Chapter 14
CO_2 Capture in Industrial Effluents. Calorimetric Studies

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Abstract In order to reduce environmental impact of CO_2 emissions, one possible option is the decarbonation of the effluents coming from fixed sources. A description of the different techniques proposed for a separation of CO_2 from gaseous effluents is explained with a focus on post-combustion processes. The design of specific separation units will require studies of gas dissolution in various selective absorbent solutions. The thermodynamic approach for CO_2 dissolution in aqueous solutions of amine is depicted, showing the physicochemical background and the main properties required in this domain. An overview of the main experimental developments for determining the enthalpy of solution of carbon dioxide in absorbent solutions is presented together with some representative results.

14.1 Introduction

Carbon dioxide is considered as a main greenhouse gas. Its contribution to global warming can be pointed up by correlations between the evolution of CO_2 in atmosphere and the average earth temperature [1]. Since the eighteenth century the concentration of CO_2 has approximately risen from 280–380 ppm when simultaneously temperature has increased by 0.6 K. Anthropogenic sources of carbon dioxide represents currently about 25 Gt per year. If we consider constant industrial development and population growth in the world, the emissions of carbon dioxide will

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not decrease without an international mobilization. In order to avoid irreversible environmental impact, CO_2 emissions have to be drastically reduced [2].

The anthropogenic carbon dioxide emissions can roughly be classified in 3 main categories: industrial, transportation and residential. The key solutions to reduce these emissions will be found in an ecologic production and rational utilization of energy. One of them will be to reduce CO_2 emissions from industrial site called"fixed sources". It mainly concerns industries using fossil energy such as cement factory, metallurgy, glass industry or power plant. For this purpose pre-combustion and post-combustion processes have been proposed. The first ones consist in using specific comburant and technology for the combustion of coal, fuel or natural gas in order to release small quantity of CO_2 in the fumes. The second ones refer to techniques of separation of carbon dioxide from industrial effluent. In this last case carbon dioxide will be valorized or stored in specific secured sites.

Capture processes were developed in the past to remove acid gases such as carbon dioxide and hydrogen sulfide (H_2S) from natural gas. They are mainly based on chemical and physical dissolution of the acid gas in aqueous solutions of amines. The technique is considered as mature enough to be adapted in next future to the treatment of post combustion effluents. The new processes should take into account difference from natural gas treatment such as temperature, pressure or composition of the effluent. However one major barrier for the integration into industrial sites in the few coming years is the economical cost of the so called *ton of* CO_2 *avoided*. Specific researches are then carried out on both the technology and the choice of the absorbent solutions.

Future absorbent solutions have to combine high carbon dioxide loading charges (moles of dissolved carbon dioxide per mole of amine) with low energies of regeneration. Characterization of new absorbent solution can be performed by calorimetric studies of gas dissolution. The experimental data collected are essential to develop thermodynamic models representative of the $\{CO_2\text{-absorbent solution}\}$ systems that will be used to design the future capture units. The dissolution properties required are the mainly the gas solubility and the enthalpy of solution. However some other properties also have to be studied, such as heat capacity, vapor pressure, chemical and thermal degradations. Then specific calorimetric techniques were set up to provide the essential experimental data.

14.2 Presentation of Techniques for CO_2 Separation from Gaseous Effluents

Adsorption on micro-porous solids is a common industrial technique used for removing impurities (e.g. CO_2 from gaseous streams such as hydrogen-rich gases resulting from gasification, steam reforming or shift of fossil hydrocarbons. The molecules to be adsorbed interact with the internal surface of microporous solids. Polar and/or condensable species like CO_2 will be strongly retained whereas "light components" such as N_2, O_2, CO will be less or not retained on the adsorbent. The regeneration, or gas desorption, is performed by running thermal cycles (Temperature Swing Adsorption, TSA) and/or pressure cycles (Pressure-Swing-Adsorption, PSA or Vacuum-Swing-Adsorption, VSA). The energy required is thus analogous to that of absorption. The most common adsorbents are activated carbons and zeolite molecular sieves, mostly used in combination [3, 4].

For separation processes, solid adsorbents are packed as fixed beds and submitted to successive adsorption and desorption steps. The operation is therefore transient instead of steady-state. To achieve a continuous production, multiple packed-beds are needed in parallel with shifted time-cycles. The technique necessitates a drastic pretreatment of gas effluent, especially for particle removal. A new class of nanoporous crystalline solids, called metal-organic framework (MOF) materials, is intensively studied as potential adsorbent materials for CO_2 capture. The interest of such material is their high internal surface area, large pore volume, and the possibility to adapt the pores with a variety of functionalities.

The membrane processes proposed for CO_2 separation consist in selective permeation of molecules through a thin layer of polymeric or mineral material. The two intrinsic criteria determining their performance are the selectivity and the permeability. Industrial membrane processes have been particularly developed for recovery of relatively concentrated CO_2 ($>20\,\%$) at high pressures from natural gas. [5, 6]. Selectivity and permeability of membranes depend on their chemical nature and their structure (microporosity, active layer thickness). Modern membranes are layered composites, with a thin dense selective layer supported by thicker, more permeable and less-selective or inert supports. There are basically two families of membrane materials: inorganic ceramic type membranes, and organic polymeric membranes. The former can stand high temperatures and pressures, and are corrosion resistant. They can be made selective for H_2/CO_2 separations, with hydrogen permeating preferentially. However the CO_2/N_2 separation selectivity remains relatively low in case of CO_2 capture from post combustion effluent.

The cryogenic process is used on a large scale for air separation but cryogenic distillation does not seem to be currently considered as an alternative for CO_2 capture, probably because of anticipated high costs when diluted streams are used [7]. However in the case oxy-fuel combustion technique where cryogenic air separation unit is implemented, it may be conveniently integrated with c ondensation units for separating water from CO_2.

Absorption in alkaline solution is a common principle used in acid gases capture processes operating for decades in natural gas treatment. The reference absorbent is aqueous solution of monoethanolamine (MEA). The mechanism of capture is a combination of chemical and physical dissolution. The chemical dissolution is based on an acido-basic reaction. The reaction must be reversible in order to regenerate the absorbent solution and recover carbon dioxide for storage. The physical dissolution, usually observed fot high partial pressure of CO_2, can be improved by addition of specific physical solvent.

Some other more emerging techniques are proposed. It includes gas hydrate crystallization [8], enzymatic capture [9] or dissolution in ionic liquids [10]. However the separation process by dissolution in amine solutions (amine washing process) is presently the most advanced technology proposed to remove carbon dioxide from industrial effluents. However the dilemma of the economic costs still constitutes a barrier for integration such processes into industrial sites.

14.3 Industrial Processes Proposed for CO_2 Capture in Post Combustion Effluents

The CO_2 capture processes will concern the industries that emit large volumes of carbon dioxide i.e. those using fossil energy. For near future integration, the most mature technologies are those based on gas separation by selective dissolution in appropriate absorbent solutions. The industrial process is schematically represented in Fig. 14.1. It consists in cycles of gas absorption and desorption that implicate a reversible reaction of gas dissolution [11]. In the first step the gaseous effluent flows counter-currently to the absorbent solution in an absorber unit. In the second step the "rich" absorbent solution containing dissolved CO_2 is pumped to the top of a stripper (or regeneration vessel). The regeneration of the chemical solvent is carried out by heating the solution using water vapor. The "lean" solvent is pumped back to the absorber.

Industrial pilots based on this principle are now under study. The design of the future installations must be tailored to the composition, flow rate, temperature and pressure of the fumes. These effluent parameters largely depend on the type of industry considered. The incoming gas flow rates will vary from 15,000 to 3,00,000 Nm^3/h

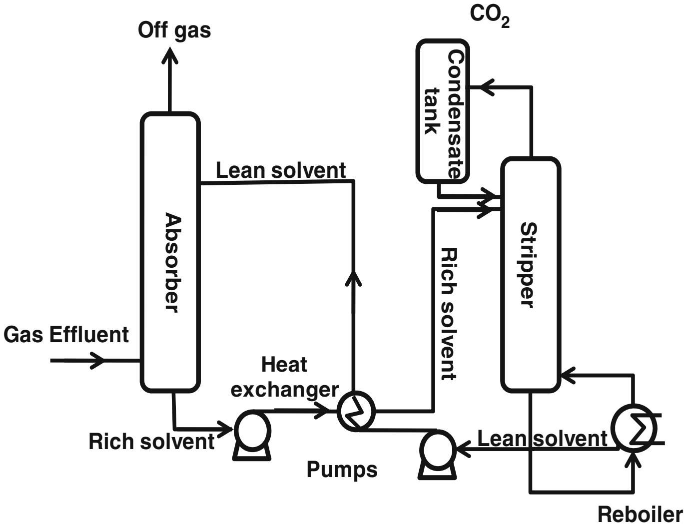


Fig. 14.1 Schematic representation of capture process

as in the same way, CO_2 compositions in the effluents will vary from 3 to 30 moles percent.

The regeneration of the solvent solution is planned to be performed at temperatures between 100 and 140 °C and at pressures not very much higher than atmospheric pressure. The costs of this step represent a major barrier to the integration of capture process into industrial sites. Then active researches are conducted to elaborate better absorbent solutions that will require less energy for regeneration.

The characterization of the new absorbent solutions will be achieved by a determination of its physical and chemical properties. We will focus here on some properties that can be investigated by calorimetric techniques.

For example, the energy of regeneration, related to the opposite of the energy of gas dissolution, will be studied through the determination of the enthalpy of solution of CO_2 in the absorbent solution. This enthalpy represents the energy needed to dissolve one mole of gas and will contribute in a great extend to the calculi of economical costs of carbon dioxide capture. Heat capacities will also be key properties for heat exchange calculations as well as the gas solubility, required to estimate solvent flux for given gas stream. In addition, the solvent characterization should be completed by studies on vapor pressure, transport properties, chemical and thermal degradations, kinetic of dissolution, corrosion...

14.4 Thermodynamic Approach of CO_2 Dissolution in Aqueous Solutions of Amine

14.4.1 Mechanism of CO_2 Dissolution

The dissolution of CO_2 in aqueous solution of amine is combination of chemical reactions and physical dissolution. The chemical reactions involved depend on the type of the amine.

In case of primary or secondary amine, the presence of hydrogen(s) branched on nitrogen atom allows formation of carbamate. The carbon dioxide reacts first with one molecule of amine to form a zwitterion (Eq. 14.1). Then the zwitterion reacts with a second amine molecule to form a carbamate (Eq. 14.2). The stoechiometry for chemical dissolution in primary or secondary amines is then limited to 2 molecules of amine per molecule of carbon dioxide (Eq. 14.3).

$$\mathrm{CO_2 + RR'NH = RR'N + HCOO^-} \tag{14.1}$$

$$\mathrm{RR'N^+HCOO^- + RR'NH = RR'NCOO^- + RR'N^+H_2} \tag{14.2}$$

$$\mathrm{CO_2 + 2RR'NH = RR'NCOO^- + RR'N^+H_2} \tag{14.3}$$

In case of sterically hindered amine the carbamate is instable and primary or secondary amines will react as the tertiary amines. The instability of carbamate also increases with temperature. With tertiary amines, carbon dioxide cannot form carbamate because of no available free proton. The reaction mechanism then results in hydration of carbon dioxide by alkaline catalysis to form hydrogenocarbonate (Eq. 14.4).

$$RR'R''N + H_2O + CO_2 = RR'R''NH^+ + HCO_3^- \tag{14.4}$$

The increase of partial pressure of carbon dioxide forces the physical dissolution. This mechanism is purely mechanical and results in the apparition of molecular CO_2 in the solution. This physical dissolution is particularly considerate in the treatment of natural gas in which partial pressure of carbon dioxide can reach hundreds of bars. In the case of CO_2 capture in industrial effluent, partial pressure of CO_2 remains below atmospheric pressure and carbon dioxide is mainly chemically absorbed with formation of carbamate and hydrogen carbonate.

The solution concentration and the choice of the amine will be adapted to the conditions of temperature, pressure and composition of the gas stream to be treated. It has been shown that amines can also be combined to improve kinetic of absorption and quantity of dissolved gas [12]. In some cases, physical solvents can also be added to the solution in order to increase physical dissolution.

14.4.2 Selection of Amines for CO_2 *Capture Processes*

The design of specific amines for CO_2 capture in industrial effluent is a difficult task as no model really exists to predict the dissolution properties from structural properties. Then current studies consist in a screening of commercial or synthesized molecules, implicating numerous experimental investigations. The absorbent solution must be characterized by properties such as density, viscosity, heat capacity, thermal and chemical stability, or corrosion aspects. The gas dissolution can be described by the determination of dissolution properties such as the limits of gas solubility, enthalpies of solution or kinetic of gas dissolution. The experimental data make it possible the development of theoretical models representative of the $\{CO_2$-water-amine$\}$ systems. These models can then be used for engineering calculations to estimate the pre-cited properties of dissolution of the absorbent solution as function of temperature, pressure or amine concentration.

First studies were carried out on alcanolamine such as monoethanolamine (*MEA*), diethanolamine (*DEA*) or methyl diethanolamine (*MDEA*). Investigations are actually extended to "new" amines chosen within families such as aliphatic, cyclic, polyfunctional … Recently demixing amines solutions were proposed for new capture process. Aqueous solutions containing such amines present a liquid-liquid phase separation with a temperature change depending on the composition of the solution. The corresponding process DMX^{TM} has been proposed and patented by IFPEN [13]. A demixing unit was added at the output of the absorber unit in which the temperature of the gas charged solution is increased until reaching demixing of the ternary solution CO_2-amine-water in two phases. Only the aqueous phase that contains dissolved carbon dioxide is sent to the stripper while the amine phase is directly returned to the absorber. In these conditions the energy required for the regeneration of the absorbent solution is significantly reduced. The characterization of these demixing amine solutions is comparable to the classic one excepted an additional determination of phase diagrams of binary {water-amine} and ternary {CO_2-water-amine} systems.

14.4.3 Calorimetric Experimental Data Required

The properties of dissolution as gas solubility and enthalpy of solution can be derived from vapor liquid equilibrium models representative of {CO_2-H_2O-amine} systems. The developments of such models are based on a system of equations related to phase equilibria and chemical reactions: electro-neutrality and mass balance. The non ideality of the system can be taken into account in liquid phase by the expressions of activity coefficients and by fugacity coefficients in vapor phase. Non ideality is represented in activity and fugacity coefficient models through empirical interaction parameters that have to be fitted to experimental data. Development of efficient models will then depend on the quality and diversity of the experimental data.

Regarding literature data reported in Tables 14.1 and 14.2 collected for classical amines (MEA-DEA-AMP), it appears that solubility data are quite available while enthalpy data remains very scarce. Solubility data in Table 14.1 are usually obtained using *pVT* measurements and provide gas solubility expressed as loading charge α (moles of gas per mole of amine) as function of temperature and pressure (CO_2 partial pressure or total pressure). The enthalpy data in Table 14.2 are obtained from measurements of heat of mixing gas with absorbent solution using calorimetric techniques. Different techniques and associated experimental protocols have been proposed and will be presented in next paragraph. Mathonat et al. [14, 15], Arcis et al. [16, 17] use a flow calorimetric technique where the heat of mixing is detected by thermopiles surrounded a mixing cell. Kim and Svendsen [18], Carson et al. [19] and Kierzkowska-Pawlak [20] use a reaction calorimeter based on power compensation of the heat of mixing. Oscarson et al. [21], Merkley et al. [22] and Helton et al. [23] use a flow technique where the heat of mixing is determined from power compensation. In another hand enthalpies of solution can be derived from solubility data or from thermodynamic model fitted to solubility data. However as shown by Arcis et al. [24] and Kim et al. [25] such calculated values can show large divergence with direct experimental.

The representation of chemical reactions in solution in the thermodynamic models [21, 26, 27] necessitates the knowledge of the equilibrium constants of CO_2 dissociations, water dissociation, amine protonation and carbamate formation. For original amines the protonation or carbamate formation equilibrium constants are usually not available and must be measured. In order to derive enthalpy properties using Van't Hoff equations, these equilibrium constants must be determined as function of temperature. Such data can be obtained from a protonation constant determined at a

Table 14.1 Literature solubility data of CO_2 in aqueous solution

Source	m mol.kg^{-1}	T K	p_{CO_2} kPa	ASD %
(a). Monethanolamine (MEA)				
Mason and Dodge [28]	0.5–12.5$^{(b)}$	273–348	1.32–100	2
Jones et al. [29]	15.3	313–413	0.0027–930	0.5
Lee et al. [30]	2.5–5.0$^{(b)}$	313–373	1.15–6621	3
Lee et al. [31]	1.0–5.0$^{(b)}$	298–393	0.1–10000	4
Lawson and Garst [32]	15.2	313–413	1.32–2750	9
Isaacs et al. [33]	2.5$^{(a)}$	353–373	0.0066–1.75	15
Austgen and Rochelle [34]	2.5$^{(a)}$	313–353	0.0934–229	NC
Shen and Li [35]	15.3–30.0	313–373	1.1–2550	12
Dawodu and Meisen [36]	4.2$^{(a)}$	373	455–3863	13.5
Jou et al. [37]	30.0	273–423	0.0012–19954	3
Song et al. [38]	15.3	313	3.1–2359	12
Jane and Li [39]	2.5$^{(a)}$	353	3.57–121.8*	5
Mathonat et al. [14]	30.0	313–393	5000–20000	7
Ma'mun et al. [40]	30.0	393	7.354–191.9	2
Arcis et al. [41]		323; 373	500–5000*	7
(b). Methyldiethanolamine (MDEA)				
Jou et al. [42]	2.00–4.28$^{(a)}$	298–393	0.001–6630	NC
Merkley et al. [22]	20.0–23.5	298–393	1121	5
Chakma and Meisen. [43]	1.69–4.28$^{(a)}$	373–473	103–4930	14
Austgen and Rochelle [34]	2.00–4.28$^{(a)}$	313	0.0056–93.6	NC
Shen and Li [35]	30	313–373	1.1–1979	12
Jou et al. [44]	35	313–373	0.963–236	3
Dawodu and Meisen [36]	4.28$^{(a)}$	373–393	162–3832	14
Oscarson et al. [21]	20.0–60.0	289–422	22-6164	5
Kuranov et al. [27]	1.95–2.00$^{(b)}$	313–413	73.5–5036.7	3
Xu et al. [45]	1.72–6.85$^{(a)}$	328–363	137.5–808.5	NC
Mathonat et al. [15]	30	313–393	2000 − 10000*	7
Rho et al. [46]	5–75	323–373	0.775–268.3	5
Silkenbäumer et al. [47]	2.632$^{(b)}$	313	12 − 4080*	2
Baek and Yoon [48]	30	313	1.02–1916	3
Rogers et al. [49]	23–50	313	0.00007–1.0018	6
Xu et al. [45]	3.04–4.28$^{(a)}$	313–373	0.876–1013	NC
Lemoine et al. [50]	23.63	298	0.02–1.636	5
Pacheco et al. [51]	35–50	298–373	73–738	NC
Kamps et al. [52]	3.95–7.99$^{(b)}$	313–353	176.5–7565	4
Park and Sandall [53]	50	298–373	0.78–140.40	10
Kierzkowska-Pawlak [20]	10-30	293–333	100–300	3
Bishnoi and Rochelle [54]	4.28$^{(a)}$	313	0.108–0.730	NC
Sidi-Boumedine et al. [55]	25.73–46.88	298–348		2
Ali and Aroua [56]	2$^{(a)}$	313–353	0.06–95.61	2
Kundu et al. [57]	23.8–30.0	303–323	1	3
Benamor and Aroua [58]	2 − 4$^{(a)}$	303–323	0.1–98.2	5
Ma'mun et al. [40]	50	328–358	65.75–813.4	2

(continued)

Table 14.1 (continued)

Source	m mol.kg^{-1}	T K	p_{CO_2} kPa	ASD %
Jenab et al. [59]	$2.0-2.5^{(a)}$	298–343	101–2320	4
Huttenhuis et al. [60]	35–50	283–298	0.054–986.80	NC
(c). Diethanolamine (DEA)				
Lee et al. [30]	0.5–8.0$^{(a)}$	273–413	0.69–6900	5
Oyevaar et al. [61]	0.984–2.463$^{(a)}$	298	1.844–14.8	5
Kennard and Meisen [62]	10.0–30.0$^{(c)}$	373-478	73.1–3746.7	10
Dawodu and Meisen [36]	4.2$^{(a)}$	373	455–3863	13.5
Lal et al. [63]	2.0$^{(a)}$	313–373	0.0026–3.336	15
Lee et al. [64]	3.0–4.0$^{(a)}$	298–403	0.001- 5000	NC
Lawson and Garst [32]	25.0$^{(c)}$	311–394	1.974–4315.79	9
Mason and Dodge [28]	0.5–8.3$^{(a)}$	273–348	1.32–100	2
Sidi-Boumedine et al. [55]	41.78$^{(c)}$	298- 348	2.46–4662.7	2
Seo and Hong [65]	30.0$^{(c)}$	313–353	4.85–357.3	3
Benamor and Aroua [58]	2.0–4.0$^{(a)}$	303–323	0.1–104.7	2
Haji-Sulaiman et al. [66]	2.0–4.0$^{(a)}$	303–323	0.1–104.7	2
Haji-Sulaiman and Aroua [67]	2.0$^{(a)}$	301–353	5–100.3	12
Arcis et al. [68]	15; 30$^{(c)}$	323; 373	500 -5000	7

$^{(a)}$ *molarity* (mol.L^{-1}); $^{(b)}$massic fraction; $^{(c)}$wt%; $^{*}p_{\text{tot}}$ in kPa

Table 14.2 Literature references for experimental enthalpy of solution

Source	*wt* %	T K	p_{CO_2} kPa	ASD %
		MEA		
Mathonat et al. [14]	30.0	313–393	2000–10000	7
Kim and Svendsen [18]	30.0	313–393	0.001	3
Carson et al. [19]	10.0–30.0	298	265	2
Arcis et al. [41]	15.0; 30.0	323; 373	500–5000*	5
		DEA		
Helton et al. [23]	20–50	300–400	87–1121	5
Carson et al. [19]	10.0–30.0	298	265	2
Oscarson et al. [21]	20.6–49.8	300–450	90–1121	5
Arcis et al. [68]	15.0; 30.0	323; 373	500–5000*	5
		MDEA		
Merkley et al. [22]	20.0–23.5	298–393	1121	5
Oscarson et al. [21]	20.0–60.0	289–422	156–1466	5
Mathonat et al. [15]	30.0	313–393	2000–10000	7
Kierzkowska-Pawlak [20]	10.0–40.0	293–333	100–300	2
Carson et al. [19]	10.0–30.0	298	265	2
Arcis et al. [17]	15.0–30.0	323	500–2000	5
Arcis et al. [16]	15.0–30.0	373	500–2000	5

$^{*}p_{tot}$ in kPa

reference temperature and the enthalpy of amine protonation. Experimental data can be obtained by combining electrochemical and calorimetric techniques [21]. For primary and secondary amine it is also essential to determine the equilibrium constants for carbamate formation. These constants can be obtained by the determination of carbamate concentration when adding CO_2 to the amine solution using available speciation techniques. As for amine protonation the study can be completed by measurements of enthalpies of carbamate formation using mixing calorimetry. Then it appears that to develop thermodynamic models for CO_2 dissolution in aqueous solution of amine, there is a real need of accurate experimental data for enthalpies of solution, enthalpy of amine protonation as well as for enthalpy of carbamate formation.

14.5 Calorimetric Studies of CO_2 Dissolution in Amine Solutions

14.5.1 Calorimetric Techniques for Measuring Heat of Mixing

The calorimetric techniques for measuring heats of mixing two fluids can be classified into their mode of measurement and their principle of heat detection. The isothermal displacement calorimetry will refer to a “static” mode and flow calorimetry, to a “dynamic mode”. The principles of heat detection in the following examples will be power compensation or heat flux determination.

Isothermal Displacement Calorimeter

The technique used by Carson et al. [19] at University of Canterbur (New Zealand) is a modification of the liquid–liquid isothermal displacement calorimeter originally developed by Stokes et al. [69]. This static technique has then been primarily used to study binary liquid mixtures. The technique consists in filling a calorimetric cell with a known amount of one of the liquids (solvent) and injecting the solute from a burette. The injection is performed after reaching thermal equilibrium in the calorimetric cell. As reaction occurs, the temperature change is compensated in order to maintain the calorimeter to its initial temperature. Heat of mixing can be determined at temperatures range from 298 to 313 K and pressures comprised between 0.1 and 0.3 MPa.

In order to make it possible the determination of enthalpies of solution of gases in organic liquid solvents, Battino and Marsh [70] set up a modified burette arrangement. This modified technique proved to be effective for the particular systems where small gas solubilities are observed. However the technique was impractical in the case of CO_2 dissolution in aqueous solution of amine. This was mainly due to high solubility of carbon dioxide and consequently, large volumes of injected gas. Then Carson

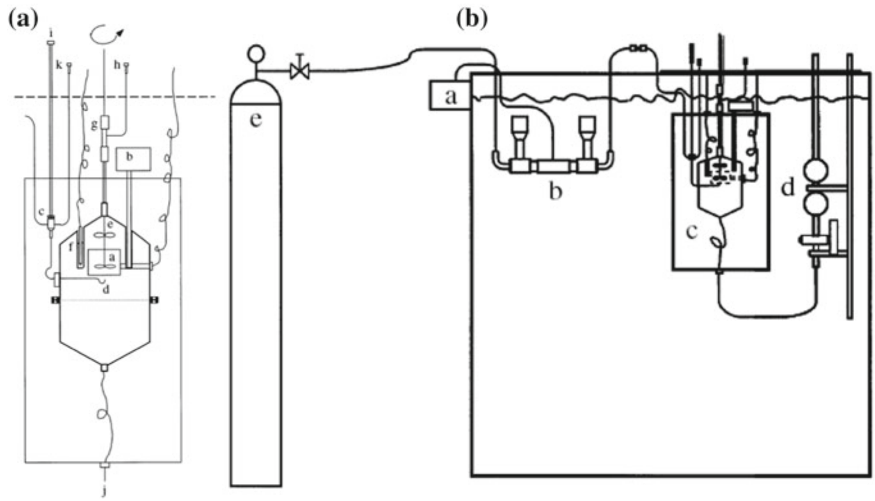


Fig. 14.2 Schematic representation of **a** classical displacement calorimeters [69]. (*a* annular heater; *b* Peltier cooling unit; *c* inlet valve; *d* injection tube; *e* stirrer; *f* thermistor; *g* stirrer gland; *h* solution outlet; *i* inlet valve control; *j* outlet to pipette; *k* by-pass outlet.) and of **b** modified calorimeter [19] (*a* pressure transducer; *b* gas injection device; *c* calorimeter; *d* pipette; *e* carbon dioxide reservoir tank)

et al. [19] carried out the last modifications of this technique. A special gas injection device constructed from stainless steel was used in place of the former burette. The mole number of gas introduced into the cell is calculated from the pressure changes after gas injection at known temperature. The exothermic effect when mixing CO_2 and amine solution is measured after successive injections of CO_2. The schematic representation of the experiment is shown Fig. a,b.

Kim and Svendsen [18] at Norwegian University of Science and Technology choose a similar technique for measuring heat of mixing of CO_2 in amine solutions. The main difference with Carson et al. modified calorimeter [19] results in a larger range of experimental temperatures (253–473 K) and pressures (up to 10 MPa) that can be investigated. Their experimental procedure (Fig. 14.3) consists as previously in multiple successive injections of CO_2 up to reach a CO_2 pressure in the gas reservoir tank close to pressure in the calorimeter vessel.

Isothermal Compensation Flow Calorimeter

This dynamic technique used by Oscarson and co-workers [21] at Brigham Young University (USA) to study CO_2 capture studies was developed in same University by Christensen and coworkers [71]. The principle of isothermal compensation calorimeter is based on the measurement of an external heat power used to maintain a reaction vessel at constant temperature during mixing. In flow mode the fluids flow to the

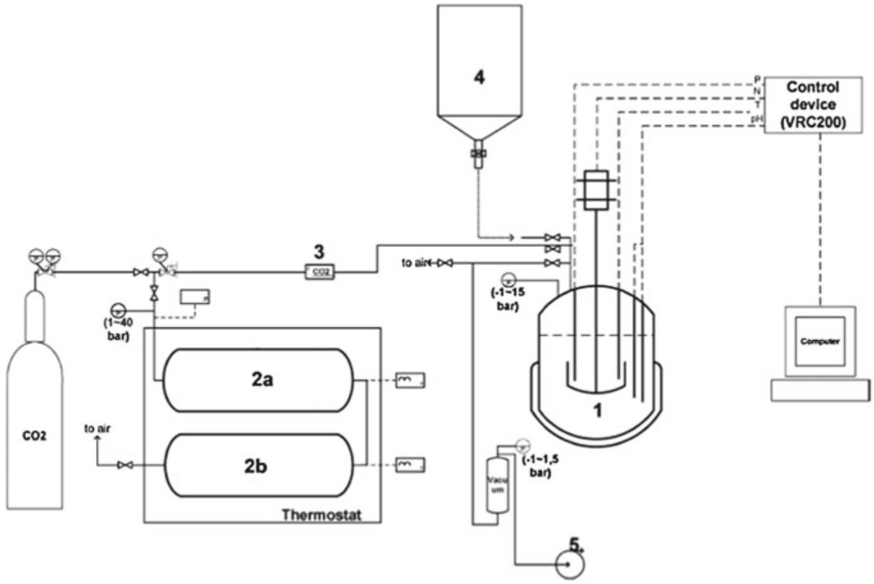


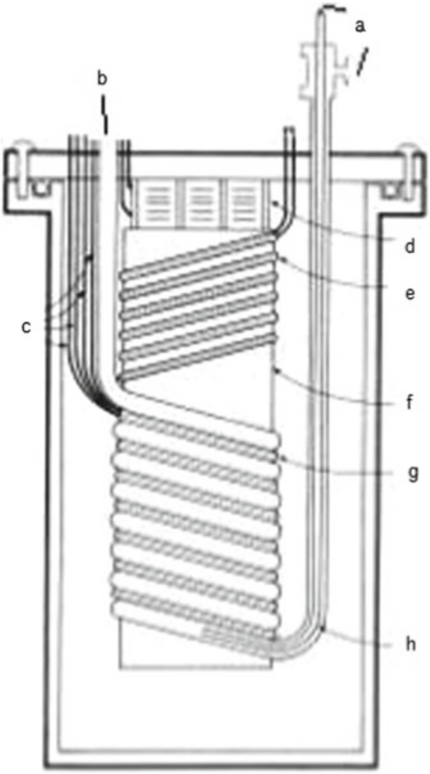
Fig. 14.3 Experimental setup of Kim and Svendsen [18] calorimeter. *1* reaction calorimeter (2000cm^3); *2a*, *2b* CO_2 reservoir tanks; *3* CO_2 mass flow controller; *4* amine solution feed bottle; *5* vacuum pump

reaction vessel where they mix. Different types of reaction vessel were proposed as for example that one described by Ott et al. [72] and represented in Fig. 14.4. In this example heaters and mixing tube are wound around and vacuum silver braised to a nickel plate cylinder. The mixing tube is made of hastelloy. Two concentric tubes drive the fluids to the mixing point located at the bottom of the cylinder. The energy generated by the reaction is balanced by adjusting the heater or the Peltier cooler device. Hence the change in heater or cooler power is proportional to the enthalpy change in the calorimeter. The two solutes are injected at defined flow rates by used of two syringe pumps. The pressure is maintained constant using a back pressure regulator. This kind of calorimetric technique can be be adapted to be used at temperature from ambient up to 473 K and at pressures up to 20 MPa.

Heat Conduction Differential Flow Calorimeter

This dynamic technique was initially developed by Mathonat and coworkers at University of Clermont-Ferrand (France). It is a flow technique where the heat of mixing is measured in a mixing cell located inside a Calvet type calorimeter (Fig. 14.5a). The Calvet sensors are a thermopiles constituted of thermocouples surrounding the mixing cell and measuring the heat power exchanged with a thermostated calorimetric block. The mixing cell represented in Fig. 14.5b consists of an hastelloy tube

Fig. 14.4 Schematic representation of a reaction vessel [72] of isothermal compensation flow calorimeter. *a* inlets; *b* outlet; *c* electrical leads; *d* Peltier cooler; *e* controlled heater; *f* isothermal cylinder; *g* calibration heater; *h* inside tube



tightly coiled inside a metallic confinement cylinder which fits into the well surrounded by the thermopile detector. For measuring the heat of dissolution of carbon dioxide in an absorbent solution, the fluids are injected at constant flow rates by used of high pressure syringe pumps. The temperature of the fluids to be mixed is controlled by pre-heaters positioned on the incoming tubes before the mixing point.

The fluids encounter following two different mixing technologies schematically represented in Fig. 14.5-c. The first one developed by Mathonat et al. [15] consists in flowing the fluids to be mixed into two concentric tubes; the fluids meet where the thinner tube ends. The second one presented by Arcis et al. [16, 17, 73] consists in two parallel hastelloy tubes silver welded on a T type brass piece represented in Fig. 14.5-c. Experiments are carried out at constant pressure range from 0.1–40 MPa. The temperature of experiment will depend on the calorimeter. Using a commercial Calvet type calorimeters from Setaram, this technique permits measurements from 200 to 573 K.

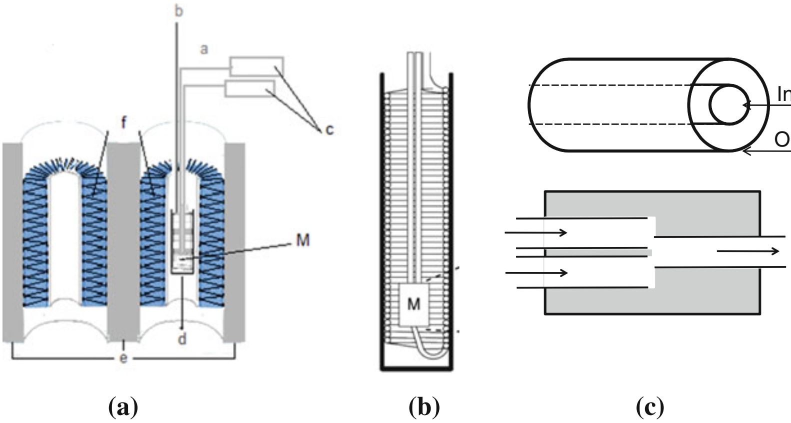


Fig. 14.5 Schematic view of the thermopiles **a**, mixing cell **b**, and mixing points **c** in the Setaram C80 or BT2.15 calorimeters *a* inlets; *b* outlet; *c* syringe pumps; *d* mixing cell; *e* thermostated calorimetric bloc; *f* thermopiles; *M* mixing point

14.5.2 Calorimetric Investigations

The experimental protocol for measuring heat of mixing of gas in liquid absorbent will depend on the chosen technique.

The static technique will consist in additions of known amount of gas in a cell containing the absorbent solution. The heat of mixing is obtained by integration of a peak corresponding to the heat power signal recorded as a function of time during gas dissolution. The end of dissolution is considered as reached when the heat power signal returns to baseline state. In the approximation of small gas addition, the heats of mixing expressed per mole of CO_2 can be assumed to be equal to differential enthalpies of solution H_{diff}. Carson et al [19] measured the enthalpy of solution of CO_2 in aqueous solutions of monoethanolamine (MEA) and methyl diethanolamine (MDEA) at 298.15 K. The experiments were carried out at atmospheric pressure for small CO_2 loading charges. In these conditions the gas is assumed to be totally dissolved in amine solution and no vapor phase was considerate. The method is particularly appropriate for the determination of enthalpy of solution at infinite dilution at atmospheric pressure. The uncertainty is estimated by the authors to $\pm 2\,\text{kJ} \cdot \text{mol}^{-1}$. The results represented in Fig. 14.6 show that the enthalpy of solution is almost constant down to $\alpha = 0.05$ and then decreases.

Kim and Svendsen determined the enthalpy of solution of MEA for higher CO_2 loading charges α (Fig. 14.7). The maximum loading charge reported in this work is close to 0.8. The uncertainty on enthalpy of solution is estimated to 2.2 %. It is observed that for loading charge below 0.5 the enthalpy of solution is more or less constant. It is usually admitted that the enthalpy derived from the plateau (Fig. 14.7) corresponds to an enthalpy of solution at infinite dilution. However this behavior must be confirmed by measurements in the domain of small loading charges to con-

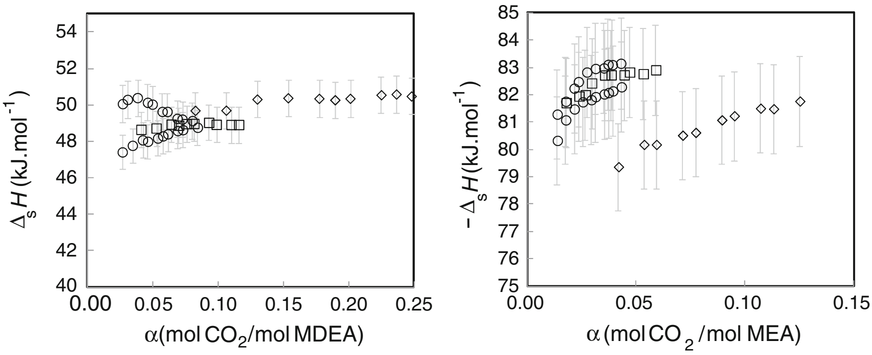


Fig. 14.6 Enthalpy of solution of CO_2 in aqueous solutions of monoethanolamine (MEA) and methyl di-ethanolamine (MDEA) at low loading charges using an isothermal displacement calorimeter [19]. Mass fractions of amine solutions ◇ 0.1, □ 0.2, ∘ 0.3

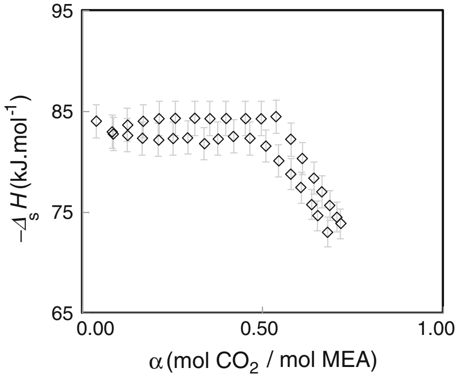


Fig. 14.7 Enthalpy of solution at 313.15 K and 0.3 MPa of CO_2 in aqueous solutions of monoethanolamine (MEA) at mass fraction 0.3, using static technique [18] on a wide range of loading charges α

firm the enthalpy decrease observed by Carson et al. [19]. This domain is particularly difficult to investigate due to problems of detection of small heat effects. The curve representing the enthalpy of solution in Fig. 14.7 shows a split at loading charge $\alpha = 0.5$. As the monoethanolamine (MEA) is a primary amine that forms carbamate with CO_2, the stoechiometric limit of gas absorption should be 0.5. However, when adding more gas, it was observed that the reaction of carbamate formation is displaced to release the amine. Then dissolution of CO_2 can continue with formation of carbonate as it is shown by the speciation curve in Fig. 14.9, representing the solution composition as function of loading charge. The change in the chemical mechanism of CO_2 absorption will modify the enthalpy of solution after loading charge 0.5 (Fig. 14.7).

Using flow techniques (or dynamic technique), the gas and the absorbent solution flow separately in narrow tubes to a mixing point. Then the mixture flows in a common mixing tube located in the sensible part of the calorimeter. The heat power due to gas dissolution is then detected along the mixing tube, by a thermopile in Calvet

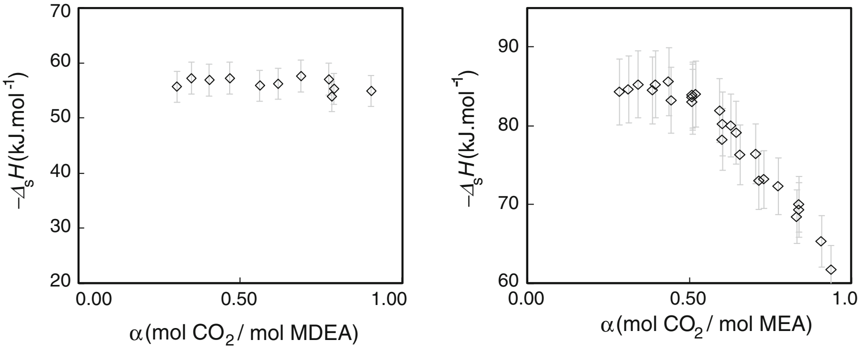


Fig. 14.8 Enthalpy of solution of CO_2 in aqueous solution of MDEA and MEA using dynamic techniques. Results for amine solutions at mass fraction of 0.30, at temperature 322.5 K and pressure 5.17 MPa [41, 74]

type calorimeter or by a compensation heat power in Picker type calorimeter. The enthalpy of solution per mole of CO_2 is obtained by dividing the heat power by the gas molar flow rate. This enthalpy of solution determined here is an integral enthalpy of solution $\Delta_s H$, related to the differential enthalpy following Eq. 14.5

$$\Delta_s H = \frac{1}{\alpha} \int_0^\alpha H_{diff} d\alpha. \tag{14.5}$$

Special care is required with dynamic technique to adjust the fluid flow rates to the kinetic of dissolution. The residence time of mixture in the sensible zone of the calorimeter must be long enough in order to reach total dissolution. The volumetric fluid flow rates are usually comprised between 0.05 and $1 \mathrm{mL} \cdot \mathrm{min}^{-1}$. The heats of mixing are measured at variable loading charges by changing fluid (gas/absorbent) flow rates ratios. The experiments are carried out increasing loading charge α up to the saturation of the absorbent solution. Investigation can be carried out at elevated pressure where physical dissolution can be observed.

The graphs reported in Fig. 14.8 represent enthalpy of solution as function of loading charge determined using fluxmetric detection; the graphs obtained with compensation detection will be similar. As initially mentioned, the enthalpies remain nearly constant in the domain of the low loading charges before decreasing when increasing loading charges. With monoethanolamine (MEA), the decrease of the enthalpy of solution starts at loading charge 0.5 corresponding to the change of chemical mechanism of absorption (Fig. 14.9). The speciation in the liquid can be estimated from thermodynamic model (Fig. 14.9). It indicates that significant physical dissolution starts for loading charge about 0.75. This is revealed by the presence of molecular CO_2 in the solution. Then enthalpy decrease is also physical dissolution of CO_2; the energy of dissolution associated to physical mechanisms is lower than the energy of chemical dissolution. On the graph representing the enthalpy of solution of CO_2 in

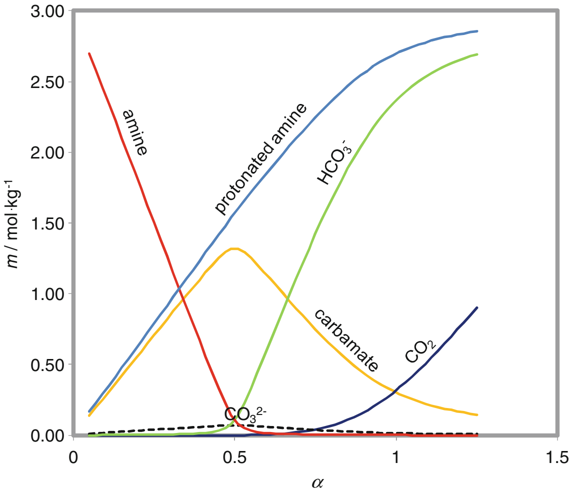


Fig. 14.9 Speciation in aqueous solution of MEA (3.00 mol · kg^{-1}) as function of CO_2 loading charge. Value calculated at 313.15 K using thermodynamic model [75]

MDEA solution, the enthalpy decrease starts at loading charge about 0.9. The MDEA is a tertiary amine and then does not form carbonate. The chemical mechanism of CO_2 absorption corresponds only to formation of carbonate. However the enthalpy of solution decreases at loading charge about 0.9. This phenomena is observed because of one part of CO_2 is physically dissolved.

The thermodynamic models developed to represent rigorously CO_2 dissolution in aqueous solution of amine consider all possible chemical reactions. Then the system is complex and numerous interaction parameters, molecule-molecule, ion-ion and molecule-ion, have to be defined. These models correlate vapor liquid equilibria data and are used to predict carbon dioxide solubility as a function of its partial pressure in the gas phase, temperature and amine concentration of the absorbent solution. In addition the models can give a detailed composition of solution as function of loading charge α as presented in Fig. 14.9. The model then predicts if gas dissolution leads to formation of hydrogenocarbonates or carbamates but experimental data of the real speciation are very scarce to validate those results. However as the energy of carbamate or carbonate reaction are different, the enthalpy data can provide some indications on the nature of the compounds produced by reaction of CO_2 with the amine. For this purpose thermodynamic models are developed to decompose the total enthalpy of solution into contribution terms associated to the formation of all the different species in solution, such as protonated amine, carbonate, bicarbonate or carbamate. Example of calculation of enthalpy contribution terms is given in Fig. 14.10 for the dissolution at 313.15 K of CO_2 in aqueous solution of MEA of composition 3.00 mol · kg^{-1}. The comparison between the enthalpy of solution obtained by summing the contribution terms and experimental data can then be used to validate the model.

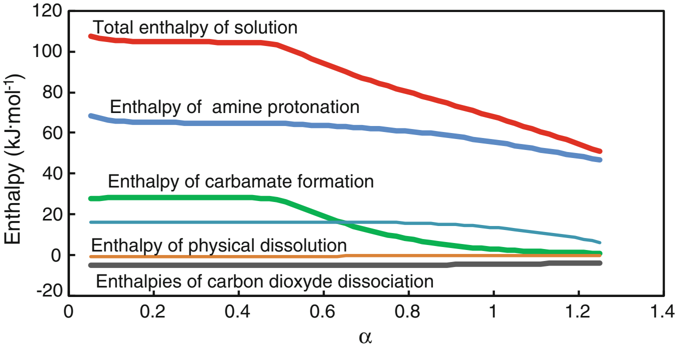


Fig. 14.10 calculated enthalpy contribution at 313.15 K for CO_2 dissolution in aqueous solution of MEA 3.00 mol · kg^{-1} as function of loading charge

Other interest of flow techniques is the short time required to obtained enthalpy of solution at given loading charge α, usually about 30 min. It is then not so much time consuming to investigate a large domain of loading charge, covering the domain of total and partial dissolutions of the CO_2 gas flux. In this way the flow techniques allow a simultaneous determination of the gas solubility at given temperature pressure and absorbent composition. For this purpose the enthalpies are expressed as energy per mole of amine and represented as function of loading charge. The graphic representation then makes it possible to identify the domains of total and partial CO_2 dissolutions. In the domain where the solution is unsaturated (all injected CO_2 is dissolved), the enthalpies expressed per mol of amine (Figs. 14.11 and 14.12) increase with gas loading charge. Over passing the loading charge corresponding to the limit of solubility, the additional CO_2 injected remains in vapor phase and the enthalpy per mole amine remains constant. It corresponds to the apparition of a plateau as showed in Fig. 14.11. The loading charge at the limit of gas solubility corresponds to the point where the plateau is reached. If the mechanism of dissolution is chemical reaction, the increase of enthalpy is almost linear and the intersection between the unsaturated and saturated domain is easily determined (Fig. 14.11-I). This determination is somewhere more difficult when physical mechanism is involved as the enthalpy slope decreases slowly before reaching the plateau (Fig. 14.11-II). In the case of primary amine as MEA (Fig. 14.12) a change in enthalpy slope is observed at loading charge $\alpha = 0.5$, due to the formation of a carbamate and only the points above $\alpha = 0.5$ must be considered to determine the linear part of the unsaturated domain that will cross the plateau. The uncertainties on the value of gas solubility are obviously more important than those obtained from direct *pVT* techniques. However it represents a simple and easy method for acquisition of solubility data at elevated pressures and temperatures. In addition the comparison of solubility obtained by mixing calorimetry with reference values obtained from *pVT* techniques will confirm that good mixing and total gas dissolution is achieved in the mixing cell.

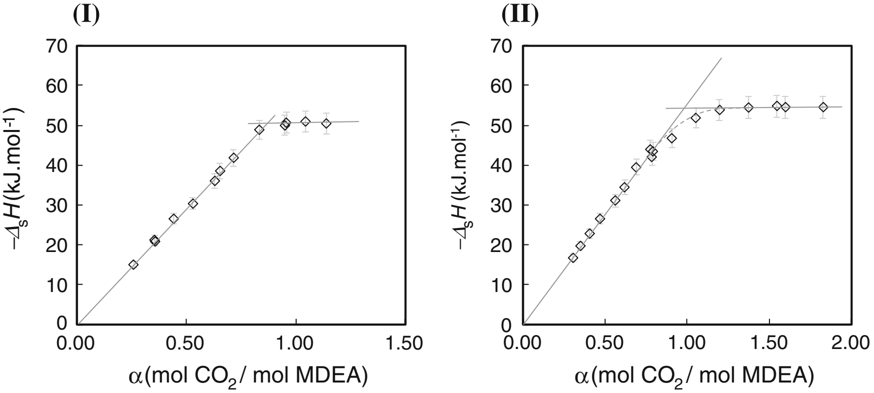


Fig. 14.11 Enthalpy of solution of CO_2 expressed as energy per mole of amine as function of loading charge. Case of gas dissolution at 322 K in aqueous solution of (I) MDEA 30 wt%, p = 0.5 MPa and (II) MDEA 30 wt%, p = 5.17 MPa

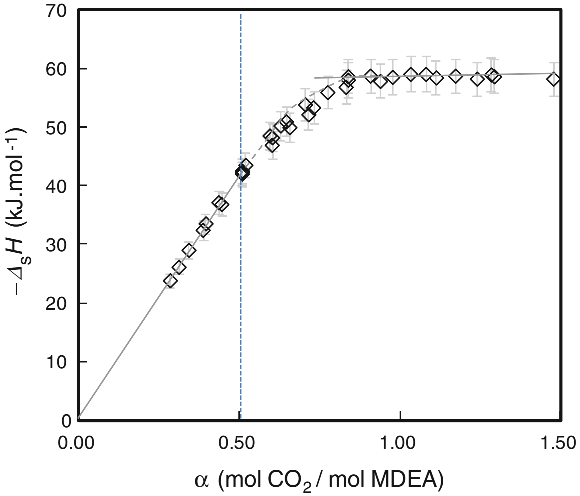


Fig. 14.12 Enthalpy of solution of CO_2 expressed as energy per mole of amine as function of loading charge. Case of gas dissolution in aqueous solution of MEA 30 wt% at 322 K and $p = 5$ MPa

14.6 Conclusion

The environmental impact of CO_2 must be considered and it is urgent to reduce its anthropogenic emission. Solutions have to be proposed for near future. One option is a decarbonation of post combustion effluents. Design and development of future industrial process for CO_2 separation from fumes will require studies of gas dissolution in various selective absorbent solutions.

Aqueous solutions of amine are considered as promising solvent but the selection of the best adapted molecule is still open. Then important experimental work will be necessary to characterize and test the dissolution of carbon dioxide. In this domain, determination of calorimetric properties such as enthalpy of solution of carbon dioxide in absorbent solutions will be essential. The enthalpies of solution are particularly important for the estimation of the energy required for the solvent regeneration step of an industrial process. For theoretical point of view, this thermodynamic property participates to the development of thermodynamic models representative of gas-absorbent systems. This chapter has focused on mixing calorimetric techniques used to investigate gas dissolution in liquid absorbents. The presented techniques can be adapted, in studies of CO_2 dissolution in aqueous solution of amines, to investigate for example each chemical reaction involved such as amine protonation or carbamate formation.

Symbols

wt %: mass percent composition
α: gas loading charge (mole of gas / moles of absorbent)
ASD: average standard deviation
$\Delta_s H$: integral enthalpy of solution
H_{diff}: differential enthalpy of solution
MEA: mono-ethanolamine
DEA: di-ethanolamine
AMP: 2-Amino-2-methyl-1-propanol
MDEA: methyl di-ethanolamine

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