Thermochimica Acta, 222 (1993) 203–207
Elsevier Science Publishers B.V., Amsterdam

Modification of the general method of determination of the heat capacity of liquids in high pressure crucibles by differential scanning calorimetry

M.D. Contreras Claramonte [a,*], F. Girela Vilchez [b] and A. Parera Vialard [a]

[a] *Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy, University of Granada, E-18071 Granada (Spain)*
[b] *Department of Applied Analytical Chemistry, Experimental Station of Zaidín, C.S.I.C. E-18008 Granada (Spain)*

(Received 6 October 1992; accepted 28 January 1993)

Abstract

With the aim of assuring a hermetic seal in high pressure crucibles, a teflon membrane has been introduced in order to allow for the determination of the heat capacity of liquids in the temperature range from 25 to 225°C. The influence of this membrane on the heat capacity values for water, methanol, i-propanol, *n*-hexane, toluene and dimethylsulphoxide was investigated.

INTRODUCTION

One of the main applications of calorimetric techniques in industry is in the determination of the heat capacity (C_p) of solid and liquid materials [1]. In the case of solids, even though it is still necessary to take precautions, their determination does not present great problems. With liquids, however, because of their volatility greater care must be taken to prevent loss of sample.

One of the accessories offered by the majority of companies producing differential scanning calorimeters (DSC) is a special type of hermetically sealed crucible for the investigation of liquids, known as a "high pressure crucible". Those produced by Mettler consist of an 80A Nimonic receptacle of 500 μl capacity with a screw top, between which a gold seal 0.3 mm in thickness has been inserted [2]. This produces a hermetic seal capable of withstanding internal pressures of up to 100 bar, thus permitting rapid and accurate measurement of the heat capacity of liquids at constant volume, even when these are at temperatures near their boiling points [3].

However, when working with these crucibles on a regular basis a

---

* Corresponding author.

complete hermetic seal is difficult to obtain with these three elements alone (receptacle, screw top and gold membrane) despite Mettler's guarantee, and a proportion of the substance is lost in the majority of tests. To obtain useful data, it is therefore necessary to repeat the test several times, prolonging excessively the duration of the experiment. Also, the gold seal, due to its great malleability, becomes deformed by the high pressure exerted upon it from the edge of the crucible, making it necessary to use a different membrane for each test, which raises considerably the price of heat capacity determinations.

In order to solve these problems, a second membrane has been introduced between the edge of the crucible and the gold membrane. This is of a more elastic, cheaper material and produces a better hermetic seal than the gold one. After selection of the material, the influence of the new membrane on the experimental values obtained for some liquids was tested.

METHODS AND MATERIALS

A Mettler TA 2000 differential scanning calorimeter was used, calibrated with respect to the fusion temperature of Indium, with 500 μl capacity high pressure crucibles (Mettler).

Teflon membranes of a diameter equal to the gold ones, were cut from a sheet of teflon (20 cm × 30 cm and 0.25 mm thick, film P.T.F.E.) supplied by SIPEM, S.A. (Valencia, Spain). Double distilled water (freshly prepared), methanol, i-propanol, *n*-hexane, toluene and dimethylsulphoxide (DMSO) (Q.P. Merck) were used as sample materials.

In all the heat capacity determinations the following conditions were applied. Both crucibles (reference and sample) contained a teflon membrane of a similar weight (29.5 mg ± 0.3 mg), the difference between the two never being greater than 0.2 mg.

The initial temperature of the test was approximately 4 or 5°C (20°C lower than the first reading taken). To obtain temperatures lower than room temperature, the furnace was placed in a chest freezer. For materials with a higher temperature of fusion, heating began a few degrees higher than 4 or 5°C, e.g. for dimethylsulfoxide.

Before undertaking the heat capacity test, the apparatus was kept at the initial temperature until an unfluctuating baseline was achieved, indicating an equal temperature in both crucibles (reference and sample). The reason for this extra precaution lies in the fact that the high pressure crucibles are larger and heavier than the aluminium ones usually used in other tests, and it is necessary to assure a constant flow of heat through them.

The rate of heating was less than 2 K min^{-1}, compatible with the data-registering capacity of the central data processor of the DSC. It is dependent on the temperature range used and the memory capacity of RAM, which is greater than 70 min.

In each case the 500 μl crucibles were completely filled with sample at

25°C. The constancy of the sample mass was checked by weighing it at 25°C on a semi-microanalytical balance before and after each test, thus assuring that there was no loss of sample.

For the heat capacity determination, the apparatus was programmed to perform the test, within the same temperature range and at the same rate, first on a blank (with the crucibles empty) and then on the sample. The experimental value for the sample was calculated from the difference of these two values followed by integration [3].

For each test substance, at least three assays were undertaken, the heat capacity values being measured at 1 K intervals. The best correlation coefficient between the temperature and the average heat calorimetry value for the three assays was calculated by using the mean-square test.

RESULTS AND DISCUSSION

When high pressure crucibles are used for heat capacity determinations of liquids with high vapour pressures over a wide temperature range, two problems become apparent: the lack of a hermetic seal and the deformation of the gold membrane. To overcome these, a second membrane has been introduced between the edge of the crucible and the gold membrane. This was made of a material more elastic, more economical and with a better ability to make a hermetic seal then gold. So that the new membrane should influence the experimental results as little as possible, the following conditions are recommended: it should not undergo any thermal change in the temperature range used, and it should be chemically inert to a range of solvents.

In order to choose this membrane, chemically inert materials such as different types of plastics, silicones, polypropylene, etc., were subjected to the DSC test and their thermal behaviour was studied.

Teflon was the only material which when tested showed only a small endothermic transformation at 20°C, with baseline recovery before 25°C (Fig. 1). The rest of the measured curve was flat up to 225°C where a second endothermic transformation, characteristic of a fusion process, took place; this continued up to 330°C. Teflon is therfore considered suitable for use in the temperature range from 25 to 225°C.

Selection of the material was followed by a study of the influence of the new membrane on heat capacity values. The heat capacities of a series of substances, water, methanol, i-propanol, *n*-hexane, toluene and dimethylsulphoxide, were determined in the new crucibles.

Three different tests were carried out on each of the liquids in the temperature range from 25°C to boiling point. The relative standard deviation of the heat capacity for each temperature change of 1 degree was never greater than 4%.

For each substance, the average heat capacity value is related to the temperature by the second-degree polynomial equation (Table 1); the

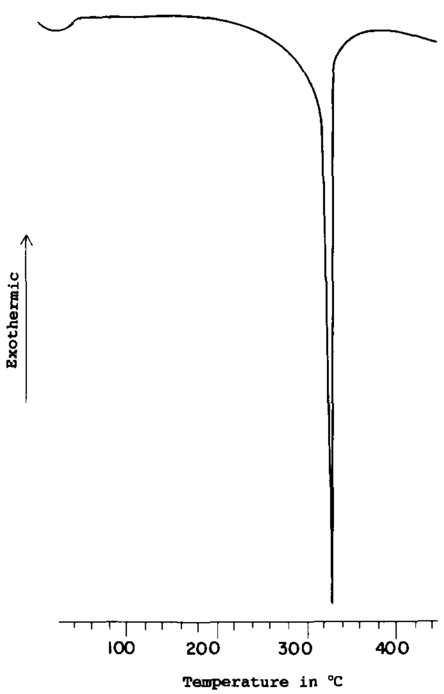

Fig. 1. DSC of teflon: $T_i = 0°C$; $T_f = 450°C$; $m = 5.78$ mg; heating rate = 10 K min^{-1}.

TABLE 1

Experimental heat capacity obtained using crucibles with a teflon membrane: $C_V = A + BT + CT^2$ (J mol^{-1} K^{-1})

Substance	T[a]/K	K min^{-1} [b]	*A*	*B*	*C*	*N*	r^2	*s*
Water	298.15							
	363.15	1.2	91.710	−0.123	1.509×10^{-4}	66	0.4820	0.3389
Toluene	298.15							
	359.15	1.2	231.215	−0.489	9.630×10^{-4}	61	0.5416	0.5738
n-Hexane	298.15							
	333.15	1.2	195.720	−0.368	1.344×10^{-3}	36	0.7623	0.8162
Methanol	298.15							
	343.15	1.2	240.511	−1.154	2.121×10^{-3}	46	0.8036	0.3354
i-Propanol	298.15							
	363.15	1.2	202.050	−0.928	2.471×10^{-3}	66	0.9744	0.5332
DMSO	298.15							
	356.15	1.2	−93.806	1.456	-2.061×10^{-3}	58	0.4245	0.4482

[a] Range of temperature.

[b] Rate of heating.

TABLE 2

Comparison between the literature and experimental heat capacity values when the teflon membrane is used

Substance	$(C_l)_p$ [a]/J mol^{-1} K^{-1} (Lit.)	$(C_l)_V$/J mol^{-1} K^{-1} (Exp.)	$(C_l)_p - (C_l)_V$	
			J mol^{-1} K^{-1}	J g^{-1} K^{-1}
Water	75.22	74.04	−1.17	−0.06
Toluene	156.04	167.96	+11.92	+0.13
n-Hexane	194.94	205.44	+10.50	+0.12
i-Propanol	143.49	144.78	+1.29	+0.02
Methanol	81.57	84.46	+2.89	+0.15
DMSO	153.52	153.23	+0.29	+0.01

[a] Ref. 4.

coefficient of determination (r^2) was never less than 0.54. Using the equation obtained, the heat capacity at 25°C was calculated for each liquid and compared with the value cited in the literature [4].

From Table 2, it can be seen that a high level of agreement exists between these results. For all the liquids studied, the difference between the values is relatively low (of the order of 0.1 J g^{-1}), in spite of the fact that the experimental values were obtained at constant pressure $(C_l)_p$ and the theoretical values at constant volume $(C_l)_V$. Thus the method may be considered to fulfil the aims of the study.

The teflon membrane did not undergo any visible transformation with any of the substances tested, and in each test a perfect seal was achieved enabling the determination of the heat capacity of the liquids even near their boiling points. The gold membrane did not undergo any deformation and the same membrane was used for many tests.

REFERENCES

1 J.L. Ford and P. Timmins, Pharmaceutical Thermal Analysis, Techniques and Applications, Ellis Horwood Limited, New York, 1989, Chapt. 2.
2 V. Schlichenmaier and G. Widmann, Thermochim. Acta, 21 (1977) 39.
3 Determination of specific heat with the Mettler TA 2000 System, Information No. 5.
4 Handbook of Chemistry and Physics, R.C. Weast (Ed.), CRC, Press Inc., Florida, 63rd edn., 1982–1983, Section D.