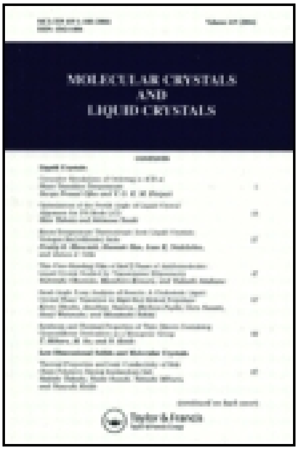

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Density Measurements in the Nematic and Isotropic Phases of 5CB and Dilute Solutions of Tetraethylmethane in 5CB

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Density as a function of temperature was measured in the nematic and isotropic phases of *p*-*n*-pentyl-*p*′-cyanobiphenyl (5CB). Similar measurements were made on six dilute solutions of the quasispherical solute Et_4C (tetraethylmethane) in 5CB. The results were used (on their own and with previous results from visual studies) to obtain β_N and β_I, the moduli of the slopes of the nematic and isotropic boundary lines in the reduced NI transition temperature (T^*) vs. solute mole fraction (x_2) diagrams. The results verify the compatibility of the density and visual methods and show that T^* vs. x_2 plots can, for all practical purposes, be considered linear in the x_2 ranges studied.

Keywords: density, phase diagram, tetraethylmethane-5CB mixtures

INTRODUCTION

The addition of a non-rodlike solute impurity to a nematogenic solvent leads, with few exceptions,[1,2] to depression of the nematic-to-isotropic transition temperature and the formation of a two-phase region. The existence of a two-phase region is in accordance with the first order nature of the nematic-to-isotropic transition.[3] From visual[3–5] methods the phase diagram shown in Figure 1 is typically obtained for a nonmesomorphic/nematogenic solvent mixture at moderately low solute mole fractions (x_2) where $T^*(=T/T_{NI})$, T^* being

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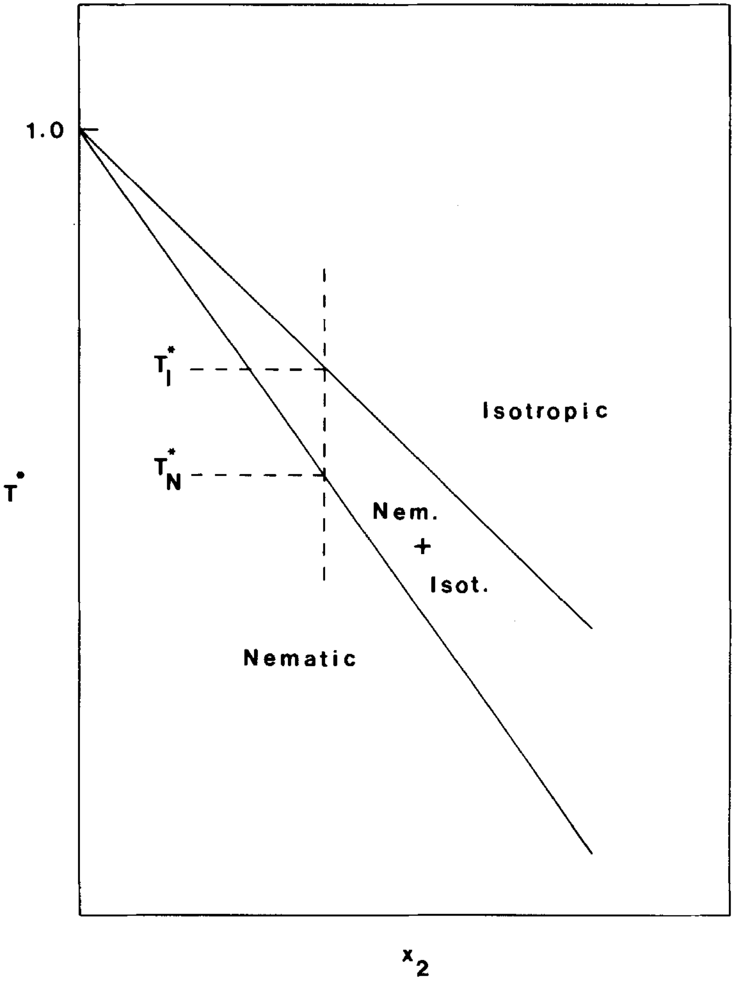

FIGURE 1 Reduced temperature (T^*)–solute mole fraction (x_2) diagram typically obtained from studies on mixtures with moderately low solute mole fractions.

the reduced temperature and T_{NI} is the nematic-to-isotropic transition temperature of the "pure" liquid crystalline solvent. The nematic and isotropic boundary lines were found to be virtually linear and their slopes (of moduli β_N and β_I respectively) reflect the solute's ability to destabilize the nematic phase.

Moduli of limiting slopes ($x_2 \to 0$) of the nematic and isotropic boundary lines, β_N^∞ and β_I^∞ respectively, are given by[3]

$$\beta_N^\infty = -(dT^*/dx_2)_N = \{(\gamma_N^\infty/\gamma_I^\infty) - 1\}\{R/\Delta S_{NI}\} \qquad (1)$$

$$\beta_I^\infty = -(dT^*/dx_2)_I = -\{(\gamma_I^\infty/\gamma_N^\infty) - 1\}\{R/\Delta S_{NI}\} \qquad (2)$$

where R is the gas constant, ΔS_{NI} is the nematic-to-isotropic transition entropy of the pure nematogenic solvent and γ_N^∞ and γ_I^∞ are the infinite dilution solute activity coefficients in the nematic and isotropic phases, respectively, each extrapolated to T_{NI} ($T^* \rightarrow 1$). Clearly β^∞ values depend on a pure solvent property, ΔS_{NI}, that can be determined from differential scanning calorimetry (DSC) and a solution property, $\gamma_N^\infty/\gamma_I^\infty$, that can be obtained from gas–liquid chromatographic (GLC) studies.[7–9] Unfortunately the high uncertainties (up to 20%) in this DSC/GLC approach to β^∞ values limit its use to that of rapid scanning of a variety of solutes in nematic solvents. Furthermore such high uncertainties in the β^∞ values combined with their closeness to the visually determined β values prohibited experimental search for possible slight curvature theoretically predicted for T^* vs. x_2 diagrams.[10–12]

More recently[13] β_N and β_I values were obtained from measurements of the variation of density as a function of temperature (in the nematic, isotropic and two-phase regions) for a pure liquid crystal and a mixture of it and a nonmesomorphic impurity. The liquid crystalline solvent studied was *p*-*n*-heptyl-*p*′-cyanobiphenyl (7CB) and the solute probes were 3,3-diethylpentane (or tetraethylmethane; Et_4C) and the tetraalkyl tin compounds R_4Sn (R = C_2H_5, *n*-C_3H_7 and *n*-C_4H_9). Results from this study are given in Table I. Unfortunately these results could not be directly compared with those from earlier visual measurements (also given in Table I) for two reasons. Firstly the visual measurements were carried out on different liquid crystalline solvents; namely *p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA) and *p*-*n*-pentyl-*p*′-cyanobiphenyl (5CB). In Table I only the 5CB results are given. Secondly the density method relied on measurements on a single 7CB/solute probe mixture using an x_2 value close to the lowest x_2 value used for the same solute in the visual study, where results from several 5CB/solute probe mixtures (with x_2 values falling within the range 0.006 to 0.05) were fitted to straight lines. Thus if, as theory predicts,[10–12] the T^* vs. x_2 plots are actually curved, and if this curvature is appreciable then the linear phase diagrams obtained from the density and visual methods, in different x_2 regions,

TABLE I

β values for systems of quasispherical solutes in 7CB[a] and 5CB[b] solvents

	7CB			5CB		
Solute	Mole fraction of solute	β_N	β_I	Mole fraction range (data points)	β_N	β_I
Et_4C	0.0151	0.568 ± 0.004	0.383 ± 0.004	0.013 – 0.049 (5)	0.728 ± 0.008	0.627 ± 0.006
Et_4Sn	0.0129	0.645 ± 0.004	0.442 ± 0.004	0.011 – 0.041 (4)	0.857 ± 0.014	0.715 ± 0.013
Pr_4Sn	0.0102	0.677 ± 0.005	0.481 ± 0.004	0.007 – 0.026 (4)	1.124 ± 0.006	0.913 ± 0.007
Bu_4Sn	0.00770	0.854 ± 0.006	0.535 ± 0.004	0.006 – 0.023 (4)	1.296 ± 0.012	1.035 ± 0.008

[a] From density study; Ref. 13.
[b] From visual study; Ref. 4.

will give different β values for even the same liquid crystal/solute probe system.

As Table I shows, for each of the quasispherical solutes studied, the β values visually obtained with 5CB as solvent are appreciably higher than those obtained from density studies on solutions in 7CB. Assuming that the 5CB and 7CB molecules are rigid spherocylinders, with nearly equal length-to-breadth ratios (2.8 and 2.95 respectively), closer β values are expected for their solutions (see Table I in Ref. 11). A fraction of these larger than expected differences in β values may be attributed to the differences between the visual and density studies, discussed in the previous paragraph, if the T^* vs. x_2 diagrams are actually appreciably curved. For rigid spherocylindrical solvent molecules theory[11] predicts that the T^* vs. x_2 diagrams are only very slightly curved. Visual measurements in 5CB solvent systems in the x_2 ranges indicated in Table I gave virtually linear T^* vs. x_2 diagrams with correlation coefficients in excess of 0.999. If appreciable curvature does not exist at lower x_2 values one may safely assume that, for all practical purposes, the T^* vs. x_2 plots are linear. If this is the case then the lower β values for systems with 7CB[13] as solvent may be due to the greater flexibility and/or aliphatic character of the 7CB molecule.

To directly compare the visual and density methods, density measurements were carried out on the 5CB/Et_4C system. To avoid missing possible curvature at low x_2 values, the density measurements were carried out on, in addition to "pure" 5CB, six 5CB/Et_4C solutions with x_2 values ranging from about 0.0028 to an upper value of about 0.014; the latter falling within the range of x_2 values used in the visual study[4] on this system.

EXPERIMENTAL SECTION

3,3-diethylpentane (Et_4C) with a purity in excess of 99% was obtained from Chemical Samples and used as received. 5CB was obtained in sealed containers from BDH Chemicals. From their sharp nematic-to-isotropic transition temperature (35.26°C for one batch and 35.15°C for another batch; labelled I and II respectively) the two batches of 5CB used in this study were assessed to be highly pure and were used without further purification. The properties of Et_4C and 5CB are given elsewhere.[4,13]

The density measurements, using an Anton Paar precision density system, have been previously described.[13] Under the conditions used the accuracy of our density measurements is better than 1.0×10^{-5} g cm^{-3}.

RESULTS

The general shapes of the density (ρ) vs. temperature (t) diagrams for "pure" 5CB (Figure 2) and 5CB/Et$_4$C mixtures (Figure 3) are similar to those previously observed in 7CB systems.[13] The nematic-to-isotropic transition temperature, T_{NI}, is that at which a sharp change in the density of the pure liquid crystal occurs (see Figure 2). The volume change at the nematic-to-isotropic transition of pure 5CB was obtained by fitting the reciprocal of the density in each phase to a quadratic function of $|T - T_{NI}|^{0.5}$ where T is the temperature and T_{NI} is the transition temperature. This procedure is suggested by Klement and Cohen.[14] In Table II our results for the two 5CB batches are given along with the results of Dunmur and Miller.[15]

T_N and T_I in Figure 3 are the temperatures at which the two-phase region begins (isotropic phase appears) and ends (nematic phase disappears) respectively. Different variations of density with temperature exist in the nematic region just before T_N is reached and the part

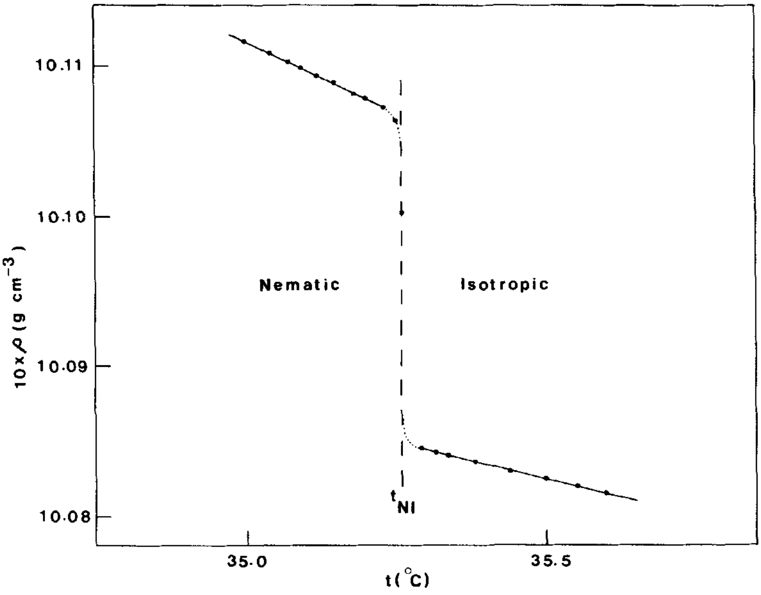

FIGURE 2 Density (ρ) in g cm^{-3} as a function of temperature for 5CB.

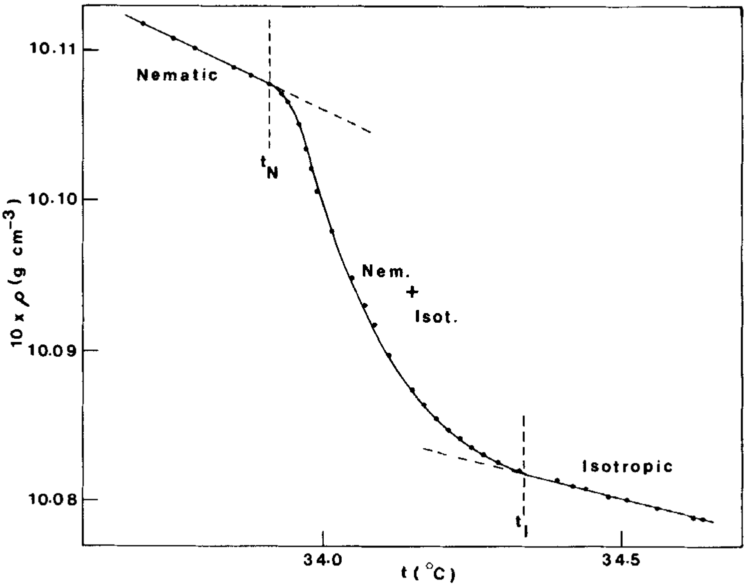

FIGURE 3 Density (ρ) in g cm^{-3} as a function of temperature for a dilute mixture of Et_4C in 5CB.

of the two-phase region immediately after T_N. T_N is determined from the intersection of best fits for the data in the two regions. T_I is similarly determined using best fits to the data in the part of the two-phase region just preceeding T_I and in the isotropic region just after T_I. Because different batches of liquid crystals exhibit different T_{NI} values, the effect of solute impurities on the nematic-to-isotropic transition temperature is investigated using the reduced temperatures T_N^* $(=T_N/T_{NI})$ and T_I^* $(=T_I/T_{NI})$, which for a pure liquid crystal have the value of unity. In Table III T_N^* and T_I^* values are given for eleven 5CB/Et_4C mixtures; six with Et_4C mole fractions ranging from

TABLE II

Transitional temperature, densities and volume change for 5CB

			Densities (g cm^{-3})		
		t_{NI} (°C)	Nematic	Isotropic	$V/V_{Nem.}$
This work	Batch I	35.26	1.01051	1.00847	0.00202
	Batch II	35.15	1.01100	1.00886	0.00212
Dunmur and Miller[15]		35.0	1.01135	1.00933	0.00200

TABLE III

T_N^* and T_I^* values at various Et_4C mole fractions (x_2) in $5CB/Et_4C$ mixtures

Study	x_2	T_N^*	T_I^*
This study (Batch I)	0.002799	0.9975	0.9984
	0.005144	0.9956	0.9970
This study (Batch II)	0.001848	0.9985	0.9990
	0.004920	0.9962	0.9977
	0.007728	0.9938	0.9955
	0.01431	0.9890	0.9920
Visual[4] study	0.01259	0.9902	0.9929
	0.02487	0.9809	0.9848
	0.03288	0.9751	0.9799
	0.04077	0.9699	0.9752
	0.04852	0.9638	0.9702

0.0028 to 0.0143 are from this study and five with Et_4C mole fractions ranging from 0.0126 to 0.0485 are from an earlier visual[4] study.

In Figure 4 we present ρ vs. *t* plots for 5CB from batch II and four $5CB/Et_4C$ mixtures prepared using batch II. Figures 3 and 4 illustrate that the addition of a solute impurity to a nematic liquid crystal broadens its nematic-to-isotropic transition region and depresses the temperature of the transition. That both these effects increase as the concentration of the solute impurity increases is evident from Figure 4. In Figure 5 linear fits of T_N^* vs. x_2 and T_I^* vs. x_2 are given.

DISCUSSION

That solute impurities broaden the nematic-to-isotropic transition region and depress the temperature of the transition has already been theoretically predicted[10–12] and experimentally observed.[3–6,13] One of the objectives of this study was to compare the visual[4] and density[13] methods. To achieve this mixtures of the nematic solvent 5CB and the nonmesomorphic solute Et_4C, previously used in a visual study,[4] were used in this density study. The second objective was to determine whether T^* vs. x_2 plots are truly linear or are slightly curved as theory[10–12] predicted. For this purpose the mole fraction of Et_4C in the $5CB/Et_4C$ mixtures ranged from as low as 0.0028 up to 0.0143. This lower range of Et_4C mole fractions complements and overlaps with the mole fraction range (0.0126–0.0485) used in the visual study.

Although results of earlier visual studies[3–6] gave virtually linear T^* vs. x_2 plots, their possible curvature (theoretically predicted)[10–12]

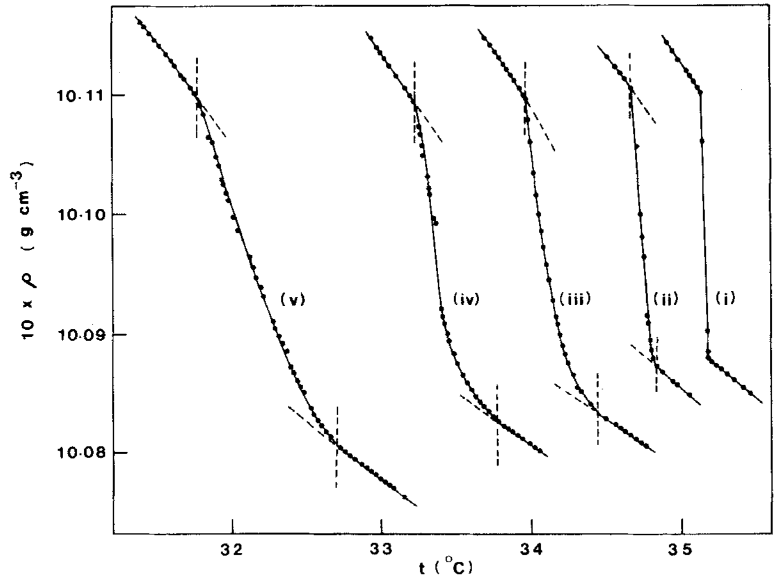

FIGURE 4 Density (ρ) in g cm^{-3} as a function of temperature for (i) 5CB and Et$_4$C/5CB mixtures with Et$_4$C mole fractions of (ii) 0.001844, (iii) 0.00492, (iv) 0.007728 and (v) 0.01431.

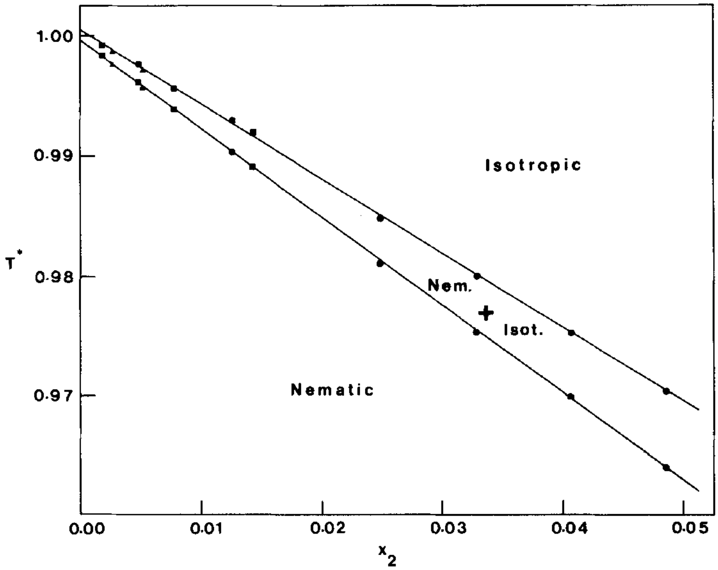

FIGURE 5 Linear least squares fits for the reduced temperatures (T^*_N and T^*_I) vs. Et$_4$C mole fractions (x_2). ▲ density studies on batch I, ■ density studies on batch II and ● results from visual studies (Ref. 4).

could not be totally excluded especially at low x_2 values that could not be conveniently reached by the visual[3,4] method. In addition differences between β^{∞} values obtained using the GLC/DSC approach[4,7] and β values obtained for the same systems using the visual[4] method pointed to possible curvature in the T^* vs. x_2 plots. Unfortunately the closeness of the β^{∞} and β values combined with the uncertainties of the two methods (especially the GLC/DSC approach) precluded a definite statement on curvature.

Given in Table IV are the results of linear least squares analyses of T_N^* vs. x_2 and T_I^* vs. x_2 (i) 6 data points from this study, (ii) 5 data points from an earlier visual[4] study and (iii) 11 data points from the above two studies. Second order fits[16] to the set of 11 data points fell very close to the linear study. No appreciable improvement was achieved by higher order fits. These results and Figure 5 clearly show that (i) the visual and density methods are of comparable precision and (ii) T^* vs. x_2 can, for all practical purposes, be considered linear.

Comparability of the density and visual methods means that the lower β values for 7CB systems relative to 5CB systems (see Table I) are real and not, as has been previously[13] suspected, due to a combination of (i) curvature in the T^* vs. x_2 diagrams and (ii) the use (then)[13] of one data point by the density method to obtain these β values. The smaller β values in 7CB systems may be due to the greater flexibility and/or aliphatic character of the 7CB molecule relative to the 5CB molecule.

Knowledge of β_N and β_I values is needed to test various theories[4,13] for mixtures of nonmesomorphic solutes in liquid crystalline solvents. The agreement between the results of this density study and the visual method means that β_N and β_I values can now be determined to a high degree of confidence from studies on the variation of density as a function of temperature (in the nematic, isotropic and two-phase regions) for a pure liquid crystal and only one mixture of it and a nonmesomorphic solute. The results of such studies, especially on systems of quasispherical solutes dissolved in nematogenic solvents, are of considerable practical importance, since small amounts of similar solutes are often added to nematogenic mixtures used in liquid-crystal displays to adjust viscosity-electrical conductivity characteristics.

We are currently involved in using the density method to obtain β_N and β_I values for systems of quasispherical solutes of different sizes (namely Et_4C and the tetraalkyl tin compounds R_4Sn where $R = C_2H_5$, n-C_3H_7 and n-C_4H_9) in 5CB as well as *p*-*n*-hexyl-cyanobiphenyl (6CB) and *p*-*n*-octyl-cyanobiphenyl (8CB). In addition to

TABLE IV

Results of linear least squares analyses of T^* vs. x_2

	T^*_{N} vs. x_2			T^*_{I} vs. x_2		
Study (data points)	Slope	Intercept	Correlation coefficient	Slope	Intercept	Correlation coefficient
This study (6)	−0.7542 ± 0.0146	0.99971 ± 0.00011	0.99906	−0.5630 ± 0.0214	1.00007 ± 0.00016	0.99641
Visual study[4] (5)	−0.7281 ± 0.0116	0.99922 ± 0.00040	0.99974	−0.6267 ± 0.0087	1.00060 ± 0.00030	0.99981
Visual study[4] and this study (11)	−0.7377 ± 0.0040	0.99957 ± 0.00010	0.99985	−0.6206 ± 0.0052	1.00041 ± 0.00012	0.99966

their practical importance the results of such measurements will, it is hoped, be used to test theories of mixtures of nonmesomorphic solutes in liquid crystalline solvents.

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16. These are: $T_N^* = 0.999747 - 0.766897(x_2) + 0.614844(x_2)^2$
    $T_I^* = 1.000275 - 0.597347(x_2) - 0.489846(x_2)^2$.