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Specific heat of carboxymethyl cellulose and Carbopol aqueous solutions

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Abstract

Aqueous solutions of polymers such as Carbopol and carboxymethyl cellulose (CMC) solutions are employed in laboratory for simulation of the thermo-rheological behaviour of complex fluids. Then, it is necessary to know their thermophysical properties with good precision. Especially, study of the constant pressure specific heat allows to undertake thermal balance and to describe the temperature field evolution under unsteady conditions.

Experimental results concerning the direct measure of the specific heat of two complex solutions in the range of temperatures (20–90 °C) are presented and detailed in this work. The temperature dependence of the specific heat is higher for CMC solutions than for Carbopol solutions. Furthermore, an energy contribution of molecular origin is put into evidence from the study of the concentration dependence of the specific heat. Thus, the excess in specific heat value can reach 8% of the water specific heat value.

Keywords: Specific heat; Complex fluids; Adiabatic calorimeter; Carboxymethyl cellulose; Carbopol

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1. Introduction

Polymer solutions generally consists of a dispersed phase (or solute) and a continuous phase (or solvent). For thermo-rheological simulations led in laboratory, the distilled or permuted water is used as continuous phase. The dispersed phase is composed of grains of resin such as Prolabo CMC or BF Goodrich Carbopol. The obtained solution shows a complex behaviour under shear stress, and the apparent viscosity reaches higher value for weak concentrations. Especially, the solution obtained with Carbopol resins takes a gel network aspect for mass concentrations lower than 1%.

The specific heat of polymer solutions, such as CMC and Carbopol solutions, has been very little studied. Cho and Hartnett [1] have observed that the specific heat value of a polymer solution for weak mass concentration is identical to that of the continuous phase. In the case of higher concentrations, Metzner [2] recommends to use the weighted value of solvent and solution specific heats.

For some aqueous polymer solutions, Bellet et al. [3] have determined, the volume specific heat at constant pressure using an analytic identification method. As indicated by these authors, the precision obtained by this method remains very modest (12%). Raynaud et al. [4] have used an inverse numerical identification based on a finite differences scheme.

Quantitative analysis of the volume specific heat data in Refs. [3,4] shows that the specific heat values

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Nomenclature

C	thermal capacity ($\mathrm{J\,K^{-1}}$)
C_p	specific heat ($\mathrm{J\,kg^{-1}\,K^{-1}}$)
ΔH	enthalpy variation (J)
m	mass (kg)
Q	energy (J)
Q^*	lost energy (J)
ΔS	entropy variation ($\mathrm{J\,K^{-1}}$)
T	temperature (K)
X	mass concentration (%)

Subscripts

0	empty calorimeter cell
1	filled calorimeter cell

of solutions are higher than the specific heat of water. We think that, there is presence of an extra energy contribution for these solutions. In other words, molecular links or molecular cohesion forces are not of hydrogen type only. Does the evaluation of molecular cohesion forces suppose the precise knowledge of the value of the specific heat?

Because of the importance of these results, we have been interested in the study of the mass specific heat of these complex solutions using a direct and precise measurement method. We have designed quasi-adiabatic calorimeter of spherical exchange symmetry, particularly adapted to viscous fluids. The development of this calorimeter, Semmar et al. [6], has shown us that precision of measures was inferior to 2%. The calculated estimation of measurement errors shows that the loss of energy by evaporation is the main cause of the error of measure. The qualitative study of the specific heat allows us to make obvious the energy molecule contribution (EMC) and to estimate its value.

2. Measurement principle

The thermodynamic definition of specific heat at constant pressure is given by

$$C_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p \qquad (1)$$

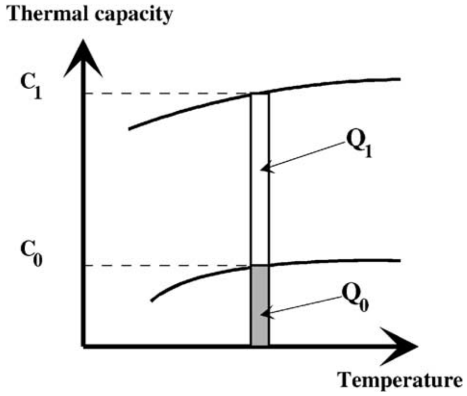


Fig. 1. Adiabatic measurement principle.

For a given system, it invite us to first measure the enthalpy variation as a function of the variation of temperature, and then to calculate its specific heat. However, it is impossible to measure infinitesimal variations of enthalpy and temperature. Moreover, in the relationship (1), the considered enthalpy is relative to the studied solution and not to the calorimetric system.

The relationship (1) can be approximated by the measure of the enthalpy variation in a reduced temperature range (ΔT). Then, the mean specific heat measured in this interval is then given by

$$C_p = \frac{1}{m}\left(\frac{\Delta H}{\Delta T}\right)_p \qquad (2)$$

As represented in Fig. 1, the enthalpy variation of the studied solution is deduced from variations of the filled calorimeter (ΔH_1) and of the empty calorimeter (ΔH_0), and can be expressed with corespondent calorific capacity functions

$$\Delta H = \Delta H_1 - \Delta H_0 = \Delta T(C_1 - C_0) \qquad (3)$$

Then the specific heat of the solution is given by

$$C_p = \frac{1}{m}(C_1 - C_0) \qquad (4)$$

With a precise measure of thermal capacities of the empty and filled calorimeter cell, it will be possible to find the mean specific heat of the sample. Nevertheless, we stress that the relationship (4) supposes a perfect adiabaticity of the calorimeter.

When the calorimetric system worked with quasi-adiabatic or isobaric conditions, lost heat is generally reproducible and quantifiable. The relationship giving the specific heat can be obtained with the following expression which takes into account heat loss:

$$C_p = \frac{1}{m}\left(\frac{C_1 - C_0}{1+\varepsilon}\right) \quad (5)$$

where the coefficient of correction ε is the ratio:

$$\varepsilon = \frac{Q_1^* - Q_0^*}{Q_1 - Q_0} \quad (6)$$

For high vapour pressure liquid, the function ε is generally known. The expression (5) is then used to calculate the specific heat value. In this work, lost energy (Q^*) is calculated by quantifying parasitic thermal exchanges (conduction and effect of fin) and losses of energy by evaporation (Appendix A).

With our calorimeter, the thermal capacity difference has to be relatively important in order to make parasitic thermal exchanges negligible. The C_1/C_0 quotient is an important parameter which determines the precision of the adiabatic method. To some degree, the reliability of the regulation system participate to it [5]. Despite the small dimension of the container (spherical cell: 30 mm of diameter and 0.5 mm thick cooper wall), the spherical symmetry that we have employed allows, to operate with a fraction C_1/C_0 close to 7/2 for water.

3. Specific heat measurements

Conception of the spherical calorimeter cell employed for measuring the specific heat of viscous liquids was described and detailed in a previous paper [6,7], nevertheless, we give some necessary precisions for the logic of this study.

The originality of our calorimetric system resides in the use of concentric spherical heater that allows to optimise the time of heating, and then the thermal stabilisation time (Fig. 2). The heater is built up of two spherical copper enclosures between which a resistance is included. The resistance is composed of adjacent spiral scrolls fixed by adapted resins (5).

This heating element (6 in Fig. 2) is stabilised in a drying oven before use. Thus, the calorimetric cell is made of different materials. The determination of the thermal capacity of calorimetric cell (C_0) has to be made with a direct measure. Furthermore, thermal capacity C_0 translates the thermodynamic balance of the cell.

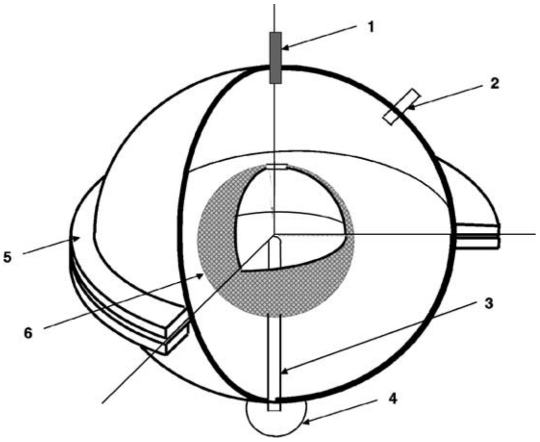


Fig. 2. Calorimetric cell.

We have made three series of measurements for different intensities of heating current in the admissible value range 0–30 mA [5]. The evolution of the thermal capacity is illustrated by Fig. 3.

The thermal capacity of the empty cell increases slightly (4%) according to the temperature with an experimental error of the order of 1%. It becomes negligible compared to solution samples thermal capacity. So as to facilitate the exploitation of results which follows, we have smoothed points of measure with a line called (baseline) of which expression is given in Fig. 3. Notice that the first points of measure situate close to the smoothing line because of the initial inertia of thermal screens [5].

3.1. *Controls of non-linear specific heat behaviour*

The calorimeter system behaviour has been controlled with pure water and with glycerol [6]. Profiles of specific heat curves are nearly linear and do not present anomaly (under atmospheric pressure) in the range of temperatures (10–90 °C). To complete this control, we have tested the studied calorimeter with a paraffin wax “Prolabo 52–54 °C”. The interest of this measure is to insure the feasibility and the reproducibility of measures for non-linear specific heat behaviour. By the way, we determine the working limits of our apparatus, too.

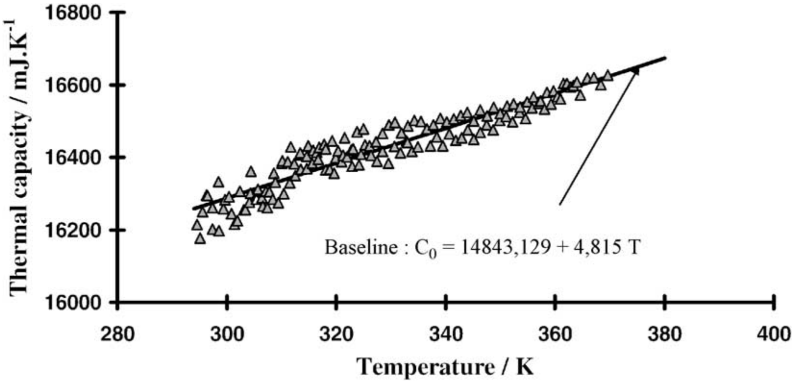


Fig. 3. Thermal capacity of the empty cell.

Results recorded in Fig. 4 are relative to three series of measures with different heating rates. Thus, we observe a first anomaly between 300 and 313 K which corresponds to a solid–solid transition (structural transformation) according to Delaunay [8]. A softening point of the texture of the paraffin is then observed.

The second anomaly is clearly more pronounced. It translates a progressive melting of the paraffin that begins at 316 K and reaches a maximum value for a temperature of 324.26 K. The chromatographic analyses undertaken by Delaunay [8] on a similar paraffin proves its structural impurity. The existence of pure paraffin with different melting points seems to be at the origin of the melting zone.

The value of the specific heat for the transition peak is measured with an absolute error of 1000 J kg^{-1} K^{-1}. The mean value of the specific heat peak is about 41,000 J kg^{-1} K^{-1}. The relative error increases with the temperature to reach a value of 2.5% at the melting point. This is due to the evolution of the increment interval of temperature during a measurement sequence: the imposed constant value of the heating current corresponds to 0.1 to 0.2 K increment for temperatures close to the melting zone, against 1–2 K increment away from melting temperatures.

3.2. *CMC aqueous solutions*

The CMC is a granular solid of yellowish white colour. Solutions of CMC are realised by dissolution of granules in distilled or permuted water. The obtained solution presents a high apparent viscosity (1000 times higher than that of water) even for small mass concentrations (of 0.5–3%).

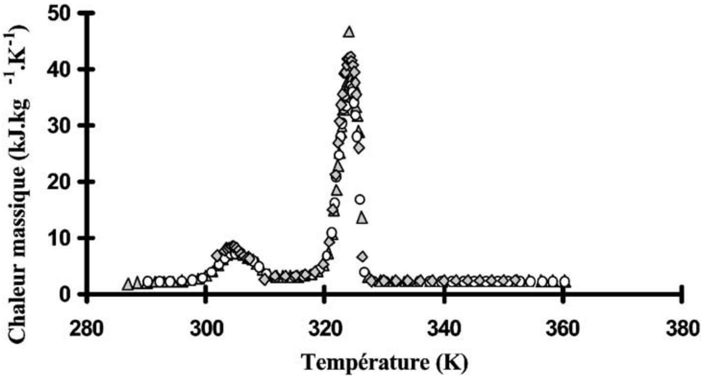


Fig. 4. Specific heat of the paraffin wax “Prolabo 52–54 °C”.

Granules of CMC used are marketed by "Prolabo" and possess a degree of substitution going from 65 to 95%. This type of product is one the most used in laboratory to simulate the pseudo-plastic behaviour of complex fluids. In aqueous solution, the CMC presents a slightly basic pH. Chains of macromolecules obtained in solution are disordered and tangled.

We have measured the specific heat of these solutions between 293 and 363 K. Because of the high viscosity of these products, the filling of the calorimetric cell has been made by spreading. The disjointable heating element, allows to insure a homogeneous distribution of the fluid inside the cell. In order to reduce degassing phenomena during measurement period, we take the precaution to put the calorimeter cell in a drying oven at 60 °C for 2 h, period after which we determine the mass of the sample.

Curves of the specific heat evolution for three solutions of CMC are presented in Fig. 5. We observe that for small concentrations, the specific heat shows a temperature dependence more pronounced than for the concentration of 8.3%. As compared to the specific heat of water, the three curves present an excess of specific heat. For the 1.8% CMC solution, the difference between its specific heat and that of the water is going more important as the temperature increases. The same observation is made for the 3.5% CMC solution. For the 8.3% CMC solution we notice a change in the curve slope of specific heat that translates a saturation of the structural effect.

3.3. *Carbopol aqueous solutions*

Before solving in water, Carbopol resins appear under the form of strongly entangled threads. In order to obtain a gel, these resins are dispersed in water under the effect of moderate agitation. Then, the obtained substance is very fluid and must be neutralised with a basic mineral such as soda. The viscosity increases strongly under the effect of the development of negative charge on the axis of the polymer [9]. There is presence of secondary connection forces of ionic origin inside the obtained gel and its pH value varies between 6 and 8. Resins of Carbopol that we have used are type 940 of BF Goodrich Company. Under its form of gel, Carbopol solutions are easily placed inside the cell.

Nevertheless, as for solutions of CMC, we undertake the same degassing operation in a drying oven. To study the specific heat of the Carbopol solutions, we have selected three different concentrations: 0.15, 0.3 and 1%. The specific heat data are recorded in Fig. 6.

Contrary to CMC solutions, we observe that Carbopol solutions possess a faintly temperature dependence of specific heat. Moreover, the curves are nearly parallel to that of water. An interesting phenomena appears for 0.15 and 1% Carbopol concentration.

For the 0.15% concentration solution, the specific heat value varies from 4480 J kg^{-1} K^{-1} at 350 K to 4400 J kg^{-1} K^{-1} at 360 K, see Appendix A.

For 1% concentration solution, the specific heat value changes from 4640 J kg^{-1} K^{-1} at 353 K to

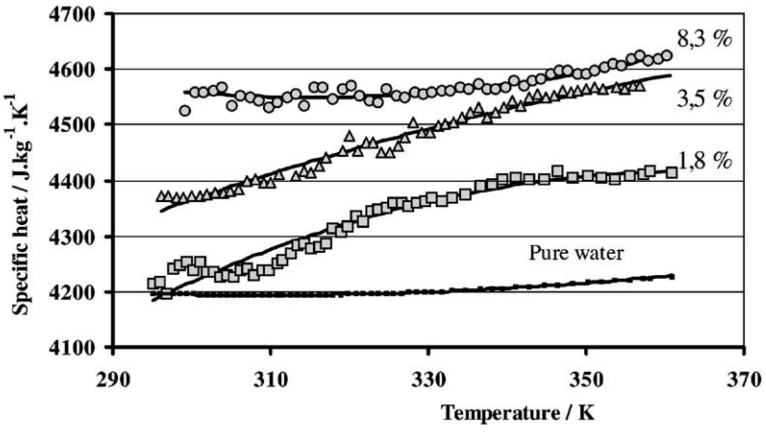


Fig. 5. Specific heat evolution for CMC solutions.

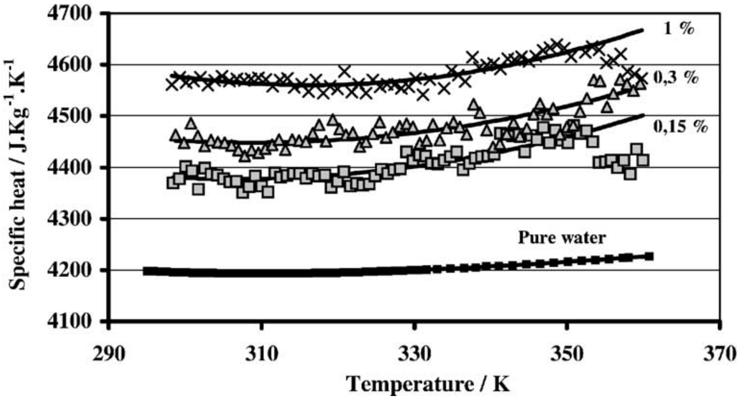


Fig. 6. Specific heat evolution for Carbopol solutions.

4570 J $kg^{-1} K^{-1}$ at 360 K. This reproducible diminution of approximately 80 J $kg^{-1} K^{-1}$, though smaller than the absolute error of measure, leaves us suppose that the gel of Carbopol structure changes which makes the threshold flow collapse. The rheological characterisation is indispensable to verify such a phenomenon, but it is difficult in this range of temperatures.

4. Comparative study

Solutions of CMC do not involve important molecular interactions forces especially for weak concentrations. They possess an enclosed structure and flocculate [10]. The thermal agitation consecutive to heating in the calorimeter, is increasing with temperature. In presence of water molecules, molecular chains of CMC possess an energy potential which increases with temperature. According to our results, this is true for concentrations smaller than 3.5%.

Nevertheless, in view of the temperature dependence of the consistency of CMC the dissolution is sufficiently advanced [1] to suspect an important thermal agitation in the static state. According to Tadros [10] the thermal agitation predominates for diluted suspensions. For concentrated suspensions, the interaction between molecules results from collisions, which explain the specific heat behaviour at 8.3% CMC concentration. The viscoelastic behaviour of this last solution seems to be closely linked to the evolution of the specific heat as a function of the temperature. Indeed, the presence of an elastic behaviour means that there exists a well ordered “micro-architecture” and consequently forces of more important interaction.

Concerning solutions of Carbopol, the interaction of ionic type molecular forces provokes a “structural order”. The structure of solutions of Carbopol is flocculated with bridges of polymers [10]. Their system is regular, and the amplitude of forces is such that the thermal agitation of the Carbopol macromolecules becomes negligible. However, the specific heat of these gels is appreciably different from that of pure water. This evolution tends to decrease for increasing concentrations. Though system remains structured even for large concentrations, it goes vibrating more and more as concentration increases. However, the vibration amplitude does not increase linearly with concentration.

As for solutions of CMC, a rheological interpretation can be associated with this behaviour. The evolution of Carbopol solutions with the temperature is weak [1]. It seems that this gel remains effectively insensitive to the temperature (in the area of room temperatures) and that, even under the effect of shear stress.

No doubt, the evolution of the specific heat with the concentration for the two studied polymer solutions indicates a contribution to the specific heat of structural origin.

5. Structural contribution

In order to estimate the energy contribution (EMC) to the specific heat due to the presence of the

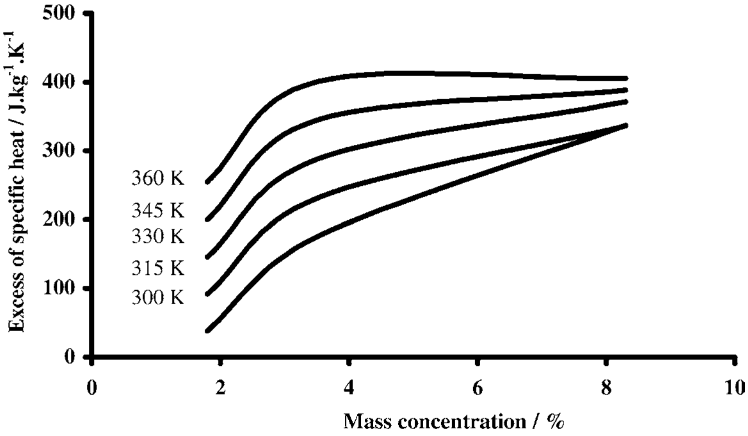


Fig. 7. Evolution of the structural contribution for CMC.

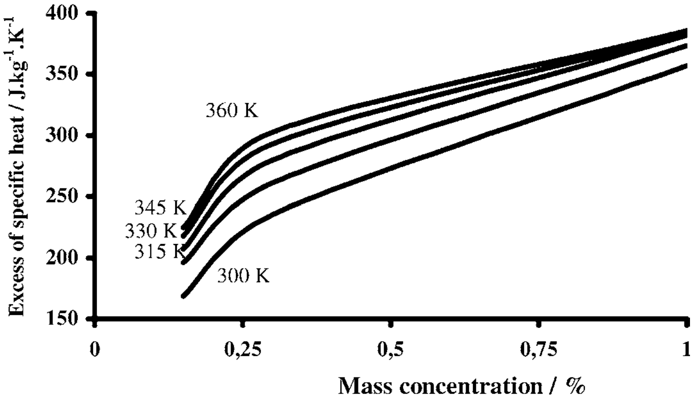


Fig. 8. Evolution of the structural contribution for Carbopol.

macromolecules of polymer in the water, we have examined the evolution of the excess specific heat [11] for a given temperature as a function of concentration.

The excess specific heat is calculated for a determined concentration. It is equal to the difference between the specific heat of the solute and that of the solvent.

Fig. 7 shows that the EMC of CMC increases with concentration in a non-linear manner to reach a limit that corresponds to a structural saturation. This limit is reached for concentrations between 3.5 and 8.3%. For higher than 8.3% concentrations, the specific heat CMC solutions has to decrease according to the additive rule [2].

Fig. 8 illustrates a different EMC behaviour for Carbopol solutions of that observed for CMC solutions. Indeed, the evolution of the excess in specific heat tends asymptotically to a contribution limit, much less pronounced than for CMC solutions.

6. Additional thermodynamic properties

Calculation of additional thermodynamic properties, such as specific entropy and specific enthalpy, asks integration of an analytical correlation: $C_p(X, T)$. The use of small temperature increments (0.5–1.5 °C) for specific heat measurement makes possible a numerical integration:

$$\Delta H(T) = \Delta H(T_0) + \int_{T_0}^{T} C_p \, \mathrm{d}T = \sum_{i=1}^{N} C_{p(i-1/2)}(T_i - T_{i-1}) \tag{7}$$

$$\Delta S(T) = \Delta S(T_0) + \int_{T_0}^{T} C_p \frac{\mathrm{d}T}{T} = \sum_{i=1}^{N} C_{p(i-1/2)}(\ln(T_i) - \ln(T_{i-1})) \tag{8}$$

As an example of calculation, Appendix B gives, the result obtained for 0.15% Carbopol solution. We used this result to evaluate the relaxation energy for the same solution. The value of this energy is about 1 kJ kg^{-1} in the temperature range (349–360 K).

7. Conclusion

In order to verify the calorimeter answer under non-linear working conditions, we have tested its behaviour with a paraffin wax of which the temperature dependence is strong. The reproducibility of its specific heat remains good, even under delicate functioning conditions. Thereafter, we have measured the specific heat of two original polymer solutions.

Curves of specific heat thus obtained, do not present well-defined anomalies between 293 and 363 K. However, we observe a faint singularity for Carbopol solutions that begins to the vicinity of 353 K. It is detectable for concentrations 0.15 and 1%. It is supposed to indicate a relaxation of the gel structure that is accompanied by the collapse of the threshold of flow. Furthermore, due to the sensitivity of the calorimeter we have been able to make into evidence the presence of a structural contribution to specific heat for the CMC and Carbopol macromolecules. This contribution is different according to whether molecular interaction forces are of ionic origin or not.

Hypotheses that consist to suppose that the specific heat of polymer solutions is equal to that of the solvent, is false in the case of aqueous polymer solutions. The water solution of CMC with 3.5 mass% concentration presents a contribution of the order of 3.5% of specific heat value at 300 K, and of the order of 8% of this same value at 345 K. The 0.15 mass% concentration Carbopol solution presents a contribution of 4% at 300 K and 6% at 345 K. This contribution increases with concentration.

If the correlation of specific heat in function of temperatures is easy to establish, we notice that an exponential model, alone, allows to take into account the complex evolution of the structural contribution. Independent of the immediate interest relative to specific heat of polymer solutions, in particular 1.8 and 3.5% CMC and the 0.15 and 0.3% Carbopol, we work currently on the development of a model for the specific heat that takes the two thermodynamic variables (X, T) into account.

Appendix A. Lost energy calculation

The computation is based on the overall heat and mass transfer equations:

- radiation and convection between the cell and the spherical shield:

$$\Phi_\mathrm{r} = \frac{\sigma S_\mathrm{c}(T_\mathrm{c}^4 - T_\mathrm{s}^4)}{(1/\varepsilon_\mathrm{c}) + (S_\mathrm{c}/S_\mathrm{s})((1/\varepsilon_\mathrm{s}) - 1)} \quad \text{and}$$

$$\Phi_\mathrm{cv} = \frac{\nu + 1}{2} \frac{c_v P_\mathrm{r}}{(2\pi R T_\mathrm{c})^{0.5}} \frac{a_\mathrm{c} S_\mathrm{c}(T_\mathrm{c} - T_\mathrm{s})}{1 + (S_\mathrm{c}/S_\mathrm{s})(1 - a_\mathrm{c})}$$

- conduction and thermal fin effect between the vent, wires and the cylinder shield:

$$\Phi_\mathrm{cd} = N \frac{\lambda \pi d^2}{4L}(T_\mathrm{c} - T_{\mathrm{s}^*}) + \lambda_\mathrm{t} s_\mathrm{t} \sqrt{\frac{\sigma p_\mathrm{t} \varepsilon_\mathrm{t} \varepsilon_{\mathrm{s}^*}}{\lambda_\mathrm{t} S_\mathrm{t}}} \sqrt{\frac{2}{5} T_\mathrm{c}^5 - 2 T_{\mathrm{s}^*}^4 T_\mathrm{c} + \frac{8}{5} T_{\mathrm{s}^*}^5}$$

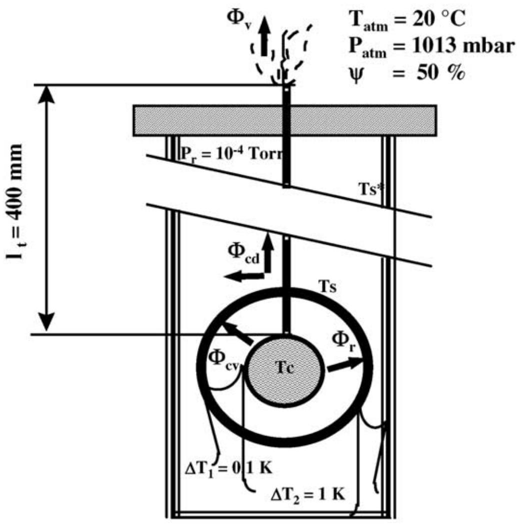
- mass transfer through the vent:

$$\Phi_\mathrm{v} = \dot{m} L_\mathrm{v} = \frac{D_\mathrm{v}}{R_\mathrm{v} T} \frac{P s_\mathrm{t}}{l_\mathrm{t}} \ln\left[\frac{P - P_\mathrm{v0}}{P - P_\mathrm{sat}(T)}\right] L_\mathrm{v},$$

$$\text{where } D_\mathrm{v} = 2.26 \times 10^{-5} \times \frac{1}{P} \left(\frac{T}{273}\right)^{1.81}$$

The lost energy is then given by: $Q^* = (\Phi_\mathrm{cd} + \Phi_\mathrm{cv} + \Phi_\mathrm{r} + \Phi_\mathrm{v})\Delta t$.

Data used in this study are summarised below:



λ (thermal conductivity of wires, W m^{-1} K^{-1})	200
N (number of wires)	10
L (mean length of wires, m)	0.2
d (mean diameter of wires, mm)	0.1
λ_t (Teflon thermal conductivity, W m^{-1} K^{-1})	0.23
l_t (length of Teflon vent, m)	0.4
s_t (cross-section 3.2/4.8 mm, mm^2)	10
S_t (heat exchange surface, cm)	60.3
$\varepsilon_c = \varepsilon_s = \varepsilon_{s^*}$ (total emmisivity, $\varepsilon_t = 0.7$)	0.1
R (air constant, J kg^{-1} K^{-1})	287
R_v (water vapour constant, J kg^{-1} K^{-1})	402
c_v (air isochore specific heat capacity, J kg^{-1} K^{-1})	715
S_c/S_s	0.25
a_c (accommodation coefficient)	0.5

Appendix B

Specific entropy and enthalpy of Carbopol solution at 0.15%

Temperature (K)	Specific heat of water (J kg^{-1} K^{-1})	Specific heat data (J kg^{-1} K^{-1})	Smooth curve of first order	Specific enthalpy of water (kJ kg^{-1})	Specific enthalpy (kJ kg^{-1})	Specific entropy percentage (kJ kg^{-1} K^{-1})
299.28	4.20E+03	4.38E+03	4.36E+03	3.61E+00	3.77E+00	1.21E+01
300.11	4.20E+03	4.40E+03	4.36E+03	7.09E+00	7.42E+00	2.37E+01
300.93	4.19E+03	4.39E+03	4.37E+03	1.05E+01	1.10E+01	3.51E+01
301.76	4.19E+03	4.36E+03	4.37E+03	1.40E+01	1.46E+01	4.67E+01
302.59	4.19E+03	4.40E+03	4.37E+03	1.75E+01	1.83E+01	5.82E+01
303.42	4.19E+03	4.39E+03	4.37E+03	2.10E+01	2.19E+01	6.97E+01
304.24	4.19E+03	4.38E+03	4.37E+03	2.44E+01	2.55E+01	8.10E+01
305.08	4.19E+03	4.38E+03	4.37E+03	2.79E+01	2.92E+01	9.26E+01
305.91	4.19E+03	4.37E+03	4.37E+03	3.14E+01	3.28E+01	1.04E+02
306.73	4.19E+03	4.37E+03	4.37E+03	3.49E+01	3.64E+01	1.15E+02
307.56	4.19E+03	4.35E+03	4.37E+03	3.83E+01	4.00E+01	1.27E+02
308.39	4.19E+03	4.36E+03	4.38E+03	4.18E+01	4.36E+01	1.38E+02
309.22	4.19E+03	4.38E+03	4.38E+03	4.53E+01	4.73E+01	1.49E+02
310.04	4.19E+03	4.36E+03	4.38E+03	4.87E+01	5.09E+01	1.60E+02
310.87	4.19E+03	4.33E+03	4.38E+03	5.22E+01	5.45E+01	1.71E+02
311.71	4.19E+03	4.39E+03	4.38E+03	5.57E+01	5.81E+01	1.83E+02
312.53	4.19E+03	4.38E+03	4.38E+03	5.92E+01	6.17E+01	1.94E+02

Appendix B (*Continued*)

Temperature (K)	Specific heat of water (J kg^{-1} K^{-1})	Specific heat data (J kg^{-1} K^{-1})	Smooth curve of first order	Specific enthalpy of water (kJ kg^{-1})	Specific enthalpy (kJ kg^{-1})	Specific entropy percentage (kJ kg^{-1} K^{-1})
313.35	4.19E+03	4.38E+03	4.38E+03	6.26E+01	6.53E+01	2.05E+02
314.18	4.19E+03	4.39E+03	4.38E+03	6.61E+01	6.90E+01	2.16E+02
315.00	4.19E+03	4.39E+03	4.39E+03	6.95E+01	7.26E+01	2.27E+02
315.82	4.19E+03	4.38E+03	4.39E+03	7.30E+01	7.62E+01	2.38E+02
316.65	4.19E+03	4.39E+03	4.39E+03	7.65E+01	7.98E+01	2.49E+02
317.47	4.19E+03	4.38E+03	4.39E+03	7.99E+01	8.34E+01	2.60E+02
318.29	4.19E+03	4.39E+03	4.39E+03	8.33E+01	8.70E+01	2.70E+02
319.12	4.19E+03	4.36E+03	4.39E+03	8.68E+01	9.06E+01	2.81E+02
319.95	4.20E+03	4.37E+03	4.39E+03	9.03E+01	9.42E+01	2.92E+02
320.77	4.20E+03	4.39E+03	4.39E+03	9.37E+01	9.78E+01	3.03E+02
321.59	4.20E+03	4.36E+03	4.40E+03	9.72E+01	1.01E+02	3.14E+02
322.42	4.20E+03	4.37E+03	4.40E+03	1.01E+02	1.05E+02	3.24E+02
323.24	4.20E+03	4.37E+03	4.40E+03	1.04E+02	1.09E+02	3.35E+02
324.07	4.20E+03	4.37E+03	4.40E+03	1.08E+02	1.12E+02	3.46E+02
324.89	4.20E+03	4.35E+03	4.40E+03	1.11E+02	1.16E+02	3.56E+02
325.72	4.20E+03	4.36E+03	4.40E+03	1.15E+02	1.19E+02	3.67E+02
326.54	4.20E+03	4.39E+03	4.40E+03	1.18E+02	1.23E+02	3.78E+02
327.37	4.20E+03	4.40E+03	4.40E+03	1.21E+02	1.27E+02	3.88E+02
328.18	4.20E+03	4.40E+03	4.41E+03	1.25E+02	1.30E+02	3.99E+02
329.01	4.20E+03	4.43E+03	4.41E+03	1.28E+02	1.34E+02	4.09E+02
329.82	4.20E+03	4.41E+03	4.41E+03	1.32E+02	1.38E+02	4.20E+02
330.64	4.20E+03	4.42E+03	4.41E+03	1.35E+02	1.41E+02	4.30E+02
331.45	4.20E+03	4.42E+03	4.41E+03	1.39E+02	1.45E+02	4.40E+02
332.27	4.20E+03	4.41E+03	4.41E+03	1.42E+02	1.48E+02	4.51E+02
333.09	4.20E+03	4.41E+03	4.41E+03	1.45E+02	1.52E+02	4.61E+02
333.91	4.20E+03	4.41E+03	4.41E+03	1.49E+02	1.56E+02	4.71E+02
334.72	4.20E+03	4.42E+03	4.41E+03	1.52E+02	1.59E+02	4.82E+02
335.54	4.20E+03	4.43E+03	4.42E+03	1.56E+02	1.63E+02	4.92E+02
336.36	4.20E+03	4.40E+03	4.42E+03	1.59E+02	1.66E+02	5.02E+02
337.18	4.20E+03	4.41E+03	4.42E+03	1.63E+02	1.70E+02	5.12E+02
337.99	4.21E+03	4.42E+03	4.42E+03	1.66E+02	1.74E+02	5.23E+02
338.81	4.21E+03	4.42E+03	4.42E+03	1.70E+02	1.77E+02	5.33E+02
339.62	4.21E+03	4.42E+03	4.42E+03	1.73E+02	1.81E+02	5.43E+02
340.44	4.21E+03	4.43E+03	4.42E+03	1.76E+02	1.84E+02	5.53E+02
341.26	4.21E+03	4.47E+03	4.42E+03	1.80E+02	1.88E+02	5.63E+02
342.08	4.21E+03	4.46E+03	4.43E+03	1.83E+02	1.92E+02	5.73E+02
342.89	4.21E+03	4.46E+03	4.43E+03	1.87E+02	1.95E+02	5.83E+02
343.69	4.21E+03	4.46E+03	4.43E+03	1.90E+02	1.99E+02	5.93E+02
344.48	4.21E+03	4.49E+03	4.43E+03	1.93E+02	2.02E+02	6.03E+02
345.28	4.21E+03	4.46E+03	4.43E+03	1.97E+02	2.06E+02	6.12E+02
346.08	4.21E+03	4.45E+03	4.43E+03	2.00E+02	2.10E+02	6.22E+02

Appendix B (*Continued*)

Temperature (K)	Specific heat of water ($J\,kg^{-1}\,K^{-1}$)	Specific heat data ($J\,kg^{-1}\,K^{-1}$)	Smooth curve of first order	Specific enthalpy of water ($kJ\,kg^{-1}$)	Specific enthalpy ($kJ\,kg^{-1}$)	Specific entropy percentage ($kJ\,kg^{-1}\,K^{-1}$)
346.89	4.21E+03	4.48E+03	4.43E+03	2.04E+02	2.13E+02	6.32E+02
347.69	4.21E+03	4.49E+03	4.43E+03	2.07E+02	2.17E+02	6.42E+02
348.49	4.21E+03	4.47E+03	4.43E+03	2.10E+02	2.20E+02	6.51E+02
349.29	4.22E+03	4.50E+03	4.44E+03	2.14E+02	2.24E+02	6.61E+02
350.10	4.22E+03	4.45E+03	4.44E+03	2.17E+02	2.28E+02	6.71E+02
350.91	4.22E+03	4.48E+03	4.44E+03	2.20E+02	2.31E+02	6.81E+02
351.72	4.22E+03	4.47E+03	4.44E+03	2.24E+02	2.35E+02	6.90E+02
352.54	4.22E+03	4.47E+03	4.44E+03	2.27E+02	2.39E+02	7.00E+02
353.36	4.22E+03	4.45E+03	4.44E+03	2.31E+02	2.42E+02	7.10E+02
354.18	4.22E+03	4.41E+03	4.44E+03	2.34E+02	2.46E+02	7.20E+02
354.99	4.22E+03	4.41E+03	4.44E+03	2.38E+02	2.49E+02	7.29E+02
355.81	4.22E+03	4.41E+03	4.45E+03	2.41E+02	2.53E+02	7.39E+02
356.63	4.22E+03	4.40E+03	4.45E+03	2.45E+02	2.57E+02	7.49E+02
357.46	4.22E+03	4.37E+03	4.45E+03	2.48E+02	2.60E+02	7.59E+02
358.28	4.22E+03	4.39E+03	4.45E+03	2.52E+02	2.64E+02	7.68E+02
359.11	4.23E+03	4.41E+03	4.45E+03	2.55E+02	2.67E+02	7.78E+02

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