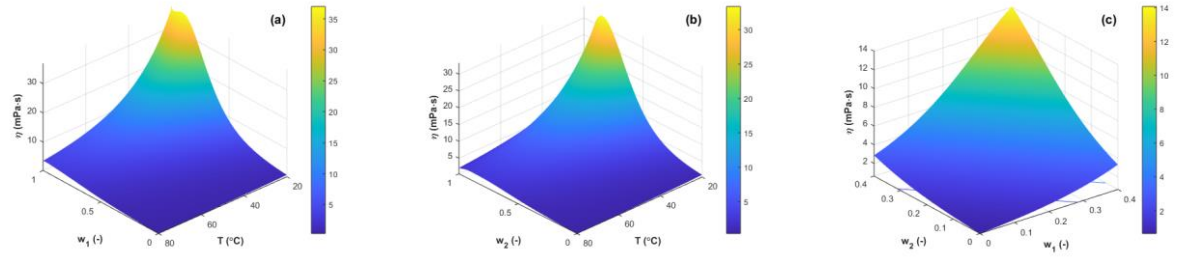

Figure 2. Viscosity profile for each solvent (a) Amine 1; (b) Amine 2; (c) Blends of amines at 40°C.

2.2. The eNRTL model

The developed e-NRTL model for the equilibrium partial pressure of CO_2 as a function of loading and temperatures for individual solvent is presented in Figure 3 for Amine 1 and in Figure 4 for Amine 2, whereas the blends are presented in Figure 5, respectively. The estimated value for the heat of absorption as a function of loading at 40°C is also presented in Figure 6.

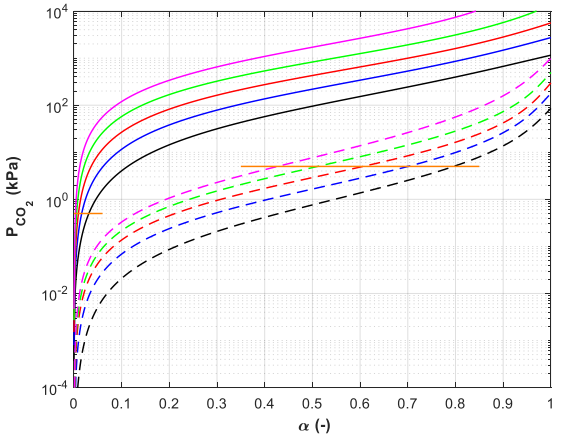

Figure 3 Representation of the eNRTL model for the absorber and stripper temperatures (40 and 120°C) for 10, 20, 30, 40 and 50 mass % of Amine 1 (Dashed lines, 40°C; Solid lines; 120°C; Black, 10mass%; Blue, 20mass%; Red, 30mass%; Green, 40mass%; Magenta, 50mass%; Horizontal lines, pCO_2 = 0.5kPa and pCO_2 = 5kPa)

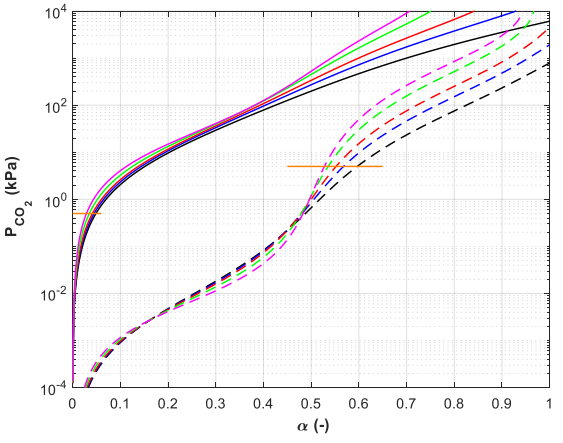

Figure 4 Representation of the eNRTL model for the absorber and stripper temperatures (40 and 120°C) for 10, 15, 20, 30 and 40 mass% of Amine 2 (Dashed lines, 40°C; Solid lines; 120°C; Black, 10mass%; Blue, 15mass%; Red, 20mass%; Green, 30mass%; Magenta, 40mass%; Horizontal lines, pCO_2= 0.5kPa and pCO_2= 5kPa)

The calculated cyclic capacity of each solvent at different concentrations is summarized in Table 1. For Amine 1, the cyclic capacity decreases with increasing concentration, whereas for Amine 2, the cyclic capacity is not too sensitive concerning concentration. The average of the heat of absorptions from the model up to 0.5 loading at 40°C are also given in Table 1, together with its physical properties. Amine 1, as a tertiary amine, has a low heat of absorption averagely at about 62 kJ/mol mol CO_2 and slightly decreases with an increasing concentration. Amine 2, as a primary amine, has shown a higher heat of absorption (107 kJ/mol CO_2) than MEA under similar conditions (84 kJ/mol CO_2) [16].

Table 1. Property of individual amines in aqueous solutions

No.	Amine 1	Amine 2	α_{rich}	α_{lean}	Cyclic capacity	(-Habs)	Viscosity	Density	Heat capacity
	(mass%)	(mass%)	(mol CO2/ mol amine)			(kJ/mol CO_2)	(mPas)	(g/cm^3)	(J/g/K)
1	10	0	0.796	0.032	0.76	67	0.95	0.9956	3.4
2	20	0	0.701	0.017	0.68	64	1.41	0.9988	3.4
3	30	0	0.606	0.045	0.56	61	2.14	1.0010	3.4
4	40	0	0.511	0.009	0.50	59	3.31	1.0022	3.4
5	50	0	0.427	0.007	0.42	58	5.09	1.0021	3.4
6	0	10	0.596	0.049	0.55	105	0.91	0.9885	3.3
7	0	15	0.568	0.045	0.52	107	1.08	0.9888	3.3
8	0	20	0.552	0.042	0.51	108	1.30	0.9893	3.3
9	0	30	0.535	0.035	0.50	108	1.90	0.9905	3.3
10	0	40	0.528	0.029	0.50	108	2.85	0.9919	3.3

The cyclic capacities of Amines blends are evaluated and summarized in Table 1. The result suggests that the cyclic capacity from 0.45 to 0.48 (mol CO_2/ mol amine) is seen for all tested blends. The estimated heat of absorptions of the amine blends at similar conditions is also given in Table 2. The heat of absorption proportionally increases with an increasing Amine 2 concentration, as expected. The lowest heat of absorption value was estimated for the blends of 40 mass% + 15 mass%, which suggests could be the best candidates.

Table 2. Property of amine blends

No.	Amine 1	Amine 2	α_{rich}	α_{lean}	Cyclic capacity	(-Habs)	Viscosity	Density	Heat capacity
	(mass%)	(mass%)	(mol CO_2/ mol amine)			(kJ/mol CO_2)	(mPas)	(g/cm^3)	(J/g/K)
1	30	15	0.501	0.019	0.48	92	3.97	1.00190	3.0
2	40	15	0.466	0.015	0.45	87	6.24	1.00214	3.0
3	25	25	0.496	0.022	0.47	93	4.82	1.00139	3.0
4	15	30	0.501	0.026	0.48	103	3.77	0.99970	3.0
5	25	30	0.474	0.020	0.45	99	5.95	1.00124	3.0

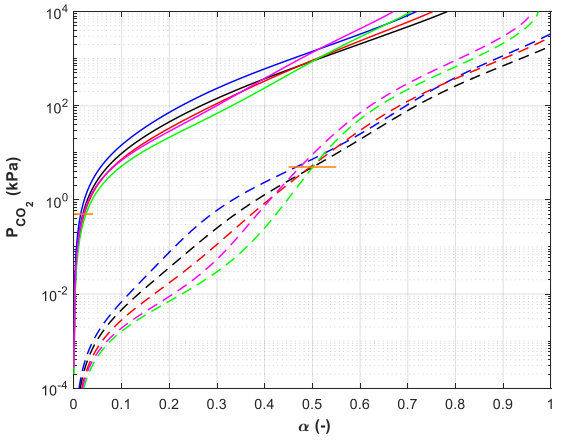

Figure 5 Representation of the eNRTL model at absorber and stripper temperatures (40 and 120°C) for blends (Dashed lines, 40°C; Solid lines; 120°C; Black, 30mass% +15mass%; Blue, 40mass% +15mass%; Red, 25mass% +25mass%; Green, 15mass% +30mass%; Magenta, 25mass% +30mass%; Horizontal lines; pCO_2= 0.5 and pCO_2= 5kPa).

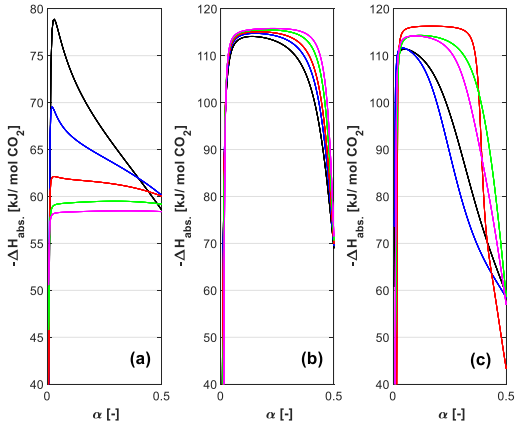

Figure 6 Representation of the eNRTL model for the heat of absorption at absorber (40°C) for a). Amine 1 (Black, 10mass%; Blue, 20mass%; Red, 30mass%; Green, 40mass%; Magenta, 50mass%). b). Amine 2 (Black, 10mass%; Blue, 15mass%; Red, 20mass%; Green, 30mass%; Magenta, 40mass%) and c): Blends (Black, 30mass% +15mass%; Blue, 40mass% +15mass%; Red, 25mass% +25mass%; Green, 15mass% +30mass%; Magenta, 25mass% +30mass%).

Tables 3 show the result of the energetic evaluation based on the Eq. 1 for individual solvent whereas Table 4 for the blends of amine respectively. For Amine 1 in Table 3, the heat requirement decreases with an increasing concentration. The increasing value is majorly affected by the sensible heat due to low amine concentration. Low solvent concentration contains more water that has higher heat capacity than amine. Low heat requirement of Amine 1, however, may have an issue in operation, such as a pinch condition where the solvent is unable to reach 90% of capture due to low kinetic property [17]. For Amine 2 in Table 3, the heat requirement also decreases with an increasing concentration. Similar reason could be lent from Amine 1, but the solvent kinetic may not be an issue. From Table 3 shows that that the energetic performance of each solvent shows lower heat requirement when the solvent concentration becomes higher, and that the heat of absorption is the major contributor.

Table 3. Energetic evaluation of single amine

No.	Amine 1 (mass %)	Amine 2 (mass %)	M (mol/L)	Q_{Sen} (MJ/ kg CO_2)	Q_{Des} (MJ/ kg CO_2)	Q_{Strip} (MJ/ kg CO_2)	Q_{Reg} (MJ/ kg CO_2)
1	10	0	0.88	1.2	1.5	0.3	3.0
2	20	0	1.72	0.7	1.5	0.3	2.4
3	30	0	2.55	0.5	1.4	0.3	2.3
4	40	0	3.41	0.5	1.3	0.3	2.1
5	50	0	4.27	0.4	1.3	0.3	2.1
6	0	10	1.33	1.0	2.4	0.3	3.7
7	0	15	2.01	0.7	2.4	0.3	3.4
8	0	20	2.66	0.5	2.4	0.3	3.3
9	0	30	4.01	0.4	2.5	0.2	3.0
10	0	40	5.28	0.3	2.5	0.2	2.9

In Table 4, five different concentrations of amine blends are studied. As previously discussed, achieving lower energy requirements with higher concentration is natural. The estimated heat requirement for each blend show low values from 2.5 to 2.9 MJ/ kg CO_2. The lowest value was obtained for the blend of 40 mass% of Amine 1 and 15 mass% of Amine 2, respectively. The reboiler duty is much lowed compared to MEA 30 mass% using similar approach (3.5 MJ/ kg CO_2) [9] is higher than these five blends. The heat of absorption (Q_{Des}) of Amine 2 gives significance contribution into the total heat of requirement, and in general, the heat of absorption, remains as the main contributor.

Table 4. Energetic evaluation of amine blends

No.	Amine 1 (mass %)	Amine 2 (mass %)	M (mol/L)	Q_{Sen} (MJ/ kg CO_2)	Q_{Des} (MJ/ kg CO_2)	Q_{Strip} (MJ/ kg CO_2)	Q_{Reg} (MJ/ kg CO_2)
1	30	15	4.61	0.3	2.1	0.3	2.7
2	40	15	5.48	0.3	2.0	0.3	2.5
3	25	25	5.51	0.3	2.1	0.3	2.6
4	15	30	5.29	0.3	2.3	0.3	2.9
5	25	30	6.17	0.2	2.3	0.3	2.8

3. Conclusions

Empirical density, viscosity, and thermal properties correlation together with the rigorous thermodynamic framework were used in the evaluation of the energetic performance of individual aquoues amines and their blends. A simplified method mimicing absorber and stripper conditions were used to evaluate the performance of each solvent. Amine 1, a tertiary amine, shows low energy requirement but potentially has kinetic issue whereas Amine 2, a primary amine, shows higher energy requirement than Amine 1, but should have higher kinetic rated compared to Amine 1. The estimated energy requirement of the Amine 2 is similarly to MEA 30 mass% case. Blends of these two amines show lower energy requirement in all tested five different ratios than MEA 30 mass%. Further, the density was not a sensitive parameter (close to unity) whereas the viscosity increases with solvent concentration. However, this difference was not that significant.

Acknowledgements

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