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"THE SPECIFIC VOLUME OF POLYMER MELTS AS A FUNCTION OF TEMPERATURE AND PRESSURE"

B. Busch, M.D. Lechner, Physikalische Chemie, Universität Osnabrück, FRG
L.A. Kleintjens, DSM Research bv, Geleen, Holland

ABSTRACT

A new vibrating tube is constructed. It allows the determination of the specific volume in the pressure range of 1 to 800 bar and in the temperature range of 20 to 200 °C. The accuracy is better than 1 ‰. Test measurements on Poly (ethylene-co-vinylacetate) (Dodiflow, BASF) with 28 % vinylacetate and a molar mass M = 10,000 g/mol demonstrate that the TAIT-equation of state fits the p-v-T-data well.

INTRODUCTION

In order to optimize the production of polymeric products one needs exact values of the specific volume v at different pressures p and temperatures T. Therefore it is necessary to develop a new apparatus which works well in the range of 20 to 200 °C and 1 to 800 bar respectively. The calculation of p-v-T-values which cannot be measured need a suitable equation of state.

EXPERIMENTAL

The essential part of the apparatus is the so called vibrating titanium tube (Fig. 1). A U-formed tube with a fixed magnet is coupled magnetically with a coil. A regulation electronics provides the resonance frequency (Ref. 1). The density of a sample is proportional to the square of the period of vibration D. After calibration one can get the desired p-v-T-values (Ref. 2). The titanium tube is connected with a pressure generator and a measuring device (Fig. 2). The density measuring apparatus (DMA) is temperature controlled in a thermostat with silicon oil. The resonance frequency is measured with a frequency counter and the temperature is measured with a Pt100-thermometer. Period of vibration, temperature and calculation of the results are carried out with a computer.

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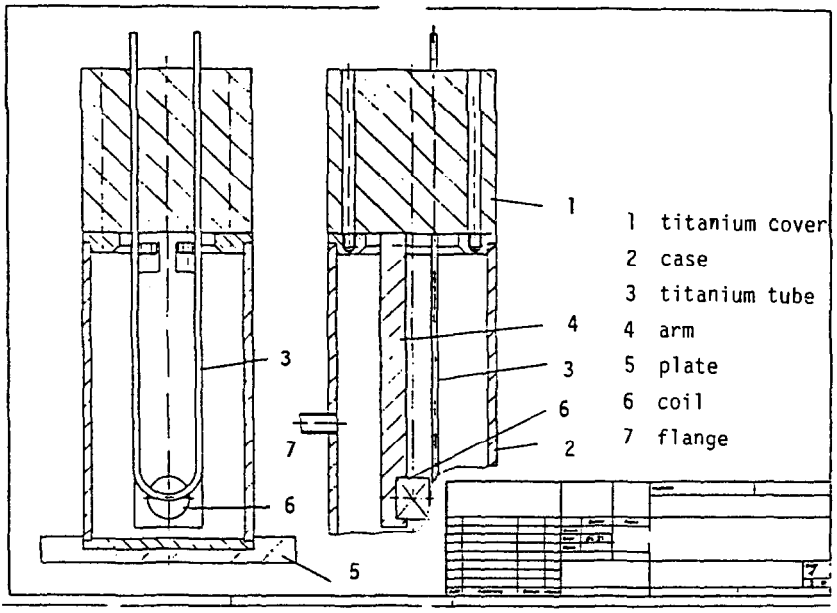

Fig. 1 : Titanium vibrating tube

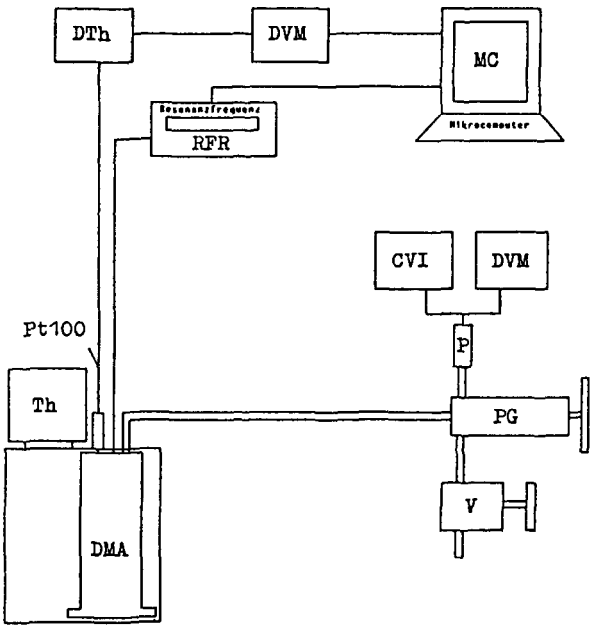

Fig. 2 : Density measuring apparatus (DMA) with Th : thermostat, Pt100, DTh : digital thermometer, DVM : digital voltmeter, RFR : resonance frequency regulator, MC : microcomputer, CVI : constant voltage instrument, P : pressure gauge, PG : pressure generator, V : valve

RESULTS AND DISCUSSION

Results of the test measurements upon distilled water agree very well with those presented in literature. Experimental errors are smaller than 1 ‰ (Fig. 3). The melting temperature of Poly (oxiethylene) 40,000 (POE) coincides with the value of 66 °C determined by thermal analysis (Fig. 4).
The p-v-T-behaviour of Dodiflow (Fig. 5) can be well described by the empirical TAIT-equation. It holds:

$$v(p,T) = (0.75181 + 1.20228 \cdot 10^{-3} \cdot T - 3.6156\ 10^{-7} \cdot T^2) \cdot$$
$$\cdot (1 - 6.4626\ 10^{-2}\ \ln[\ 1 + p/\{3.8692 \cdot 10^{3} \cdot \exp(-4.9032\ 10^{-3} \cdot T)\}\ ])$$

with v in cm^3/g, p in bar and T in K.
The deviation of the determined values from the calculated ones is less than 2 ‰ .

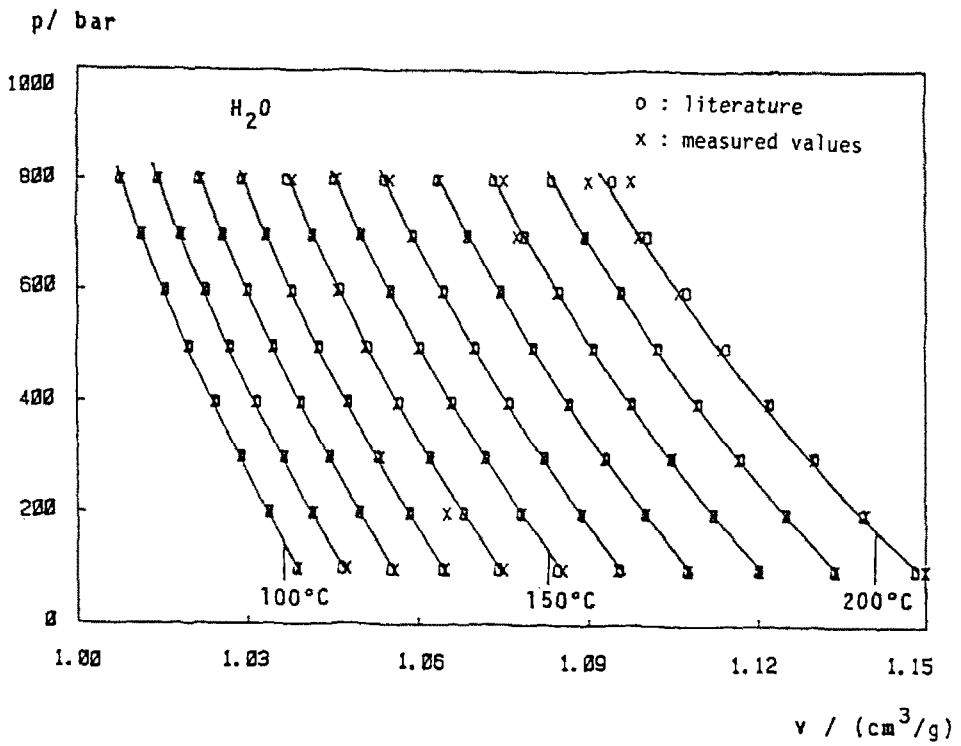

Fig. 3 : Specific volume of distilled water

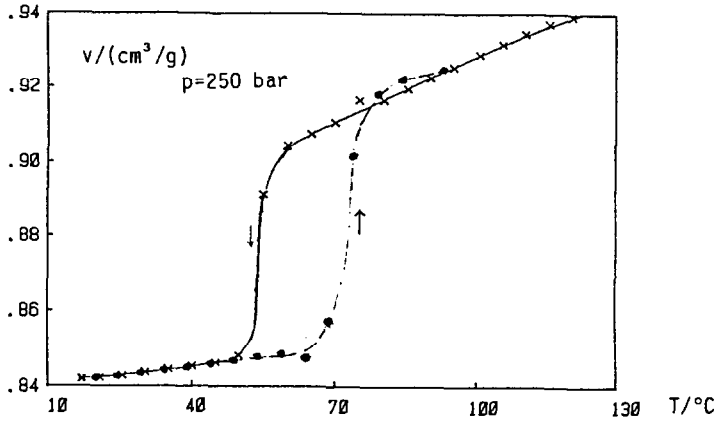

Fig. 4 : Melting diagram of Poly (oxiethylene) 40,000 (POE)

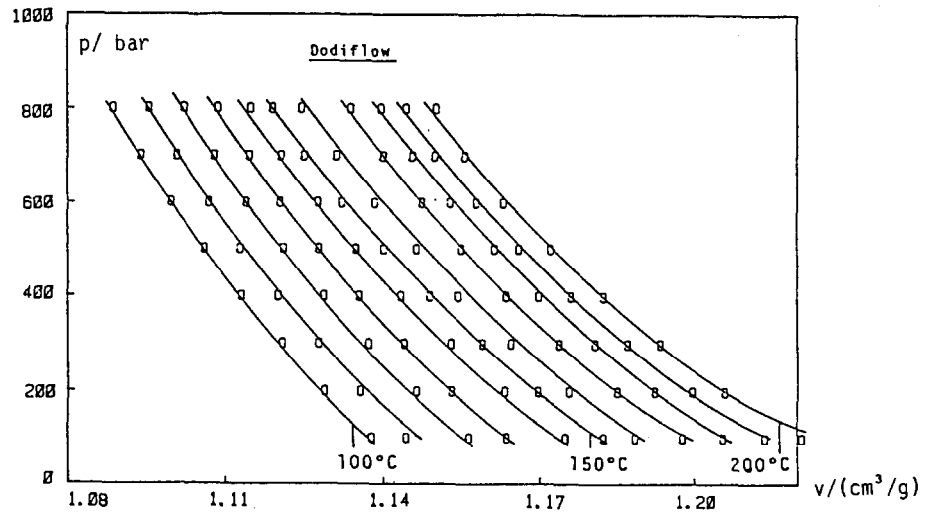

Fig. 5 : Specific volume of Poly (ethylene-co-vinylacetate) as function of pressure and temperature

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