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Different salinities water characterization by DSC-cooling

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Abstract Water is a fundamental element of life. Its multiple uses are indispensable for a wide spectrum of human activities. This study aims to characterize water from different salinities obtained in the Cariri region of Paraíba, Brazil. The samples were analyzed using the DSC-coupled to the Peltier system (DSC-Cooling) and physical–chemical water tests performed employing reactive kits, using the Spectroquant Merck® specific for each test. The calorimetric curves showed crystallization phase transitions with different characteristics in peak format and crystallization temperatures between the samples of different salinities. The calorimetric data obtained in the process of crystallization of water is directly correlated to the physico-chemical parameters of conductivity and total dissolved solids, showing that the analytical technology DSC-cooling/heating is suitable for characterization of different salinities water.

Keywords DSC-cooling · Water · Crystallization

Introduction

Water is a fundamental element of life. Its multiple uses are indispensable for a wide spectrum of human activities. The industrial and demographic expansion observed in recent decades has resulted in impairment of rivers, lakes, and reservoirs, making it necessary to conduct tests of their quality monitored through the assessment of physical, chemical, and biological characteristics.

Water has a melting point of 0 °C and boiling at atmospheric pressure. It shows the latent heat of fusion of 1.436 kcal/mol and latent heat of vaporization of 9.717 kcal mol^{-1} [1].

During the cooling, water is solidified to ice and the solutes are concentrated in the liquid phase. The ice usually forms nucleus and crystallizes after supercooling at about −10 to −15 °C below the equilibrium freezing point at 0 °C [2].

Thermal analytical methods prove to be a rapid and reproducible method that can be used, alone or combined with other techniques, with different purposes [3–6].

This study aimed to evaluate the thermal characterization of different salinities water by DSC-cooling.

Experimental

Samples

The samples were collected in Serra Branca city, state of Paraíba. Three well water samples from different salinities

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were obtained, and denominated as samples A1, A2, and A3.

Thermal analysis studies

The curves were obtained on a Shimadzu calorimeter, model DSC-60, coupled to a Peltier cooling system, model EK90/SH with nitrogen flow of 350 mL min^{-1}. Dodecane was used as standard for equipment calibration, where expected value is −20 °C. Analysis involved 2 μL of samples in aluminum crucible hermetically sealed in a Shimadzu press, model SSC-30. Rising temperature experiments were conducted in the temperature range from 25 to −35 °C at heating rate of 5 °C min^{-1}.

Physical–chemical tests

The determination of aluminum, ammonium, bromine, lead, chlorine, chloride, chromium, hardness (Ca), iron, fluoride, manganese, sodium, and nitrate in water samples A1, A2, and A3 were performed employing reactive kits, using the Spectroquant Merck® specific for each test. The pH was measured using pH meter, Tecnal, model Tec-3MP and the conductivity and total solids were obtained using a conductivimetry, Tecnal, model Tec-4MP.

Results and discussion

The thermal profile of the well water samples studied by DSC-cooling showed different behavior compared to that cited in the traditional literature, considering the crystallization temperature, which is 0 °C and the nucleation phenomenon which occurs in the range of −10 to −15 °C [2].

The calorimetric curves showed the presence of two phase transitions, the first corresponding to an exothermic event, and the second to an endothermic, Fig. 1.

The calorimetric data obtained showed onset temperature of crystallization (nucleation) in the temperatures of −9.19, −16.15, and −19.16 °C for the samples A1, A2, and A3, respectively. According to Hilllgren [2], during the cooling process, water is solidified to ice and the solutes are concentrated in the liquid phase. The ice usually forms nucleus and crystallizes after supercooling at about −10 to −15 °C, below the equilibrium cooling point which is 0 °C. According to the results obtained in this study, the crystallization temperatures of the water samples disagree with the values cited in literature.

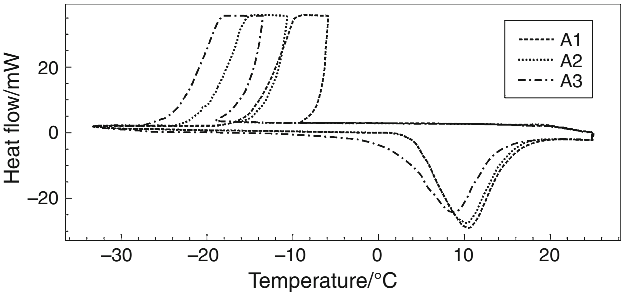

Fig. 1 DSC-cooling curves of different salinities water samples (A1, A2, A3), at a heating rate of 5 °C min^{-1}

The transition energies obtained in these crystallization processes were −32.75, −32.74, and −32.05 mW corresponding to the crystallization temperatures ranges of −5.89 to −15.06, −10.58 to −20.76 and −13.37 to −24.23 °C, for the samples A1, A2, and A3, respectively. The crystallization peak formats showed a behavior quite typical for the water samples, because it was possible to observe that the onset crystallization temperature occurs below values (plus negatives) in the curves and that the heat produced causes an increase of the temperature measured in the calorimeter system, deforming the peak characteristic of a normal phase transition. Figure 2 shows the crystallization phase transition of the samples, with the temperatures cited above.

The cooling process of the water sample reaches the onset nucleation to crystallization temperatures depending on the salinity of the sample. The crystallization process is exothermic and when it releases energy into the system it interferes in the thermocouple reader temperature, which begins to move towards heating up the whole process of crystallization has occurred.

After the crystallization process the temperature returns to the programmed cycle cooling system and finalizes the crystallization process with a variation range between the

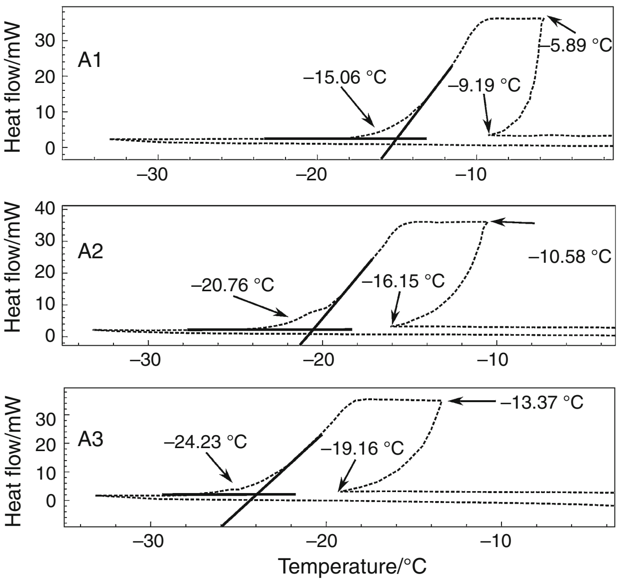

Fig. 2 Crystallization phase transition of the samples A1, A2, and A3

Table 1 Results of physico-chemical analysis of water potability

Parameters	Units	MAV[a]	A1	A2	A3
Aluminum	mg L^{-1}	0.2	0.064	0.040	0.072
Ammonia	mg L^{-1}	1.5	12	9	18
Bromine	mg L^{-1}	2.0	0.225	0.253	0.224
Lead	mg L^{-1}	0.01	0.24	0.61	1.73
Chlorine	mg L^{-1}	5	0.91	0.80	1.5
Chloride	mg L^{-1}	250	1120	3450	3845
Conductivity	µs cm^{-1}	100	3740	10430	24820
Chromium	mg L^{-1}	0.05	0.032	0.018	0.127
Hardness	mg L^{-1}	500	830	1060	1691
Iron	mg L^{-1}	0.3	0.022	0.063	0.044
Fluoride	mg L^{-1}	1.5	1.17	0.94	4.1
Manganese	mg L^{-1}	0.1	0.135	0.141	0.22
Nitrate	mg L^{-1}	10	82.5	88	175
pH	–	6–9.5	7.44	7.48	7.57
Sodium	mg L^{-1}	200	790	2320	4700
Total solids	ppm	1000	1690	5210	12524

[a] Maximum allowed value

onset and endset temperatures from 4.6 to 5.9 °C depending on salinity.

The transition energies involved in the process were close to the samples A1, A2, and A3; around −32 mW. The melt occurrance of water crystal needs of heat, different of the crystallization process. The onset melting temperatures also differed from the cited literature.

The melting points of samples studied were: 4.10, 3.94, and 1.89 °C and the transition energies were 27.64, 26.10, and 21.99 mW for samples A1, A2, and A3, respectively (Table 1).

Electrical conductivity tests and total dissolved solids present the results for (3.740 µs cm^{-1} and 1.690 mg L^{-1}), (10.430 µs cm^{-1} and 5.2100 mg L^{-1}), and (24 820 µs cm^{-1} and 12524.0 mg L^{-1}) the samples A1, A2, and A3, respectively.

Comparison of the calorimetric curves and crystallization temperatures ranges of −5.89 to −15.06, −10.58 to −20.76 and −13.37 to −24.23 °C for samples A1, A2, and A3, respectively, is shown in Figs. 1 and 2, which demonstrated an ascending order in the negative temperature values of crystallization A1 < A2 < A3. The electrical conductivity data and total dissolved solids showed increasing values of these two parameters obeying the following salinity order: A1 < A2 < A3.

Conclusions

The calorimetric data obtained in the process of crystallization of water is directly correlated to the physico-chemical parameters of conductivity and total dissolved solids, showing that the analytical technology DSC-cooling/heating is suitable for characterization of different salinities water.

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