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Experimental Study and Modelling of Cyclopentane Hydrates in the presence of NaCl, KCl and a mixture of NaCl - KCl

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Abstract

Results from an experimental study of cyclopentane hydrate in the presence of NaCl (0 – 23% wt), KCl (0 - 20% wt) and an equi-mass mixture of NaCl-KCl (0 - 22% wt) following a quick and a slow dissociation procedures are reported. The results show that the equilibrium temperatures of cyclopentane hydrate dropped significantly with an increase in salt concentration. A temperature shift between the equilibrium temperatures following the quick and the slow procedure was also observed. Two thermodynamic approaches are then presented to predict the equilibrium temperatures. The predicted-equilibrium temperatures are in good agreement with the experimental ones.

Introduction

Clathrate hydrates, which we henceforth term hydrates, are crystalline solids composed of water and guest molecules [1]. In hydrates, cage-like structures formed by hydrogen-bonded water molecules enclose different guest molecules that stabilize the structures. The guest molecules can be small molecules such as CO₂, H₂, CH₄, C₂H₆, N₂ or relatively large molecules such as Cyclopentane, Neohexane, Dimethyl sulfide, Tetrahydrofuran (THF) or Tetra-n-butyl ammonium bromide (TBAB). Three different well-known hydrate structures are identified: Structure I, Structure II and Structure H. In the structure I, each unit cell has 46 water molecules generating 8 cavities, 2 small 5¹² cavities and 6 large-sized 5¹²6² cavities (*the polyhedra n^m has m faces containing n edges*). In the structure II, one unit cell contains 136 water forming 16 small 5¹² cavities and 8 large-sized 5¹²6⁴ cavities, while in the structure H, 34 water molecules creating 3 small 5¹² cages, 2 medium 4³5⁶6³ cages and 1 large 5¹²6⁸ cages [1].

Hydrates are mostly stable at low temperature and high pressure conditions which are similar to the deep-sea petroleum operation conditions (0 to 10 °C, tens to hundreds of bars). Hydrate formation can be an issue in the oil and gas industry where it can cause blockages in the oil and gas pipelines. It can lead to a damage instruments and environment [2], [3].

Besides this problem, hydrates have many potentially beneficial applications in natural gas storage [4], [5]; hydrogen storage [6]; carbon dioxide capture [7]; gas separation [8], [2]; refrigeration and cold thermal energy [9]–[11]. Desalination, or water treatment, is another interesting application. Because the hydrate formation process requires only pure water and guest molecules, hydrates are used to remove salt in laboratory procedures and also on an industrial scale [12], [13].

Hydrate formation generally occurs under high pressure when the guest molecules are gases such as CO₂, H₂, CH₄, C₂H₆, N₂ [1]. This is an undesirable condition on an industrial scale regarding material and instrument costs. It has been required to find the way to reduce the pressure of hydrate formation. Cyclopentane is a favorable hydrate former candidate due to its ability to form hydrate at atmospheric pressure [1], [14]. It is a liquid at ambient conditions and immiscible with water, therefore it can be recovered easily after a dissociation process.

Before considering cyclopentane hydrate in water treatment processes, more data in the presence of different salts are needed. Unfortunately, there are still few studies in the literature. Kishimoto et al. [15] performed some experiments in NaCl, while Zylyftari et al. [16] reported the effect of brine on the thermodynamic of hydrates.

Therefore, this study aims to investigate cyclopentane hydrate formation and dissociation processes. Two salts were considered, NaCl, and KCl, with a wide range of concentrations: NaCl (0 – 23% wt), KCl (0 – 20% wt) and an equi-mass mixture of NaCl-KCl (0 – 22% wt). Two procedures were applied to determine the equilibrium temperatures. One is at quick dissociation rate; another is at slow dissociation rate. The aim of the quick procedure is to provide an initial estimate of the equilibrium temperature. The slow procedure is then used to obtain more accurate data. Temperature and salt concentration were measured respectively using Pt100 probes, ionic

chromatography, and a drying oven. The time-temperature figures during formation and dissociation are generated. Two thermodynamic approaches are then used to predict the equilibrium temperatures.

Experimental part

Materials

Relevant physical properties of the materials used in this study are provided in Table 1. Ultrapure water is provided by Milli-Q® Advantage A10 Water Purification System. This system can produce water with conductivity $\sigma \leq 0.055 \mu\text{S}\cdot\text{cm}^{-1}$ and TOC (total organic carbon content) less than 5 ppm. Cyclopentane (98% pure), sodium chloride (99.5% pure) and potassium chloride (99.0% pure) are all supplied by Sigma-Aldrich.

Table 1: Materials physical properties

Material	Chemical formula	Density $\text{g}\cdot\text{cm}^{-3}$	Viscosity	Solubility in water	Purity	Manufacturer
Cyclopentane	C_5H_{10}	0.751 (25°C)	0.44 (20°C)	156 mg/l (25 °C)	95%	Sigma-Aldrich
Sodium chloride	NaCl	2.16 (25°C)	-	36.0 g/l (20°C)	99.5%	Sigma-Aldrich
Potassium chloride	KCl	1.98 (25°C)	-	344 g/l (20°C)	99.0%	Sigma-Aldrich
Water	H_2O	1.00 (4°C)	1.00 (20°C)	-	-	-

Experimental apparatus

The experimental apparatus installed to study the thermodynamic of cyclopentane hydrates is presented on Figure 1. The main device is a jacketed batch glass vessel (1) provided by Verre Equipments (France) with a volume of approximately one liter. The vessel is equipped with a double jacket in order to control temperature of the solution thanks to a chiller (2). This chiller (Ministat 240) supplied by Huber has an operating temperature from -45 °C to 200 °C with the temperature stability ± 0.02 °C. The coolant of the chiller is ethylene glycol 44% wt.

The solution inside the vessel is mixed by an impeller (3) powered by a motor (6). The temperature of the aqueous mixture is monitored by two temperature probes which are positioned inside the vessel and immersed partly in the solution. The data are then transferred to a computer thanks to a transmitter (7). A Labview software is also installed in order to observe the digital data throughout the experiment.

An ion chromatography (Dionex DX-500 IC) system (11) and a drying oven (Binder) (10) are also used to measure salt concentration of the liquid samples taken at the bottom of the vessel at the end of the hydrate dissociation.

Quick dissociation procedure

For each experiment, a solution containing 500g pure water and a certain amount of salt was prepared by mixing for 10min. The solution was then injected into the vessel, followed by cyclopentane with a theoretical stoichiometric composition (the molar ratio water/cyclopentane is 17).

The solution was agitated continuously throughout the experiment by an impeller at 300 – 400 rpm. For cooling down the solution, the cryostat was started at a set-point above the ice equilibrium temperature of the salt solution approximately 1-2 °C in order to ensure that no ice of salt solution is present in the solution. Once the temperature of solution reached a value close to the set-point, hydrate formation was initiated by injecting 2 - 3g of ice (made previously from deionized water), and an amount of salt to keep salt concentration of the solution constant. Visual observations were also performed by both naked eyes and a camera. After approximately 1-2 hours, when a sufficient amount of cyclopentane hydrate was observed, the cryostat was stopped. Cyclopentane hydrates then dissociate by consuming heat from the environment. As soon as cyclopentane hydrate could not be observed inside the vessel, the temperature of the solution increased suddenly, the equilibrium temperature corresponding with the salt concentration being studied was recorded. At this time, mixing was stopped in order to separate salt solution phase from cyclopentane phase. Two samples with 1 ml and 5 ml of salt solution were taken at the bottom of the vessel to measure salt concentration. The objective of this step is to verify the correctness of the recorded equilibrium temperature. If the beginning salt concentration before the experiment and the finishing salt

concentration at the end of the hydrate dissociation process are identical, the recorded equilibrium temperature is considered as a correct value following the quick dissociation.

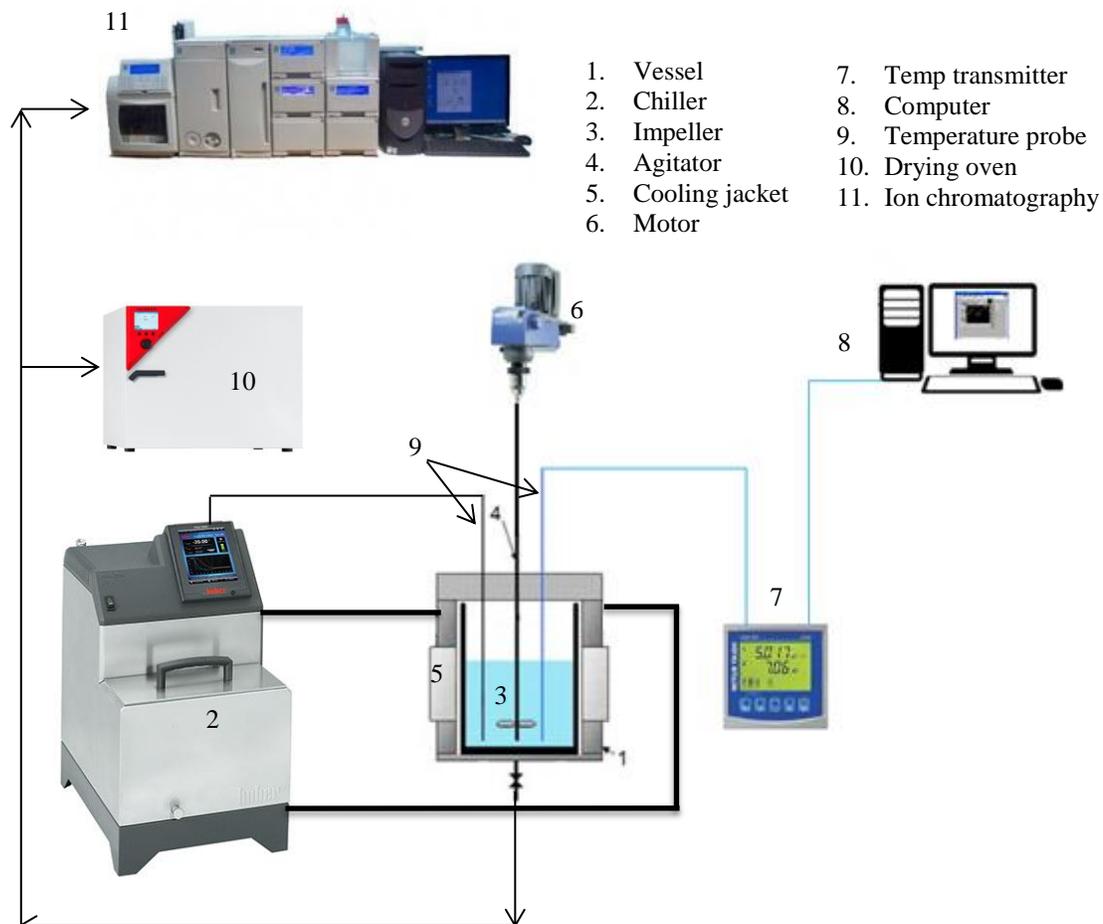


Figure 1: Simplified schematic diagram of the main experimental apparatus

Slow dissociation procedure

After each experiment following a quick procedure, another experiment following a slow procedure at the same salt concentration was performed. In the slow procedure, the main principles of process are almost the same. However, the hydrate dissociation process takes place in a different way. After a sufficient amount of hydrate formed in the vessel, the chiller was controlled manually according to a temperature program as follows: the temperature inside the vessel was increased with an increment of 0.1 °C instead of heating by environment as in a quick procedure. The temperature was then kept constant for at least 1 hour. If there was still hydrate to be observed within 1 hour, the temperature was increased. The procedure was repeated until the final step once no hydrate was observed. The equilibrium temperature of cyclopentane hydrate is the temperature of the previous step having still three phases including cyclopentane above, hydrate at the interface, and salt solution below.

The images of the solution were taken in every step through a small window to analyze and compare with others in order to determine the final step in which only two transparent phases of salt solution and cyclopentane were observed as at the beginning of the experiment. Two samples with 1 ml and 5 ml were also taken at the bottom of the vessel at the final step to measure salt concentration in order to check the correctness of the recorded equilibrium temperatures as mentioned in the quick dissociation procedure

Results and discussion

Time-temperature behavior of cyclopentane hydrate formation and dissociation

The time-temperature behavior of cyclopentane hydrate formation and dissociation in pure water following the quick procedure is presented on figure 2. The horizontal axis indicates the time lapse from the beginning of the experiment.

It can be seen from Figure 2 that the temperature decreased rapidly at the beginning due to cooling by the chiller. Hydrate formed after injecting ice, this led a small increase in temperature due to the exothermic nature of the crystallization. A noticeable amount of hydrate was then observed over time.

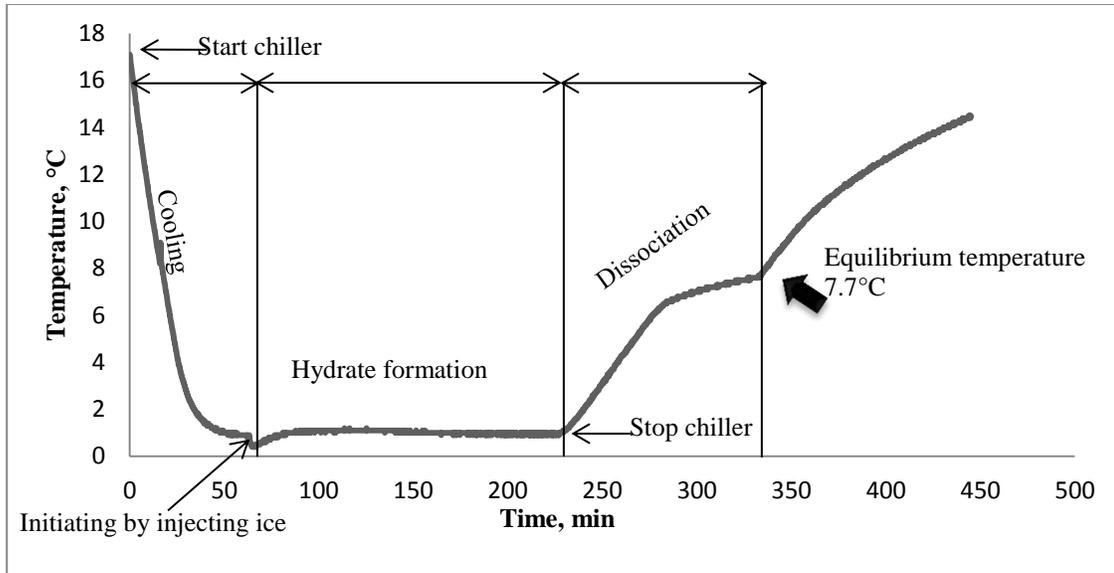


Figure 2: Time-temperature behavior in pure water following a quick dissociation procedure

After stopping the chiller, the temperature increased quickly during a period from 225 to 275 min due to heat-consuming from the environment. From 300 – 330 min, cyclopentane hydrate dissociated intensely. The temperature remained nearly stable due to the endothermic nature of this process. Theoretically, during this period, the temperature remains constant. This unexpected non-constant temperature dissociation can be explained only by a non-equilibrium dissociation.

As soon as no hydrate could be observed inside the vessel, the temperature rose suddenly. The equilibrium temperature was simultaneously recorded at 7.7 °C.

In this paper, the time-temperature behavior of cyclopentane hydrate formation and dissociation in the presence of NaCl is presented because the same behaviors were also observed in KCl and a mixture NaCl - KCl.

Figure 3 presents the time-temperature in the presence of NaCl following a quick procedure. It is apparent that at relatively high concentrations, dissociation time is shorter than that at lower concentrations. Indeed, the temperature gap between the environment and the solution at high concentrations is great because hydrate formation occurs at lower temperatures, meaning the driving force of the dissociation process is significant. After stopping the chiller, hydrate dissociation process takes place quickly and dissociation time is, therefore, short. At the final dissociation point, no hydrate was observed and the temperature increased suddenly, providing valuable evidence to determine the equilibrium temperatures.

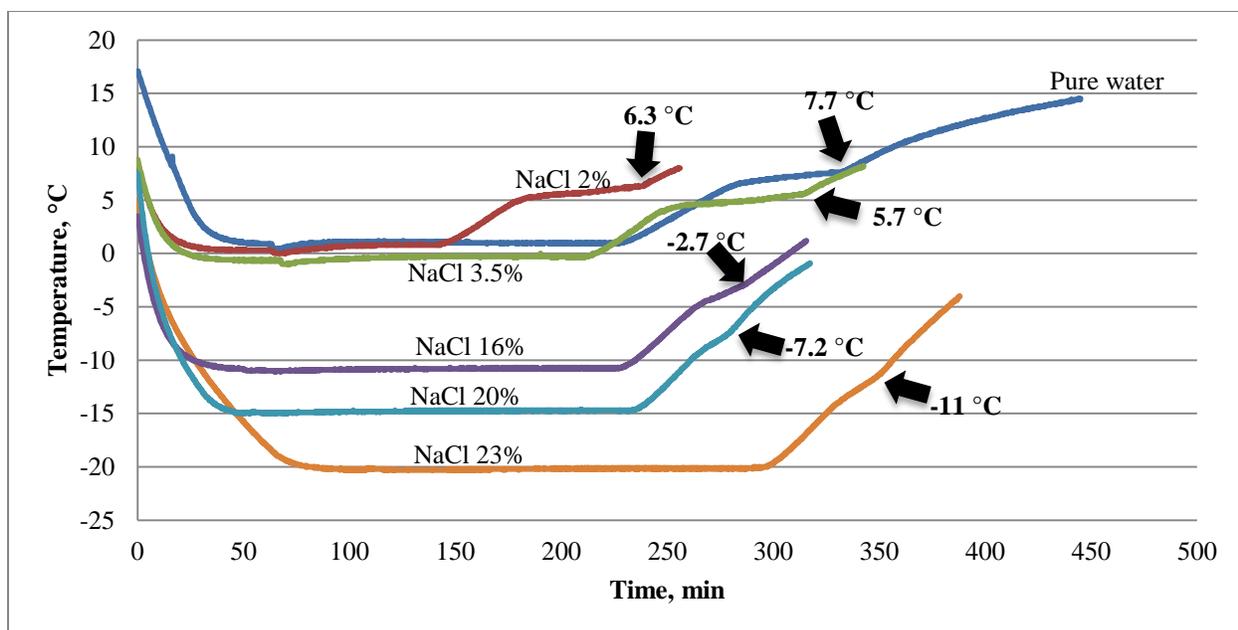


Figure 3: Time-temperature behavior in the presence of NaCl following a quick dissociation procedure, and total dissociation temperatures.

Figure 4 presents the time-temperature behavior in pure water and NaCl 23% following a slow procedure. It is apparent that the same behaviors of the temperature during the cooling and hydrate formation stages compared with the quick procedure can be observed. However, the temperature behaviors in the hydrate dissociation process are completely different. After approximately 1 – 2 hours of hydrate formation, the temperature was firstly increased up to a value near the equilibrium temperature following a quick procedure at the same concentration. It was then increased stepwise. The dissociation process took, therefore, a relatively long time. In pure water and NaCl 5%, the dissociation processes both ended after approximately one day. This typical behavior is expected in the slow procedure. Based on this, the equilibrium temperatures were then determined accurately.

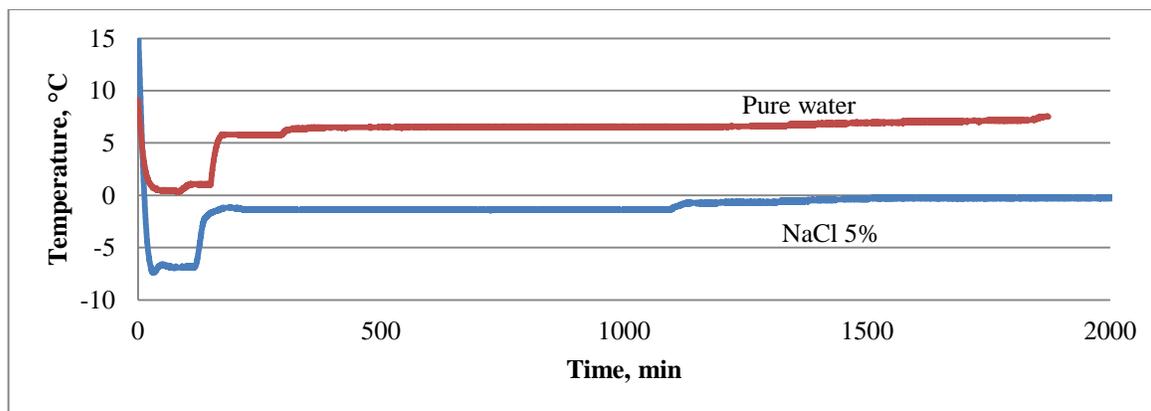


Figure 4: Time-temperature behavior following a slow dissociation procedure

The equilibrium temperature of cyclopentane hydrate in the presence of salts

As mentioned in the experimental procedure, for determining the equilibrium temperature, two procedures (quick and slow) were proposed. In the quick procedure, the equilibrium temperatures were recorded when no hydrate was observed and the temperature had a sudden increase as can be seen obviously on Figure 3. In addition, after each experiment the comparison between the beginning salt concentration and the finishing salt concentration was performed in order to ensure that the recorded temperature is correct following the quick dissociation procedure.

Figure 5 presents the equilibrium temperatures of cyclopentane hydrate in the presence of salts. It can be seen that the equilibrium temperatures following a quick procedure are always higher than ones following slow procedure. In comparison with literature, the equilibrium temperature following quick procedure in pure water in this study, 7.7 °C, is identical to the data published by Dendy Sloan et al. [1], Dirdal et al. [17] and Sefidroodi et al. [18], while Han et al. [12] reported a small different value of 7.8 °C. Moreover, the equilibrium temperature in the presence of 3.5% NaCl according to our study following a quick procedure (5.7 °C) is less than the value reported by Han nearly 1 °C (6.6 °C) [12]. In fact, Sefidroodi et al. applied a slow dissociation method with a stepwise of 0.1°C/30 min for determining the equilibrium value. However, in their study, hydrates were first warmed rapidly to 7.3°C in 5 min, this is probably a reason having the same result compare with our value following the quick procedure.

Indeed, the quick procedure itself has a risk in providing the equilibrium data because the high rate of the dissociation. This means we might miss the real equilibrium temperature before it is recorded. However, this method provides a first valuable estimate for the slow one that then provide more accurate data.

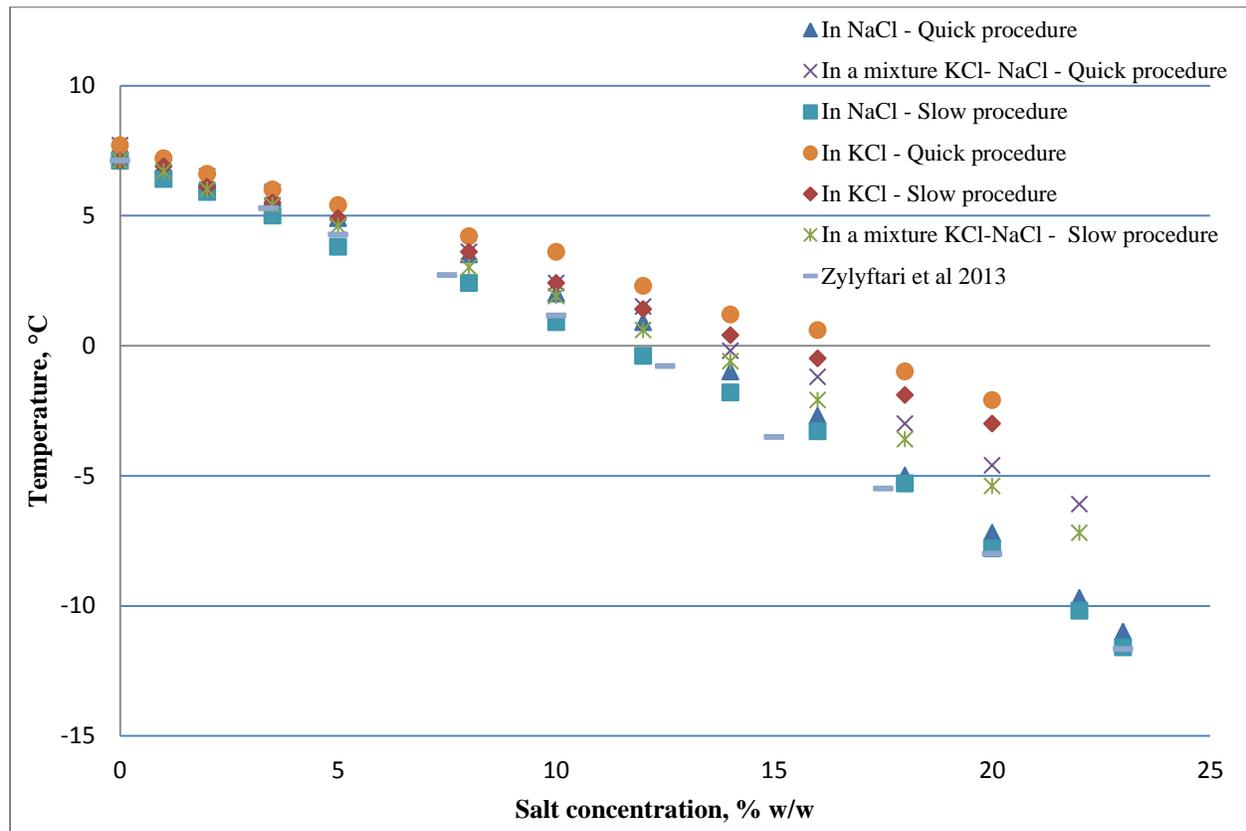


Figure 5: Equilibrium temperature of cyclopentane hydrate in the presence of salts.

In the slow dissociation procedure, the equilibrium temperatures were determined based on the analysis and comparison of the observations by both naked eyes and a camera in order to identify the final dissociation point. As in the quick procedure, the comparison between the beginning and the finishing salt concentrations was also performed.

Figure 7 presents the images of solution from the cooling to the dissociation process in the presence of NaCl 14%. In order to observe the solution clearly, the mixing rate was decreased down to approximately 120 rpm at each time taking photos of the solution.

It can be seen from Figure 7 that in the cooling process, the solution was clear due to the absence of hydrate. By contrast, it was cloudy at the beginning of the dissociation process because of the presence of hydrate suspended small-crystals in the solution that were invisible to the naked eye

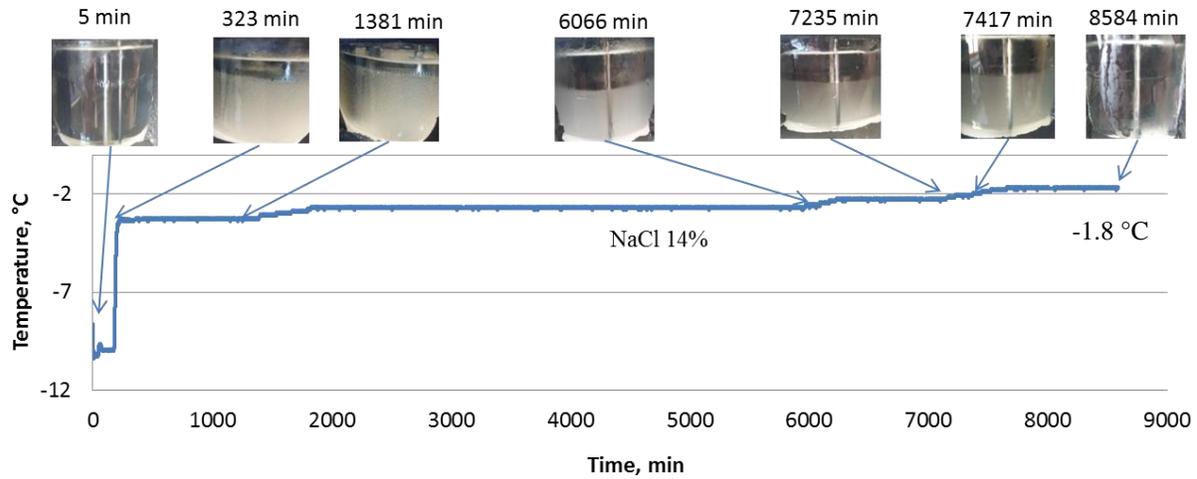


Figure 7: Images of the solutions in the experiments of cyclopentane in the presence of NaCl 14% following a slow dissociation procedure

The turbidity of the aqueous solution including hydrate crystals and salt solution changed over time with increasing gradually of temperature. The solution was then more and more clear after each step of an increment 0.1 °C / hour due to the dissociation of hydrate crystals. At the final step, the phases were totally clear without any turbidity, the equilibrium temperature was recorded of -1.8 °C in NaCl 14%. The comparison of salt concentrations showed also that the beginning and the finishing salt concentrations have the approximately same value (the relative percentage difference is less than 1%), meaning that all hydrate crystals dissociated completely and the recorded equilibrium data is, therefore, accurate following this procedure.

Table 2 summarizes the experimental equilibrium temperatures in the presence of salt following both quick and slow procedures. Two literature data reported by Zilyftari and Kishimoto are also listed in order to compare with experimental ones.

Table 2: Equilibrium temperature of cyclopentane hydrate in the presence of NaCl, KCl and an equi-weight mixture of NaCl and KCl

Salt concentration, % w/w	$T_{e\text{-quick}}$ in NaCl, °C	$T_{e\text{-slow}}$ in NaCl, °C	T_e in NaCl, °C [16]	T_e in NaCl, °C [15]	$T_{e\text{-quick}}$ in KCl, °C	$T_{e\text{-slow}}$ in NaCl, °C	$T_{e\text{-quick}}$ in a mixture of NaCl-KCl, °C	$T_{e\text{-slow}}$ in a mixture of NaCl-KCl, °C
0 (pure water)	7.7	7.1	7.11	-	7.7	7.1	7.7	7.1
1	6.9	6.4	-	-	7.2	6.9	7	6.7
2	6.3	5.9	-	-	6.6	6.1	6.5	6.0
3.5	5.7	5	-	-	6	5.5	5.9	5.4
5	4.9	4.1	-	4.45	5.4	4.9	5.1	4.6
8	3.5	2.4	-	-	4.2	3.6	3.6	3.0
10	2	0.9	1.16	1.25	3.6	2.4	2.4	1.9
12	0.9	-0.4	-	-	2.3	1.4	1.5	0.6
14	-1	-1.8	-	-	1.2	0.4	-0.2	-0.6
16	-2.7	-3.8	-	-	0.6	-0.5	-1.2	-2.1
18	-5	-5.3	-	-	-1	-1.9	-3	-3.6
20	-7.2	-7.8	-8.00	-	-2.1	-3	-4.6	-5.4
22	-9.7	-10.2	-	-	-	-	-6.1	-7.2
23	-11	-11.6	-11.66	-	-	-	-	-

$T_{e\text{-quick}}$ and $T_{e\text{-slow}}$ are the equilibrium temperatures following the quick and the slow dissociation procedure
The uncertainty is ± 0.1 °C

Table 2 shows clearly a temperature shift between the quick and the slow procedures for all kinds of salts. The equilibrium temperatures following the slow dissociation are all higher than ones following the quick procedure at the same concentrations. Moreover, the equilibrium temperature in NaCl are all lower than ones in KCl and a mixture NaCl-KCl, this indicates that NaCl has a greater impact on the equilibrium temperature at the same salt quantity.

In comparison with literature, the equilibrium temperature in pure water from our study, 7.1 °C, is close to the values of 7.11 °C reported by Zyllyftari et al. [16] and 6.6 °C, 6.8 °C, 7.1 °C reported by Masahiro et al. [14] by using the Differential Scanning Calorimetry (DSC). We have also the approximately same values in NaCl 5%, 10%, 20% and 23% compared with the values in [15], [16]. Figure 5 presents clearly also the similarity between our data in NaCl and data from Zyllyftari et al. This comparison indicates that our recorded equilibrium temperatures are very close to the literature data in which both DSC and the slow dissociation procedures were all applied, meaning that our data are accurate and reliable.

Modelling Part

For predicting the equilibrium temperatures of cyclopentane hydrate in the presence of salts, this study follows two approaches. One is based on Hildebrand and Scott's equation for determining freezing point depression; another is based on the classical model of van der Waals and Platteeuw.

First approach

Water activity can be expressed from the freezing point of cyclopentane hydrate by the following equation [19]:

$$\ln a_w = \frac{\Delta h_{fusion}}{R} \frac{(T_f - T)}{T_f T} + \frac{\Delta C_p}{R} \left[\frac{(T_f - T)}{T} - \ln\left(\frac{T_f}{T}\right) \right] \quad (1)$$

Where T is the freezing point or equilibrium temperature of cyclopentane hydrate (K) at a certain salt concentration; T_f is the freezing point of cyclopentane hydrate in pure water (279.95K [14]); Δh_{fusion} is the latent heat of cyclopentane hydrate (283.9 kJ/kg hydrate [14]); R is the gas constant; ΔC_p is the change of specific heat of cyclopentane hydrate and the subcooled liquid phase. Because it has not been published in the literature, in this study, the correlation $\Delta C_p = F(T)$ is calculated by using the experimental data in NaCl following the slow procedure. PHREEQC [20] is used to predict water activity in NaCl at the equilibrium temperature with the database "pitzer.dat" as presented in Table 3.

Table 3: Water activity in NaCl solution by using PHREEQC

Salt concentration, % w/w	Equilibrium temperature	Water activity
0	7.7	1.000
1	6.9	0.994
2	6.3	0.989
3.5	5.7	0.980
5	4.9	0.971
8	3.5	0.951
10	2	0.937
12	0.9	0.922
14	-1	0.906
16	-2.7	0.888
18	-5	0.869
20	-7.2	0.848
22	-9.7	0.824
23	-11	0.812

ΔC_p is then expressed as a function of the temperature as follow:

$$\Delta C_p = F(T) = (-10^{-19}) \cdot \exp(0.1813 \cdot T) \quad (2)$$

The equilibrium temperatures of cyclopentane hydrates in salts are then calculated by using both equations (1) and (2). Because the water activity is temperature-dependent, therefore at first step, the value of water activity in the presence of salts at 273.15 K is used. At each later step, after predicting the equilibrium temperature, PHREEQC is used to re-calculate the water activity. The calculation ends once PHREEQC gives the same value of water activity. The predicted equilibrium temperature is then recorded.

In this study, the absolute average deviation (AAD) is defined as follows:

$$AAD = \frac{1}{n} \sum_{i=1}^n Abs \left(\frac{T_{i,pred} - T_{i,exp}}{T_{i,exp}} \right) \quad (3)$$

where n is the number of experimental data points, $T_{i,pred}$ (K) is the predicted equilibrium temperature, and $T_{i,exp}$ (K) is the experimental measured equilibrium temperatures.

Figure 8 presents the predicted temperatures following the approach 1. The predicted data are in good agreement with the experimental ones in all kinds of salts. The absolute average deviations in NaCl, KCl and a mixture are 0.11%, 0.10%, and 0.09% respectively. This indicates that the phase equilibrium temperature conditions are well reproduced using the new correlation of the change of specific heat and temperature $\Delta C_f = F(T)$ for cyclopentane hydrate not only in NaCl but also in KCl and a mixture of NaCl-KCl.

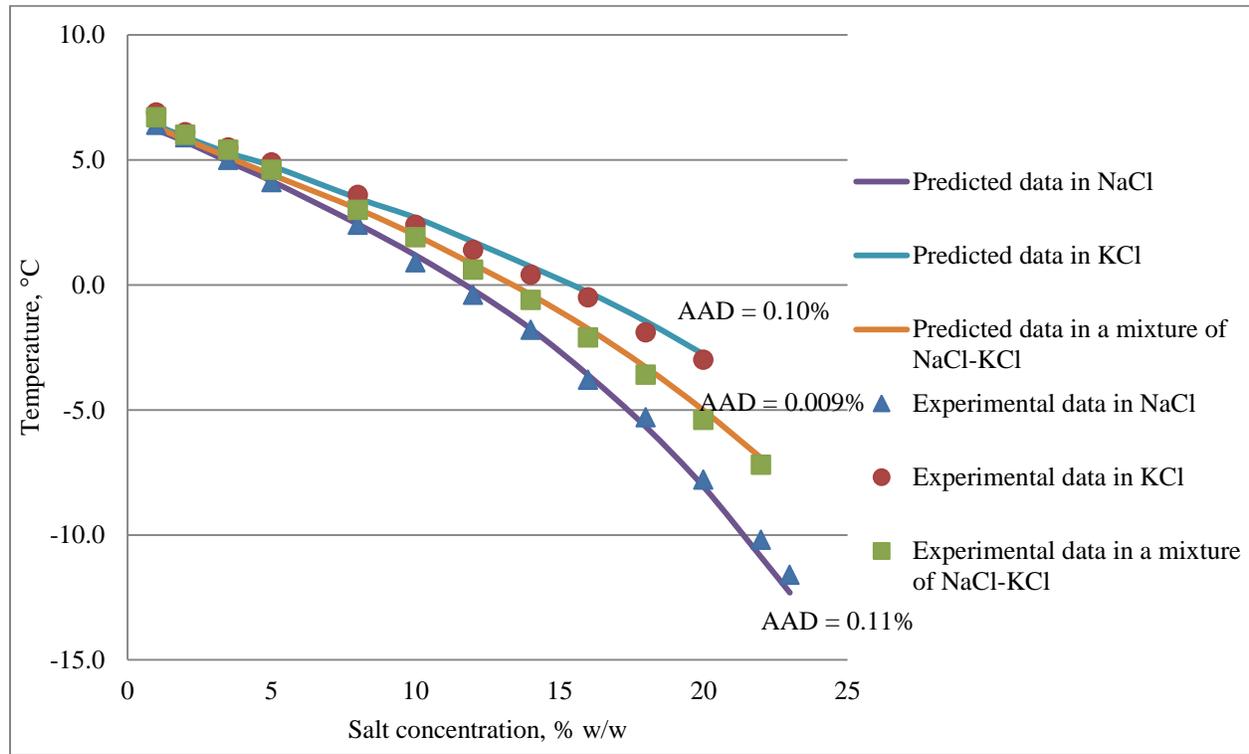


Figure 8: Predicted - equilibrium temperatures of cyclopentane hydrate in the presence of salts: Approach 1

Second Approach

In this approach, the classical van der Waals and Platteeuw model is used to describe the hydrate phase. Thermodynamic equilibrium between the hydrate phase (H) and the aqueous liquid phase (L_w) can be written as follows:

$$\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta} \quad (4)$$

where $\Delta\mu_w^H$ and $\Delta\mu_w^{Lw}$ are the differences of the chemical potentials between water in hydrate or liquid phase and water in the reference phase, respectively.

The chemical potential difference $\Delta\mu_w^{Lw}$ is then determined from statistical thermodynamic:

$$\Delta\mu_w^{H-\beta} = RT \sum_i v_i \ln \left(1 - \sum_i \theta_j^i \right) \quad (5)$$

where R is the universal constant, T is the absolute temperature, v_i is the number of type i cavities per water molecule in the hydrate (8/136 for cyclopentane hydrate), and θ_j^i is the occupancy factor of the cavities of type i by the guest molecule j (the guest molecule here is cyclopentane).

On the other hand, $\Delta\mu_w^H$ can be calculated by means of the Gibbs-Duhem of classical thermodynamic:

$$\begin{aligned} \Delta\mu_w^{Lw} = & \frac{T}{T^0} \Delta\beta^L \mu_w^0 + (bT^0 - \Delta C_{p,w}^{L,0}) T \ln \left(\frac{T}{T^0} \right) + \frac{1}{2} b T (T^0 - T) + (\Delta\beta^L h_0^w + (b T^0 - \Delta C_{p,w}^{L,0}) T^0 \\ & - \frac{1}{2} b T^0 (1 - \frac{T}{T^0}) + \Delta v_{p,w}^{L,0} (P - P^0) - RT \ln(a_w) \end{aligned} \quad (6)$$

where $\Delta\beta^L \mu_w^0$, $\Delta\beta^L h_0^w$, $\Delta C_{p,w}^{L,0}$, and $\Delta v_{p,w}^{L,0}$ are the differences in chemical potential, molar enthalpy, isobaric molar heat capacity and molar volume between water in the pure liquid and the pure metastable hydrate phase (index β) under reference conditions for temperature and pressure of $T^0 = 273.15$ K and $P^0 = 0$. a_w is the water activity, b is the empirical constant reported by Sloan [1]. P has a value of 101325 Pa due to cyclopentane hydrate forms at the atmospheric pressure.

Table 4 specifies the parameters used in this study. Because cyclopentane hydrate is the structure II, the parameters in Table 4 are presented for only this structure.

Table 4: Parameters used for the hydrate-phase equilibrium calculations

Parameters	Unit	Value	Citation
$\Delta\beta^L \mu_w^0$	J.mol ⁻¹	1068	Handa and Tse [21]
$\Delta\beta^L h_0^w$	J.mol ⁻¹	-5247	Handa and Tse [21]
$\Delta C_{p,w}^{L,0}$	J.mol ⁻¹ .K ⁻¹	-38.12	Sloan [1]
B	J.mol ⁻¹ .K ⁻²	0.141	Sloan [1]
$\Delta v_{p,w}^{L,0}$	10 ⁻⁶ m ³ .mol ⁻¹	4.99644	John et al. [22]

In this approach, the correlation between the occupancy factor and the water activity, $\theta = F(a_w)$, is calculated by using the equations (4 - 6) and the experimental equilibrium data in NaCl. PHREEQC is used to compute the water activity of salt solution as presented in Table 3.

The occupancy factor is then expressed as a function of the water activity as follow:

$$\theta = F(a_w) = m^*(a_w^2) + n^*(a_w) + p \quad (7)$$

where $m = -0.0004772$; $n = 0.0004731$; $p = 0.9998800$

The equilibrium temperatures in the presence of salts are then predicted by using the correlation $\theta = F(a_w)$ (7) and the equations (4-6). As mentioned in the approach 1, because the water activity is temperature-dependent, the value of water activity at 273.15 K is used at the first step. PHREEQC is then used to calculate the water activity at each step later. The predicted equilibrium is recorded once PHREEQC has the same value of water activity.

The predicted-equilibrium temperatures of cyclopentane hydrate in the presence of salts following the approach 2 are presented in Figure 9. It can be seen that, the predicted-equilibrium temperatures are in very good agreement with experimental ones. The average absolute deviations are 0.04% in NaCl, 0.05% in KCl and 0.05% in a mixture of NaCl-KCl. In comparison with the approach 1, the approach 2 provides data much closer to the experimental data in all kinds of salts.

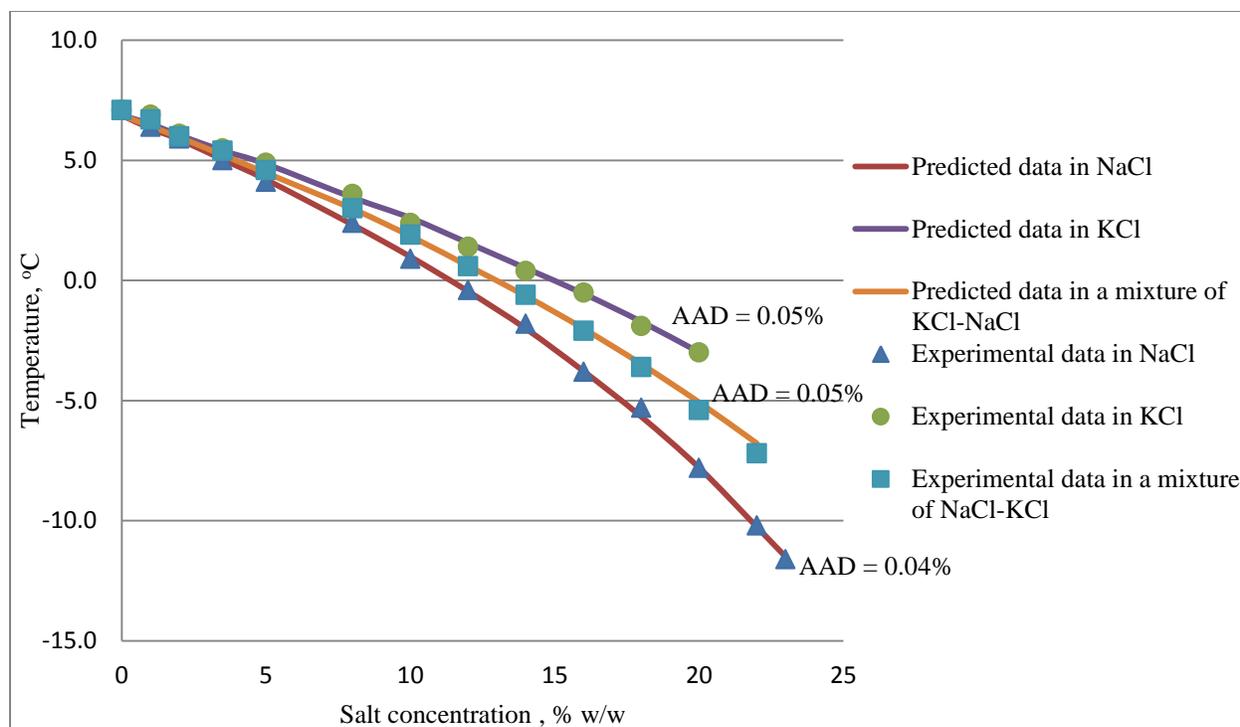


Figure 9: Predicted - equilibrium temperatures of cyclopentane hydrate in the presence of salts: Approach n°2

Conclusions

In this work, two procedures were applied to determine the equilibrium temperatures of cyclopentane hydrate in the presence of salts. One is at quick dissociation rate; another is at slow dissociation rate. The aim of the quick procedure is to provide an initial estimate of the equilibrium temperature. The slow procedure is then used to obtain more accurate data.

The time-temperature figures during formation and dissociation were also generated. A small increase in the temperature of the solution inside the reactor was observed during the hydrate formation process due to a typical exothermic property of the crystallization process. In contrast, the temperature remained nearly constant during the hydrate dissociation in the quick dissociation procedure because of the endothermic nature of the dissociation process. As soon as no hydrates were observed, the temperature rose suddenly, providing valuable evidence to determine the equilibrium temperatures.

The results also show that the equilibrium temperatures dropped significantly with an increase in salt concentration, whatever the kinds of salt. In addition, the equilibrium temperatures of cyclopentane hydrate in the presence of NaCl were always lower than ones in the presence of KCl and a mixture of KCl and NaCl at the same concentration, indicating that NaCl has a greater impact on the equilibrium temperature of cyclopentane hydrate at the same quantity.

A temperature shift between the equilibrium temperatures following two procedures was also observed. Because the quick procedure tends to miss the right temperature, the results are therefore slightly higher. In comparison with the literature, the slow procedure in pure water provides the same value reported by Masahiro and Zyllyftari, while in the presence of NaCl at 5%, 10%, 20%, 23% wt the results are close to Kishimoto and Zyllyftari, obtained either by slow dissociation or micro Differential Scanning Calorimetry (μ -DSC).

Two thermodynamic models were proposed to predict the equilibrium temperatures following two different approaches. The phase equilibrium temperature conditions are well reproduced using both approaches, while the second approach provides data with lower AAD values in all kinds of salts.

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