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CARBON DIOXIDE ABSORPTION BY MEA
A preliminary evaluation of a bubbling column reactor

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Biogas generally contains significant quantities of carbon dioxide in addition to methane. A bubbling column reactor operating at atmospheric pressure is proposed for cheap separation and a Mettler RC1 reaction calorimeter was used to build a simplified empirical model for measuring the molar heat of solubility of CO_2 in aqueous solutions of monoethanolamine (MEA). Determinations were performed in 12 mass% MEA solutions regenerated at atmospheric pressure and reflux temperature for 3 h. Flows of CO_2 from 174 to 917 mL min^{-1} were used at a reactor temperature of 283 to 353 K.

Keywords: *absorption, biogas, carbon dioxide, monoethanolamine*

Introduction

Biogas production is a promising means of achieving multiple environmental benefits and producing an energy carrier from renewable resources. Replacing fossil fuels with biogas normally reduces the emission not only of greenhouse gases, but also of nitrogen oxides, hydrocarbons, and particles [1]. Biogas typically consists of 60% methane and 40% CO_2 with up to 1% H_2S [2]. It has been demonstrated that the biogas-based fuel cell power plant with PAFC and SOFC is a technically feasible option for power generation [3, 4]. To improve the efficiency and life time of biogas-based fuel cell power plants it is necessary to remove CO_2 by the 'cheapest' available technology. At the present time, absorption of CO_2 and/or H_2S or 'acid gases' into alkanolamines (i.c. MEA) is of significant industrial importance. This technique is generally applied during natural gas sweetening to meet pipeline standards as well as in the removal of CO_2 from flue gases of power plants [5] and other industrial plants for environmental reasons [6]; a pressure rise of 0.4–4.0 MPa is used to minimize the plant volume. Usually, in fact, a high pressure 'scrubber' is employed industrially for the separation and a system operating at atmospheric pressure is considered less convenient. On the other hand, if we use a low cost raw material (i.e. biogas), 'bubbling' technology can be cheaper. No data on this system are available in the literature. In the past, direct calorimetric data were not available and the enthalpy of absorption of CO_2 in MEA solutions was obtained from solubility measurements with fairly low accuracy (±20%) [7]. More recently, Mathonat *et al.* [8] have obtained highly accurate and reproducible values using a differential heat conduction calorimeter with a flow mixing unit. However, the data refer to microcalorimetric measurements in experimental conditions of flow greatly different from current industrial practice. No calorimetric measurements are known which do simulate the absorption process in a bubbling column reactor operating at atmospheric pressure that can be economically advantageous for biogas purification [9]. Consequently, a preliminary study on the interaction between CO_2 and MEA at atmospheric pressure has now been carried out using a reaction calorimeter.

Theoretical model

The stoichiometry of absorption of CO_2 in MEA is described by the following reaction sequence [5, 8]:

$$2CO_2+2EtONH_2 \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} 2EtONH_2^+COO^- \qquad (1)$$

$$EtONH_2^+COO^-+B \underset{k_b}{\overset{k_{-b}}{\leftrightarrows}} EtONHCOO^-+BH^+ \qquad (2)$$

$$\begin{gathered} EtONH_2^+COO^-+EtONH_2 \rightarrow \\ EtONH_3^++EtONHCOO^- \end{gathered} \qquad (3)$$

$$EtONH_2^+COO^-+H_2O \rightarrow H_3O^++EtONHCOO^- \qquad (4)$$

The reaction between CO_2 and MEA solutions has been described by zwitterion and termolecular mechanisms [5]. The former consists of the reaction of CO_2 with primary amines such as MEA to form a zwitterion intermediate ($EtONH_2^+COO^-$) followed by

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deprotonation by a base B to form a carbamate (EtONHCOO$^-$), where B corresponds to any species in solution that can abstract a proton from the zwitterion intermediate. The main contributions to deprotonation of Zwitterions in an aqueous solution of primary amines are from MEA, hydroxide (OH$^-$) and water [10–13]. The general rate of reaction of CO$_2$ with a primary amine solution such as MEA by the zwitterion mechanism, under loading absorption conditions, can be given by [12, 14, 15]:

$$-\frac{\mathrm{d[MEA]}}{\mathrm{d}t}=\frac{[\mathrm{CO_2}][\mathrm{MEA}]}{\dfrac{1}{k_{\mathrm{MEA}}}+\dfrac{k_{-1}}{k_{\mathrm{MEA}}\sum k_{\mathrm{b}}[\mathrm{B}]}} \tag{5}$$

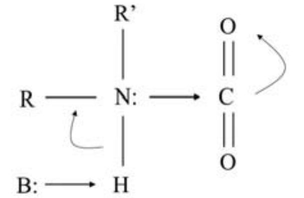

Fig. 1 Single-step termolecular reaction mechanism for carbamate formation [16]

On the other hand, the termolecular mechanism assumes that the reaction takes place in a single step, where the initial product is not a zwitterion but a loosely bound encounter complex, as shown in Fig. 1. Versteeg *et al.* [15] and Crooks and Donnellan [16] presented the forward reaction rate for this mechanism by the following equation:

$$-\frac{\mathrm{d[MEA]}}{\mathrm{d}t}= =(k_{\mathrm{H_2O}}[\mathrm{H_2O}]+k_{\mathrm{MEA}}[\mathrm{MEA}])[\mathrm{MEA}][\mathrm{CO_2}] \tag{6}$$

The simplified empirical model used by us for the bubble reactor assumes that the reaction rate is directly proportional to the concentration of free MEA. Consequently:

$$-\frac{\mathrm{d[MEA]}}{\mathrm{d}t}=(k^{\mathrm{I}}F_{\mathrm{CO_2}}+k^{\mathrm{II}}T_{\mathrm{r}}+k^{\mathrm{III}})[\mathrm{MEA}] \tag{7}$$

where k^{I}, k^{II} and k^{III} are instrumental constants, which are a function of the geometry of the systems and of the calorimeter used. Integrating Eq. (7) over time and assuming that for each mole of MEA reacted $\Delta H^*_{\mathrm{MEA}}$ is generated in conditions of excess CO$_2$, we obtain:

$$-\Delta H_{\mathrm{MEA}}=[1-\mathrm{e}^{-(\mathrm{k^IF_{CO_2}}+\mathrm{k^{II}T_r}+\mathrm{k^{III}})\,\mathrm{t}}]\Delta H^*_{\mathrm{MEA}} \tag{8}$$

for the heat evolved at time *t*. In this expression $\Delta H^*_{\mathrm{MEA}}$ is also a linear function of temperature:

$$\Delta H^*_{\mathrm{MEA}}=k^{\mathrm{IV}}T_{\mathrm{r}}+k^{\mathrm{V}} \tag{9}$$

Using a differential heat conduction calorimeter Mathonat *et al.* [8] have proposed various procedures for extrapolation of the molar heat of solubility of CO$_2$ in excess MEA ($\Delta H^*_{\mathrm{MEA}}$). In particular, $\Delta H^*_{\mathrm{MEA}}$ can be derived (imposing $\alpha\to\infty$) considering the relationship between the measured molar enthalpies and related CO$_2$ loading (α):

$$\alpha=\frac{F_{\mathrm{CO_2}}t}{24500\mathrm{MEA_0}}=\frac{F_{\mathrm{CO_2}}t}{73500} \tag{10}$$

This method, also proposed by other authors [17–19], has also been used in this study for evaluation of the results gathered from a Mettler RC1 reaction calorimeter and has allowed the determination of the five constants of the semi-empirical model, namely:

$k^{\mathrm{I}}=2.81\cdot10^{-5}\pm5.13\cdot10^{-7}$ mL^{-1}

$k^{\mathrm{II}}=3.00\cdot10^{-4}\pm8.40\cdot10^{-5}$ min^{-2}

$k^{\mathrm{III}}=-0.085\pm1.79\cdot10^{-3}$ min^{-1}

$k^{\mathrm{IV}}=0.66\pm1.72\cdot10^{-2}$ kJ mol^{-1} K^{-1}

$k^{\mathrm{V}}=-148.50\pm3.41$ kJ mol^{-1}

Experimental

The measurements were performed at atmospheric pressure using a reaction calorimeter Mettler Mod. RC1, equipped with a 2 L glass reactor mod. AP01. The RC1 works according to the heat flow rate principle resumed by Nomen *et al.* [20]. Following Cavallaro [21] the heat flow of reaction (Q_{r}) was calculated accounting for all contributions, such as the experimental value, the sensible heat accumulated and the additional values resulting from mixing and stirring of the reagents, together with the subtractive factor due to the instrumental losses. The differential thermal signal from heat-resistance inside the reactor is proportional to the heat effect measured and can be related to the amount of energy after electrical calibration. The process variables, i.e. inner temperature of the reactor (T_{r}), temperature of the heating jacket (T_{j}), stirring rate (R), etc., were monitored and acquired on-line through an IBM PS2/80 computer, in QNX language.

In order to enhance the reproducibility of the results, it would be useful to boil distilled water for at least 20 min in order to eliminate CO$_2$ residues before adding MEA. The immediate use of a fresh solution (12 mass%) guarantees maximum absorption capacity and heat evolution. As fresh solutions are not used industrially, absorption experiments have been carried out using recycled solutions saturated with CO$_2$ from the previous run. Before each run, the exhausted solution of MEA was heated at 374 K (reflux temperature) for 180 min and then cooled down to reaction temperature T_r. Anyhow, for comparison some runs were also carried out using freshly prepared CO_2-free solutions. Two electrical calibrations before and after the reaction were used to estimate the product *UA* of the overall heat transfer coefficient *U* and heat exchange area *A*. Pure CO_2 was supplied to the system by a flow-meter. During each test-run, six moles of CO_2 (twice the mole content of MEA in aqueous solution) were bubbled. The stirrer rate *R* was set at 300 rpm.

Results and discussion

In order to minimize handling of the solutions, all runs were carried out in situ in the same water–MEA 12 mass% solution regenerated each time. Figure 2 compares experimental runs carried out at baseline conditions (T_r=303 K, F_{CO_2}= 522 mL min^{-1}) with fresh and recycled solutions and shows a net difference in the heat evolved after boiling for 180 min and the first run; the heat flow of the fresh solution is always higher than after subsequent desorption of CO_2. Moreover, the figure indicates the high reproducibility of the experiments with recycled MEA and denotes the feasibility of an industrial bubbling process. The time integrals of the various curves, which represent the maximum heat evolved, show that about 70% of the initial amine is recyclable whereas the remaining fraction is neutralized irreversibly after the first absorption process. Figure 2 also shows rapid heat evolution (Q_r) obtained with the decarbonated solution, followed by asymptotic slowdown of the kinetics and nihil heat evolution at saturation. Figure 3 shows Q_r as a function of CO_2 flow. Taking into account heat losses and thermal effects not inherent to the reaction the experimental data have been evaluated according to the mathematical model of the experimental part. As a result, Fig. 4 shows maximum values of Q_r at different times depending upon the CO_2 flow; in particular at high F_{CO_2} values, Q_r is maximum for short reaction times. This can be attributed to the inverse dependence of contact time between CO_2 and MEA with respect to F_{CO_2}. At variance to the differential heat conduction calorimeter [8], use of the present method does not allow to determine the discontinuity of $-\Delta H_{MEA}$ which identifies the solubility of CO_2 in MEA very accurately as each data point is obtained by an independent

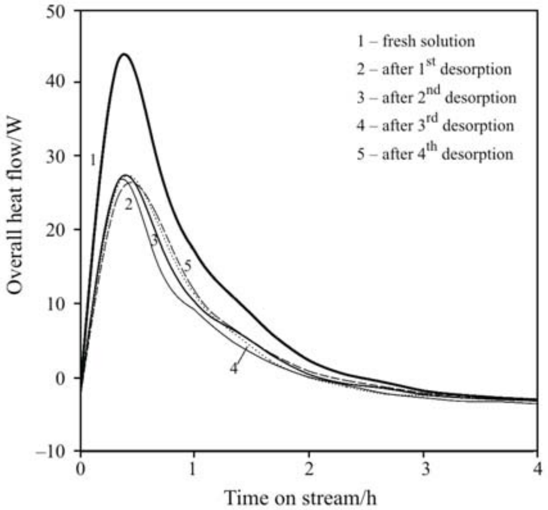

Fig. 2 Heat flow (W) *vs.* time on stream (h) for absorption of CO_2 in fresh and recycled aqueous solutions of 12 mass% MEA. Reaction conditions: T_r=303 K, p_r=0.1013 MPa and F_{CO_2}=522 mL min^{-1}

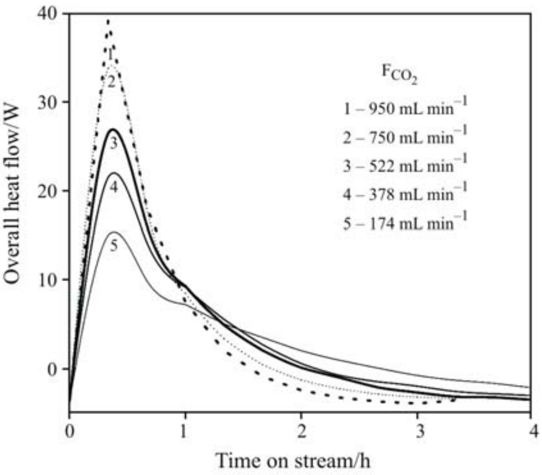

Fig. 3 Heat flow (W) at different flows of CO_2 between 174–917 mL min^{-1} *vs.* time on stream (h) for absorption of CO_2 in aqueous solutions of 12 mass% MEA at T_r=303 K and p_r=0.1013 MPa

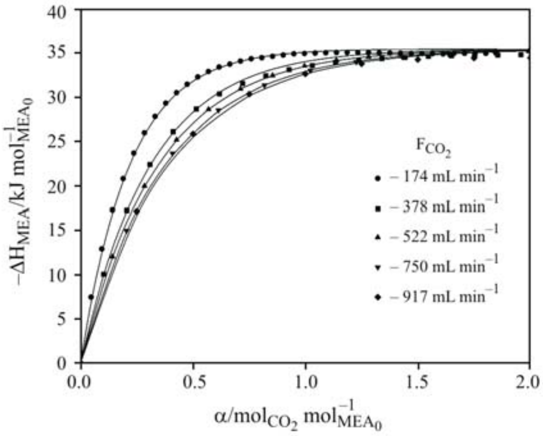

Fig. 4 Measured enthalpies, $-\Delta H_{MEA}$ (kJ $mol^{-1}_{MEA_0}$) at CO_2 flows of 174 to 917 mL min^{-1} *vs.* CO_2 loading, α (mol CO_2 $mol^{-1}_{MEA_0}$) for absorption of CO_2 in aqueous solutions of 12 mass% MEA at T_r=303 K and p_r=0.1013 MPa. Continuous lines and dots represent theoretical and experimental values of kJ $mol^{-1}_{MEA_0}$, respectively

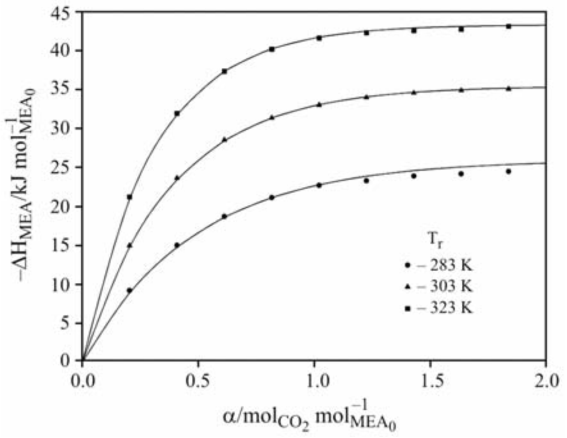

Fig. 5 Measured enthalpies $-\Delta H_{MEA}$ (kJ $mol^{-1}_{MEA_0}$) at absorption temperatures of 283 to 323 K *vs*. CO_2 loading (α, mol CO_2 $mol^{-1}_{MEA_0}$) for absorption of CO_2 in aqueous solutions of 12 mass% MEA at F_{CO_2}=522 mL min^{-1} and p_r=0.1013 MPa. Continuous lines and dots represent theoretical values and experimental values of kJ $mol^{-1}_{MEA_0}$, respectively

measurement. Theoretical fitting of the continuous experimental data points of Fig. 4 allows to estimate the error in the constants k^I, k^{II} and k^{III} of Eq. (8) as ±3%. The same precision was derived for k^{IV} and k^V by fitting of ΔH^*_{MEA} as $f(\alpha)$ at various temperatures (Fig. 5). The experimental method used (bubbling of CO_2 in MEA solutions) does not allow to operate at constant CO_2 and MEA=$f(t)$; consequently, plots of ΔH_{CO_2} as $f(\beta)$ cannot be obtained in the same way. Use of the RC1 calorimeter, even though not improving the great precision and accuracy of the microcalorimetric data [8], more closely reflects the conditions in bubbling experiments and provides useful indications for the design of an industrial separation plant. Approximate $\Delta H^*_{CO_2}$ values may be derived from ΔH^*_{MEA} if we consider that $\Delta H^*_{CO_2}$ (for $\beta\rightarrow\infty$) is roughly equal to $3/2\Delta H^*_{MEA}$ (for $\alpha\rightarrow\infty$) [8]. Figure 6 shows the $\Delta H^*_{CO_2}$ values calculated on the basis of this assumption in comparison with literature data, which represent a reference in terms of precision. Although the data obtained with the Mettler RC1 calorimeter differ significantly from the microcalorimetric data obtained by Mathonat *et al*. [8], nevertheless the agreement is considered acceptable if we consider the different operating conditions (T_r, p_r) and assumptions and interpolations made. Anyhow, our approach is characterized by higher speed of measurement and closer affinity to the real operative conditions. Moreover, as recycled solutions have been used, $\Delta H^*_{CO_2}$ is lower than the values obtainable from fresh solutions, as used in case of the differential heat calorimeter experiments used elsewhere [8].

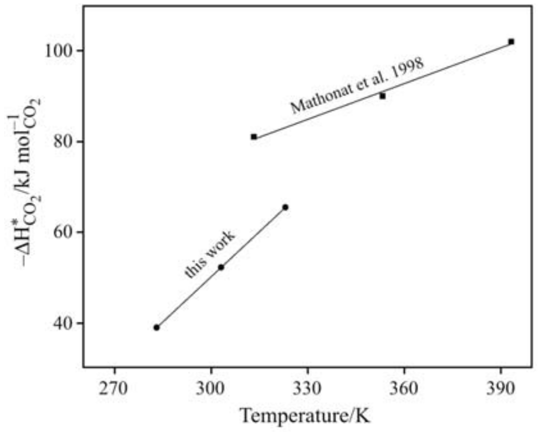

Fig. 6 Enthalpies of solution of CO_2 ($-\Delta H^*_{CO_2}$) in aqueous solutions of MEA (kJ $mol^{-1}_{CO_2}$) *vs*. absorption temperatures (K) for absorption of CO_2 in aqueous solutions of 12 mass% MEA at F_{CO_2}=522 mL min^{-1} and p_r=0.1013 MPa. ● – This work and ■ – Mathonat *et al*. [8]

Conclusions

A bubble reactor has been proposed for absorption of CO_2 in MEA solutions at atmospheric pressure for economic purification of biogas. The enthalpy of absorption of CO_2 in a 12 mass% aqueous solution of MEA has been measured for various temperatures and gas flows. Analysis of calorimetric data allows to draw the following conclusions:

- MEA solutions may be recycled, at 374 K for 3 h, even though this leads to a partial loss of absorbent power with respect to fresh solutions.
- A simplified semi-empirical model, first-order in MEA concentration, describes the absorption of CO_2 in MEA as a function of temperature, CO_2 flow and time.
- The value of $-\Delta H^*_{CO_2}$ increases linearly with temperature, in accordance with literature data [8]; however, because of the incomplete regeneration of MEA solutions the values of $-\Delta H^*_{CO_2}$ measured in this study are somewhat lower.

List of symbols and acronyms

A	heat exchange area, m^2
B	any basic species in the reaction solution
EtO^-	$CH_3CH_2O^-$
F_{CO_2}	flow of CO_2 inlet, mL min^{-1}
k_1	forward rate coefficient for reaction (1)
k_{-1}	backward rate coefficient for reaction (1)
k_b	forward rate coefficient for reaction (2)
k_{-b}	backward rate coefficient for reaction (2)
k^I	numerical constant in Eqs (8) and (9), mL^{-1}
k^{II}	numerical constant in Eqs (8) and (9), min^{-2}
k^{III}	numerical constant in Eqs (8) and (9), min^{-1}

k^{IV}	numerical constant in Eq. (10), kJ mol^{-1} K^{-1}
k^{V}	numerical constant in Eq. (10), kJ mol^{-1}
MEA	monoethanolamine
MEA_0	initial amount of MEA (i.e. 3 moles), moles
p_{r}	operating pressure
PAFC	phosphoric acid fuel cell
Q_{r}	heat flow of reaction, Watt
R	effective stirrer speed, rpm
SOFC	solid oxide fuel cell
t	time on stream, h
T_{j}	temperature of the heat exchange medium, K
T_{r}	temperature of the reaction mass, K
U	overall heat transfer coefficient, W m^{-2} K^{-1}
α	moles of CO_2 on initial amount of MEA (MEA_0), $\mathrm{mol}_{\mathrm{CO_2}}\ \mathrm{mol}^{-1}_{\mathrm{MEA}}$
β	moles of water plus monoethanolamine per moles of CO_2, $\mathrm{mol}_{\mathrm{H_2O+MEA}}\ \mathrm{mol}^{-1}_{\mathrm{CO_2}}$
$-\Delta H_{\mathrm{MEA}}$	mean evolving heat during the test , kJ $\mathrm{mol}^{-1}_{\mathrm{MEA_0}}$
$\Delta H^{*}_{\mathrm{MEA}}$	absorption heat per mol of MEA, kJ $\mathrm{mol}^{-1}_{\mathrm{MEA}}$
$\Delta H^{*}_{\mathrm{CO_2}}$	absorption heat per mol of CO_2, kJ $\mathrm{mol}^{-1}_{\mathrm{CO_2}}$

References

1 G. Lastella, C. Testa, G. Cornacchia, M. Notornicola, F. Voltasio and V. K. Sharma, Energy Conv. Managm., 43 (2002) 63.
2 P. Börjesson and M. Berglund, Biomass Bioenergy, 30 (2006) 469.
3 S. T. Naumann and C. Myrén, J. Power Sources, 56 (1995) 45.
4 J. Staniforth and K. Kendall, J. Power Sources, 71 (1998) 275.
5 A. Dallos, T. Altsach and L. Kotsis, J. Therm. Anal. Cal., 65 (2001) 419.
6 N. Ramachandran, A. Aboudheir, R. Idem and P. Tontiwachwuthikul, I&EC Res., 45 (2005) 2608.
7 J. I. Lee, F. D. Otto and A. E. Mather, Can. J. Chem. Eng., 52 (1974) 803.
8 C. Mathonat, V. Majer, A. E. Mather and J.-P. E. Grolier, I&EC Res., 37 (1998) 4136.
9 W.-R. Zhao, H.-X. Shi and D.-H. Wang, J. Zhejiang Univ. Sci., 5 (2004)714.
10 E. B. Rinker, S. S. Ashour, H.A. Al-Ghawas and O. C. Sandall, I&EC Res., 39 (2000) 4346.
11 C.-H. Liao and M. H. Li, Chem. Eng. Sci., 57 (2002) 4569.
12 P. M. Blauwhoff, G. F. Versteeg and W. M. van Swaaij, Chem. Eng. Sci., 39 (1984) 207.
13 G. F. Versteeg and W. P. M. van Swaaij, Chem. Eng. Sci., 43 (1988) 587.
14 D. A. Glasscock, J. E. Critchfield and G. T. Rochelle, Chem. Eng. Sci., 46 (1991) 2829.
15 G. F. Versteeg, A. J. Van Dijck and W. P. M. van Swaaij, Chem. Eng. Commun., 144 (1996) 113.
16 J. Crooks and J. P. Donnellan, J. Chem. Soc., Perkin Trans., 2 (1989) 331.
17 S. P. Christensen, J. J. Christensen and R. M. Izatt, Thermochim. Acta, 106 (1986) 241.
18 K. E. Merkley, J. J. Christensen and R. M. Izatt, Thermochim. Acta, 121 (1987) 437.
19 J. L. Oscarson, R. H. van Dam, J. J. Christensen and R. M. Izatt, Thermochim. Acta, 146 (1989) 107.
20 R. Nomen, J. Sempere and E. Serra, J. Thermal Anal., 49 (1997) 1707.
21 S. Cavallaro, J. Therm. Anal. Cal., 58 (1999) 3.

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