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Isobaric Thermal Expansivity of Highly Polar Nitrogen Compounds at Temperatures from (278.15 to 348.15) K and at Pressures from (5 to 55) MPa

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Isobaric thermal expansivity α_p for a set of highly polar nitrogen compounds was experimentally determined by means of a calorimetric method in the temperature T and pressure p intervals (278.15 to 348.15) K and (5 to 55) MPa. The selected liquids were propionitrile, nitromethane, nitroethane, nitropropane, benzonitrile, and nitrobenzene. The experimental results were compared to available literature data, obtaining good results for most of the studied liquids. It was found that the α_p trends against temperature highly depend on the studied pressure: α_p increases at low pressure; however, as pressure is raised, the dependence on T becomes milder, and for some cases, it is obtained that α_p clearly decreases against T at the highest pressures. The results are interpreted based on the phase-transition properties of the compounds, concretely, on vapor pressure and on distance of the experimental pressure and temperature from the critical coordinates.

Introduction

There is not a solid knowledge about isobaric thermal expansivity α_p for organic solvents over extended temperature and pressure ranges, mainly due to the scarcity and low accuracy of the available literature data, since it is usually obtained from density measurements. To obtain fairly accurate values of α_p using this technique, highly accurate density measurements are needed,[1] which is not an easy task, especially at high pressure.[2] It would be very desirable to possess high quality data of this magnitude since α_p expresses the variation of density against temperature, which has high importance from an applied point of view since, for an accurate design of any system which operate with fluids, an, at least, elementary knowledge of the behavior of their isobaric thermal expansivity is strongly required. From a fundamental point of view, highly precise α_p data are also very interesting since they can be used for testing statistical mechanics models and equations of state.[3] Moreover, an accurate α_p characterization against T and p can give insight about microscopic processes that happen in the fluid since this magnitude is directly related to fluctuations, concretely, to cross-correlations of enthalpy and volume.[4]

It is the aim of this work to provide directly measured, highly precise α_p data for a set of nitrogen compounds with high polarity, concretely, propionitrile, nitromethane, nitroethane, nitropropane, benzonitrile, and nitrobenzene, in the temperature and pressure interval (278.15 to 348.15) K and (5 to 55) MPa. To this end, a previously described calorimetric method,[5] which is based on recording the heat emitted or received by the sample due to pressure variations, was used. To check the accuracy of the experimental values, they are compared to available literature data. Finally, the results are discussed based on properties concerning vapor−liquid phase transition, concretely, vapor pressure at 298.15 K, p_v, and location of the critical temperature and pressure T_c and p_c, facts motivated mainly due to the relation between α_p and fluctuations, which are very important as the system becomes close to critical conditions.

Experimental Section

Chemicals. Nitromethane (purity > 0.985 in mass fraction) was obtained from Fluka. Nitroethane (purity > 0.995 in mass fraction), nitropropane (purity > 0.98 in mass fraction), propionitrile (purity > 0.99 in mass fraction), benzonitrile (purity > 0.99 in mass fraction), and nitrobenzene (purity > 0.99 in mass fraction) were purchased from Aldrich. All liquids were degassed and passed through molecular sieves to remove traces of water.

Experimental Methodology. Isobaric thermal expansivity was obtained using a DSC II microcalorimeter from Setaram coupled with a Ruska 7610 pressure controller. The method for determining α_p basically consisted of recording the heat flux that appeared between the sample and the calorimetric block due to pressure variations. α_p is thus obtained using the next equation

$$\alpha_p = -\frac{1}{VT}\frac{d'Q}{dp} \tag{1}$$

where V is the cell volume, and $d'Q/dp$ is the variation of the heat introduced in the sample against change in pressure. This

Table 1. Fitting Coefficients of Equation 3 and Standard Deviation of the Fits *s* for the Studied Compounds

	propionitrile	nitromethane	nitroethane
$a_0 \cdot 10^3/\mathrm{K}^{-1}$	1.8463	0.6125	0.7315
$a_1 \cdot 10^6/\mathrm{K}^{-2}$	−10.3037	1.1162	0.59094
$a_2 \cdot 10^9/\mathrm{K}^{-3}$	26.5688	−9.1080	−8.6035
$a_3 \cdot 10^{12}/\mathrm{K}^{-4}$	−29.5713	7.6801	8.9799
$a_4 \cdot 10^6/\mathrm{K}^{-1} \cdot \mathrm{MPa}^{-1}$	1.4215	1.1469	1.0063
$b_1 \cdot 10^3/\mathrm{K}^{-1}$	−2.4602	−2.4348	−2.2728
$b_2 \cdot 10^3/\mathrm{MPa}^{-1}$	3.0397	2.3404	2.5391
$s \cdot 10^6/\mathrm{K}^{-1}$	3	3	3

	nitropropane	benzonitrile	nitrobenzene
$a_0 \cdot 10^3/\mathrm{K}^{-1}$	2.2229	−0.1235	0.8053
$a_1 \cdot 10^6/\mathrm{K}^{-2}$	−14.7402	7.5153	−1.7343
$a_2 \cdot 10^9/\mathrm{K}^{-3}$	41.1236	−30.3296	0.0049
$a_3 \cdot 10^{12}/\mathrm{K}^{-4}$	−44.5535	32.9087	0.2566
$a_4 \cdot 10^6/\ \mathrm{K}^{-1} \cdot \mathrm{MPa}^{-1}$	1.1959	0.6449	0.7360
$b_1 \cdot 10^3/\mathrm{K}^{-1}$	−2.4388	−2.2134	−2.1722
$b_2 \cdot 10^3/\mathrm{MPa}^{-1}$	2.7078	1.8795	2.1538
$s \cdot 10^6/\mathrm{K}^{-1}$	2	3	2

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pressure variation was performed using a pressure ramp of 1.5 MPa·min^{-1}, which induced a heat flux ϕ^{x} for the unknown sample. To calibrate the instrument, two experiments for two standards of known α_p were needed: hexane and water were used due to the quality of the available literature data.[6,7] From the obtained fluxes, ϕ^{h} and ϕ^{w}, and from the literature α_p data $\alpha_p{}^{h}$ and $\alpha_p{}^{w}$, for the calibration fluids, the isobaric thermal expansivity of the unknown liquid $\alpha_p{}^{x}$ was obtained from

$$\alpha_p^{x} = \alpha_p^{w} + \frac{\phi^{w} - \phi^{x}}{\phi^{w} - \phi^{h}}(\alpha_p^{h} - \alpha_p^{w}) \qquad (2)$$

From the analysis of all involved magnitudes, the expanded uncertainty in α_p is estimated in 2 %, which is mainly due to the uncertainty of literature data for hexane since a significantly lower value of $5 \cdot 10^{-6}$ K^{-1} was obtained for the repeatability of α_p measurements. The instrument as well as experimental

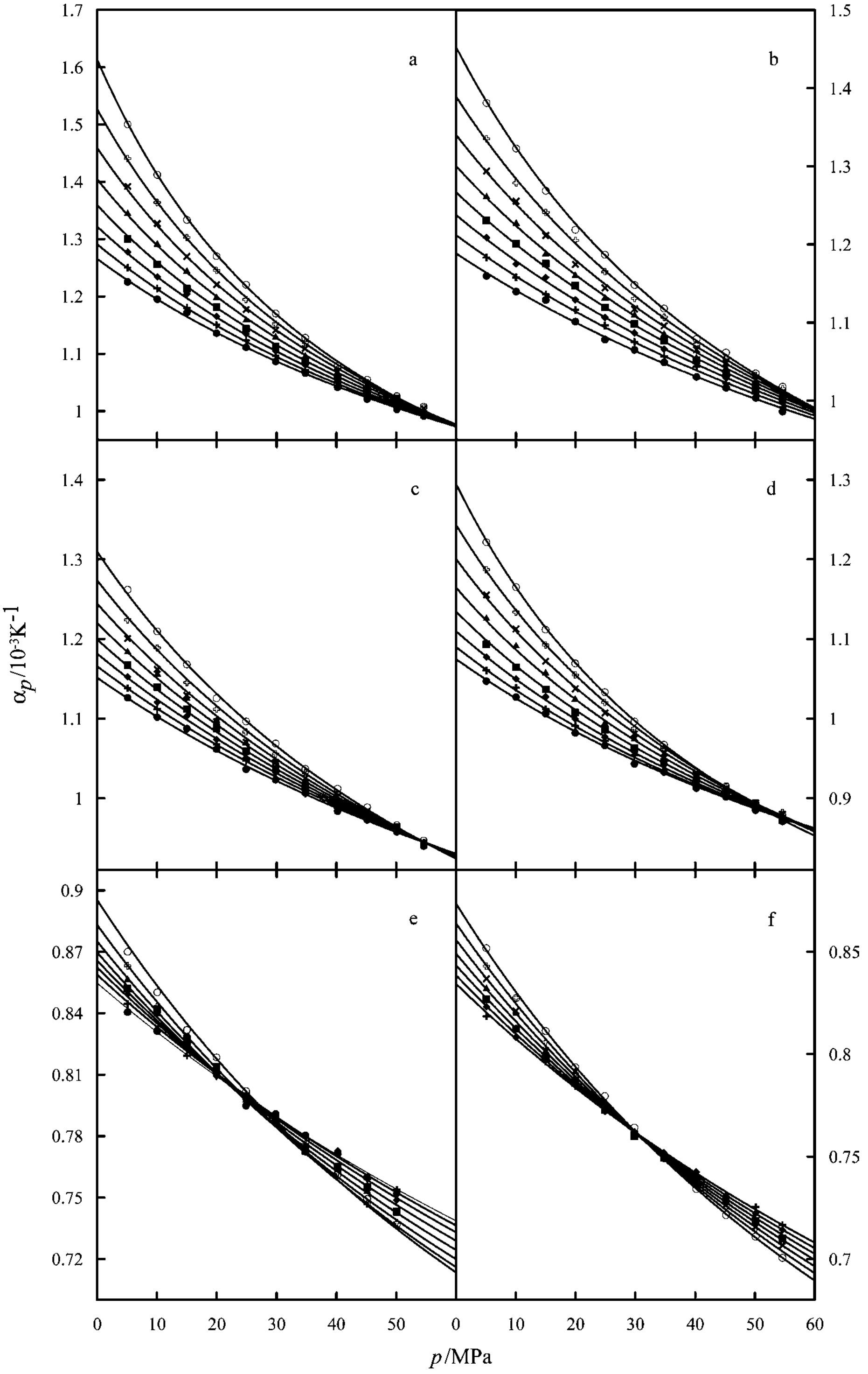

Figure 1. α_p values as a function of pressure at several temperatures for: (a) propionitrile; (b) nitromethane; (c) nitroethane; (d) nitropropane; (e) benzonitrile; and (f) nitrobenzene. ●, T = 278.15 K; +, T = 288.15 K; ◆, T = 298.15 K; ■, T = 308.15 K; ▲, T = 318.15 K; ×, T = 328.15 K; open plus sign, T = 338.15 K; ○, T = 348.15 K.

methodology were described in detail elsewhere,[5,8] and it was successfully used for determining α_p for alcohols[9,10] and ionic liquids.[11,12]

Results and Discussion

The isobaric thermal expansivity was determined in temperature and pressure steps of 10 K and 0.35 MPa, respectively, within the temperature and pressure interval (278.15 to 348.15) K and (5 to 55) MPa for propionitrile, nitromethane, nitroethane, nitropropane, benzonitrile, and nitrobenzene. All experimental data were fitted to the next function in T and p

$$\alpha_p(p, T) = \frac{a_0 + a_1T + a_2T^2 + a_3T^3 + a_4p}{1 + b_1T + b_2p} \qquad (3)$$

The values of a_i and b_i coefficients as well as standard deviation of the fits are given in Table 1. Experimental values at representative temperatures and pressures are reported as Supporting Information.

Figure 1 shows the obtained values for all studied liquids as a function of pressure at several isotherms. Negative dependence was found for all compounds, although, remarkably, there is, for some cases, curve crossing, which corresponds to a change

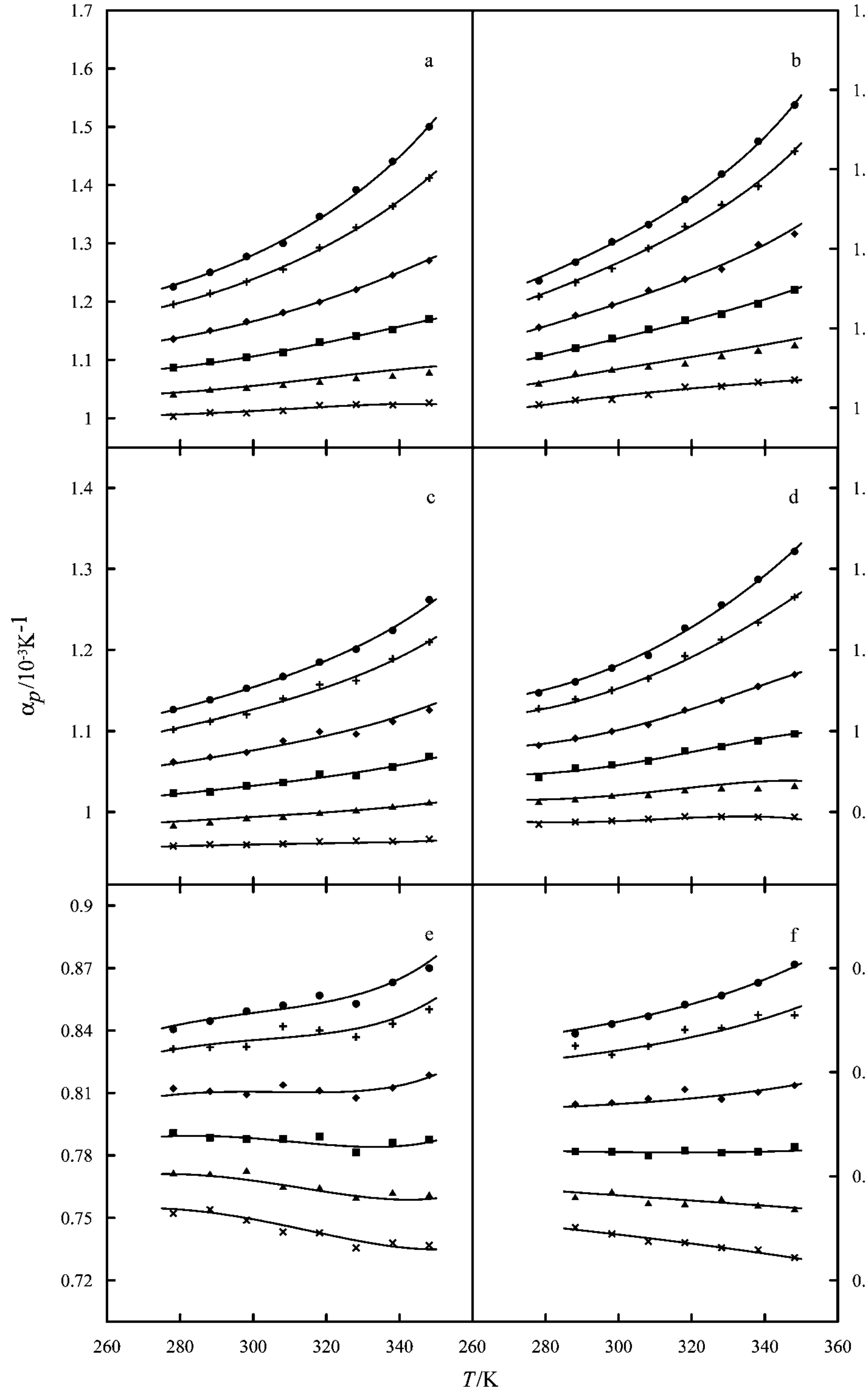

Figure 2. α_p values as a function of temperature at several pressures for: (a) propionitrile; (b) nitromethane; (c) nitroethane; (d) nitropropane; (e) benzonitrile; and (f) nitrobenzene. ●, $p = 1$ MPa; $+$, $p = 10$ MPa; ◆, $p = 20$ MPa; ■, $p = 30$ MPa; ▲, $p = 40$ MPa; $\times$, $p = 50$ MPa.

Table 2. Vapor Pressure at 298.15 K, p_v, Critical Temperature, T_c, and Critical Pressure, p_c, for the Studied Liquids

	propionitrile	nitromethane	nitroethane	nitropropane	benzonitrile	nitrobenzene
p_v/kPa	5.950[21]	4.888[21]	2.790[21]	1.364[21]	0.1[21]	0.0379[21]
T_c/K	564.4[21]	588[21]	592[22]	606[22]	699.4[21]	732[21]
p_c/MPa	4.18[21]	6.31[21]	5.12[22]	4.04[22]	4.22[21]	4.400[23]

in the behavior against temperature—from positive T dependence at low pressure to negative at high pressure—trend already observed for other organic solvents.[13−18] This becomes clearer in Figure 2, in which α_p is shown against T for several isobars. It is seen that for low-pressure isobars α_p increases against T; however, as pressure is increased, this dependence becomes milder, and for some cases, namely, benzonitrile and nitrobenzene, the T dependence reverts, obtaining undoubtedly that α_p decreases against T.

To check the reliability of the experimentally obtained values, they were compared to available literature data,[19] obtained from density correlations using the next equation

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{4}$$

This comparison was made by means of the average absolute deviation Δ, defined as

$$\Delta = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\alpha_{p,i}^{\mathrm{exptl}} - \alpha_{p,i}^{\mathrm{lit.}}}{\alpha_{p,i}^{\mathrm{exptl}}}\right| \tag{5}$$

where superscripts exptl and lit. denote this work and literature data, respectively. A deviation of 0.03 for propionitrile, 0.2 for nitromethane, 0.006 for nitroethane, 0.09 for nitropropane, 0.003 for nitrobenzene, and 0.47 for benzonitrile was found. With a view on the quality of the literature data—some correlations were based on data in a narrow temperature range, which makes the use of eq 4 not very accurate—the results are compatible within the experimental uncertainty of both data sources.

As it is stated above, there is a strong connection between isobaric thermal expansivity and fluctuations: α_p is proportional to cross-correlations of enthalpy and volume. Therefore, as experimental conditions are closer to the critical point—where fluctuations become infinite ranged—it is expected that α_p increases to a greater extent. α_p was determined for all studied liquids at temperatures significantly lower than T_c; therefore, from this point of view, increasing temperature implies approaching to critical conditions, and thus, positive temperature dependence is expected. However, if experimental p and T are very far from the critical point, fluctuations become very small, and other effects can have greater importance, which could induce the experimentally observed negative temperature dependence at high pressure. In fact, for an ideal gas, which does not show vapor−liquid equilibrium, α_p decreases against T ($\alpha_p = 1/T$). This behavior can also be obtained for the hard-sphere fluid,[20] another model which does not have vapor−liquid transition and constitutes a quite good approximation of highly compressed fluids since they are dominated for short-range repulsive forces. Thus, the observed behavior can be explained as follows: for low pressure, fluctuations dominate, producing positive T dependence, but as pressure is raised, the system becomes more compressed and less fluctuations are allowed. Thus, repulsive forces are more important, and the behavior of the system is more similar to that of a hard sphere fluid, characterized by negative α_p temperature dependence.[20] To check these statements on the studied fluids, it would be useful to compare phase transition properties with the obtained results. Table 2 gives the vapor pressure p_v at 298.15 K, critical temperature, and critical pressure for the liquids of this work. We see a clear correlation between T_c and the α_p behavior: α_p is greater, and the change in α_p temperature dependence happens at higher pressure for compounds with lower T_c—in fact, for propionitrile and nitromethane, it is not observed, although it seems to appear at higher pressures than those of this work. Also, there is a strong correlation between p_v and α_p temperature behavior but opposite to that found for T_c: the higher p_v, the higher the crossing pressure is, a fact expected due to the close relationship between vapor pressure and critical temperature—p_v is higher for compounds that show lower T_c. By contrast, the value of critical pressure does not seem to have an important role.

Conclusion

The isobaric thermal expansivity was directly determined for six highly polar nitrogen compounds within the temperature and pressure intervals (278.15 to 348.15) K and (5 to 55) MPa. α_p temperature behavior highly depends on pressure, obtaining for some of the studied liquids a change in temperature dependence within the experimental pressure interval. Since α_p is highly influenced by fluctuations, the obtained data were compared with phase transition properties. It was found that the α_p behavior against T as well as α_p itself for the studied liquids are strongly correlated with their critical temperature and vapor pressure.

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Supporting Information Available:

Experimental data for isobaric thermal expansivities for the studied compounds as a function of temperature and pressure. This material is available free of charge via the Internet at http://pubs.acs.org.

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