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Mitigating phase changes in the gas-phase that disrupt CO_2 capture in membrane contactors: CO_2-NH_3-H_2O as a model ternary system

B.A. Luqmani [a], V. Nayak [a], A. Brookes [b], A. Moore [c], P. Vale [d], M. Pidou [a], E.J. McAdam [a,*]

[a] Cranfield Water Science Institute, Cranfield University, Vincent Building, Bedfordshire MK43 0AL, UK
[b] Anglian Water, Block C-Western House, Peterborough Business Park, Lynch Wood, Peterborough PE2 6FZ, UK
[c] Northumbrian Water, Boldon House, Wheatlands Way, Durham DH1 5FA, UK
[d] Severn Trent Water, 2St. Johns Street, Coventry CV1 2LZ, UK

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ABSTRACT

Solid and liquid products can form in the gas phase of membrane contactors applied to reactive ternary systems for CO_2 absorption, which poses a critical barrier for carbon capture applications. The mechanism initiating these unwanted phase changes in the gas phase is unclear. This study therefore systematically characterises CO_2 absorption in distinct regions of the vapour-liquid equilibrium (VLE) within an illustrative ternary system (CO_2-NH_3-H_2O), to provide an explanation for the formation and mitigation of these solid and liquid products in the gas-phase. Unstable CO_2 absorption and increased pressure drop indicated product formation within the gas-phase, which occurred at high CO_2 capture ratios. Temporal analysis of gas-phase composition enabled gas-phase products to be related to the relative ternary composition. This was subsequently correlated to distinct regions of the VLE. Consequently, mitigation strategies can be developed with recognition for where products are least likely to form. Pressurisation was proposed to modify the relative gas-phase ammonia composition to reposition conditions within the VLE. The commensurate increase of CO_2 into the solvent shifts the ammonia-ammonium equilibrium towards ammonium to indirectly reduce vapour pressure. This synergistic strategy allows sustained operation of membrane contactors for CO_2 separation within reactive ternary systems which are critical to delivering carbon capture economically at scale.

1. Introduction

Hollow fibre membrane contactors (HFMC) are an emerging alternative to packed columns for CO_2 absorption due to their higher interfacial area which lowers installed capacity (capital cost) and solvent requirements (separation energy) (Belaissaoui et al., 2016; Houlker et al., 2021). Chemical solvents have been studied in HFMC to facilitate higher CO_2 absorption capacities and enhanced mass transfer (Khaisri et al., 2011, 2009; Scholes et al., 2015). Aqueous ammonia ($NH_{3(aq)}$) has a CO_2 capacity which is three times greater than amines, whilst also being cheaper, less corrosive and requiring less energy for regeneration (Chin Yeh and Hsunling, 1999; Jilvero et al., 2012; Mani et al., 2006). However, its higher volatility leads to greater 'slip' into the treated gas which has been linked to difficulties with achieving stable CO_2 separation in HFMC (Table 1) (Bavarella et al., 2022; Cui and DeMontigny, 2017; Villeneuve et al., 2018a). Makhloufi et al. (2014) reported a decline in CO_2 capture from 94 to 20 % vol during absorption using $NH_{3(aq)}$. The authors associated this with the visible precipitation of solids in the gas-side of the membrane, and this phenomenon has since been observed by others (Cui and DeMontigny, 2017; Makhloufi et al., 2014). The mechanism of solids formation was postulated to arise from a gas-phase CO_2—NH_3 reaction followed by deposition onto the membrane surface which modified the hydrophobicity sufficiently to initiate liquid breakthrough into the pore structure, as indicated by an increase in the membrane mass transfer resistance (Cui and deMontigny, 2017). The crystalline solid formed within the gas-phase was presumed to be ammonium bicarbonate using compositional analysis (Bavarella et al., 2022). However, there is recognition that the reaction pathways are dependant on the conditions employed, leading to the possible formation of several solid products which include ammonium carbamate (NH_2COONH_4) (Eq. (1)), ammonium carbonate ($(NH_4)_2CO_3H_2O$) (Eq. (2)) and ammonium bicarbonate (NH_4HCO_3) (Eq. (3)) (Mani et al., 2006):

* Corresponding author.
E-mail address: e.mcadam@cranfield.ac.uk (E.J. McAdam).

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Table 1
Literature summary for CO_2 absorption using $NH_{3(aq)}$ in HFMC.

Membrane	C_{NH3}	pH	T	p_{NH3}	p_{H2O}	CO_2 in	Process	Observations	Source
	mol_{NH3} L^{-1}		°C	mbar	mbar	%vol	instability		
PP	0.6–3.0	>11[b]	21	8–42	23–24	15 %	Yes	Gas-side solids formation	Makhloufi et al. (2014)
PTFE	3–5	11	25	51–85	29–30	50 %	Yes	Gas-side solids formation	McLeod et al. (2015)
PTFE	1.0–2.0	>11[b]	21	14–28	24	15 %	Yes	Gas-side solids formation and pore wetting	Cui and DeMontigny (2017)
PMP/PP[a]	3	>11[b]	10–40	23–101	12–69	15 %	Yes	Gas-side solids and liquid formation	Villeneuve et al. (2018a)
PP	3.3	13	20	45	21	50 %	Yes	Suspected pore wetting	Houlker (2019)
PP	3.3	9–13[c]	6	3–22	8	50 %	No	–	
PTFE	2.3–3.0	10	20	25–32	22	100 %	Yes	Gas-side solids and liquid formation	Bavarella et al. (2022)
PTFE	0.6	10	20	6	23	100 %	No	–	
PTFE	2.3	7.5–10[c]	20	1–25	22	100 %	No	–	
PTFE	3.0	7.5–10[c]	5	1–11	8	100 %	No	–	

C_{NH3} – solvent concentration; T – solvent temperature; p_{NH3} and p_{H2O} – ammonia and water partial pressures in the gas-phase at equilibrium (Appendix A2); PP – polypropylene; PMP – polymethylpentene; PTFE – polytetrafluoroethylene.
[a] Nonporous polymethylpentene skin (0.1 μm) on polypropylene matrix.
[b] Solvent pH not reported - presumed to exceed pH 11 based on ammonia concentration.
[c] Solvent pH declined over time due to recirculation and increased CO_2 loading (Darde et al., 2010).

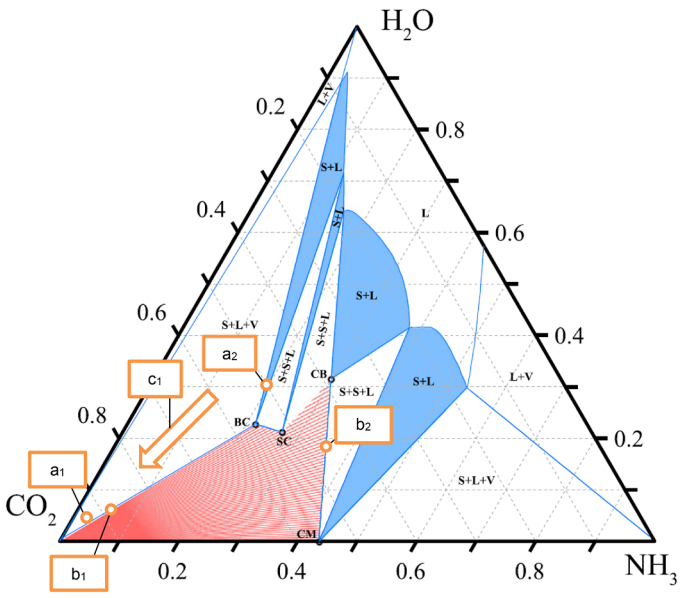

Fig. 1. Ternary vapour-liquid-equilibrium for CO_2-NH_3-H_2O based on the output of the extended UNIQUAC model at 10 °C developed by Thomsen and Rasmussen (1999). S – solid; L – liquid; V – vapour; BC – ammonium bicarbonate; SC – ammonium sesqui-carbonate; CB – ammonium carbonate; CM – ammonium carbamate. Annotations added using orange boxes and an orange arrow. Red-white shaded region could not be resolved within the model. Reproduced from Sutter et al. (2015) with permission from Elsevier Ltd.

$$2NH_3 + CO_2 \leftrightarrow NH_4^+ + NH_2COO^- \leftrightarrow NH_2COONH_{4(s)} \quad (1)$$

$$2NH_3 + CO_2 + 2H_2O_{(l)} \leftrightarrow 2NH_4^+ + CO_3^{2-} + H_2O_{(l)} \leftrightarrow (NH_4)_2CO_3H_2O_{(s)} \quad (2)$$

$$NH_3 + CO_2 + H_2O_{(l)} \leftrightarrow NH_4^+ + HCO_3^- \leftrightarrow NH_4HCO_{3(s)} \quad (3)$$

Gas-phase precipitation could be mitigated by lowering the ammonia vapour pressure through solvent chilling (Bavarella et al., 2022). Increasing CO_2 loading of the solvent also reduced NH_3 slip by shifting the ammonia-ammonium equilibrium toward non-volatile ammonium (Bavarella et al., 2022; Darde et al., 2010; Houlker, 2019). Villeneuve et al. (2018a) observed that raising humidity within the gas feed (comparable to industrial flue gases) diminished gas-phase precipitation but a concentrated ammonia solution was formed inside the fibre lumen (gas-side). Stable CO_2 capture was nevertheless observed, and the liquid could be continuously drained from the lumen without contributing to pore wetting or introducing an increased resistance to mass transfer (Villeneuve et al., 2018a, 2018b). The authors proposed that solids formation occurred through gas-phase reactions between CO_2, NH_3 and water, which then dissociate to release gaseous components when the CO_2 partial pressure lowers along the HFMC length (Villeneuve et al., 2018a). The liquid product was suggested to be formed by over-saturation of the gas-phase, leading to the condensation of a concentrated salt solution which exhibits an osmotic pressure sufficient to drive water from the solvent across the membrane into the gas-phase (Villeneuve et al., 2018a).

While a causal link has been established between the presence of an elevated ammonia vapour concentration and the development of both solid and liquid ammonia products within the gas-phase (Table 1), a method to predict the reaction mechanisms is yet unclear (Bavarella et al., 2022; Villeneuve et al., 2018a). Capture of CO_2 by ammonia is illustrative of a ternary system comprising CO_2–NH_3–H_2O. Many other ternary solvent systems are emerging for CO_2 capture, where a wider series of complex and competing reactions may occur (Zhao et al., 2023). In ternary systems, the relative fractions of the three components in the gas-phase will determine reaction kinetics and products (Sutter et al., 2015). The ternary vapour-liquid equilibrium (VLE) for CO_2-NH_3-H_2O (Darde, 2010; Thomsen and Rasmussen, 1999) has been resolved to accurately describe interaction between phases, and enables specific regions to be isolated where solid, liquid and vapour products could most likely form (Fig. 1) (Sutter et al., 2015). Since the gas phase in membrane contactors is typically within the lumen, membrane contactors can be considered as more sensitive to the formation of solid and liquid products than within conventional contacting processes, since the lumen for gas flow is typically only several hundred microns in diameter. Consequently, the aim of this study is to evidence the mechanisms that underpin gas-phase reactions in the CO_2-NH_3-H_2O system by using the VLE for diagnostic characterisation. The outcome is intended to explain previous literature observations and provide a foundation on which to develop mitigation strategies for stable CO_2 absorption in HFMC which has wider relevance for reactive ternary systems.

2. Methodology

This study employed a similar experimental set-up to previous work (Cui and deMontigny, 2017). An 8 % vol CO_2 gas was fed counter-current into the HFMC lumen, with deionised (DI) water (15 MΩ cm) or aqueous ammonia (1–3 mol_{NH3} L^{-1}) in the shell-side (6.5 ± 0.5 °C). The system was operated at a fixed volumetric gas-liquid (G/L) ratio of 4.4. At the end of each experiment, a mass balance was conducted to determine ammonia transfer into the gas-phase. Four fractions were characterised: (i) the solvent; (ii) the liquid condensate (collected in a gas-liquid separator) (Villeneuve et al., 2018a); (iii) the gas-phase

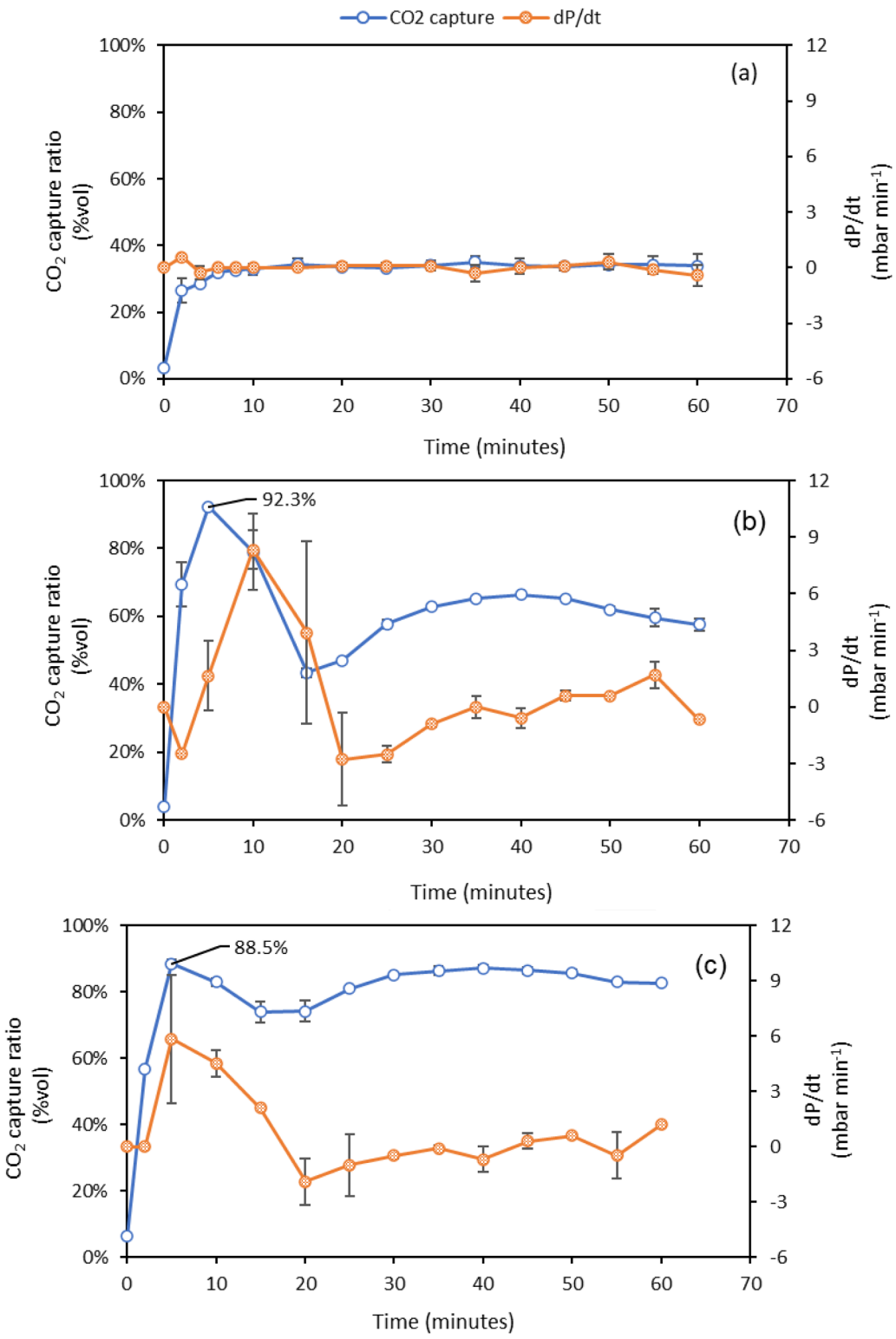

Fig. 2. CO_2 capture ratio and gas-side pressure drop using: (a) DI water; (b) 1 mol_{NH3} L^{-1}; and (c) 3 mol_{NH3} L^{-1} solvents. Operating conditions: liquid flowrate, 0.25 L min^{-1}; liquid temperature, 6.5 ± 0.5 °C; CO_2 in feed gas, 8 % vol; feed gas flowrate, 1.1 L min^{-1}; gas temperature, 21 °C.

outlet (captured in an acid trap); and (iv) the residual ammonia in the HFMC lumen (using an acid rinse). All experiments were conducted in triplicate. Full details of the methodology are available in Appendix A.

3. Results and discussion

3.1. $NH_{3(aq)}$ associated with chemical enhancement and process instability

The absorption of CO_2 by $NH_{3(aq)}$ was compared directly to DI water to evaluate the potential for chemical enhancement. When using DI

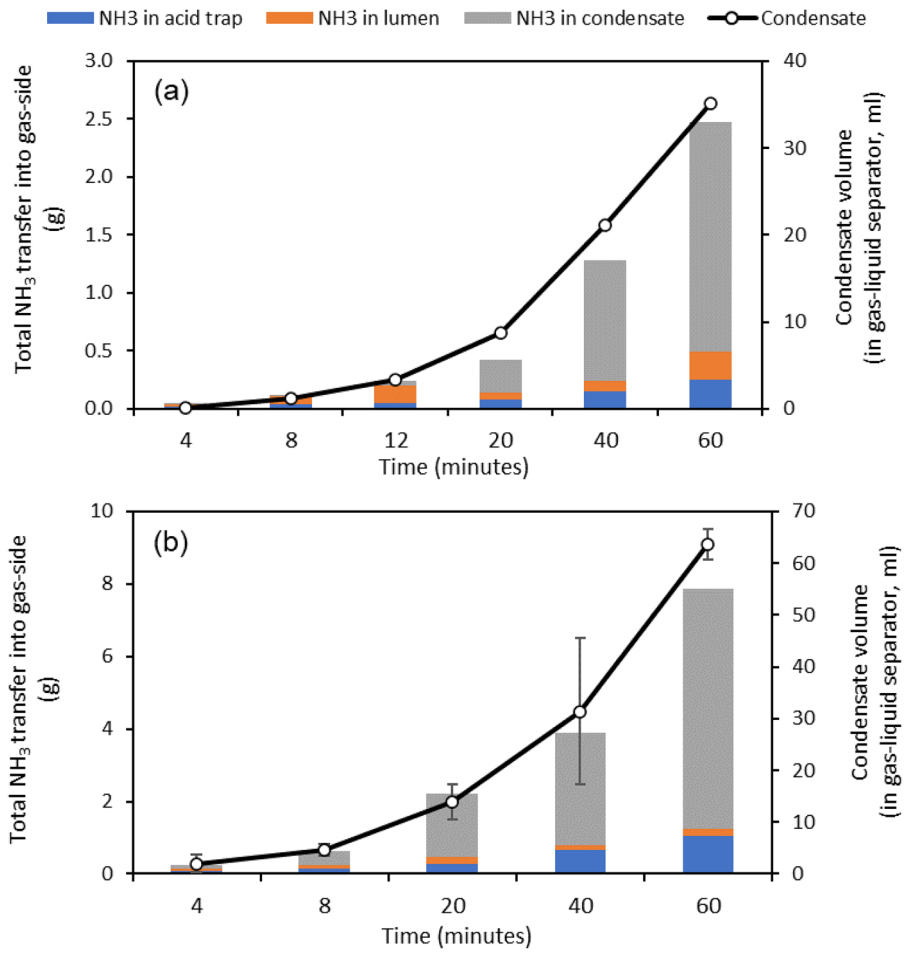

Fig. 3. Temporal analysis of ammonia transfer into the gas-side during experimentation with: (a) 1 mol_{NH3} L^{-1}; and (b) 3 mol_{NH3} L^{-1} solvents. Ammonia was recovered from the lumen (via acid elution), condensate (collected in a gas-liquid separator), and the outlet gas (captured using an acid trap). Operating conditions: liquid flowrate, 0.25 L min^{-1}; liquid temperature, 6.5 ± 0.5 °C; CO_2 in feed gas, 8 % vol; feed gas flowrate, 1.1 L min^{-1}; gas temperature, 21°C.

water, a consistent CO_2 capture ratio of 35 % vol was established (Fig. 2). An $NH_{3(aq)}$ solvent (1 mol_{NH3} L^{-1}) initially increased the CO_2 capture ratio up to 92 % vol but was unstable, gradually achieving a pseudo steady-state value of 58 % vol toward 60 min, equivalent to chemical enhancement (J_{chem}/J_{phys}) of 1.7 (Appendix A2). A similar trend was observed for 3 mol_{NH3} L^{-1}, where following an initial peak in CO_2 capture ratio of 89 % vol, CO_2 capture became unstable, eventually reaching a pseudo steady-state value of 83 % vol (J_{chem}/J_{phys}, 2.4). The CO_2 enhancement increased with solvent reactivity but the initial peak in CO_2 capture ratio observed for both $NH_{3(aq)}$ solvents correlated to an increased pressure drop in the fibre of between 45 and 85 mbar and was coincident with liquid droplets at the gas-outlet (collected as condensate in the gas-liquid separator). Formation of solid or liquid products within the lumen will reduce the effective diameter, thereby increasing the pressure drop (Chan et al., 2020; Villeneuve et al., 2018a). Since the gas flowrate was fixed throughout, a reduction in the effective diameter will also increase the superficial gas velocity. This will restrict the time for CO_2 to diffuse from the gas bulk to the liquid interface, and is consistent with the observed reduction and instability in mass transfer (Houlker, 2019; Makhloufi et al., 2014).

3.2. Condensate formation and composition evidences gas-phase reactions

Over 60 min, a total of 2.5 and 7.9 g ammonia was transferred to the gas-phase from the 1 and 3 mol_{NH3} L^{-1} solvents respectively (Fig. 3). The increase in ammonia transfer from the 3 mol_{NH3} L^{-1} solvent is due to the higher ammonia vapour pressure (7 versus 21 mbar) (Appendix A2). Through sacrificial sampling, the ammonia identified within the lumen through acid extraction of the hollow-fibre indicated early formation of solid ammonium salts as evidenced in previous work (Bavarella et al., 2022; Villeneuve et al., 2018a). However, the amount of ammonia located within the lumen did not change markedly over time. This reduced as a relative fraction of the total ammonia products as the system migrated toward the preferential formation of an ammonia-rich condensate. The final condensate produced from the 3 mol_{NH3} L^{-1} solvent was 63.7 ml, around 80 % higher than recorded at 1 mol_{NH3} L^{-1}, despite comparable water vapour pressures for both solvents (~10 mbar). We therefore propose that the intensification in water vapour mass transfer was driven by the increase in the solvent concentration and volatility, consistent with reaction pathways for ammonium salt formation (Eq. (1)–(3)) (Sutter et al., 2015). The sustained salt concentration may therefore arise from the condensate partially dissolving solid products as suggested by previous researchers (Villeneuve et al., 2018a), or from the composition favouring condensate formation.

Ammonia concentration within the condensate was two to three times greater than in the solvent (Fig. 4). This is inconsistent with previous proposals that liquid is present in the gas-side due to breakthrough following pore wetting (Bavarella et al., 2022; Cui and DeMontigny, 2017) or water transfer promoted by an osmotic gradient (Villeneuve et al., 2018a) since both propositions would result in condensate concentrations less than or equal to the solvent. It is also incompatible with physical condensation driven by the binary ammonia-water mixture, since the vapour composition (40–66 %wt ammonia) and gas-side conditions (21 °C, 1.1 bar) are insufficient to facilitate a phase-change

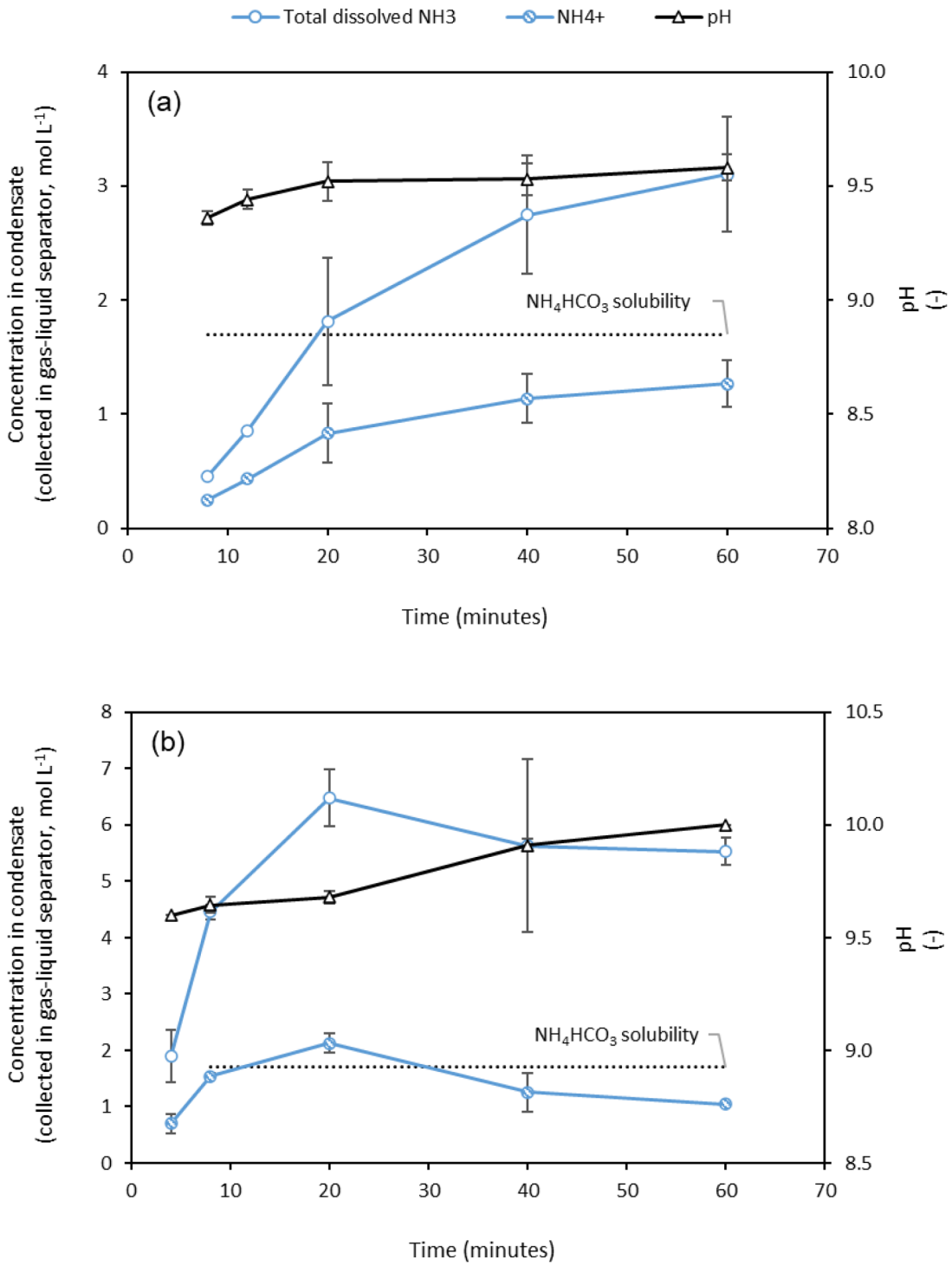

Fig. 4. Composition of condensate collected at the gas-outlet using a gas-liquid separator for: (a) 1 mol_{NH3} L^{-1}; and (b) 3 mol_{NH3} L^{-1}. Operating conditions: liquid flowrate, 0.25 L min^{-1}; liquid temperature, 6.5 ± 0.5 °C; CO_2 in feed gas, 8 % vol; feed gas flowrate, 1.1 L min^{-1}; gas temperature, 21 °C. Dotted lines indicated NH_4HCO_3 solubility at 21 °C (O'Neil, 2006; Perry and Green, 2007).

(Pátek and Klomfar, 1995) (Appendix A2). For both solvents, ammonium concentration in the liquid did not consistently exceed 1.7 mol_{NH4+} L^{-1} required to precipitate NH_4HCO_3, which is the least soluble of the ammonium salts under these conditions (Eq. (3)) (Bates and Pinching, 1950; Mani et al., 2006). This confirmed that the liquid would have the capacity to dissolve crystallised salts and capture ammonia from the lumen over time as observed in this study (Fig. 3). Ammonia collected from the gas outlet (using an acid-trap) was in close agreement with the 'slip' expected at equilibrium (Fig. 5). Consequently, this indicates that despite considerable ammonia fractionation into the solid and liquid products within the lumen, equilibrium was re-established along the fibre length according to Le Châtelier's principle. Hence, ammonia and water vapour will be continuously drawn across the membrane to sustain the formation of unwanted solid and liquid products in the gas-phase, the rate of which will be dependant on the solvent ammonia vapour pressure.

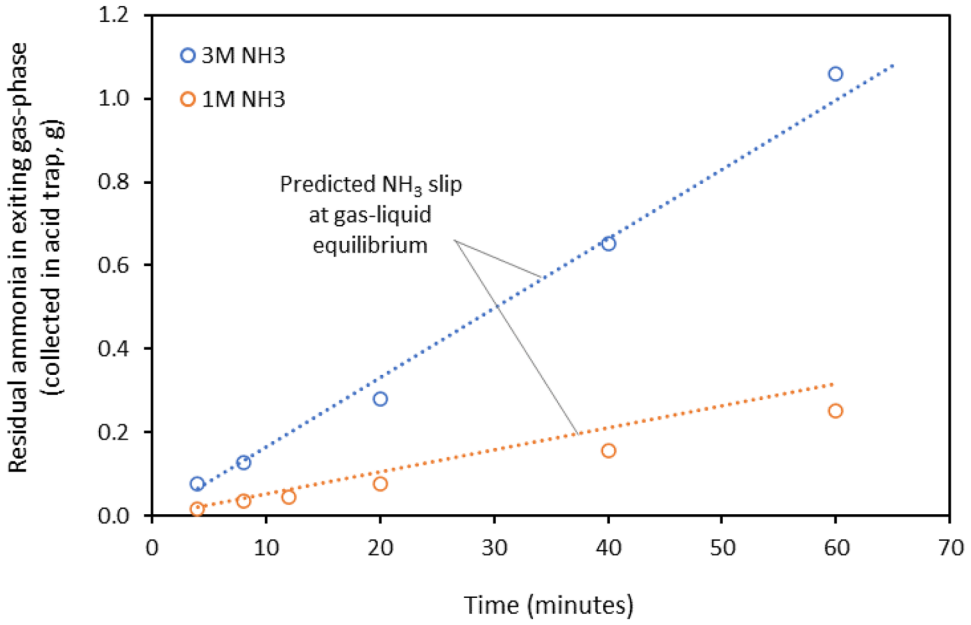

Fig. 5. Ammonia transfer at the gas outlet (captured using an acid trap) over time when using aqueous ammonia solvents. Operating conditions: liquid flowrate, 0.25 L min^{-1}; liquid temperature, 6.5 ± 0.5 °C; CO_2 in feed gas, 8 % vol; feed gas flowrate, 1.1 L min^{-1}; gas temperature, 21 °C. Dotted lines represent ammonia slip over time at gas-liquid equilibrium estimated using Henry's Law (Appendix A2).

3.3. High CO_2 capture can trigger gas-phase reactions in the ternary system

During operation of microporous membranes, the saturation for ammonia and water may be quickly established at the lumen inlet. Consequently, conditions for NH3-water condensation can occur soon after, resulting in a shift equilibrium vapour pressure that will encourage further transfer of water and ammonia which can lead to subsequent product formation, particularly when operating at low gas velocities (0.04 m s^{-1}) (Chan et al., 2020; Gabelman and Hwang, 1999). Absorption of CO_2 across the fibre length reduced the CO_2 fraction and lowered the overall gas volume (Fig. 6), shifting the gas-phase composition within the ternary system. This will impact the fugacity of each gaseous component and the activity coefficients associated with each of the potential aqueous species, therefore determining the preferential reaction sequence as described by the VLE (Darde et al., 2010; Sutter et al., 2015). This is the basis of urea production, which fosters the conditions for the gas-phase interaction of CO_2 and NH_3 in the presence of water to form a highly concentrated aqueous solution based upon NH_3COONH_4 (Verbrugge, 1979). When using 1 mol_{NH3} L^{-1}, the initial gas-phase composition (prior to CO_2 separation) is in a region of the VLE where components can exist in vapour, liquid or solid phases (Fig. 1: a_1). Without the external energy required to initiate a phase-change, the components can be expected to transit through the lumen as a vapour mixture. However, the early peak in CO_2 capture (92 % vol) reduced the CO_2 mass fraction, shifting the system into a thermodynamic region where only liquid and solid reaction products (NH_4HCO_3) are viable (Figs. 1: a_2; 7). This corresponded with the sudden increase in pressure drop and the observation of liquid at the outlet. Since the relative water fraction in the gas-phase at this condition (x_{H2O}=0.3) was slightly greater than required for solid NH_4HCO_3 precipitation, the VLE predicts a concentrated aqueous solution to be the primary product which is consistent with analysis of the liquid composition (Fig. 4). The 3 mol_{NH3} L^{-1} solvent exhibited a higher ammonia vapour pressure, leading to an initial gas-side composition which was richer in ammonia (Fig. 7b). Consequently, a lower CO_2 capture threshold (86 % vol) was necessary to transition the system into a region of the VLE where liquid and solid reaction products are predicted to form (Fig. 1: b_2). This is corroborated by the lower peak in CO_2 capture (88 % vol) for this solvent, despite its higher reactivity, prior to observation of liquid at the gas outlet (Fig. 2c). The associated salts were $(NH_4)_2CO_3H_2O$ and NH_2COONH_4 which are highly soluble (>32 g L^{-1}), and so minimal deposition in the lumen was expected as observed throughout the experiment (Fig. 3b) (Mani et al., 2006).

4. Proposed mitigation strategies

This study has identified the probable mechanism underpinning the formation of liquid and solid products that disrupt CO_2 absorption by $NH_{3(aq)}$ in HFMC. It is proposed that two pre-conditions must be met to initiate reactions: (i) ammonia and water vapour must be present alongside CO_2 in the gas-phase, and (ii) the gas-phase composition must exceed a system specific threshold necessary to promote the formation of liquid and solid reaction products (Fig. 1). Previous researchers have targeted the first pre-condition by lowering ammonia vapour pressure to reduce the extent of gas-phase reactions (Table 1) (Bavarella et al., 2022; Houlker, 2019). This can be achieved by solvent chilling and high CO_2 loading (Bavarella et al., 2022; Darde et al., 2010) both of which are complimentary to the chilled ammonia process where NH_4HCO_3 precipitation is mediated within the solvent to reduce the equipment size and energy demand related to regeneration (Milella et al., 2018; Sutter et al., 2017). However, some 'slip' is inevitable in practice, particularly since highly reactive, concentrated solvents are necessary to favour process intensification and economics (Augustsson et al., 2017). This work highlights the relevant role of the ternary VLE phase diagram as a diagnostic tool to identify compositions which set the second pre-condition for gas-phase reactions and can therefore better inform mitigation strategies. For example, pressurisation will increase CO_2 concentration in the gas-phase and since 'slip' is independent of pressure, this will lower the relative amount of ammonia (and water) in the gas-phase at equilibrium (Fig. 8) (Fang et al., 2015). Pressurisation will therefore shift the system towards the CO_2-rich region in the ternary VLE (Fig. 1: c_1) where formation of gas and liquid products cannot proceed via gas-phase reactions even under high CO_2 capture ratios. Since commercial CO_2 absorption columns operate under pressurised conditions (4–10 bar) for process intensification (Angelidaki et al., 2018), pressurisation offers a strategy to improve stability whilst intensifying mass transfer and increasing the commercial competitiveness of HFMC

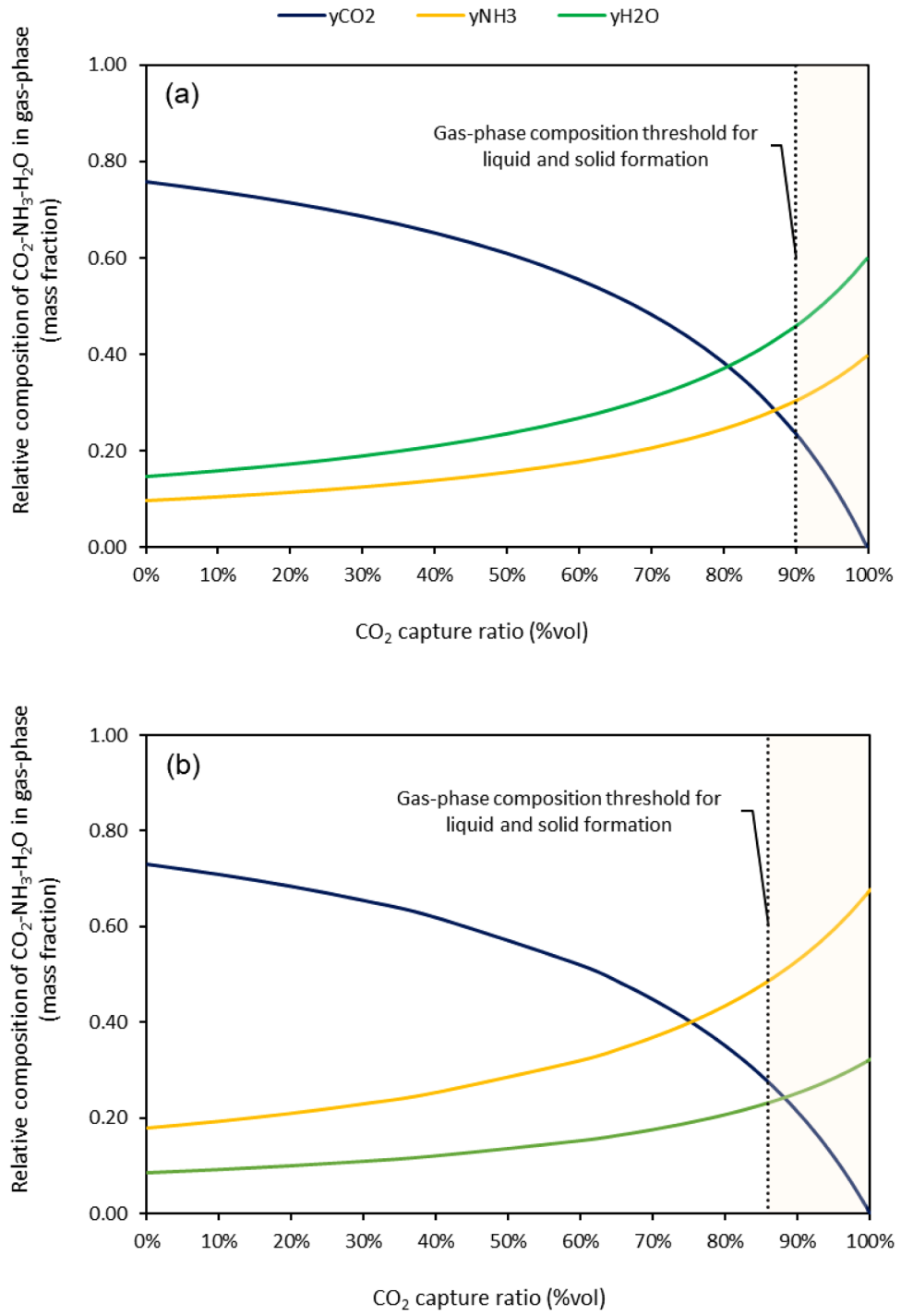

Fig. 6. Projected ternary system composition based upon gas-liquid equilibrium vapour pressures for ammonia and water and the influence of CO_2 capture ratio for: (a) 1 mol_{NH3} L^{-1}; and (b) 3 mol_{NH3} L^{-1} solvents. Based on the output from the extended UNIQUAC model at 10 °C (Sutter et al., 2015; Thomsen and Rasmussen, 1999) and equilibrium vapour pressures for NH_3 and H_2O (Appendix A2).

for reactive CO_2 absorption in ternary systems. The probability for the formation of gas phase products maybe higher within discrete locations of the lumen due to the transient concentration gradients that exist. Consequently, the modelling of localised mass transfer effects that can take consideration of the VLE, may be beneficial to the scale-up of membrane contactors for CO_2 separations using ternary systems.

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CRediT authorship contribution statement

B.A. Luqmani: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **V. Nayak:** Writing – review & editing, Formal analysis, Data curation. **A. Brookes:** Writing –

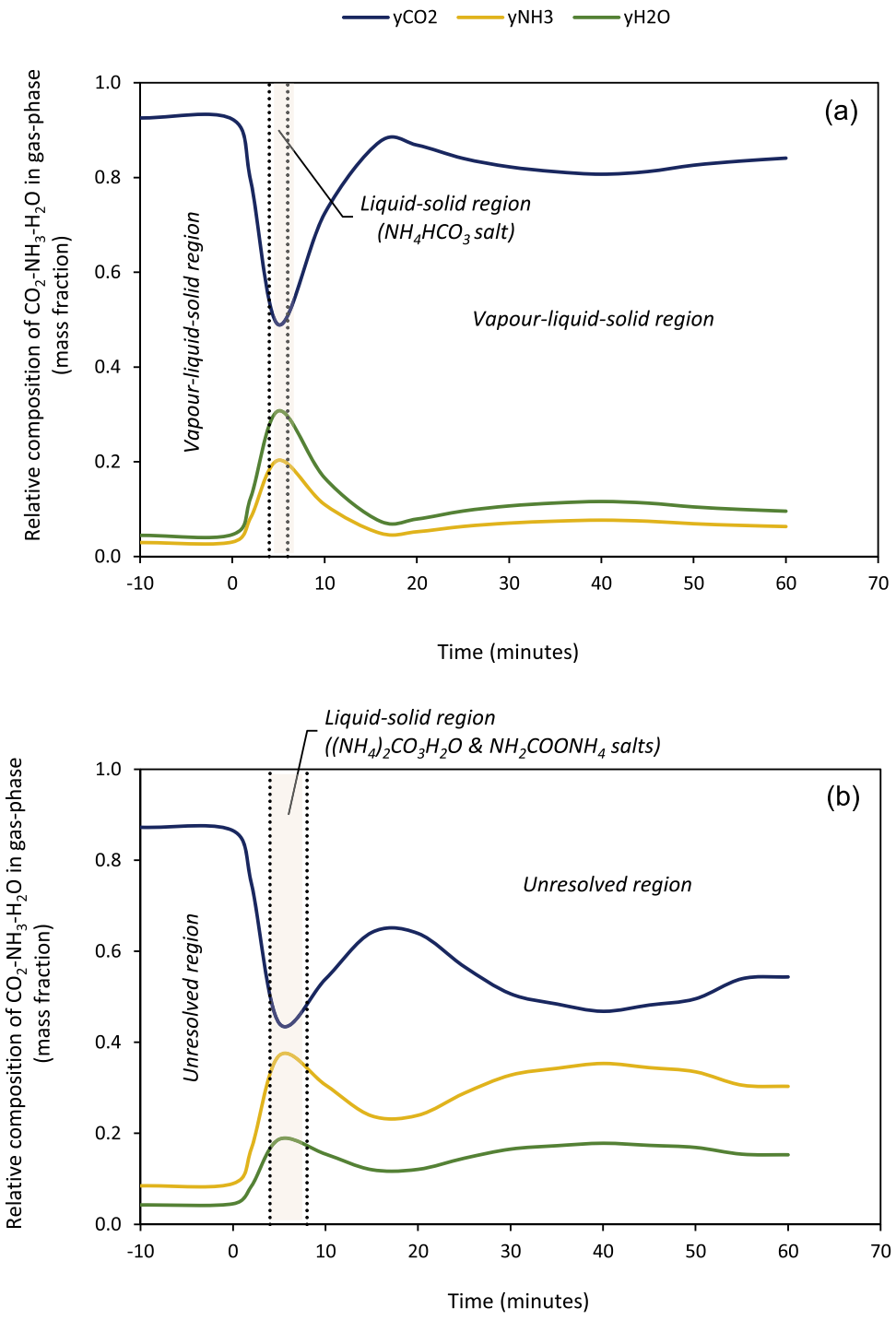

Fig. 7. Experimental ternary system composition based upon the CO_2 capture ratio when using: (a) 1 mol_{NH3} L^{-1}; and (b) 3 mol_{NH3} L^{-1} solvents. Relevant regions based on the output from the extended UNIQUAC model at 10 °C (Sutter et al., 2015; Thomsen and Rasmussen, 1999) and equilibrium vapour pressures for NH_3 and H_2O (Appendix A2).

review & editing, Resources, Project administration, Conceptualization. **A. Moore:** Writing – review & editing, Funding acquisition, Conceptualization. **P. Vale:** Writing – review & editing, Resources, Funding acquisition, Conceptualization. **M. Pidou:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **E.J. McAdam:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Link provided to data in manuscript.

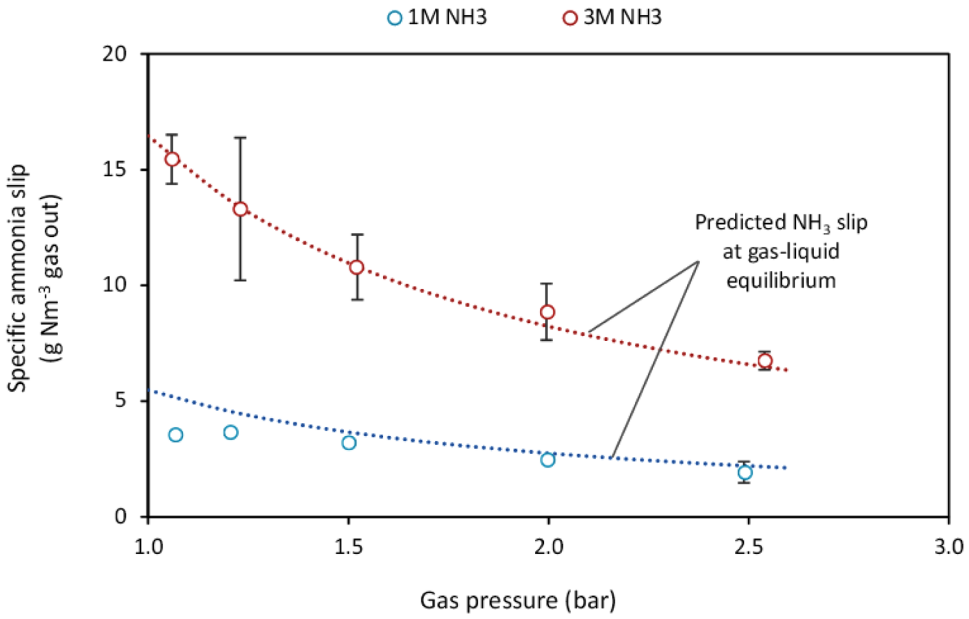

Fig. 8. Influence of pressurisation on ammonia slip into the treated gas (pure N_2). Operational conditions: liquid flowrate, 0.25 L min^{-1}; liquid temperature, 6.5 ± 0.5 °C; gas flowrate, 1.1 L min^{-1}; gas temperature, 21 °C. Dotted lines represent ammonia slip over time at gas-liquid equilibrium estimated using Henry's Law (Appendix A2).

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.memlet.2024.100076.

References

Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P.G., 2018. Biogas upgrading and utilization: current status and perspectives. Biotechnol. Adv. 36, 452–466.

Augustsson, O., Baburao, B., Dube, S., Bedell, S., Strunz, P., Balfe, M., Stallmann, O., 2017. Chilled ammonia process scale-up and lessons learned. In: Proceedings of the 13th International Conference on Greenhouse Gas Control Technologies. Lausanne, Switzerland.

Bates, R.G., Pinching, G.D., 1950. Dissociation constant of aqueous ammonia at 0 to 50° from E. m. f. studies of the ammonium salt of a weak acid. J. Am. Chem. Soc. 72, 1393–1396.

Bavarella, S., Luqmani, B., Thomas, N., Brookes, A., Moore, A., Vale, P., Pidou, M., McAdam, E.J., 2022. CO_2 absorption into aqueous ammonia using membrane contactors: role of solvent chemistry and pore size on solids formation for low energy solvent regeneration. Sep. Purif. Technol. 290, 120786.

Belaissaoui, B., Claveria-Baro, J., Lorenzo-Hernando, A., Albarracin Zaidiza, D., Chabanon, E., Castel, C., Rode, S., Roizard, D., Favre, E., 2016. Potentialities of a dense skin hollow fiber membrane contactor for biogas purification by pressurized water absorption. J. Membr. Sci. 513, 236–249.

Chan, Z.P., Li, L., Kang, G., Manan, N.A., Cao, Y., Wang, T, 2020. Discussion on water condensation in membrane pores during CO_2 absorption at high temperature. Membranes 10, 407.

Chin Yeh, A., Hsunling, B, 1999. Comparison of ammonia and monoethanolamine solvents to reduce CO_2 greenhouse gas emissions. Sci. Total Environ. 228, 279–284.

Cui, Z., DeMontigny, D, 2017. Experimental study of carbon dioxide absorption into aqueous ammonia with a hollow fiber membrane contactor. J. Membr. Sci. 540, 297–306.

Darde, V., Thomsen, K., van Well, W.J.M., Stenby, E.H., 2010. Chilled ammonia process for CO_2 capture. Int. J. Greenh. Gas Control 4, 131–136.

Fang, M., Xiang, Q., Yu, C., Xia, Z., Zhou, X., Cai, D., Wang, Z, 2015. Experimental study on CO_2 absorption by aqueous ammonia solution at elevated pressure to enhance CO_2 absorption and suppress ammonia vaporization. Greenh. Gases Sci. Technol. 5, 210–221.

Gabelman, A., Hwang, S., 1999. Hollow fiber membrane contactors. J. Membr. Sci. 159, 61–106.

Houlker, S., 2019. Scale Up of Hollow Fibre Membrane Contactors for Biogas Upgrading. Cranfield University. EngD thesis.

Houlker, S., Rutherford, T., Herron, D., Brookes, A., Moore, A., Vale, P., Pidou, M., McAdam, E., 2021. Demonstrating commercial hollow fibre membrane contactor performance at industrial scale for biogas upgrading at a sewage treatment works. Water 13, 172 (Switzerland).

Jilvero, H., Normann, F., Andersson, K., Johnsson, F, 2012. Heat requirement for regeneration of aqueous ammonia in post-combustion carbon dioxide capture. Int. J. Greenh. Gas Control 11, 181–187.

Khaisri, S., DeMontigny, D., Tontiwachwuthikul, P., Jiraratananon, R, 2009. Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor. Sep. Purif. Technol. 65, 290–297.

Khaisri, S., DeMontigny, D., Tontiwachwuthikul, P., Jiraratananon, R, 2011. Membrane contacting process for CO_2 desorption. Energy Procedia 4, 688–692.

Makhloufi, C., Lasseuguette, E., Remigy, J.C., Belaissaoui, B., Roizard, D., Favre, E., 2014. Ammonia based CO_2 capture process using hollow fiber membrane contactors. J. Membr. Sci. 455, 236–246.

Mani, F., Peruzzini, M., Stoppioni, P., 2006. CO_2 absorption by aqueous NH3 solutions: speciation of ammonium carbamate, bicarbonate and carbonate by a 13C NMR study. Green Chem. 8, 995–1000.

McLeod, A., Buzatu, P., Autin, O., Jefferson, B., McAdam, E., 2015. Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. J. Membr. Sci. 473, 146–156.

Milella, F., Gazzani, M., Sutter, D., Mazzotti, M., 2018. Process synthesis, modeling and optimization of continuous cooling crystallization with heat integration - application to the chilled ammonia CO_2 Capture Process. Ind. Eng. Chem. Res. 57, 11712–11727.

O'Neil, M.J., 2006. The Merck Index - an Encyclopedia of Chemicals, Drugs, and Biologicals, (1st ed. Merck & Co., Inc., Rahway, NJ, USA, pp. 88–100.

Pátek, J., Klomfar, J., 1995. Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system. Int. J. Refrig. 18, 228–234.

Perry, R.H., Green, D.W., 2007. Perry's Chemical Engineers' Handbook, 8th ed. McGraw-Hill, New York, NY, USA, pp. 2–126.

Scholes, C.A., Kentish, S.E., Stevens, G.W., DeMontigny, D, 2015. Comparison of thin film composite and microporous membrane contactors for CO2 absorption into monoethanolamine. Int. J. Greenh. Gas Control 42, 66–74.

Sutter, D., Gazzani, M., Mazzotti, M., 2015. Formation of solids in ammonia-based CO_2 capture processes — Identification of criticalities through thermodynamic analysis of the CO_2–NH_3–H_2O system. Chem. Eng. Sci. 133, 170–180.

Sutter, D., Gazzani, M., Pérez-Calvo, J.F., Leopold, C., Milella, F., Mazzotti, M., 2017. Solid formation in ammonia-based processes for CO_2 capture - turning a challenge into an opportunity. In: Proceedings of the 13th International Conference on Greenhouse Gas Control Technologies. Lausanne, Switzerland.

Thomsen, K., Rasmussen, P., 1999. Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. Chem.Eng. Sci. 54, 1787–1802.

Verbrugge, P., 1979. Vapour-Liquid Equilibria of the Ammonia-Carbon dioxide-Water System. Delft University. PhD thesis.
Villeneuve, K., Roizard, D., Remigy, J.C., Iacono, M., Rode, S., 2018a. CO_2 capture by aqueous ammonia with hollow fiber membrane contactors: gas phase reactions and performance stability. Sep. Purif. Technol. 199, 189–197.
Villeneuve, K., Torres Hernandez, A.A., Albarracin Zaidiza, D., Roizard, D., Rode, S, 2018b. Effects of water condensation on hollow fiber membrane contactor performance for CO_2 capture by absorption into a chemical solvent. J. Membr. Sci. 556, 365–373.
Zhao, D., Dong, S., Bai, L., Li, D., Liu, H., 2023. Experimental method and mathematical method for VLE plots in 3DMA1P-CO_2-H_2O system. Sep. Purif. Technol. 307, 122800.

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Liqmani, Ben A.; Nayak, Vignesh; Brookes, Adam; Moore, Andrew; Vale, Peter C. J. ...

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