J. Chem. Eng. Data **1981**, *26*, 13-16

Literature Cited

(1) Pitzer, K. S.; Lippmann, D. Z.; Curl, R. F., Jr.; Huggins, C. M.; Peterson, E. D. *J. Am. Chem. Soc.* **1955**, *77*, 3433.
(2) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977.
(3) Wieczorek, S. A.; Kobayashi, R. *J. Chem. Eng. Data* **1980**, *25*, 302.
(4) Wieczorek, S. A.; Kobayashi, R. *J. Chem. Eng. Data*, previous paper in this issue.

Received for review June 30, 1980. Accepted October 17, 1980. The Electric Power Research Institute provided financial support for this work.

Densities of Molten $K_2S_2O_7$–$KHSO_4$ and $K_2S_2O_7$–$KHSO_4$–V_2O_5

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Densities of the molten salt systems $K_2S_2O_7$–$KHSO_4$ and $K_2S_2O_7$–$KHSO_4$–V_2O_5 were measured by using the automated float method. Ten different compositions of the $K_2S_2O_7$–$KHSO_4$ system were measured. The obtained densities were fitted to equations of the form $\rho = A(X) + B(X)(t - 400)$. $A(X)$ and $B(X)$ were again fitted by polynomials of the mole fraction, X_{KHSO_4}, in each of the composition ranges $0.0000 \leq X_{KHSO_4} \leq 0.5000$, $0.5000 \leq X_{KHSO_4} \leq 1.0000$, and $0.0000 \leq X_{KHSO_4} \leq 1.0000$. Furthermore, all the measured data in each range were fitted to equations of the form $\rho = \sum_0^n A_n X^n + (\sum_0^m B_m X^m)(t - 400)$. It was shown that a linear relationship exists between molar volume at 400 °C and X_{KHSO_4} at all compositions. Two different compositions of the $K_2S_2O_7$–$KHSO_4$–V_2O_5 system were measured. The observed densities were at each composition fitted to a linear equation of the form $\rho = A(X_1,X_2) + B(X_1,X_2)(t - 400)$, where X_1 and X_2 are $X_{V_2O_5}$ and X_{KHSO_4}, respectively. Finally all the measured data for this system were fitted to the equation $\rho = A + BX_2 + CX_2^2 + (D + EX_2 + FX_2^2)X_1(t - 400)$.

The molten $K_2S_2O_7$–$KHSO_4$ system plays a major role as solvent for various vanadium(V) and vanadium(IV) complexes during the catalytic conversion of SO_2 to SO_3 for the manufacture of sulfuric acid. As part of a larger investigation (*1–3*) of the catalytic vanadium oxide-pyrosulfate melts, the present paper supplies density data for the $K_2S_2O_7$–$KHSO_4$ system in the whole composition range $0.0000 \leq X_{KHSO_4} \leq 1.0000$ and for the $K_2S_2O_7$–$KHSO_4$–V_2O_5 at compositions around $X_{KHSO_4} = 0.6$. The method employed is the previously described "automated float method" for determination of densities of molten salts (*4*, *5*). This method is very well suited for the present systems, which at the employed temperatures have high vapor pressures. Especially the pure molten $KHSO_4$ is believed to exert a high vapor pressure at higher temperatures. One of the quartz cuvettes containing 100% $KHSO_4$ broke when the temperature reached 430 °C possibly due to the internal pressure. The high pressure is probably the reason that only measurements of the density of molten $KHSO_4$ at temperatures very close to the melting point have been performed (*6*). The melts containing V_2O_5 are furthermore very dark colored, thus making visual observations of floats impossible.

Experimental Section

The densities were measured by the automated float method (*4*, *5*). The method is based on magnetic detection of quartz floats with iron cores, as they pass a differential transformer. The furnace and its regulation have been described in detail previously (*4*). Passage temperatures were detected by platinum resistance thermometers (from Degussa) and by chromel-alumel thermocouples (from Pyrotenax) which were calibrated at the freezing points of pure (99.99%) zinc and lead to within ±0.5 °C.

$K_2S_2O_7$ was made by thermal dissociation of $K_2S_2O_8$ (*7*) (Merck, Pro Analysi) in a stream of pure N_2 in order to avoid contamination by H_2O. The synthesized potassium pyrosulfate was sealed under vacuum into Pyrex ampules and stored in a glovebox. It is important to ensure that the hygroscopic potassium pyrosulfate is kept out of contact with atmospheric air—a commercial analytical-grade $K_2S_2O_7$ (Riedel-de Haën) was shown by Raman spectroscopy to consist of more than 60 mol % $KHSO_4$ (*1*). By weighing it was determined that $K_2S_2O_7$ did not give off any SO_3 at the employed dissociation temperature (290 °C). $KHSO_4$ (Merck, Pro Analysi) was dried at 110 °C in 3 days and stored in a glovebox. V_2O_5 (Merck, Extra Pure) was recrystallized under vacuum in a quartz ampule by quick heating to just above the melting point (658 °C), followed by slow cooling.

All handling of the solid salts was performed in a nitrogen-filled glovebox with a measured water content of ~5 ppm and continuous gas purification by forced recirculation through external molecular sieves.

Results

The experimental densities and temperatures of the $K_2S_2O_7$–$KHSO_4$ system are given in Table I. The densities of the used floats are calculated on the basis of 8–10 determinations at room temperature and corrected for the thermal expansion of quartz at the measured temperature. In Table II the results for the $K_2S_2O_7$–$KHSO_4$–V_2O_5 are given in a similar way. The standard deviations of the measured temperatures are calculated in accordance with the procedure described previously (*4*).

In Table III the measured densities for the $K_2S_2O_7$–$KHSO_4$ system are at each composition expressed by $A(X)$ and $B(X)$, where $\rho = A(X) + B(X)(t - 400)$. ρ is the density in g/cm^3, $A(X)$ is the density at the composition X_{KHSO_4} at 400 °C, $B(X)$ is the density change per degree at the composition X_{KHSO_4}, and t is the temperature in °C. As described previously (*5*) this expression gives a more satisfactory representation of the measured data than the usually employed equation $\rho = A(X) + B(X)t$. In Table IV the results for the $K_2S_2O_7$–$KHSO_4$–V_2O_5 are given analogously by $A(X_1,X_2)$ and $B(X_1,X_2)$ ($X_1 = X_{KHSO_4}$, $X_2 = X_{V_2O_5}$).

0021-9568/81/1726-0013$01.00/0

Table I. Experimental Densities and Temperatures of the Molten $K_2S_2O_7$-$KHSO_4$ System

densities of floats, g/cm³		measured temperatures at the given X_{KHSO_4} mole fractions, °C									
at 20 °C	at measd temp	0.0000	0.1000	0.3000	0.4000	0.5000	0.6000	0.7000	0.7750	0.9000	1.0000
1.9697	1.9682								475.8(8)[a]		
1.9697	1.9683									441.6(9)	
1.9697	1.9684										410.8(10)
2.0019	2.0004					496.4(5)					
2.0019	2.0005						471.0(8)				
2.0019	2.0006								429.4(9)		
2.0019	2.0007									395.8(10)	
2.0172	2.0154	562.4(9)									
2.0172	2.0159								407.1(7)		
2.0176	2.0159		541.5(8)								
2.0172	2.1060									373.3(8)	
2.0176	2.1060			506.8(7)	491.1(5)						
2.0172	2.0161										343.3(6)
2.0176	2.0161					473.4(18)					
2.0176	2.0162							423.5(7)			
2.0317	2.0301		520.9(11)								
2.0317	3.0302			485.5(12)		470.0(12)					
2.0317	2.0305							403.5(11)			
2.0343	2.0327		517.2(8)								
2.0343	2.0328			482.3(17)							
2.0343	2.0329				464.3(16)						
2.0343	2.0331							401.4(11)			
2.0398	2.0381	528.5(21)									
2.0398	2.0386								375.3(6)		
2.0398	2.0388									342.9(6)	
2.0398	2.0389										311.1(5)
2.0504	2.0488		493.4(9)								
2.0504	2.0489			459.3(11)							
2.0504	2.0490				441.4(10)						
2.0504	2.0492							376.4(10)			
2.0730	2.0715		459.4(17)								
2.0730	2.0716			426.0(25)							
2.0730	2.0717				408.1(26)	392.1(6)					
2.0730	2.0718						366.8(21)				
2.0730	2.0719							343.0(10)			
2.0744	2.0728	447.0(18)									
2.0744	2.0733								325.7(5)		
2.0744	2.0734									294.5(6)	
2.0744	2.0735										263.5(5)
2.0981	2.0966	440.7(20)									
2.1114	2.1103					338.1(7)					
2.1114	2.1104						311.1(8)				

[a] i.e., 475.8 ± 0.8.

Table II. Experimental Densities and Temperatures of the Molten $K_2S_2O_7$-$KHSO_4$-V_2O_5 System

density of floats, g/cm³			measured temperatures at the given mole fractions		
at 20 °C	at measd temp	X_{KHSO_4}:	0.6000	0.5920	0.5734
		$X_{K_2S_2O_7}$:	0.4000	0.3946	0.3829
		$X_{V_2O_5}$:	0	0.0134	0.0447
2.0019	2.0004		471.0(8)		
2.0176	2.0160				489.0(20)
2.0176	2.0161			463.4(8)	
2.0317	2.0303			442.4(9)	460.8(6)
2.0504	2.0490				434.7(6)
2.0504	2.0491			413.8(8)	
2.0730	2.0717				398.5(5)
2.0730	2.0718		366.8(21)	379.8(20)	
2.1114	2.1104		311.1(8)		

Table III. Linear Density Equations and Molar Volumes of the Molten $K_2S_2O_7$-$KHSO_4$ System[a]

mole fraction $KHSO_4$	$A(X)$,[b] g/cm³	$10^3B(X)$,[b] g/(cm³ deg)	SD, g/cm³	molar vol at 400 °C, cm³/mol
0.0000	2.1240(3)	−0.669(3)	0.0002	119.73
0.1000	2.1119(4)	−0.677(3)	0.0002	114.82
0.3000	2.0897(4)	−0.691(5)	0.0003	104.74
0.4000	2.0769(6)	−0.672(9)	0.0006	99.69
0.5000	2.0669(3)	−0.693(5)	0.0006	94.46
0.6000	2.0492(2)	−0.687(2)	0.0003	89.50
0.7000	2.0330(3)	−0.687(12)	0.0007	84.41
0.7750	2.0212(1)	−0.700(2)	0.0002	80.89
0.9000	1.9977(3)	−0.715(5)	0.0005	74.08
1.0000	1.9759(4)	−0.713(4)	0.0004	68.92

[a] For the measured temperature ranges, see Table I. [b] $\rho = A(X) + B(X)(t - 400)$.

From the molar volumes listed in Table III, it is observed that for the $K_2S_2O_7$–$KHSO_4$ system a linear relationship between the molar volume at 400 °C and composition exists in the whole composition range $0.0000 \le X_{KHSO_4} \le 1.0000$. This is illustrated in Figure 1 and indicates that the molten salt system $K_2S_2O_7$–$KHSO_4$ is ideal.

In Figure 2 $A(X)$ and $B(X)$ are shown as functions of the composition of the $K_2S_2O_7$–$KHSO_4$ system. Here are shown the best $A(X)$ polynomial fitted to the data (by the least-squares

Table IV. Linear Density Equations and Molar Volumes of the Molten $K_2S_2O_7$-$KHSO_4$-V_2O_5 System[a]

mole fraction $KHSO_4$ (X_1)	mole fraction $K_2S_2O_7$	mole fraction V_2O_5 (X_2)	$A(X_1,X_2)$,[b] g/cm^3	$10^3B(X_1,X_2)$,[b] g/(cm^3 deg)	SD, g/cm^3	molar vol at 400 °C, cm^3/mol
0.6000	0.4000	0	2.0492(2)	−0.687(2)	0.0003	89.50
0.5920	0.3946	0.0134	2.0584(2)	−0.664(4)	0.0003	89.09
0.5734	0.3823	0.0443	2.0706(2)	−0.616(4)	0.0003	88.55

[a] For the measured temperature ranges, see Table II. [b] $\rho = A(X_1,X_2) + B(X_1,X_2)(t - 400)$.

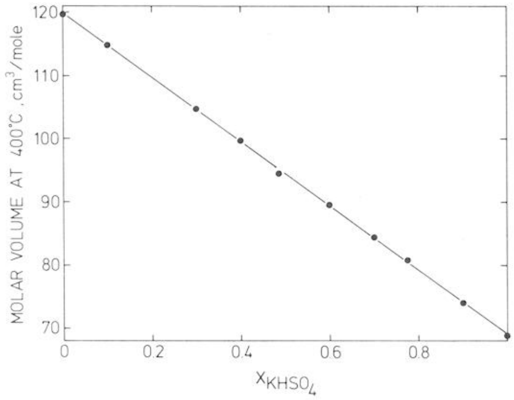

Figure 1. Molar volume of the $K_2S_2O_7$–$KHSO_4$ system at 400 °C vs. mole fraction X_{KHSO_4}.

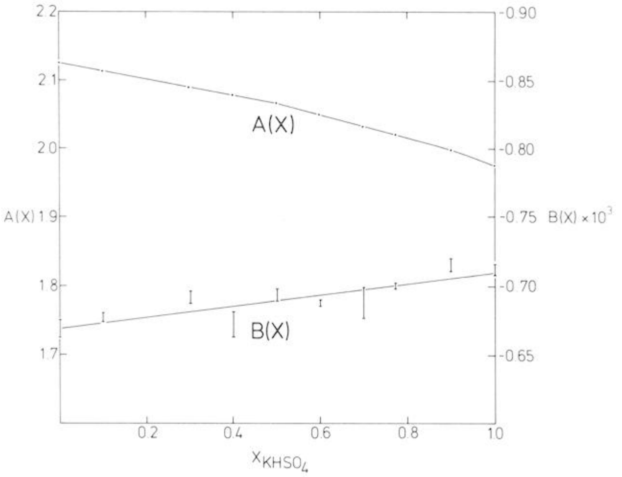

Figure 2. Variations of the parameters $A(X)$ and $B(X)$ vs. mole fraction X_{KHSO_4} in the $K_2S_2O_7$–$KHSO_4$ system: $0.0000 \leq X_{KHSO_4} \leq 0.5000$, $A(X) = 2.12372 - 0.11476X$ (SE = 0.00073); $0.5000 \leq X_{KHSO_4} \leq 1.0000$, $A(X) = 2.33308 - 0.54667X + 0.56754X^2 - 0.27815X^3$ (SE = 0.00036); $0.0000 \leq X_{KHSO_4} \leq 1.0000$, $B(X) = -0.66877 \times 10^{-3} - 0.04110 \times 10^{-3}X$ (SE = 0.00840×10^{-3}).

method) in each of the mole-fraction ranges $0.0000 \leq X_{KHSO_4} \leq 0.5000$ and $0.5000 \leq X_{KHSO_4} \leq 1.0000$, and the best $B(X)$ polynomial that fits the data in the total mole-fraction range $0.0000 \leq X_{KHSO_4} \leq 1.0000$. The used parameters and the standard errors are given in the figure captions, and it is noted that a slightly better representation is obtained when employing two mole fraction ranges for the $A(X)$ polynomial than by fitting all the data to a single polynomial (in this case the SE is equal to 0.00129 on $A(X)$). In connection with the use of computer programs, it is especially convenient if all the density data obtained at different temperatures and different compositions can be combined into a single empirical equation of the form $\rho = \sum_0^n A_nX^n + (\sum_0^m B_mX^m)(t - 400)$. In the present case an expression with $n = m = 1$ could be employed in the composition range $0.0000 \leq X_{KHSO_4} \leq 0.5000$, while $n = 3$ and $m = 1$ in the range $0.5000 \leq X_{KHSO_4} \leq 1.0000$. To obtain a satisfactory representation of the data in the total mole-fraction range $0.0000 \leq X_{KHSO_4} \leq 1.0000$, we found the values of n and m to be 6 and 1, respectively. These results are given in Table V. If the expressions that apply to the ranges $0.5000 \leq X_{KHSO_4} \leq 1.0000$ or $0.0000 \leq X_{KHSO_4} \leq 1.0000$ are extrapolated to the temperatures employed by Rogers and Ubbelohde (*6*) (210–230 °C) in their determinations of the density of pure potassium hydrogen sulfate, deviations of −1.9 to −3.1% are observed.

Table V. Values of Coefficients in Empirical Polynomial[a] for Densities of the Molten $K_2S_2O_7$–$KHSO_4$ System in Different Composition Ranges

	$0.0000 \leqslant X_{KHSO_4} \leqslant 0.5000$ (n=1, m=1)	$0.5000 \leqslant X_{KHSO_4} \leqslant 1.0000$ (n=3, m=1)	$0.0000 \leqslant X_{KHSO_4} \leqslant 1.0000$ (n=6, m=1)
A_0	2.123 41	2.239 19	2.123 96
A_1	−0.113 55	−0.574 91	−0.122 79
A_2		0.608 67	−0.152 56
A_3		−0.297 20	1.309 99
A_4			−3.357 34
A_5			3.393 21
A_6			−1.218 44
B_0	$-0.668\,59 \times 10^{-3}$	$-0.660\,88 \times 10^{-3}$	$-0.667\,27 \times 10^{-3}$
B_1	$-0.053\,79 \times 10^{-3}$	$-0.052\,78 \times 10^{-3}$	$-0.042\,58 \times 10^{-3}$
SE, g/cm^3	0.0006	0.0006	0.0009

[a] $\rho = \Sigma_0{}^nA_nX^n + (\Sigma_0{}^mB_mX^m)(t - 400)$.

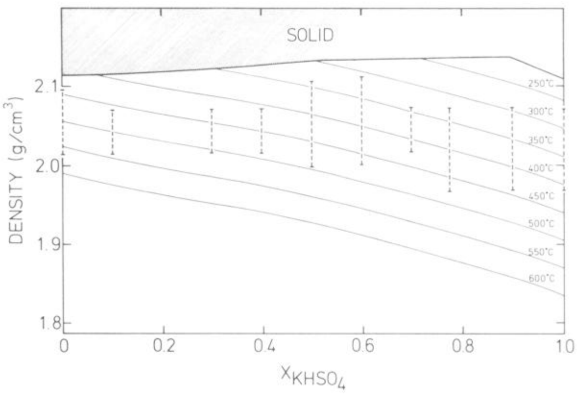

Figure 3. Density isotherms for the molten $K_2S_2O_7$–$KHSO_4$ system. The dashed lines show the experimental ranges.

In Figure 3 are shown the measured temperature ranges and density isotherms calculated on the basis of the parameters of Table V. The liquidus curve is constructed from the phase diagram given by Hagisawa and Takai (*8*). As a linear relationship between density and temperature is found for all the measured compositions, it seems reasonable to conclude that the expressions given in Tables III and V can be extrapolated to temperatures considerably beyond the temperature ranges employed in this investigation.

The density measurements on the $K_2S_2O_7$–$KHSO_4$–V_2O_5 system can, by analogy with the $K_2S_2O_7$–$KHSO_4$ system, be described by an equation of the form $\rho = A(X_2) + B(X_2)X_1(t - 400)$, where $A(X_2)$ is the density at the mole fraction $X_{V_2O_5}$, $B(X_2)$ is the change in density per unit of mole fraction of $KHSO_4$ per degree, X_1 is the mole fraction of $KHSO_4$, and t is the temperature in °C. In this case ρ does not vary linearly with X_2, and the expression for ρ becomes $\rho = A_0 + A_1X_2 +$

Table VI. Values of Coefficients for Empirical Polynomial[a] for Densities of the Molten $K_2S_2O_7$-$KHSO_4$-V_2O_5 System at Compositions around $X_{KHSO_4} = 0.6$ and $0.0000 \leq X_{V_2O_5} \leq 0.0450$

A_0	2.049 12
A_1	0.781 56
A_2	−6.700 15
B_0	−0.114 68 × 10^{-2}
B_1	0.322 00 × 10^{-2}
B_2	−1.210 90 × 10^{-2}
SE, g/cm³	0.0003

[a] $\rho = A_0 + A_1X_2 + A_2X_2^2 + (B_0 + B_1X_2 + B_2X_2^2)X_1(t - 400)$; $X_1 = X_{KHSO_4}$, $X_2 = X_{V_2O_5}$.

$A_2X_2^2 + (B_0 + B_1X_2 + B_2X_2^2)X_1(t - 400)$. The values for the employed parameters are given in Table VI. The nonlinearity of the system suggests that depending on concentration different complexes of vanadium(V) are formed. In contrast to the $K_2S_2O_7$–$KHSO_4$ system, the $K_2S_2O_7$–$KHSO_4$–V_2O_5 system is not ideal.

Literature Cited

(1) Hansen, N. H. Thesis (in Danish) The Technical University of Denmark, Chemistry Department A, Lyngby, Denmark, 1979.
(2) Bjerrum, N. J.; Hansen, N. H.; Fehrmann, R. "Journeés d'Etude des Sels Fondus", 6-8 Jun 1979, Université de Liege.
(3) Hansen, N. H; Fehrmann, R.; Bjerrum, N. J., to be submitted to *Inorg. Chem.*
(4) Andreasen, H. A.; Bjerrum, N. J.; Foverskov, C. E. *Rev. Sci. Instrum.* **1977**, *48*, 1340.
(5) Andreasen, H. A.; Bjerrum, N. J.; Hansen, N. H. *J. Chem. Eng. Data* **1980**, *25*, 236.
(6) Rogers, S. E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1951**, *46*, 1051.
(7) Baumgarten, P.; Tullo, E. *Ber.* **1938**, *71*, 2596.
(8) Hagisawa, H.; Takai, T. *Bull. Inst. Phys. Chem. Res., Tokyo* **1937**, *16*, 27.

Received for review January 11, 1980. Accepted September 2, 1980. We acknowledge financial support from Statens teknisk-videnskabelige Forskningsråd.

Vapor–Liquid Equilibria of the NaCl–H_2O System in the Temperature Range 300–440 °C

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A complete apparatus is described for the phase study of saltwater systems at high pressures and temperatures. An original technique is presented for the direct sampling of solutions with high salt concentration. These have been applied to the liquid–vapor equilibrium determination of the system NaCl–H_2O in the range 300–440 °C at concentrations up to quasisaturation. The data obtained confirm previously published work and solve the uncertainty in several sources of data. Diagrams and correlations are presented for eight isotherms.

Introduction

Since the late thirties, a large amount of work has been published on saltwater systems at high temperatures and pressures. The interest of these studies is scattered in such different fields as fundamental geology, geothermal power plant technology, high-pressure steam power plants, hydrothermal synthesis, fundamental thermodynamics of solutions, and seawater desalination processes.

High-temperature distillation has been mentioned by several authors (*1*–*3*) as a possible alternative to water (especially seawater) desalination, and some work has been published in the field (*4*–*6*). However, some thermodynamic parameters, such as phase equilibria in the high-concentration range and the latent heat of vaporization under these conditions, have not been determined up to now and are the focus of our present investigations (*7*). We have limited our interest to the system NaCl–H_2O, which is the best-known binary system at high temperature, the knowledge of which is fundamental for extrapolation to seawater.

Previous Work

The system NaCl–H_2O has been extensively studied up to 300 °C, allowing publication of preliminary steam tables for NaCl solutions by Haas (*8*, *9*).

At higher temperatures, under the conditions of coexisting liquid and vapor phases, the system has been investigated by Keevil (*10*), who studied the parameters of the saturated solution in the range 180–650 °C. Oelander et al. (*2*) determined the liquid–vapor equilibria between 350 and 475 °C, at liquid-phase concentration up to 25%, work which has been extended up to 700 °C by Sourirajan et al. (*1*). Using radioisotopes, Khaibullin et al. (*11*, *12*) measured the same equilibria in the range 100–440 °C. Other results have been presented by Urosova (*13*), Copeland et al. (*14*), and Styrikovich et al. (*15*).

However, there are large divergences among the three major contributions (*1*, *2*, *12*) as pointed out in the Gmelins Handbuch (*16*). Moreover a lack of data at concentrations higher than 25%, which is attributed to the difficult handling of solutions under these conditions, encouraged us to reascertain the vapor–liquid equilibria and extend the measurements up to the saturation point.

Apparatus

Our measurements are based on the sampling method described in the literature (*1*, *2*). This technique has important advantages over other indirect methods as long as the ratio of the weight of the sample to the total weight of the phase remains low. For this purpose we have designed a complete high-pressure, high-temperature apparatus which is schematically represented in Figure 1.

A 1-L 316 SS autoclave with standard ¼-in. o.d. tubing and high-pressures valves has been used throughout this investigation. The autoclave is fitted out with two heating devices: an internal coaxial insulated heater CH1 driven by a high-precision PID regulator and an external heater CH2 made of two half-cylindrical aluminum blocks equipped with coaxial heating elements, piloted by a PI regulator. The conjugated use of two

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