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Short communication

Comments on “volumetric studies of aqueous polymer solutions using pressure perturbation calorimetry . . . ” [Macromolecules 34 (2001) 4130]

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Abstract

Although, pressure perturbation calorimetry has been applied to a novel problem by Kujawa and Winnik [Macromolecules 34 (2001) 4130], their failure to appreciate earlier work on this method led to instrumental and methodological errors of unknown magnitude discussed in this note. The design and operation of the commercial instrument used by Kujawa and Winnik is shown to be flawed.

Keywords: Pressure perturbation calorimetry; Maxwell relations; Calorimetric vessels; Differential mounting; Pressure effects; Symmetry; Transitiometry

1. Introduction

In a recent study on poly(*N*-isopropylacrylamide) + water (or D_2O), Kujawa and Winnik [1] used a technique which they call pressure perturbation calorimetry (PPC). The technique is based on measuring the heat exchanged at constant temperature between the calorimetric vessel and the thermostat resulting from a pressure change above a polymer solution contained in the vessel. On the basis of such measurements performed at different temperatures and the Maxwell relation, $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$, the isobaric coefficient of thermal expansion (α_p) and its temperature and pressure derivatives can be determined. Existing literature shows this method [2–17] has been known for more than 30 years. Moreover, it has been applied in investigations of various systems and substances, including polymers [18] and solutions [19–21]. Kujawa and Winnik [1] imply the technique is new by not giving any references to the extensive literature on the subject. Moreover, the manufacturer of the instrument claims their technique has recently been patented [22]. The method was first called *the piezothermal technique* [4,5] by the Ter Minassian group, later with incorporation of automatic pressure control (both for step-wise and continuous linear variations) [14] it was called *pressure-scanning* [6] or *pressure-controlled calorimetry* [8], when it became possible [15,16] to measure simultaneously the mechanical derivative of a process or a change it became known as *scanning transitiometry* [17,23,24].

Kujawa and Winnik and the manufacturer of their instrument apparently failed to appreciate some of the subtleties of the method, thus leading to errors of unknown magnitude. The purpose of this note is to

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discuss the methodological errors in the paper under discussion [1].

2. Significance of the calorimetric signal

2.1. In a homogeneous phase

The heat effect $\mathrm{d}Q_{\mathrm{cal}}$ recorded by the calorimetric signal is always proportional to the mass m of the substance contained in the calorimetric vessel and reacted or submitted to a thermodynamic change of state: $\mathrm{d}Q_{\mathrm{cal}} = m\,\mathrm{d}Q_{\mathrm{m}}$, where Q_{m} is the molar heat of reaction or of the change under investigation. The mass m is of crucial importance in calorimetric experiments, in which the change in the thermodynamic state of the substance under investigation is induced by pressure variation. The manner by which the pressure variation is transmitted to the investigated substance affects the thermodynamic significance of the calorimetric signal recorded. Fig. 1 presents two limiting situations, one in which the pressure is transmitted through the investigated substance itself and the other where the pressure is transmitted directly through a piston placed in the calorimetric vessel [25]. The technique used by Kujawa and Winnik is an example of the first situation. When the pressure is transmitted through the substance under investigation, the active internal volume V_{cal} of the calorimetric vessel is approximately constant. In such an experiment the mass contained in the active part of the calorimetric vessel changes with pressure and is equal to the ratio $V_{\mathrm{cal}}/V_{\mathrm{m}}$, where V_{m} is the molar volume of the investigated substance. Due to compressibility, V_{m} varies with pressure. As the equations given in Fig. 1 show, the amount of heat ΔQ_{cal} exchanged between the calorimetric vessel and the thermostat due to a pressure change Δp (or the thermal power $\mathrm{d}Q_{\mathrm{cal}}/\mathrm{d}t$ induced by a linear pressure variation at a rate (b) is proportional to the isobaric coefficient of thermal expansion α_p of the substance under investigation. This property has been used in numerous investigations of various liquids and liquid solutions by different authors over wide ranges of both pressure and temperature [9,19–21,25,26]. Contrary to this, Eq. (4) in the paper [1] under consideration assumes both the molar volume V_{m} and α_p are invariant with pressure. V is also incorrectly defined as “the volume of the system”.

To make the significance of the pressure perturbation calorimetric signal completely clear, a constant mass configuration of the calorimetric vessel is also analyzed. Such a situation is modeled in Fig. 1 where a piston placed in the calorimetric vessel exerts pressure on the sample. The sample mass remains

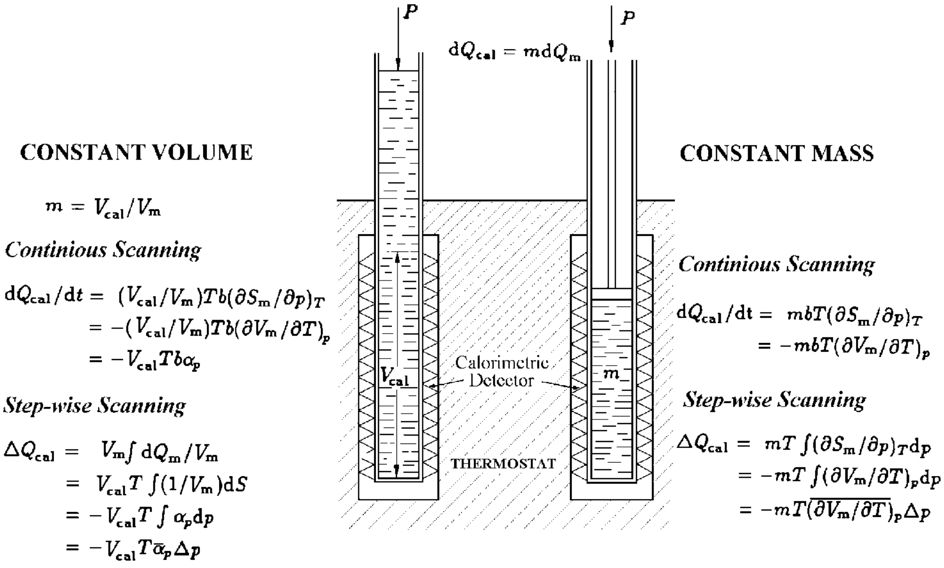

Fig. 1. Modeling of constant volume (open mass) and of constant mass calorimetric pressure vessels.

constant during pressure action and thus both ΔQ_{cal} and $\mathrm{d}Q_{\mathrm{cal}}/\mathrm{d}t$ are proportional to $(\partial V_{\mathrm{m}}/\partial T)_p$, so, in order to determine α_p one must know the molar volume $V_{\mathrm{m}}(p, T)$ of the sample.

In practice, placing a piston in the calorimetric vessel would cause a large heat effect from friction. For this reason mixed techniques are often used. For example a given mass of sample is placed in a flexible closed ampoule and the pressure is transmitted through a hydraulic fluid. In another configuration, a given amount of sample is placed in the calorimetric vessel over a non-miscible/non-reacting liquid (for example mercury) which transmits the pressure. In such mixed techniques the calorimetric signal is a sum of a constant mass contribution from the investigated substance and of a constant volume contribution from the pressurizing liquid present in the remaining part of the active volume V_{cal}. This case is described by Eq. (1) for the continuous pressure-scanning mode [18]:

$$\frac{\mathrm{d}Q_{\mathrm{cal}}}{\mathrm{d}t} = -bT[\alpha_{p,\mathrm{s}} V_{\mathrm{m,s}} + \alpha_{p,\mathrm{h}}(V_{\mathrm{cal}} - m_{\mathrm{s}} V_{\mathrm{m,s}})] \quad (1)$$

where m_{s}, $\alpha_{p,\mathrm{s}}$, $V_{\mathrm{m,s}}$ are respectively the mass, coefficient of thermal expansion and specific (or molar) volume of the investigated sample, $\alpha_{p,\mathrm{h}}$ is the coefficient of thermal expansion of the pressure transmitting fluid. A similar equation can be easily derived for the step-wise pressure-scanning mode by integration of Eq. (1).

It is important to notice that in temperature-scanning calorimetric experiments one must always balance the heat capacities of the calorimetric vessel and contents between the measuring and reference cells, while in pressure-scanning experiments the volume must be balanced in all analyses of data. Contrary to the above analysis, Kujawa and Winnik do not define the limits of their thermal system. V in Eq. (4) in their paper is incorrectly defined as "the volume of the system". They do not distinguish between the molar (or specific) volume of the investigated sample and the volume in which it is confined.

2.2. *With a phase change*

The analysis of pressure-scanning calorimetric data obtained in investigations of phase transitions, such as in the study of Kujawa and Winnik [1], must take into consideration the fact that in the course of the transition at least three domains are present in the calorimetric vessel: the pre-transition phase; the post-transition phase; and the interface; which is the domain of the transition itself [8,17]. The contribution to the calorimetric signal from the interface depends on the order of the transition. In first order transitions $(\partial V_{\mathrm{m}}/\partial T)_p$ and α_p are discontinuous, and it is erroneous to write that one can derive the coefficient of thermal expansion at the transition from pressure-scanning calorimetric data. Also, in the study [1] under discussion, differential mounting of the calorimetric vessels with respect to the action of pressure was done to eliminate the contribution from the solvent, so that only the contribution from the solute would be recorded. But this can only be done reliably if the active volumes V_{cal} of measuring and reference vessels are exactly equal and a proper balance of volumes is made, neither of which condition was verified in the study in question. In their paper, Kujawa and Winnik state that the cell volumes are identical, but that does not mean that the active cell volumes are equal.

3. Contribution from the calorimetric vessel

Reference [1] presents an example of the calorimetric response to pressure variations in their Fig. 2 (reproduced here as Fig. 2a), but does not discuss these curves. The first peak that appears after the pressure change (negative on compression and positive on decompression) is caused by asymmetry between the measuring and reference vessels [13]. When an increase of pressure dp is applied inside a cylinder of internal volume V_{cal}, the volume of the wall of the cylinder V_{w} will increase by an amount that can be approximated by [27]:

$$\mathrm{d}V_{\mathrm{w}} = V_{\mathrm{cal}} \kappa_{T,\mathrm{w}}\, \mathrm{d}p \quad (2)$$

where $\kappa_{T,\mathrm{w}}$ is the isothermal coefficient of compressibility of the material from which the calorimetric vessel is made. When introducing Eq. (1) into the Maxwell relation $(\partial S/\partial V)_T = (\partial p/\partial T)_V = \alpha_p/\kappa_T$, Eq. (3) is obtained:

$$\mathrm{d}Q_{\mathrm{w}} = V_{\mathrm{cal}} T \alpha_{p,\mathrm{w}}\, \mathrm{d}p \quad (3)$$

Thus, in the constant volume vessel (see Fig. 1) the total heat effect recorded is the sum of two effects,

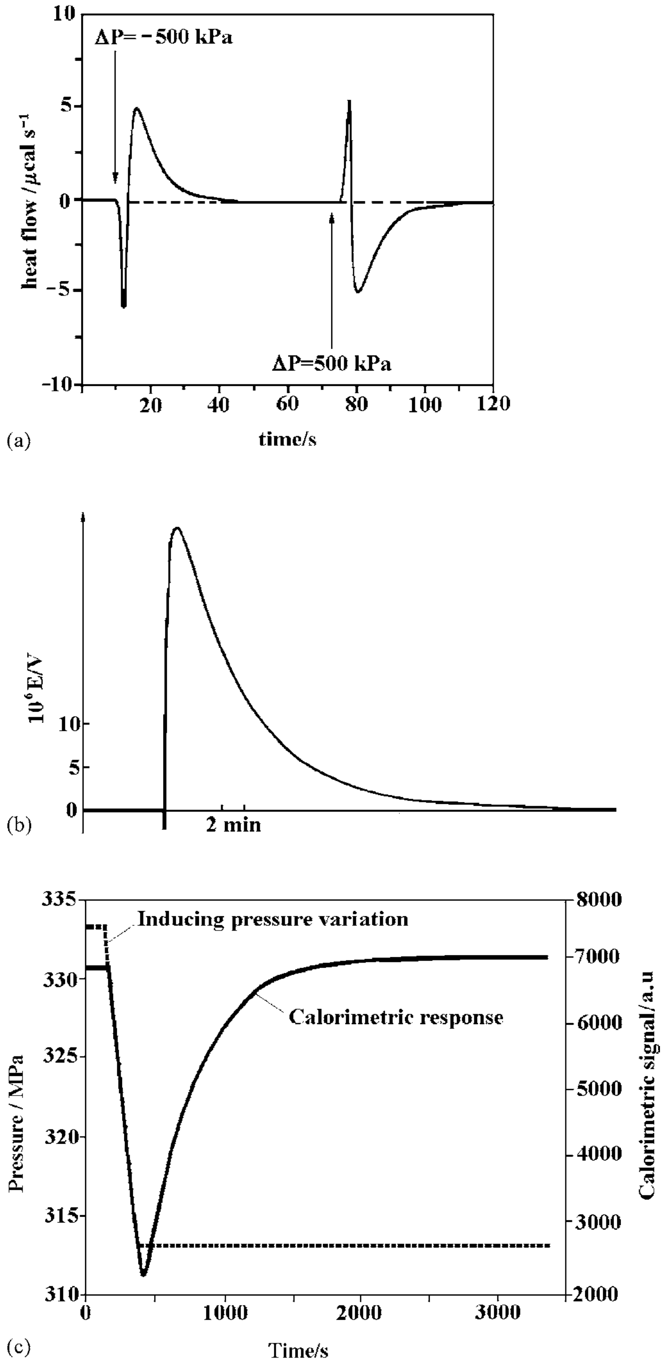

Fig. 2. Calorimetric responses to various methods of a step-wise pressure variation: (a) by a fast valve opening [1]; (b) by a hand pump action [5]; (c) by a feedback control action [20].

one from the sample (exothermic with positive α_p) and one from the vessel (endothermic):

$$dQ = V_{\text{cal}} T \alpha_{p,\text{w}}\, dp - V_{\text{cal}} T \alpha_p\, dp \tag{4}$$

If the pressure variation is fast (as it is in the study under discussion [1]) and there is a phase change or other reaction that requires a finite time, the vessel responds faster than the sample and the two effects are separated in time. The relative magnitudes of the two terms is nearly independent of pressure or the pressure change, so the contribution from the vessel is not negligible at low pressures as assumed by Kujawa and Winnik.

The fact that the calorimeter used by Kujawa and Winnik has a lower detection limit (which in heat conduction calorimeters implies a longer time response) than most calorimeters previously used with this method also actually exacerbates rather than alleviates this problem. The compression and decompression in the experiments done by Kujawa and Winnik was done rapidly compared to the time constant of the calorimeter which makes the process adiabatic and not isothermal as required by the Maxwell relation. Thus, at least part of the recorded heat is described incorrectly by the equations used to analyze the data. Fig. 2b presents an example where the pressure variation was realized with a hand pump, and the pressure variation was a bit too fast. The data show only a small peak from expansion of the vessel [5] similar to that seen in the data of Kujawa and Winnik [1]. Fig. 2c gives an example [20] of a step-wise pressure variation realized at a slow constant rate with a feedback pressure controller, and not as a result of a fast valve opening [1] or of a hand pump action [5]. The data in Fig. 2c show a unidirectional calorimetric response. Such a form can be taken as a verification that the proper thermodynamic conditions (i.e. very nearly isothermal) existed during the pressure-scanning experiment. It is also worth noting that, if the internal volumes of the differential vessels are exactly equal, the heat developed in the walls of the vessels (Eq. (2)) should also be exactly equal, but of opposite sign, and thus should compensate exactly. The data given in the paper [1] under discussion demonstrate that the vessels are asymmetric and thus the differential solvent correction is incorrect. The form of the calorimetric response found by Kujawa and Winnik thus calls into question the accuracy of variable pressure data collected with the MicroCal VP-DSC.

In conclusion, Kujawa and Winnik [1] used an erroneous thermodynamic description of the calorimetric response of their open (for mass transfer, but constant volume) experimental vessels, performed pressure variations under adiabatic rather than isothermal conditions (as required by the Maxwell relation), and the asymmetry of their vessels suggests the differential correction is not accurate. To answer the question of how much these problems influenced their results would require much more detailed information on the experiments than is given in the publication or in the personal communication provided by the authors.

It is hoped that both the paper under discussion and this note will contribute to a wider, but proper, use of pressure-controlled calorimetry and of its more developed forms such as scanning transitiometry in furthering macromolecular science.

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