International Journal of Thermophysics, Vol. 5, No. 3, 1984

Thermal Pressure Coefficients of Ethanenitrile, Propanenitrile, and Butanenitrile in the Region 295–395 K

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Received January 17, 1984

The thermal pressure coefficient $(\partial p/\partial T)_V$ has been measured for ethanenitrile from 299 to 364 K, for propanenitrile from 295 to 377 K, and for butanenitrile from 297 to 398 K. The results are discussed in terms of the diminishing role of polarity in the alkanenitrile series and of a corresponding-states approach using gas–liquid critical properties as reduction factors. Although $(\partial p/\partial T)_V$ varies unevenly with chain length, the reduced quantity shows a more regular behavior similar to that of the related quantity the cohesive energy density.

KEY WORDS: butanenitrile; cohesive energy density; corresponding-states principle; ethanenitrile; hydrogen-bonding; polar liquids; internal pressure; propanenitrile; thermal pressure coefficient.

1. INTRODUCTION

In order to compare the results of our measurements of the excess enthalpies H^E [1] and excess volumes V^E [2] for alkanenitrile + alkane mixtures with the predictions of the modification of the solubility parameter version of the regular solution theory [3] that was devised by Prausnitz, Anderson, and Weimer [4] for polar + nonpolar mixtures, it is necessary to calculate the excess energy at constant volume U_V^E. Of several routes to U_V^E the

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simplest is based on

$$U_V^{\mathrm{E}} = H^{\mathrm{E}} - T\gamma_V V^{\mathrm{E}} \tag{1}$$

where T is temperature and γ_V is the thermal pressure coefficient $(\partial p/\partial T)_V$ of the mixture. Our measurements of H^{E} and V^{E} cover seven mixtures, and rather than measure γ_V as a function of composition for each, we elected to calculate it with sufficient accuracy from the expression for an ideal binary mixture

$$\gamma_V^{\mathrm{id}}(\mathrm{mix}) = (\phi_1\alpha_1 + \phi_2\alpha_2)/(\phi_1\beta_1 + \phi_2\beta_2) \tag{2}$$

where ϕ_i is the volume fraction, α_i is the isobaric thermal expansivity, and β_i is the isothermal compressibility of component i of the mixture. At low pressures, close to 0.1 MPa, the best values of β are usually obtained from $\beta = \alpha/\gamma_V$. The pVT coefficients for the alkanes are well known; pVT coefficients for the alkanenitriles, by contrast, are almost unknown, and for this reason we determined γ_V directly for ethanenitrile from 299 to 364 K, for propanenitrile from 295 to 377 K, and for butanenitrile from 297 to 398 K.

There is continuing interest in the properties of homologous series, particulary in terms of the principle of corresponding states. This interest has found greatest expression in terms of analyses of pVT coefficients, and although our data are insufficient at this stage to permit a full analysis, some preliminary remarks are made.

2. EXPERIMENTAL

The ethanenitrile was Fisons SLR grade; the propanenitrile was obtained from Koch-Light Laboratories and the butanenitrile from BDH Chemical. All were initially of stated purity 99 mole %; they were further purified by fractionation in an all-glass 70-cm packed column. Reactivated Molecular Sieve of grade 4A was used as the drying agent. The impurity levels detected by gas–liquid chromatography (Poropak Q column with nitrogen carrier gas and flame-ionization detection) were less than 0.1 mole %. Immediately before use all the liquids were degassed by repeated freeze–pump–thaw cycles. The thermal pressure coefficients were determined with an apparatus consisting of a constant-volume thermometer in which the pressure is controlled and measured for a series of temperatures at a series of different densities. The details of the method have already been described [5].

3. RESULTS

The results of our measurements of γ_V are given in Table I. They are the outcome of converting the raw dp/dT gathered at almost but not quite constant volume to isochore slopes at a temperature corresponding to a pressure of 0.1 MPa using the usual correction equation [5]. The expansivi-

Table I. Thermal Pressure Coefficients of Ethanenitrile, Propanenitrile, and Butanenitrile

T (K)	γ_V(exp) (MPa · K^{-1})	γ_V(calc) (MPa · K^{-1})
Ethanenitrile		
297.80	1.249	1.247
306.90	1.176	1.179
312.76	1.140	1.137
315.95	1.109	1.115
325.66	1.054	1.049
339.36	0.965	0.964
351.91	0.890	0.892
364.23	0.829	0.828
Propanenitrile		
294.77	1.218	1.211
298.24	1.180	1.186
304.78	1.138	1.140
309.64	1.108	1.107
322.01	1.035	1.028
333.03	0.948	0.962
337.43	0.941	0.937
347.39	0.886	0.884
352.90	0.856	0.856
363.25	0.812	0.807
372.29	0.768	0.768
377.37	0.744	0.747
Butanenitrile		
296.76	1.230	1.227
310.81	1.127	1.132
319.49	1.081	1.076
331.04	1.007	1.005
343.57	0.922	0.933
354.13	0.883	0.875
363.19	0.826	0.828
374.25	0.769	0.774
385.02	0.741	0.725
398.02	0.661	0.670

ties for the nitriles were taken from Ref. 6 and the α and β for Pyrex glass and mercury from Ref. 7.

The values of γ_V are well described by the following equations:

$$\gamma_V(\text{ethanenitrile}) = 5.3398 - 1.9826 \times 10^{-2}T + 2.043 \times 10^{-5}T^2 \qquad (\sigma = 3 \times 10^{-3}) \tag{3}$$

$$\gamma_V(\text{propanenitrile}) = 5.1334 - 1.9310 \times 10^{-2}T + 2.037 \times 10^{-5}T^2 \qquad (\sigma = 6 \times 10^{-3}) \tag{4}$$

$$\gamma_V(\text{butanenitrile}) = 4.5571 - 1.5480 \times 10^{-2}T + 1.436 \times 10^{-5}T^2 \qquad (\sigma = 8 \times 10^{-3}) \tag{5}$$

where γ_V is in MPa · K^{-1}, T is in K, and σ (standard deviation) is in

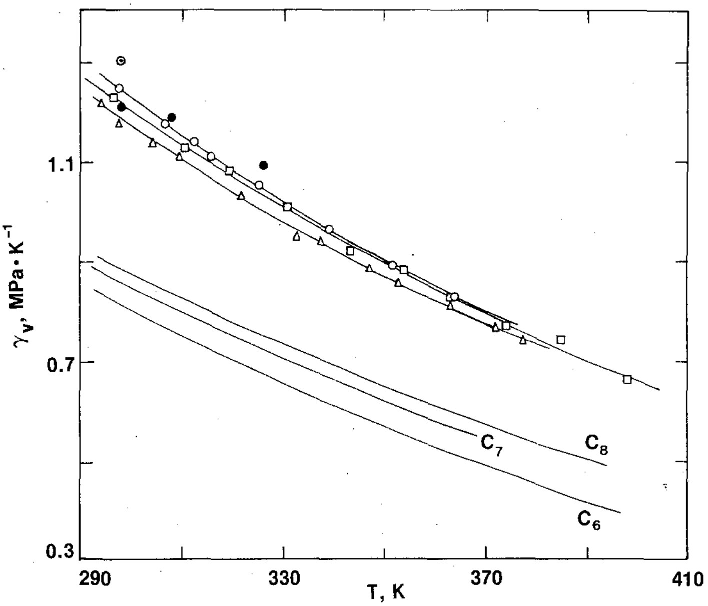

Fig. 1. Thermal pressure coefficient γ_V as a function of temperature T for ethanenitrile (○), propanenitrile (△), and butanenitrile (□); ●, values for ethanenitrile from Ref. 9; ⊙, value for ethanenitrile from Ref. 10. The lower three curves are for hexane, heptane, and octane as indicated.

MPa · K^{-1}. The γ_V given by these expressions are listed in the third column of Table I. Repeat determinations establish the precision of our results to be close to 0.6% and comparison measurements on benzene establish their accuracy to be close to 1%.

The results of our measurements of γ_V are shown as a function of temperature T in Fig. 1, which also displays curves representing γ_V for hexane [7], heptane [8], and octane [7]. The values of γ_V for ethanenitrile reported by Grant and McDonald [9] are shown. Although the agreement between our and their results is good near 300 K, there is evidently a disagreement in the temperature dependence. The single value for ethanenitrile reported by Dack [10] is higher than either our results or those of Grant and McDonald. We have found no other reports of measurements of γ_V for alkanenitriles.

4. DISCUSSION

The large magnitude of the thermal pressure coefficients of the alkanenitriles compared to those of the normal alkanes or other nonpolar homologous or chain-molecule series can be simply and convincingly ascribed to the high polarity of the alkanenitriles that is illustrated by their dipole moments listed in Table II.

Magnitudes apart, the most noteworthy feature of our results is the drop in γ_V from ethanenitrile to propanenitrile followed by the increase for butanenitrile. This contrasts sharply with the behavior of nonpolar homologous series, for which at a given temperature γ_V increases smoothly with chain length [16]. The chain-length dependence of γ_V is harder to account for than its magnitude, and it is helpful to preface a partial explanation with one for the chain-length dependence of the cohesive energy density (c.e.d.) defined by $-U/V$, where U is the energy and V the volume of a

Table II. Dipole Moment μ for the Gas Phase, Gas–Liquid Critical Volume V_c, and a Measure of Effective Polarity $P = \mu^2/V_c$ for Some Alkanenitriles[a]

	$10^{30}\mu$ (C · m)	V_c (cm^3 · mol^{-1})	$10^{56}P$ (C^2 · m^{-1} · mol)
Ethanenitrile	13.14	173	9.98
Propanenitrile	13.48	229	7.93
Butanenitrile	13.51	285	6.40
Pentanenitrile	13.64	340	5.47

[a] Values of μ from Refs. 11 and 12; values of V_c from Ref. 13 if known or estimated from methods quoted in Ref. 15 if unknown. For critical properties and comments on the thermal stability of ethanenitrile see Ref. 14.

given amount of substance. Frank [17] has proposed the general relation between U and V:

$$U = -a/V^n \tag{6}$$

where n and a are constants characteristic of a given substance. Invoking the approximations (1) that the internal pressure $T\gamma_V$ greatly exceeds atmospheric pressure and (2) that $-U \simeq \Delta U_{\text{vap}} \simeq \Delta H_{\text{vap}} - RT$, where ΔU_{vap} is the energy and ΔH_{vap} the enthalpy of vaporization, we find that Eq. (6) becomes

$$T\gamma_V = n\,\Delta U_{\text{vap}}/V = n(\Delta H_{\text{vap}} - RT)/V \tag{7}$$

where R is the gas constant.

For a van der Waals fluid n is equal to unity and this is the value found for many substances, especially those composed of nonpolar molecules that are either small or large but quasispherical. For nonpolar chain molecules n is close to 1.2. For polar substances n is usually less than unity, and for hydrogen-bonded liquids it can be as small as 0.32, as, for example, for methanol [16].

From the accurate enthalpies of vaporization at 298.15 K reported by Howard and Wadso [18] for the nitriles containing two to six carbon atoms and densities of Smith and McLure [6], Eq. (7) gives $n = 0.643$, 0.747, and 0.866 for the alkanenitriles in order of increasing chain length. These values conform to the usual pattern of values less than unity that is characteristic of highly polar substances, and indeed so much less than unity are they as to offer evidence for hydrogen bonding in the lower alkanenitriles. The upward trend toward unity confirms the decrease in polarity of successive alkanenitriles. This trend is echoed in the dependence on chain length of the naive but useful measure of effective polarity $P = \mu^2/V_c$, where μ is the dipole moment in the gas phase and V_c is the gas–liquid critical volume. As Table II shows, although μ is essentially independent of chain length, as would be expected since the CN group is largely unaffected by the size of the attached alkyl group, P decreases with chain length. Lack of accurate enthalpies of vaporization for the nitriles at temperatures other than 298.15 K precludes further discussion of n.

We turn now to the c.e.d. itself. From the enthalpies of vaporization for the alkanenitriles referred to above and those of Stridh *et al.* [19] for the even-numbered nitriles containing from eight to 14 carbon atoms and the densities of Dreisbach [20] it has been shown that the c.e.d. of the alkanenitriles decrease smoothly from ethanenitrile to at least tridecanenitrile [21]. A plausible explanation is based on the decrease in the density of polar CN groups in the liquid as the chain length increases. The associated decrease in the polar contribution to the overall cohesion of the liquid is not compensated by the increase in the contribution from chain–chain interactions as relatively weak methyl–methyl intermolecular contacts between adjacent ends of different chains are replaced by stonger intramolecular contacts between adjacent methylene groups on the same (longer) chain and thus the cohesive energy density decreases.

More difficult to explain is the apparent minimum in γ_V at propanenitrile, assuming that it is real and that the increase from propanenitrile to butanenitrile is the forerunner of a general increase similar to that for nonpolar series. More experimental information about γ_V for alkanenitriles of greater chain length would be valuable to confirm this assumption, but since our investigation was limited to supporting measurements on mixtures containing either propanenitrile or butanenitrile, it is unlikely that we shall be able to furnish it. Despite this uncertainty, an explanation similar to that for the c.e.d. relying on the balance between a decreasing contribution to γ_V from polarity and an increasing contribution from the replacement of intermolecular by intramolecular interactions can be adduced. When applied to γ_V the argument requires that diminishing the contribution from polarity is balanced at propanenitrile by the increasing contribution from chain–chain interactions and is outweighed thereafter, thus resulting in a rise in γ_V for the higher alkanenitriles. There is a difficulty, however, in that the same explanation that accounts for the overall decrease in the c.e.d. must simultaneously account for the minimum in γ_V for a member of the series in which the c.e.d. is still dropping. The apparent inconsistency can perhaps be resolved by recalling, as Ross and Hildebrand [22] pointed out, that although γ_V and the cohesive energy density are both measures of the cohesion of the liquid, they probe different regions of density. The c.e.d. reflects the expansion of the liquid all the way to the ideal gas and it thus tests a very different part of the density range than does γ_V, which reflects only densities close to those for close-packing. It is therefore not inconsistent, and perhaps not even surprising, that two quantities sharing the same general explanation should, because of differences in the details, exhibit somewhat different dependences on chain length.

We turn, lastly, to the possibility of analyzing our results in terms of the principle of corresponding states (c.s.p.). Although evidently we have results for too few alkanenitriles to permit us to embark on a full corresponding-states analysis, there are a few useful comments to be made. The simplest form of corresponding-states treatment uses the gas–liquid critical parameters as reduction factors. Thus, using p_c/T_c as reduction factor for

Table III. Gas–Liquid Critical Temperature T_c and p_c from Ref. 13, Thermal Pressure Coefficient γ_V at 298.15 K, and Reduced Thermal Pressure Coefficient $\tilde{\gamma}_V = \gamma_V T_c / p_c$ and Reduced Temperature $\tilde{T} = T/T_c$ for Some Alkanenitriles and Alkanes

	T_c (K)	p_c (MPa)	γ_V(298.15 K) (MPa · K^{-1})	$\tilde{T}$	$\tilde{\gamma}_V$
Ethanenitrile	545.5	4.83	1.244	0.5466	140.5
Propanenitrile	564.4	4.18	1.187	0.5283	160.3
Butanenitrile	582.2	3.79	1.218	0.5121	187.1
Hexane	507.5	3.00	0.814	0.5875	137.2
Heptane	540.3	2.736	0.858	0.5518	169.4
Octane	568.8	2.482	0.888	0.5241	203.5

γ_V and T_c for T, we obtain the results given in Table III, taking 298.15 K as the base temperature. For the alkanes hexane, heptane, and octane, chosen because their critical temperatures are close to those of the three alkanenitriles studied here, the reduced thermal pressure coefficient $\tilde{\gamma}_V = \gamma_V T_c / p_c$ increases with chain length at a given T; for the alkanenitriles, in contrast to the seeming aberrant behavior of γ_V itself, it also increases with chain length. This is more clearly shown on Fig. 2, where γ_V is shown over a fuller range of reduced temperature $\tilde{T} = T/T_c$. Since the temperature reduction factors for all the liquids studied are in the same range, it is not unlikely that the cause of the minimum in γ_V operates also on the critical pressure in such a way as to remove the aberrant behavior in $\tilde{\gamma}_V$. This tends to support the assumption above that γ_V for nitriles higher than propanenitrile increases with chain length.

Although the order of increasing $\tilde{\gamma}_V$ is the same for both the normal alkanenitriles and the normal alkanes and, roughly, so is the dependence on reduced temperature, the actual conformity with the principle of corresponding states is not very impressive. Little more could have been expected, however, in view of the very great difficulty of devising a full analysis for chain-molecule liquids as polar as the alkanenitriles. At least two more reduction factors besides T_c and p_c would certainly be needed. The first extra factor would take account of those aspects of the chain character not already included, for example, the effect of flexibility reflecting the growing number of external degrees of freedom as the chain length increases. This term would be of an entropic nature similar to those used for the alkanes by Patterson and Bardin [23] and by Dickinson *et al.* [24] for the linear dimethylsiloxanes. The second extra factor would be needed to take account of polarity, probably in a fashion similar to that employed by Gubbins and others in the theory of mixtures containing polar liquids

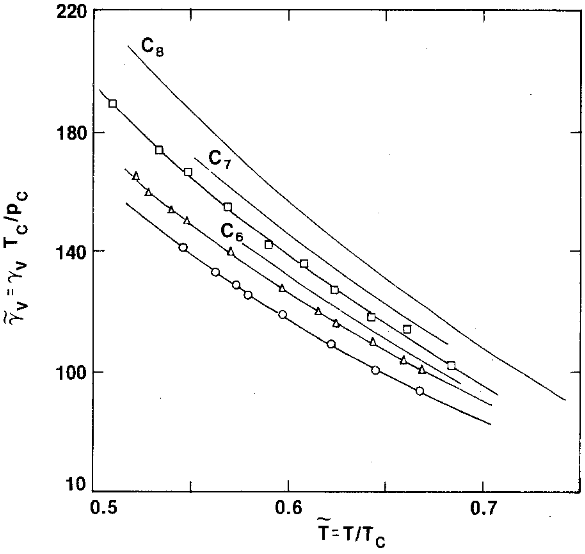

Fig. 2. Reduced thermal pressure coefficient $\tilde{\gamma}_V = \gamma_V T_c/p_c$ as a function of reduced temperature $\tilde{T} = T/T_c$ for ethanenitrile (○), propanenitrile (△), and butanenitrile (□). The corresponding curves for hexane, heptane, and octane are indicated.

[24] using a reduced dipole moment $(\mu^2/\epsilon\sigma^3)^{1/2}$, where ϵ and σ are the characteristic energy and size parameters, respectively, of the pairwise intermolecular potential function. Perhaps in the light of these requirements for a full c.s.p. analysis including both chain flexibility and polarity in an unambiguous way the conformity shown in Fig. 2 is reasonably acceptable.

It is not the purpose of this discussion to claim that the normal alkanenitriles obey a simple two-parameter principle of corresponding states, much less that the alkanenitriles and the alkanes conform to the same c.s.p., but merely to point out that a simple step toward a comprehensive c.s.p. treatment apparently eliminates the most puzzling feature of our results for the unreduced quantity. There is no reason to doubt that the apparently unusual dependence of γ_V on chain length thus removed would not also disappear in a more sophisticated analysis.

ACKNOWLEDGMENTS

One of the authors (J.L.A.C.) is grateful to the Consejo Nacional de Ciencia y Tecnologia, Mexico, for a studentship that permitted him to participate in this investigation.

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