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# Isobaric Thermal Expansivity and Isothermal Compressibility of Several Nonsaturated Hydrocarbons at 298.15 K

**Emilio Aicart* and Elena Junquera**

Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense,
28040 Madrid, Spain

**Trevor M. Letcher**

Department of Chemistry, Faculty of Science, University of Natal, Durban 4001, South Africa

The isobaric thermal expansivity $\alpha_P$ and the isothermal compressibility $\kappa_T$ have been measured at 298.15 K for several nonsaturated hydrocarbons: 1-hexene, 1-hexyne, 1-heptene, 1-heptyne, 1-octene, 1-octyne, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene (1,3,5-trimethylbenzene). The results, together with previous data from our laboratory, are discussed in terms of the chain length of the hydrocarbons, the degree of unsaturation (-ane, -ene, -yne), the degree of methylation, and the position of the methyl groups on the aromatic ring.

## Introduction

The isobaric thermal expansivity $\alpha_P$ and the isothermal compressibility $\kappa_T$ are defined as

$$\alpha_P = V^{-1}(\partial V/\partial T)_P \tag{1}$$

$$k_T = -V^{-1}(\partial V/\partial P)_T \tag{2}$$

The ratio between both of them is known as the thermal pressure coefficient $\gamma = \alpha_P/\kappa_T$. Both quantities, $\alpha_P$ and $\kappa_T$, are of great interest since these properties have direct application in the determination of different parameters used in recent liquid-state theories. Among these, the Prigogine–Flory theory (Prigogine, 1957; Flory et al., 1964; Abe and Flory, 1965) is perhaps the most commonly used for apolar liquids (pure and mixed) of different molecular shape and size. The characteristic parameters of this theory $P^*$, $V^*$, and $T^*$ for the pure substances are obtained from $\alpha_P$, $\kappa_T$, and the molar volume $V_m$. The Prigogine–Flory theory, which gives fairly good results for the prediction of excess functions for binary systems, has been recently generalized by Patterson et al. (1968 and 1970) to relate the energy with the volume through different potentials. The Prigogine–Flory–Patterson theory (PFP) allows an interpretation of the discrepancies between the theoretical predictions and the experimental results in terms of effects of creation–destruction of order when the mixtures are formed. Applying this generalized model (Costas et al., 1988; Matilla et al., 1990), it is essential to have $\alpha_P$, $\kappa_T$, and $V_m$ values for the pure substances. Other theories, such as those of Sánchez and Lacombe (Lacombe and Sánchez, 1976; Sánchez and Lacombe, 1978) or the generalized van der Waals (Svejda and Kohler, 1983; Siddiqi et al., 1983; Kohler and Svejda, 1984), also require experimental values for $\alpha_P$, $\kappa_T$, or both in order to calculate the characteristic parameters of the pure substances. However, the PFP and analogous theories fail in the prediction of the thermodynamic properties of associated liquids (i.e., alcohols, amines, etc.), it being necessary to use other models such as those of Kretschmer and Wiebe (1954) or Renon and Prausnitz (1967). In an effort to develop a generalized model for mixed liquids (associated or nonassociated), Heintz (1989) recently proposed the ERAS model (extended real association solution), which combine the basic idea of the association model taking into account the interaction due to the presence of polar molecules, and the ideas of the Prigogine–Flory theory, which uses an equation of state for nonpolar molecules. The final result is a mixed equation of state which allows the ERAS model to predict excess functions for solutions, such as hydrocarbon + alcohol, hydrocarbon + amine (Funke et al., 1989), and alcohol + amine (Reimann and Heintz, 1991). As a result of this development, experimental values for $\alpha_P$ and $\kappa_T$ are necessary for the pure substances. However, the measurement of $\alpha_P$ and $\kappa_T$ is somewhat tedious, and for that reason the availability of these values are limited. Different experimental techniques are used to determine these properties. Thus, $\alpha_P$ is measured with dilatometric or with densitometric techniques. Most researchers determine the volume $V$ or the density $\varrho$ at four to six temperatures in a range slightly below 40 °C, fit these values as a function of $T$, and obtain $\alpha_P$ using eq 1 or ($\alpha_P = -(\partial \ln \varrho/\partial T)_P$). On the other hand, $\kappa_T$ can be directly obtained through the adiabatic compressibility $\kappa_S$ by using the expression

$$\kappa_T = \kappa_S + \alpha_P^2 TV/C_P \tag{3}$$

where $C_P$ is the heat capacity at constant pressure. The adiabatic compressibility is easily determined through a knowledge of the speed of sound $u$ and the density $\varrho$ ($\kappa_S = 1/\varrho u^2$), but it is necessary to know $\alpha_P$ and $C_P$ values, which are not always available.

In this work, both $\alpha_P$ and $\kappa_T$ have been simultaneously determined on the same sample using a direct piezometric technique, which allows a greater number of measurements of the volume in the low-pressure range and over a limited temperature range around the desired temperature. The pure substances chosen were the linear alkenes and alkynes with six to nine carbon atoms, xylenes, and 1,3,5-trimethylbenzene (mesitylene). It is important to have $\alpha_P$ and $\kappa_T$ values for these compounds in order to make calculations on binary alcohol + alkene, alcohol + alkyne, or alcohol + xylene mixtures, using the theoretical models

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* To whom correspondence should be addressed.

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**Table 1. Experimental Values of Pure Liquids at 298.15 K**

| substance | $10^6\varrho$ (kg m$^{-3}$) this work | $10^6\varrho$ (kg m$^{-3}$) lit. | $10^6V_m$ (m$^3$ mol$^{-1}$) | $10^3\alpha_P$ (K$^{-1}$) this work | $10^3\alpha_P$ (K$^{-1}$) lit. | $\kappa_T$ (TPa$^{-1}$) this work | $\kappa_T$ (TPa$^{-1}$) lit. | $10^6\gamma$ (K$^{-1}$ TPa$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1-hexene | 668.05 | 668.5[a] | 125.976 | 1.415 | 1.414[c] | 1690 | 1689[c] | 0.837 |
| 1-heptene | 692.97 | 692.7[a] | 141.670 | 1.267 | 1.273[d] | 1447 | | 0.876 |
| 1-octene | 711.05 | 710.9[a] | 157.826 | 1.170 | 1.195[d] | 1297 | | 0.902 |
| 1-hexyne | 710.34 | 710.0[a] | 115.658 | 1.372 | 1.371[c] | 1405 | 1404[c] | 0.976 |
| 1-heptyne | 728.30 | 728.3[a] | 132.006 | 1.249 | 1.212[d] | 1256 | | 0.994 |
| 1-octyne | 742.29 | 742.6[a] | 148.519 | 1.162 | 0.993[d] | 1148 | | 1.012 |
| *o*-xylene | 875.72 | 875.9[a] | 121.295 | 0.965 | 0.956[d] | 803 | 811[g] | 1.202 |
| *m*-xylene | 859.80 | 860.0[a] | 123.529 | 0.999 | 0.967[d] | 867 | 855[g] | 1.152 |
| *p*-xylene | 857.15 | 856.7[a] | 123.869 | 1.019 | 1.019[c] | 884 | 908[d] | 1.153 |
| mesitylene | 861.19 | 861.1[a] | 139.588 | 0.951 | 0.940[d] | 826 | 868[d] | 1.151 |
| *n*-hexane | | 655.04[b] | 131.576 | | 1.381[c] | | 1669[h] | 0.827 |
| *n*-heptane | | 679.81[b] | 147.427 | | 1.256[e] | | 1438[h] | 0.873 |
| *n*-octane | | 698.56[b] | 163.495 | | 1.160[c] | | 1282[h] | 0.905 |
| toluene | | 862.14[b] | 106.893 | | 1.086[c] | | 914[i] | 1.188 |
| benzene | | 873.69[b] | 89.441 | | 1.218[c] | | 966[h] | 1.261 |
| ethylbenzene | | 862.43[b] | 123.105 | | 1.019[f] | | 868[f] | 1.174 |

[a] TRC Thermodynamic Tables Data Base, 1994. [b] Determined in our laboratory. [c] Tardajos et al., 1986. [d] Determined from densities at various temperatures of TRC Thermodynamic Tables Data Base, 1994. [e] Blinowska and Brostow, 1975. [f] Matilla et al., 1989. [g] Determined using eq 3 and TRC Thermodynamic Tables Data Base, 1994. [h] Díaz Peña and Tardajos, 1978. [i] Garbajosa et al., 1982.

for the liquid state briefly reviewed in this section.

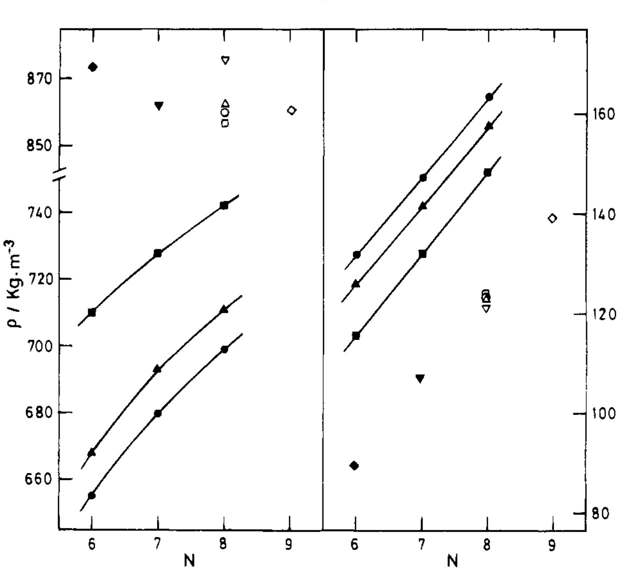

**Figure 1.** Experimental values of densities $\varrho$ and molar volumes $V_m$ as a function of the number of carbon atoms of the hydrocarbon $N$: (●) alkanes; (▲) alkenes; (■) alkynes; (▽) *o*-xylene; (○) *m*-xylene; (□) *p*-xylene; (◇) mesitylene; (◆) benzene; (▼) toluene; (△) ethylbenzene.

## Experimental Section

The solvents used in this work were all from Fluka. Their purities, determined by liquid gas chromatography, were 98.8 mass % for 1-octene, 99.0 mass % for mesitylene, 99.4 mass % for o-xylene, 99.6 mass % for 1-hexene, 1-heptene, 1-octyne and *m*-xylene, 99.8 mass % for 1-hexyne and *p*-xylene, and 99.9 mass % for 1-heptyne. All were stored over 0.4 nm molecular sieves and were used without further purification.

Experimental densities were determined at 298.15 K using a vibrating-tube densitometer (Anton-Paar DMA 601), with a reproducibility of 0.01 kg m$^{-3}$, and all are in agreement with literature data (TRC Tables 1994), also reported in Table 1.

The isobaric thermal expansion $\alpha_P$ and the isothermal compressibility $\kappa_T$ were determined using a direct piezometric technique, whose experimental details, including the degassifying process and the piezometric filling, have been described previously (Díaz Peña and McGlashan, 1961; Díaz Peña and Tardajos, 1978; Tardajos et al., 1985). The mercury used to seal the liquid in the piezometer does not interact with the compounds. The experimental procedure to obtain $\alpha_P$ and $\kappa_T$ consists of measuring the volume changes produced when the temperature is varied at constant pressure and when the pressure is changed at constant temperature, respectively. At least 12 measurements of the volume changes were made in a range of ±1.5 K centered at 298.15 K for $\alpha_P$ and from 0 to 2 MPa for $\kappa_T$. The expansivity and compressibility of the mercury and the glass of the piezometer have been considered in the determination of $\alpha_P$ and $\kappa_T$ of the compounds (Díaz Peña and McGlashan, 1961; Díaz Peña and Tardajos, 1978; Tardajos et al., 1985). The temperature in the thermostated bath was held constant at 298.15 K (±1 mK) using a TRONAC controller. $\alpha_P$ and $\kappa_T$ were measured twice for all the liquids studied here, the reproducibility for both quantities being estimated to be better than ±0.3%.

## Results and Discussion

Table 1 reports densities $\varrho$, molar volumes $V_m$, isobaric thermal expansivities $\alpha_P$, isothermal compressibilities $\kappa_T$, and thermal pressure coefficient $\gamma$ at 298.15 K, together with available literature values for all the liquids studied in this work and for various *n*-alkanes (hexane, heptane, and octane), benzene, toluene, and ethylbenzene. The quantities $(\partial V_m/\partial T)_P$ and $(\partial V_m/\partial P)_T$, which are directly related with $\kappa_T$ and $V_m$, through eqs 1 and 2, are not reported in Table 1. The values of $\varrho$ and $V_m$, $\alpha_P$ and $\kappa_T$ are plotted as a function of the number of carbon atoms of the hydrocarbon (N) in Figures 1 and 2.

Most of the $\alpha_P$ literature data reported in Table 1, which are obtained from measurements of densities as a function of temperature (TRC Tables 1994), are affected by a higher uncertainties (from 1% to 3%) than our data. The high discrepancy for 1-octyne, whose $\alpha_P$ literature data deviate 16% from our value, may be due to the density values used to obtain $\alpha_P$, most of them reported more than 50 years ago. In Table 1, the $\kappa_T$ literature data obtained from eq 3 deviate from our values similarly to $\alpha_P$ results (less than 4%). It confirms that it is better to obtain $\kappa_T$ directly (this work) than through eq 3, where uncertainties in the involved quantities are accumulated.

An increase in the density $\varrho$ usually implies a decrease in the molar volume with the corresponding decrease in the free intermolecular space. As a consequence, the capacity of the liquid to expand ($\alpha_P$) or compress ($\kappa_T$) will

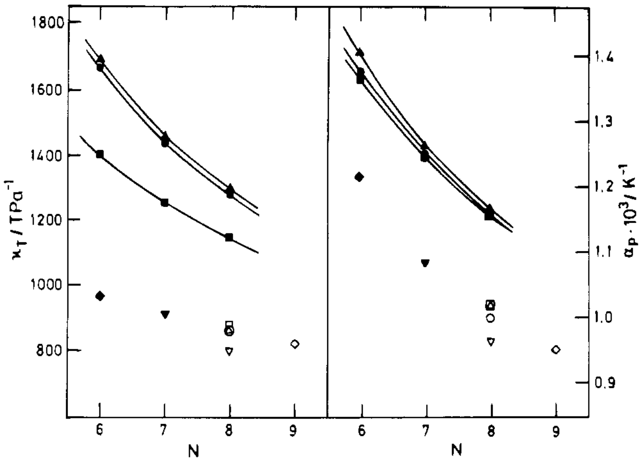

**Figure 2.** Experimental values of $\alpha_P$ and $\kappa_T$ as a function of the number of carbon atoms of the hydrocarbon $N$: (●) alkanes; (▲) alkenes; (■) alkynes; (▽) *o*-xylene; (○) *m*-xylene; (□) *p*-xylene; (◇) mesitylene; (◆) benzene; (▼) toluene; (△) ethylbenzene.

also decrease. $\alpha_P$ and $\kappa_T$ can present a nonexpected or nondefined behavior, when the trend of $V_m^{-1}$ and $(\partial V_m/\partial T)_P$ or $-(\partial V_m/\partial P)_T$ is opposite. This behavior is corroborated by the results of Table 1 or Figures 1 and 2. Hence, it can be observed that for a given number of carbon atoms, as long as the insaturation degree increases (from alkane to alkene, to alkyne, to aromatic hydrocarbon), $\varrho$ increases, while $V_m$ (Figure 1) decreases. In this particular case, the combination of the increase in $V_m^{-1}$ and the decrease in $(\partial V_m/\partial T)_P$ and $-(\partial V_m/\partial P)_T$ result in the expected decrease in $\alpha_P$ and $\kappa_T$ (Figure 2) for alkynes and mainly for aromatic substances, although these quantities are similar for alkanes, alkenes, and even alkynes in the case of $\alpha_P$.

In Figure 1 $\varrho$ increases with $N$ for alkanes, alkenes, and alkynes and not so clearly for aromatic hydrocarbon, while $V_m$ increases with $N$ for all hydrocarbons. On the other hand, as can be noticed in Figure 2, $\alpha_P$ and $\kappa_T$ decrease with $N$ in all the cases (alkanes, alkenes, alkynes, and aromatic hydrocarbon). This decrease can be explained assuming that the increase in $(\partial V_m/\partial T)_P$ and in $-(\partial V_m/\partial P)_T$ is not enough to counteract the sharp decrease in $V_m^{-1}$ when $N$ increases (Figure 1). Thus, although for a given number of carbon atoms $\varrho$ and $V_m$ vary in the opposite way, they behave similarly as a function of the number of carbon atoms, where the packing effects (increase in $\varrho$) are decisive in $\alpha_P$ and $\kappa_T$ (Díaz Peña and Tardajos, 1978).

Other remarkable feature is that the values for the studied aromatic substances of eight carbon atoms are pretty similar for m-xylene, p-xylene and ethylbenzene, the values for *o*-xylene being slightly out of the observed trend. *o*-Xylene, with two methylene groups close to each other, allows a higher packing from an steric point of view, the data for $\varrho$ being the highest (Figure 1), and consequently $V_m$, $\alpha_P$, and $\kappa_T$ data the lowest (Figures 1 and 2).

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