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A simple method to determine the specific volumes of liquids and melts as a function of the temperature

Application to four *n*-alkanes ($C_{16}H_{34}$, $C_{18}H_{38}$, $C_{19}H_{40}$ and $C_{21}H_{44}$) under saturating vapour pressure in the 298–573 K range

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Abstract

A simple method to measure the specific volume of liquids as a function of the temperature is described. In order to validate the method, measurements are carried out in the 298–573 K range on four *n*-alkanes and the results are compared with previous experimental data from the literature.

Keywords: Specific volumes; Liquids; *n*-Alkanes; Water; Vapour pressure

1. Introduction

A previous paper [1] showed how specific volume values can be used to determine the slopes dp/dT of two-phase equilibrium curves, and subsequently construct topological p,T diagrams accounting for the stability hierarchy of polymorphs in one-component systems. With regards to the solid–liquid equilibriums related to polymorphs, it becomes necessary to know the volume change upon melting if the Clapeyron equation is to be used. Thus, a simple method was designed to measure the specific volume for any body in the liquid state as a function of the temperature.

For comparison as well as validation purposes, this method is applied to compounds for which data on the temperature dependence of the liquid density (or specific volume) are available from the literature.

This paper reports specific volume values determined in the (298–573) K temperature range for four *n*-alkanes and for water the specific volume data of which are well known.

2. Experimental

The *n*-alkanes were purchased from Aldrich for $C_{16}H_{34}$ (>99%) and from Alfa Aesar for $C_{18}H_{38}$ (99%), $C_{19}H_{40}$ (99%) and $C_{21}H_{44}$ (99%). All were used without any further purification.

The following scheme was used to determine the specific volume (and thus the density) of each *n*-alkane as a function of the temperature: the mass, m of an aliquot (typical masses were about 5–10 g) was weighed by means of a balance sensitive to 0.1 mg after being introduced in a calibrated cylindrical silica tube from Heraeus (Germany), whose inner diameter, d (typical diameters were about 5–10 mm) was measured by means of an alesometer sensitive to 0.001 mm. The tube was maintained overnight at room temperature under a vacuum of about 10^{-3} Pa and then sealed. Afterwards, it was suspended in an XU 75/300 oven from Climats (France), working at a $\pm x$ K-controlled temperature within 298–573 K ($x = 1$ up to 473 K, and 0.5 from 473 K). The temperature of the liquid was also measured by means of a chromel–alumel thermocouple close to the tube. The liquid was alternately heated or cooled slowly and held at isothermal steps during which h_m, the height of the meniscus, and h_b, that of the flat bottom of the inner part of the tube, were read by means of a cathetometer sensitive to 2 μm ($h_m - h_b$ values were typically about 100 mm).

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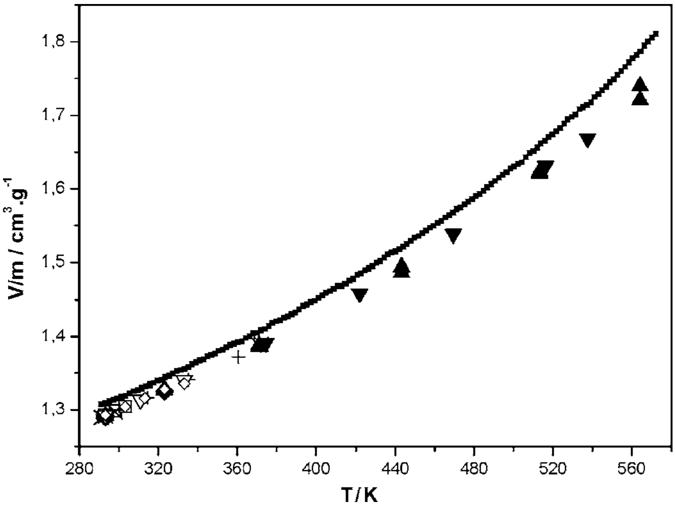

Fig. 1. Specific volume of *n*-hexadecane ($C_{16}H_{34}$) as a function of temperature. *Experimental*: (■) this work; (▼) Ref. [5]; (▲) Ref. [6]; (+) Ref. [7]; (×) Ref. [8]; (♦) Ref. [9]; (▽) Ref. [10]; (△) Ref. [11]; (●) Refs. [12,13]; (◯) Ref. [14]; (□) Ref. [15]; (◇) Ref. [16].

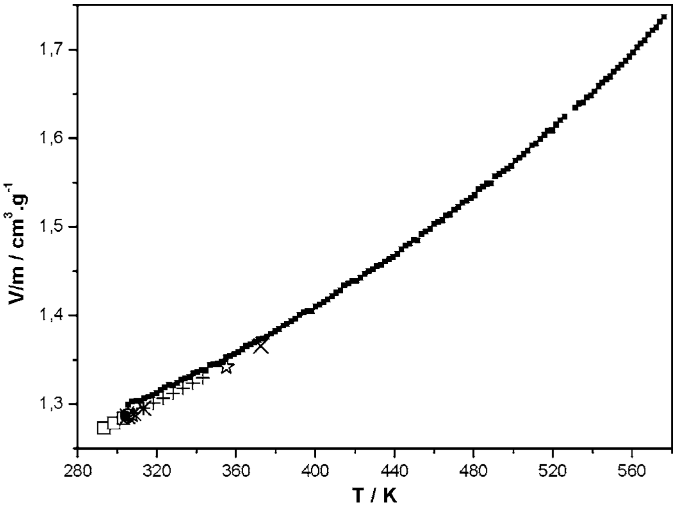

Fig. 3. Specific volume of *n*-nonadecane ($C_{19}H_{40}$) as a function of temperature. *Experimental*: (■) this work; (×) Ref. [8]; (△) Ref. [11]; (●) Ref. [12]; (◯) Ref. [14]; (□) Ref. [15]; (☆) Ref. [17]; (+) Ref. [18].

The specific volume of the melt is given by $v_l = \pi d^2(h_\mathrm{m} - h_\mathrm{b})/4m$, and the inaccuracy on v_l is calculated by $\Delta v_l/v_l \approx 2\,\Delta d/d + 2\,\Delta h/h + \Delta m/m$, where $2\,\Delta d/d \approx 0.06/5$, $2\,\Delta h/h \approx 0.06/80$ and $\Delta m/m \approx 4/1000$. It follows that $\Delta v_l/v_l$ is of about 1.5%. It should be noticed that, even though the silica glass expands as the temperature increases, its expansion was neglected since it has been proven negligible (see Le Châtelier [2] and Brückner [3]) in the temperature range under consideration (the linear expansion coefficient of the silica glass changes from 4×10^{-7} at 298 K to $\approx 5.5 \times 10^{-7}$ at 500 K) [4].

3. Results and discussion

Experimental dependence of the specific volume on (the) temperature for $C_{16}H_{34}$, $C_{18}H_{38}$, $C_{19}H_{40}$ and $C_{21}H_{44}$ is presented in Figs. 1–4, respectively. With regard to the 298–573 K range, the results for $C_{18}H_{38}$, at low temperature, and for $C_{21}H_{44}$ are in close agreement with the literature. The results for $C_{16}H_{34}$ and $C_{19}H_{40}$ are slightly greater than those from the literature by a difference that does not exceed 3.7% at high temperature for $C_{16}H_{34}$, and an average error of 1.5%. For $C_{19}H_{40}$ and $C_{21}H_{44}$, measurements were carried out on a range of temperature 200 K above the experimental data from the literature.

Since the presence of some “dead volume” after sealing each silica tube cannot be avoided, heating induces some vaporization that should be accompanied with a decrease of the mass of liquid. To check whether the difference in experimental versus extrapolated data was due to an increased loss of condensed matter while heating, the mass of the vapour phase (assumed to behave ideally) was estimated in each dead volume. It was found that, whichever the *n*-alkane, the vaporization-related mass loss was less than about 0.2% of the initial mass at 573 K.

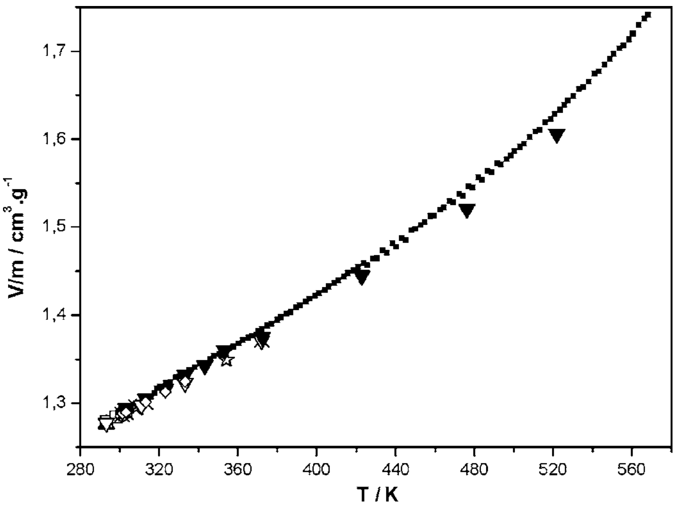

Fig. 2. Specific volume of *n*-octadecane ($C_{18}H_{38}$) as a function of temperature. *Experimental*: (■) this work; (▼) Ref. [5]; (×) Ref. [8]; (▽) Ref. [10]; (△) Ref. [11]; (●) Ref. [12]; (◯) Ref. [14]; (□) Ref. [15]; (◇) Ref. [16]; (☆) Ref. [17].

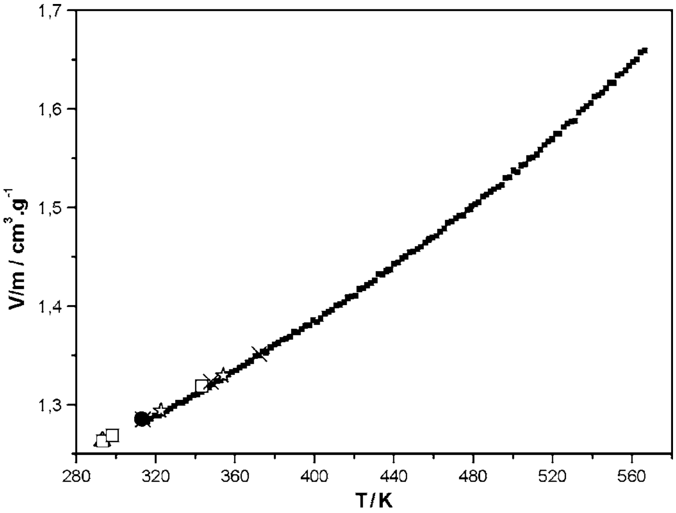

Fig. 4. Specific volume of *n*-heneicosane ($C_{21}H_{44}$) as a function of temperature. *Experimental*: (■) this work; (×) Ref. [8]; (△) Ref. [11]; (●) Ref. [12]; (◯) Ref. [14]; (□) Ref. [15]; (☆) Ref. [17].

Table 1
Coefficients of the third-order polynomials $v = a + bT + cT^2 + dT^3$ (v in cm^3 g^{-1} and T in K), that fit the specific volumes v of four liquid n-alkanes as a function of the temperature in the 298–573 K range

	a	b	c	d	r^2
$C_{16}H_{34}$	0.856332	23.5×10^{-4}	-4.413456×10^{-6}	5.62052×10^{-9}	0.999931
$C_{18}H_{38}$	0.533831	44.44×10^{-4}	-9.038316×10^{-6}	8.720324×10^{-9}	0.999818
$C_{19}H_{40}$	1.108915	4.1779×10^{-4}	1.136861×10^{-7}	1.811378×10^{-9}	0.9999
$C_{21}H_{44}$	0.917645	14.69×10^{-4}	-18.79738×10^{-7}	2.82448×10^{-9}	0.999851

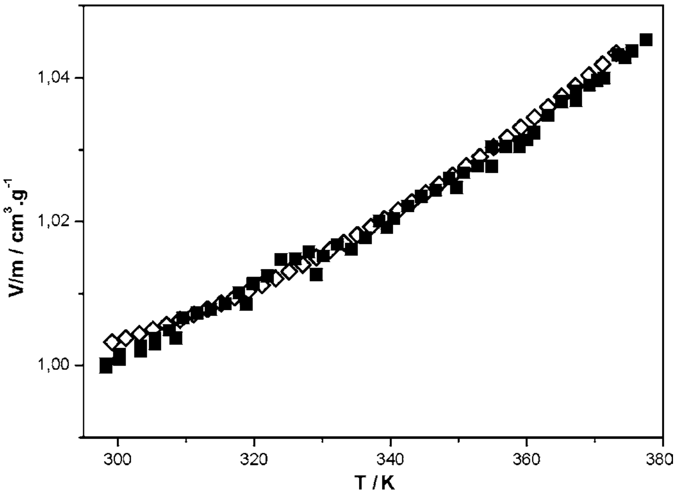

Fig. 5. Specific volume of liquid water as a function of temperature. *Experimental*: (■) this work; (◇) Ref. [19].

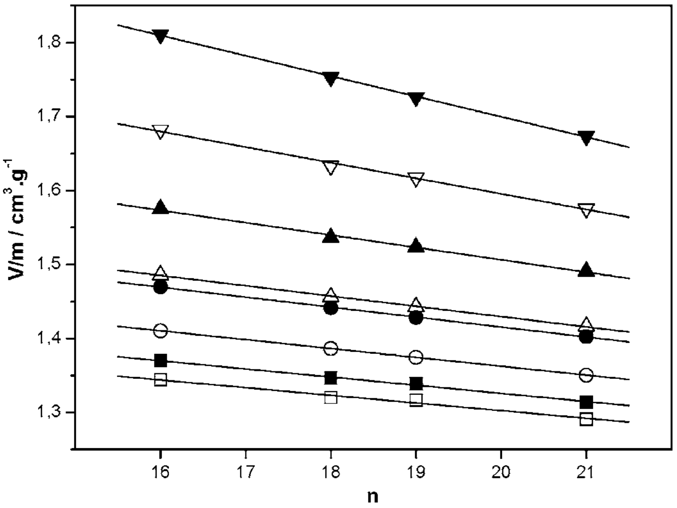

Fig. 6. Specific volumes of four n-alkanes ($C_{16}H_{34}$, $C_{18}H_{38}$, $C_{19}H_{40}$ and $C_{21}H_{44}$) at several temperatures as a function of the number n of C-atoms per chain. (□) 323 K; (■) 343 K; (○) 373 K; (●) 413K; (△) 423 K; (▲) 473 K; (▽) 523 K; (▼) 573 K.

As an additional test on the efficiency and accuracy of the method, the dependence of the specific volume of distilled water on the temperature was determined in the 300–380 K range. Fig. 5 shows that the data obtained virtually fit the usually admitted data [19].

The best empirical fits to the experimental data in Figs. 1–4 are obtained from third-order polynomials whose coefficients are listed in Table 1.

Then the isothermal dependence of the specific volume, v on the chain length was examined at several temperatures. In every case, a linear relationship, $v(n, T) = a(T)n + v_0(T)$, was found between v and the number, n of C-atoms in the chain (Fig. 6). Since the negative value of $a = (\partial v/\partial n)$ indicates how v decreases at constant temperature when each n-alkane chain is incremented with a CH_2-unit, the changes in $(\partial v/\partial n)_T$ and v_0 as a function of the temperature were addressed. $|(\partial v/\partial n)_T|$ and v_0 were found to increase exponentially as the temperature increases (see Table 2). That allows expressing by a unique empirical equation the specific volume of the four studied n-alkanes as a function of the temperature and the chain length (i.e. the number, n of C-atoms per n-alkane):

$$v(n, T)\,(\mathrm{cm^3\,g^{-1}}) = \left[1.22 + 0.06\,\exp\left(\frac{T\,(\mathrm{K})}{201}\right)\right] - \left[0.0076 + 0.00024\,\exp\left(\frac{T\,(\mathrm{K})}{130}\right)\right] n$$

Table 2
Exponentials ($y = A\exp(T\,(\mathrm{K})/B) + y_0$) that empirically describe the dependence of $a(T) = (\partial v/\partial n)_T$ and $v_0(T)$ on the temperature in the linear equations $v(n, T) = a(T)n + v_0(T)$ for the straight lines in Fig. 6

	A	B	y_0	r^2
$y = (\partial v/\partial n)_T$	−0.00024 ± 0.00003	130 ± 4	−0.0076 ± 0.0002	0.99979
$y = v_0(T)$	0.060 ± 0.007	201 ± 7	1.22 ± 0.02	0.99983

4. Conclusion

The validation of the presented method to measure specific volumes is done with four liquid n-alkanes whose densities are in close agreement with experimental points from literature values and the deviation is no greater than 3.7% at high temperature. The advantage of the presented method compared to other methods (especially to other dilatometric methods [20,21] is that nothing but heating or cooling is to be changed for measurements at various temperatures.

With this method, measurements could be carried out on a large range of temperatures whose upper limit is the maximum temperature allowed by the oven. In fact, the limiting factor could be the wall of the silica container. Nevertheless, the latter should resist the vapour pressure of the liquids all the better as its thickness is increased.

In addition, measurements on water as a reference allowed getting further insight on the accuracy of the method (the deviation is less than 0.3% from literature values). Thus, this simple method could be efficiently used to measure specific volumes versus temperature of any liquid or molten compound under its own vapour pressure. Moreover, it could apply to any mixture of solids leading to complete miscibility in the molten state, as mixtures of *n*-alkanes do, or even to any mixture of immiscible liquids below and above the critical mixing temperature. This should also be an incentive to apply this method to density measurements on molten drugs provided they do not significantly degrade in the molten state.

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