The Salting-out Effect in Some Physical Absorbents for CO_2 Capture

Ricardo R. Wanderley[a], Sigvart Evjen[b], Diego D. D. Pinto[a], Hanna K. Knuutila[a,*]

[a]Department of Chemical Engineering, NTNU, Norway
[b]Department of Chemistry, NTNU Norway
hanna.knuutila@ntnu.no

The solubility of CO_2 in organic solvents N-methyl-2-pyrrolidone (NMP), methanol and monoethylene glycol (MEG) at 30 °C was measured together with its heat of absorption. The salts lithium nitrate ($LiNO_3$), lithium chloride (LiCl) and tetraethylammonium bromide (TEABr) were then dissolved in different proportions to these solvents to analyze their salting-out/salting-in effects. Results from pure and salt containing solvents were compared to those found for CO_2 solubility in fully loaded hybrid solvents of each diluent plus monoethanolamine (MEA), wherein carbamate and protonated amine coexist, presumably causing similar salting-out/salting-in effects. Interestingly, an unexpected persistent enhancement in CO_2 capacity was observed through all of the latter solutions, suggesting that physical absorption is not the only mechanism through which CO_2 is absorbed after full theoretical amine loading. Vapour-liquid equilibrium (VLE) curves and heat of absorption data are provided for these hybrid solvents at 30 °C as well.

1. Introduction

A lot of effort has been invested on the development of novel alternatives for CO_2 capture in efficient and environmentally friendly ways. One of these alternatives is through hybrid solvents. Among the many reasons for the interest in these solutions is the claim that advantages of both chemical and physical absorbents could be brought together into a hybrid solvent. That is to say, hybrid solvents could capture CO_2 not only through chemical absorption, which is constrained by stoichiometry, but also by physical absorption, a function only of CO_2 partial pressure (MacGregor and Mather, 1991; Kohl and Nielsen, 1997).

However, it is unreasonable to assume that these physical and chemical capacities are merely additive. On the contrary, as chemical absorption is deranged by having an organic diluent (Hamborg et al, 2010), it could also be presumed that the formation of electrolytes in the medium – the amine carbamate and the protonated amine – will decrease the physical solubility of CO_2 through the salting-out effect (Browning and Weiland, 1994).

The extent of this effect is what this work set out to analyze. The chief supposition behind the methodology applied here is that there is no direct involvement from the organic diluent in the chemical reaction between amine and CO_2. As such, in non-aqueous hybrid solvents, the only mechanism for CO_2 absorption after the amine has fully reacted would be physical absorption (Versteeg and van Swaaij, 1988). This not being true, the CO_2 capacity after full theoretical amine loading will still be an interplay between chemical and physical absorption. That is precisely what the results found in this work suggest. For all solutions proposed, what is left of salting-out deranged CO_2 physical solubility is compensated by what could well be chemical reactivity.

2. Theory

A hybrid solvent is a solvent containing both an organic diluent and an amine, being low or null in water content. In this work, only non-aqueous hybrid solvents shall me discussed. In those, there can be found two mechanisms for CO_2 absorption: chemical absorption and physical absorption. If the solvent contains fast-reacting amines such as monoethanolamine, it is suggested that, until every molecule of amine has reacted, all CO_2 captured is found chemically bonded. Thus, CO_2 absorption can be treated as occurring in two definite, successive steps.

In non-aqueous hybrid solvents, the only base available for the deprotonation step is the amine itself (Versteeg and van Swaaij, 1988), though some authors suggest the diluent may act as a base as well (Ali et al., 2000; Zheng et al., 2012). In case these latter claims are dismissed, during chemical absorption the amine reacts with CO_2 according to the reaction Eq(1), where R_1R_2NH denotes an arbitrary primary or secondary amine.

$$2R_1R_2NH + CO_2 \longrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{1}$$

After all amine has reacted, what is left in solution is an amount of ions equal to the amount of amine molecules divided into cations (protonated amine) and anions (carbamate). This is the initial setup for physical absorption.

Physical absorption in its inception occurs roughly following Henry's law, Eq(2), through which Henry's constant is defined. In this scenario, CO_2 molecules steadily transition from vapour to liquid phase as the partial pressure of CO_2 increases. All cases analysed in this work are dilute enough such that Henry's law should be valid.

$$p^* = H \cdot x \tag{2}$$

Eq(2) shows that, the lower Henry's constant is, the higher the solubility of CO_2 in the solvent. If not because of carbamate formation, one could assume that physical solubility of CO_2 in a hybrid solvent would be the same as its solubility in pure organic diluent in terms of mol CO_2/mol solvent. However, this is not observed experimentally. In fact, hybrid solvents with distinct amine compositions show distinct CO_2 physical solubilities after full theoretical amine conversion.

The usual way of explaining the effect of electrolytes on gas solubility in solvents is through the salting-out effect. Bockris and Egan (1948) suggest that, as more molecules of solvent are drawn around the ions to provide solvation, less of them are available to solvate the incoming gas. Salting-in can be explained in converse terms when the electrolyte shifts the structure of the solvent, generating a configuration with more void spaces.

According to Browning and Weiland (1994), in the context of aqueous amine solvents, the increase in ionic strength brought by the formation of electrolytes causes a decrease in CO_2 solubility. While this has been observed in aqueous amine solutions, studies regarding this effect in hybrid solvents are lacking.

The shift in solubility of a gas as a function of the presence of electrolytes, at least in dilute solutions, can be described by the Sechenov equation, written below as Eq(3) in its simplest form. There, h is the salting-out factor and I is the ionic force brought by the ions in solution. The factor h is strongly dependent on the nature of both electrolytes and solvent, but weakly dependent on the nature of the gas (Browning and Weiland, 1994).

$$\ln(H/H_0) = h \cdot I \tag{3}$$

Bockris and Egan (1948) showed that, for dilute solutions, the decrease of Henry's constant due to salting-out is exponentially proportional to how the dielectric constant of the pure solvent decreases with the addition of gas. Besides this, no clear relationship was found between CO_2 salting-out in water and that in organic diluents.

3. Methodology

An array of different salts – LiCl, $LiNO_3$ and TEABr – was proposed so that general impressions could be drawn on the causes and particularities of CO_2 salting-out in all of the proposed solvents, which are NMP, methanol and MEG. Although historically ammonium ion has been employed to simulate the salting-out effect of protonated amine and carbonate that of carbamate, fewer salts are soluble in organic diluents than in water. All chemicals used in this work were obtained from Sigma Aldrich. These are: N-methyl-2-pyrrolidone (NMP) 99.8% purity, methanol (MeOH) 99.8% purity, monoethylene glycol (MEG) 99.5% purity, monoethanolamine (MEA) 99% purity, lithium nitrate (LiNO3) 99% purity, lithium chloride (LiCl) 99% purity and tetraethylammonium bromide (TEABr) 98% purity.

The equipment employed for VLE data acquisition consisted of a calorimeter model CPA 202 provided by ChemiSens AB. Both set-up and procedure in this work are very similar to those employed by Hartono et al. (2017). Heat of absorption data was compared to and found in agreement with the results of Kim et al. (2014) and Svensson et al. (2014), while VLE data has been further validated by comparison to results from Jou et al. (1995) and Aronu et al. (2011) for aqueous MEA. In addition to VLE data, viscosity and density data were measured when possible with the use of a Lovis 2000 ME viscosimeter and a DMA 4500 M densimeter apparatus, both provided by Anton Paar.

4. Results

4.1 Pure solvents with LiNO₃, LiCl and TEABr

Results from solubility, viscosity and density carried at 30 °C with NMP, methanol and MEG plus the salts LiNO$_3$, LiCl and TEABr are shown in Tables 1, 2 and 3. The definition of solubility employed here is the inverse of Henry's constant in mass basis, and the mass of solvent S is that of diluent alone once salt is discounted. As LiCl is only partially soluble in NMP and TEABr is not soluble at all, fewer data points for NMP were obtained in comparison to methanol and MEG.

Table 1: Data acquired for electrolytic solutions of N-methyl-2-pyrrolidone at 30 °C

	C (%mol/mol)	s (kg CO$_2$/ton S)/bar	ρ (g/cm^3)	η (mPa.s)
		6.4 ± 0.2	1.023 ± 0.00001	1.55 ± 0.03
LiNO$_3$	7.87	4.7 ± 0.2	1.063 ± 0.00001	3.16 ± 0.06
	15.28	3.7 ± 0.2	1.100 ± 0.00001	7.0 ± 0.1
	22.26	2.9 ± 0.2	1.135 ± 0.00001	18.2 ± 0.4
	28.87	2.3 ± 0.2	1.169 ± 0.00001	58 ± 1
LiCl	7.88	4.7 ± 0.2	1.052 ± 0.00001	3.24 ± 0.06
	15.28	3.6 ± 0.2	1.079 ± 0.00001	7.9 ± 0.2

Table 2: Data acquired for electrolytic solutions of methanol at 30 °C

	C (%mol/mol)	s (kg CO$_2$/ton S)/bar	ρ (g/cm^3)	η (mPa.s)
		8.9 ± 0.2	0.782 ± 0.00001	0.53 ± 0.01
LiNO$_3$	2.69	7.3 ± 0.2	0.821 ± 0.00001	0.82 ± 0.02
	5.51	6.0 ± 0.2	0.860 ± 0.00001	0.86 ± 0.02
	8.47	5.3 ± 0.2	0.899 ± 0.00001	0.90 ± 0.02
	11.59	4.5 ± 0.2	0.940 ± 0.00001	0.94 ± 0.02
LiCl	2.69	7.3 ± 0.2	0.810 ± 0.00001	0.83 ± 0.02
	5.51	5.9 ± 0.2	0.837 ± 0.00001	1.32 ± 0.03
	8.47	4.7 ± 0.2	0.866 ± 0.00001	2.26 ± 0.05
	11.60	3.6 ± 0.2	0.896 ± 0.00001	4.06 ± 0.08
TEABr	2.69	8.5 ± 0.2	0.836 ± 0.00001	0.68 ± 0.01
	5.51	8.4 ± 0.2	0.882 ± 0.00001	0.86 ± 0.02
	8.47	8.3 ± 0.2	0.923 ± 0.00001	1.09 ± 0.02
	11.59	7.9 ± 0.2	0.959 ± 0.00001	1.41 ± 0.03

Table 3: Data acquired for electrolytic solutions of monoethylene glycol at 30 °C

	C (%mol/mol)	s (kg CO$_2$/ton S)/bar	ρ (g/cm^3)	η (mPa.s)
		1.3 ± 0.2	1.106 ± 0.00001	13.8 ± 0.3
LiNO$_3$	5.08	1.2 ± 0.2	1.138 ± 0.00001	20.7 ± 0.4
	10.15	1.1 ± 0.2	1.170 ± 0.00001	31.0 ± 0.6
	15.20	1.0 ± 0.2	1.202 ± 0.00001	48 ± 1
	20.26	0.8 ± 0.2	1.234 ± 0.00001	75 ± 1
LiCl	5.08	1.1 ± 0.2	1.127 ± 0.00001	22.8 ± 0.5
	10.14	0.9 ± 0.2	1.148 ± 0.00001	39.6 ± 0.8
	15.21	0.7 ± 0.2	1.170 ± 0.00001	78 ± 2
	20.29	0.6 ± 0.2	1.192 ± 0.00001	122 ± 2
TEABr	5.08	1.5 ± 0.2	1.123 ± 0.00001	14.3 ± 0.3
	10.15	1.7 ± 0.2	1.136 ± 0.00001	15.2 ± 0.3
	15.21	1.9 ± 0.2	1.147 ± 0.00001	16.8 ± 0.3
	20.26	2.3 ± 0.2	1.157 ± 0.00001	19.5 ± 0.4

Figure 1a shows the molar density of both pure and electrolytic solutions, wherein anions and cations are taken into consideration together with solvent molecules. Figure 1b shows the relative change in Henry's constant.
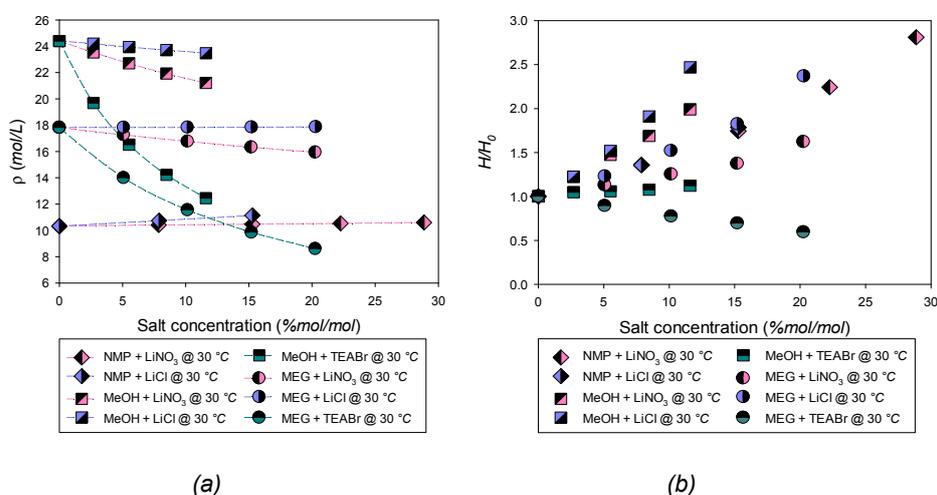

(a)   *(b)*

Figure 1: Molar densities and relative change in Henry's constant of different solvents with varying concentrations of electrolytes at 30 °C

Heat of absorption of CO_2 at 30 °C was measured at around 15 ± 1 *kJ/mol* CO_2 in NMP, 15 ± 1 *kJ/mol* CO_2 in methanol and 14 ± 1 *kJ/mol* CO_2 in MEG. The value for NMP agrees with that published by Svensson et al. (2014) of 16 ± 1 *kJ/mol* CO_2 at 25 °C. Heat of absorption in mixtures of NMP and salts decreased slightly with the addition of both $LiNO_3$ and LiCl, but the reduction was within the measurement uncertainties.

4.2 Hybrid solvents with MEA

The vapour-liquid equilibrium (VLE) curves for methanol, NMP and MEG with MEA can be seen in Figures 2a, 2b and 3. In the same figures the differential heat of absorption is also shown. Confidence intervals are given for all values displayed. The dashed lines correspond to the maximum theoretical amine loading of 0.5 *mol* CO_2/*mol* MEA for each slope. Final CO_2 solubilities are calculated on organic diluent basis for each curve by fitting a line through the last four experimental data points, and their values are presented in Table 4 along with that for the pure diluent.
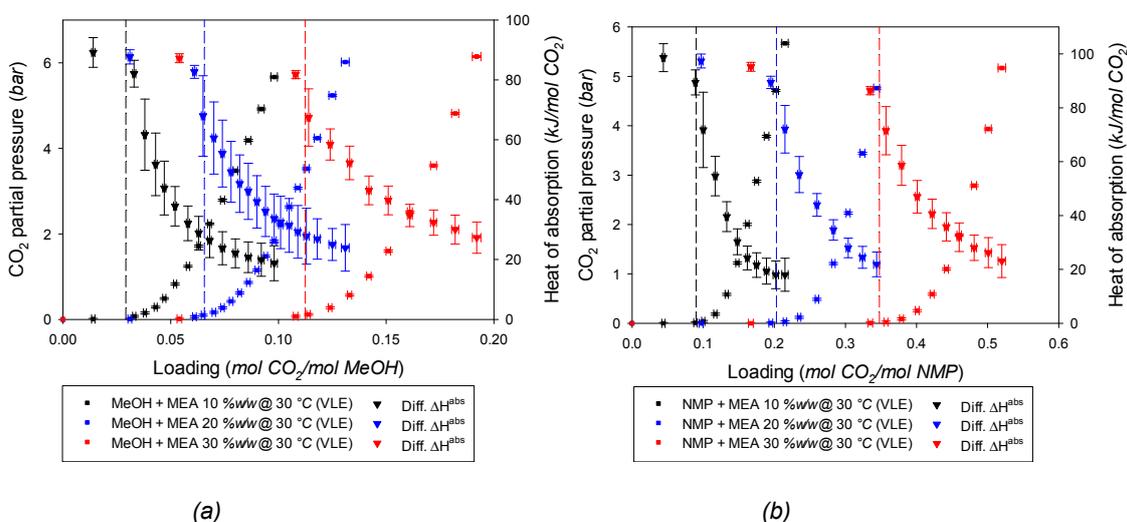

(a)   *(b)*

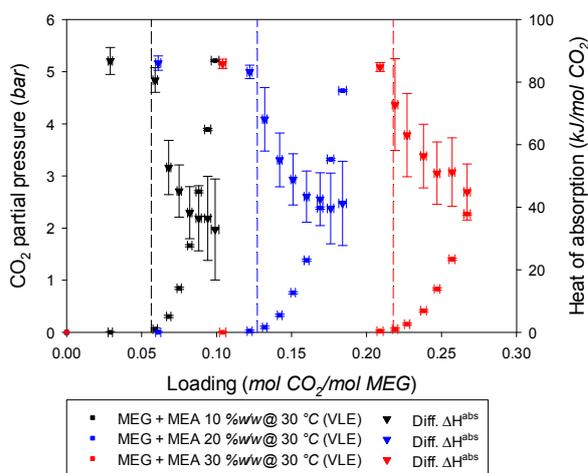*Figure 2: VLE and heat of absorption curves in hybrid solvents of methanol, NMP and MEA at 30 °C*

Figure 3: VLE and heat of absorption curves in hybrid solvents of MEG and MEA at 30 °C

Table 4: Final CO_2 solubilities for pure diluents and fully loaded hybrid solvents (mmol CO_2/mol S)/bar

Solvent	Pure	10 %w/w MEA	20 %w/w MEA	30 %w/w MEA
NMP	14.6 ± 0.6	14 ± 2	17 ± 1	25 ± 2
Methanol	6.5 ± 0.2	6.8 ± 0.8	7.2 ± 0.8	8.5 ± 0.6
MEG	2.1 ± 0.7	4.7 ± 0.7	7.3 ± 0.8	15 ± 1

5. Discussion

Data from Carvalho et al. (2015) shows that the solubility of CO_2 in water at 30 *°C* is of approximately 1.03 *(kg CO_2/ton water)/bar*. As expected, both NMP and methanol display better capacity for CO_2 absorption even when salting-out is involved. MEG has the worst CO_2 solubility among the solvents tested.

The nature of salting-out and how it connects to the increase in viscosity caused by introducing salts to the solution is not completely clear. On one hand, this increase is often related with "structure-making", a reduction of the system entropy brought by coordination between solvent molecules and electrolytes, consequently rendering non-electrolytic molecules less soluble (Desnoyers and Perron, 1972). In accordance to this, Tables 1, 2 and 3 show a similar pattern between increase in viscosity and decrease in solubility for most salts and solutions. However, TEABr promotes salting-in of CO_2 in MEG even though it also seems to fit the definition of structure-making salt. The salting-in phenomenon is much less understood, and explanations range from void spaces (Bockris et al., 1951) to ion-solute interactions (Zhang et al., 2017). According to the first theory, electrolytes that generate an excess of empty space in the solvent may facilitate the solvation of non-electrolytes, a phenomenon typically related to large cations. In this sense, the slope for TEABr in MEG in Figure 1a can be seen as showing how this salt decreases the apparent molecular density of MEG. According to the second theory, the strength of interactions between CO_2 and one or more of the electrolytes of TEABr could be high enough to justify an enhancement in solubility brought by its addition to the solvent. Curiously, CO_2 solubility order in electrolytic organic diluents follows the Hofmeister series (Cacace et al., 1997), with Cl^- ions reducing it more than NO_3^- anions for the same cation (Li^+). This has also been observed by Zhang et al. (2017). Heat of absorption values measured in NMP, methanol and MEG are very similar. Interestingly, Svensson et al. (2014) also reported a similarity in their heat of absorption results for CO_2 in both NMP and tetraethylene glycol dimethyl ether (TEGDME), another commonly employed physical absorbent. The differential heat of absorption in organic solvents has been observed to be somewhat constant throughout all loadings. This is an unsurprising result: in dilute solute scenarios, where Henry's law is valid, the presence of more or less CO_2 in solution does not affect too strongly the energy of the breaking/making of intermolecular bonds. At last, heat of absorption of all solvents was found not to vary too much with the addition of salts.

Under this light, results seen in Figures 2a, 2b and 3 are unexpected. First, an increase in solubility of CO_2 in all solvents has been observed with the addition of MEA and consequent formation of more carbamate/protonated amine ions, a clear case of what could be called salting-in. However, this seems to be a strange, unexpected case of salting-in: in NMP + MEA 30 *%w/w* solutions at 40 *°C*, viscosity after CO_2 loading was seen to increase more than 12 times, a good indication of structure-making. Second, the differential heat

of absorption in all hybrid solvents never reach quite as low as the heat of absorption in pure organic diluents, even after all chemical conversion has theoretically ceased. This gives weight to claims of Ali et al. (2000) and Zheng et al. (2012) that the diluent molecules in hybrid solvents indeed play a part in the chemical absorption of CO_2. However, it is difficult to affirm if this is indeed what happens without speciation data.

6. Conclusions

The salting-out/salting-in behavior of CO_2 in some typical organic solvents due $LiNO_3$, LiCl and TEABr has been studied and its causes have been proposed. Comparison between this data and that of similar electrolytes in water, readily available in literature, may help tracing connections between phenomena in aqueous and in organic diluents. The interest for these solvents in the CO_2 absorption industry may furthermore justify an in-depth analysis of how solubility is affected by electrolytic impurities. Mostly, however, the relevance of this work is in showing how salting-out/salting-in looks like in organic diluents and how different it is from what is observed in hybrid solvents containing these very compounds. This suggests that phenomena observed in hybrid solvents are indeed not due to solvation effects alone, but also to chemical reactivity. To check the validity of these claims, future work is suggested on the chemical speciation during CO_2 absorption in hybrid solvents.

References

Ali S.H., Merchant S.Q., Fahim M.A., 2000, Kinetic study of reactive absorption of some primary amines with carbon dioxide in ethanol solution, Separation and Purification Technology, 18(3), 163-175.

Aronu U.E., Gondal S., Hessen E.T., Haug-Warberg T., Hartono A., Hoff K.A., Svendsen H.F., 2011, Solubility of CO2 in 15, 30, 45 and 60 mass% MEA from 40 to 120 °C and model representation using the extended UNIQUAC framework, Chemical Engineering Science, 66(24), 6393-6406.

Bockris J.O'M., Egan H., 1948, The salting-out effect and dielectric constant, Transactions of the Faraday Society, 44, 151-159.

Bockris J.O'M., Bowler-Reed J., Kitchener J.A., 1951, The salting-in effect, Transactions of the Faraday Society, 47, 184-192.

Browning J.G., Weiland R.H., 1994, Physical solubility of carbon dioxide in aqueous alkanolamines via nitrous oxide analogy, Journal of Chemical & Engineering Data, 39(4), 817-822.

Cacace M.G., Landau E.M., Ramsden J.J., 1997, The Hofmeister series: salt and solvent effects on interfacial phenomena, Quarterly Reviews of Biophysics, 30(3), 241-277.

Carvalho P.J., Pereira L.M.C., Gonçalves N.P.F., Queimada A.J., Coutinho J.A.P., 2015, Carbon dioxide solubility in aqueous solutions of NaCl: Measurements and modeling with electrolyte equations of state, Fluid Phase Equilibria, 388, 100-106.

Desnoyers J.E., Perron G., 1972, The viscosity of aqueous solutions of alkali and tetraalkylammonium halides at 25 °C, Journal of Solution Chemistry, 1 (3), 199-212.

Hamborg E.S., van Aken C., Versteeg G. F., 2010, The effect of aqueous organic solvents on the dissociation constants and thermodynamic properties of alkanolamines, Fluid-Phase Equilibria, 291(1), 32-39.

Hartono A., Kim I., Knuutila H.K., van der Ham L.V., Goetheer E., 2017, Calorimetric Studies of Precipitating Solvent System, Energy Procedia, 114, 744-755.

Jou F.-Y., Mather A.E., Otto F. D., 1995, The solubility of CO_2 in a 30 mass percent monoethanolamine solution, The Canadian Journal of Chemical Engineering, 73(1), 140-147.

Kim I., Hoff K.A., Mejdell T., 2014, Heat of absorption of CO_2 with aqueous solutions of MEA: New experimental data, Energy Procedia, 63, 1446-1455.

Kohl A.L., Nielsen R.B., 1997, Physical solvents for acid gas removal, Chapter In: A.L. Kohl, R.B. Nielsen (Eds.), Gas Purification, 5th Edition, Gulf Professional Publishing, Houston, USA, 1187-1237.

MacGregor R.J., Mather A.E., 1991, Equilibrium solubility of H_2S and CO_2 and their mixtures in a mixed solvent, The Canadian Journal of Chemical Engineering, 69(6), 1357-1366.

Svensson H., Velasco V.Z., Karlsson H.T., 2014, Heat of absorption of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents, International Journal of Greenhouse Gas Control, 30, 1-8.

Versteeg G., van Swaaij, W., 1988, On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions – I. Primary and secondary amines, Chemical Engineering Science, 43(3), 573-585.

Zhang X., Zhang L., Jin T., Pan Z.-J., Chen Z.-N., Zhang Q., 2017, Salting-in/Salting-out mechanism of carbon dioxide in aqueous electrolyte solutions, Chinese Journal of Chemical Physics, 30(6), 811-816.

Zheng C., Tan J., Wang Y.J., Luo G.S., 2012, CO2 solubility in a mixture absorption system of 2-amino-2-methyl-1-propanol with ethylene glycol, Industrial & Engineering Chemistry Research, 52(34), 12247-12252.