Critical Phenomena in Ternary Mixtures of Near-Critical Carbon Dioxide, o-Nitrophenol and Certain 1-Alkanols

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ABSTRACT

Experimental results of fluid multiphase equilibria occurring in a series of ternary systems (carbon dioxide + o-nitrophenol + 1-alkanol) are presented and discussed. The 1-alkanols considered were octanol, heptanol, hexanol and pentanol. Special attention was given to the determination of critical endpoints of the three-phase equilibria liquid-liquid-vapor occurring in these systems. A comparison was made with previous measurements in a series of ternary mixtures (carbon dioxide + tetradecane + 1-alkanol) with as the 1-alkanol octanol, heptanol, hexanol and pentanol.

The binary subsystem (carbon dioxide + o-nitrophenol) has been found to show type-V fluid phase behavior according to the classification of Van Konynenburg and Scott, whereas the binary subsystem (carbon dioxide + pentanol) has type-II. All the other binary subsystems (carbon dioxide + 1-alkanol) show type-III fluid phase behavior. The transformation of type-V fluid phase behavior into type-II or type-III suggests that the binary system (carbon dioxide + o-nitrophenol) has type-IV fluid phase behavior.

KEY WORDS: carbon dioxide, critical, data, experiments, liquid-liquid-vapor equilibria, o-nitrophenol, 1-alkanols

1 INTRODUCTION

Compared to binary mixtures, experimental information of ternary mixtures is only limited. Particularly, data on critical phenomena in ternary mixtures are rare. Since in ternary mixtures molecular interactions are much more complex, unexpected phase behavior may occur accordingly. For instance, Patton et al. (1993), examining the fluid multiphase behavior of the system (carbon dioxide + tetradecane + decanol), in the near-critical region of the solvent, discovered a closed loop two-phase region liquid-vapor (lg) in the three-phase surface liquid-liquid-vapor (l_1l_2g). This closed loop was completely bounded with a critical endpoint locus of the nature $l_1 = l_2 + g$. Further investigations of this phenomenon were reported by Peters et al. (1995, 1996), Gauter et al. (1996). In these studies, experimental results of the ternary systems (carbon dioxide + tetradecane + 1-alkanol), with as the 1-alkanols decanol, octanol, heptanol, hexanol and pentanol, were compared and discussed with the systems (carbon dioxide + o-nitrophenol + 1,4-dichlorobenzene), (carbon dioxide + o-nitrophenol + dodecane) and (carbon dioxide + o-nitrophenol + n-octanol). The results obtained were represented in T,x*-diagrams, where x* is the mole fraction of one of the low-volatile solutes on a carbon dioxide (CO_2)-free basis.

For the binary system (carbon dioxide + o-nitrophenol) strong evidence was found that its fluid phase behavior belongs to type-IV. Earlier findings of Baylé (1951) suggested that this system has type-V fluid phase behavior. In order to collect more evidence for this phenomenon, experimental work was carried out on the systems (carbon dioxide + o-nitrophenol + 1-alkanol), with as the 1-alkanols heptanol, hexanol and pentanol.

In this paper the experimental results of the four systems (carbon dioxide + o-nitrophenol + 1-alkanol) will be presented and discussed. The experimental setup will be described briefly. Some conclusions and recommendations for further work will be given.

2 EXPERIMENTAL

In this study the critical end-points of the ternary systems (carbon dioxide + o-nitrophenol + 1-alkanol) with either octanol, heptanol, hexanol or pentanol as the alkanol, were investigated experimentally. The measurements were carried out in a Cailletet-apparatus, which has been described elsewhere (Peters et al., 1993).

The sample inside a Cailletet-tube has a fixed overall composition, i.e. many samples for one ternary system have to be prepared. The mole fraction x^*_{NP} of nitrophenol on a CO_2-free basis varies from zero to one. Starting with one of the binary CO_2-subsystems, the nature of the mixture is gradually changed into that of the other binary CO_2-subsystem. As pointed out by Patton et al. (1993), the concentration of the solvent (CO_2) is of little influence on the location of the critical endpoints since the solvent is much more volatile than the solutes. Nevertheless, in order to keep this influence as small as possible, the mole fraction of carbon dioxide was kept constant at $x_{CO2} = 0.95$ for all mixtures investigated.

In Table 1 the suppliers and purities of the substances used are summarized. All chemicals were used without further purification.

2.1 PREPARATION OF THE SAMPLE

As mentioned before, the samples are examined at fixed overall composition, i.e. specified amounts of the components have to be dosed into the Cailletet-tube. In preparing the sample, in all cases we have to deal with one solid component (o-nitrophenol), one liquid component (1-alkanol) and one gaseous component (CO_2). First the solid and the liquid substances are dosed into the high-pressure tube and their amounts are determined by weighing. After the degassing of both low-volatile components, the proper amount of gas is dosed volumetrically into the Cailletet-tube, using a gas-dosing apparatus.

Throughout the measuring procedure an expansion of the sample into the non-observable part of the Cailletet-tube should be avoided.

2.2 EXPERIMENTAL PROCEDURE

In order to determine the location of a critical endpoint, pressure and temperature of phase transitions from three phases to two phases were observed. Because of the transparency of the sample part of the Cailletet-apparatus phase transitions can easily be observed visually.

In the measuring procedure, first a pressure-temperature combination is adjusted for which the three fluid phases liquid 1 (l_1), liquid 2 (l_2) and vapor (g) are coexisting at equilibrium conditions. Then, the boarder of this three-phase region is searched for the occurrence of critical endpoints. During this search, temperature is kept constant whereas pressure is changed gradually. The temperature and the pressure at which one of the three phases disappears, along with the nature of the phase transition, are established. After changing the temperature, the described procedure is repeated, until a critical endpoint is reached. In cases the critical endpoint could not be found exactly, average values of the pressures and temperatures lying slightly above and below this point were taken as the critical endpoint data. The latter procedure has to be applied if the susceptibility of the meniscus for pressure and temperature changes exceeds the detectability by the equipment.

3 RESULTS AND DISCUSSION

The critical endpoint data of the systems measured are presented in Tables 2 to 5. Figures 1 to 6, and 8 to 10 show the transitions of fluid phase behavior occurring in the various ternary systems. In all figures the mole fraction of o-nitrophenol is on a CO_2-free basis (x^*_{NP}). As can be seen from the various T,x^*_{NP}- and p,x^*_{NP}-diagrams, all ternary systems

qualitatively show a similar behavior. In the various figures, critical endpoints of the character $l_1 = l_2 + g$ are indicated by open circles, whereas those of the character $l_1 = l_2 + g$ are represented by open or filled triangles.

From our previous work (Peters et al., 1995, 1996 and Gauter et al., 1996), it is known that type-IV fluid phase behavior has two three-phase regions l_1l_2g. The tree-phase region at lower temperature ends with a critical endpoint of the nature $l_1 = l_2 + g$ (open triangles in the various figures). The three-phase region at higher temperature begins with a critical endpoint of the same nature (filled triangles). As pointed out previously (Peters et al., 1995, 1996 and Gauter et al., 1996), coincidence of a filled and an open triangle represent a double critical endpoint (DCEP).

The binary systems (carbon dioxide + 1-alkanol) with as the 1-alkanol octanol, heptanol and hexanol, show type-III fluid phase behavior. Therefore, in the related diagrams of the ternary systems (carbon dioxide + o-nitrophenol + 1-alkanol), shown in Figures 1 to 6 respectively, transitions of type-III into type-V fluid phase behavior can be observed with increasing x^*_{NP}. In type-III fluid phase behavior of the classification of Van Konynenburg and Scott (see Scott and Van Konynenburg, 1970; Van Konynenburg and Scott, 1980) only a critical endpoint of the nature $l_1 = g + l_2$ is present. However, characteristic for type-V is the presence of two critical endpoints: at lower temperature one of the nature $l_1 = l_2 + g$ and at higher temperature one of the nature $l_1 = g + l_2$. The critical endpoint data of the binary subsystems (carbon dioxide + 1-alkanol) are taken from Lam et al. (1990).

In Figure 1 it can be seen that a continuous locus $l_1 = g + l_2$ exists in the ternary system (carbon dioxide + o-nitrophenol + octanol). This locus passes through a maximum in temperature at T = 317 K and $x^*_{NP} = 0.72$. Another critical endpoint line of the nature $l_1 = l_2 + g$ starts at the axis $x^*_{NP} = 1$. First this locus goes to higher temperatures with decreasing

mole fraction x^*_{NP} and, without touching the critical endpoint locus $l_1 = g + l_2$, bends back to lower temperatures again. The temperature maximum of this locus is located at about T = 314 K and $x^*_{NP} = 0.60$. In addition, it can be observed that this locus reaches a minimum of x^*_{NP} at 0.40. In previous contributions (Peters et al., 1995, 1996 and Gauter et al., 1996), it was pointed out that this minimum of x^*_{NP} can be identified as a DCEP. Finally, the extension of this locus to lower temperatures and higher x^*_{NP} is hidden by the occurrence of solid o-nitrophenol. For completeness, the p,x^*_{NP}-diagram of this ternary system is given in Figure 2. It shows a similar behavior to the T,x^*_{NP}-diagram (Figure 1).

For the system with heptanol as the 1-alkanol (Figures 3 and 4), qualitatively the same behavior is obtained. In analogy to what was already found for the ternary systems (carbon dioxide + tetradecane + 1-alkanol), see Peters et al. (1995, 1996) and Gauter et al. (1996), the "hole" in the three-phase surface l_1l_2g becomes larger with decreasing carbon number of the 1-alkanol. In the T,x^*_{NP}-diagram (Figure 3) the DCEP is situated at lower mole fraction ($x^*_{NP} = 0.20$). Furthermore, it can be seen that both critical endpoint loci $l_1 = g + l_2$ and $l_1 = l_2 + g$ seem to coincide at their maximum in temperature (Figure 3) or pressure (Figure 4). Compared to the ternary system with octanol as the 1-alkanol, this temperature maximum is shifted to a lower mole fraction ($x^*_{NP} = 0.57$). Finally, it can be observed that in the T,x^*_{NP}-diagram (Figure 3) both critical endpoint loci approach each other ar close as 1 K.

In Figures 5 and 6 the phase behavior of the ternary system (carbon dioxide + o-nitrophenol + hexanol) is shown. As expected, the size of the two-phase “hole” liquid-vapor in the three-phase surface l_1l_2g has increased further. The two critical endpoint loci $l_1 = g + l_2$ and $l_1 = l_2 + g$ are about to intersect. In case of intersection tricriticality is the result. In order to decide whether tricritical points (TCPs) are present the extended classical theory

of tricritical phenomena (Scott, 1987) can be used. From this theory it follows that:

$$\Delta T = 2 \cdot j_2 \cdot (\Delta x^*_{NP})^{3/2} + 2 \cdot j_4 \cdot (\Delta x^*_{NP})^{5/2} + 0 \cdot (\Delta x^*_{NP})^{7/2} \quad (1)$$

where j_2 and j_4 are constants, while

$$\Delta x^*_{NP} = |x^*_{NP} - x^*_{NP,t}| \quad (2)$$

For a certain value of x^*_{NP}, in Eq. (1) ΔT is the temperature difference between both critical endpoint loci $l_1 = g + l_2$ and $l_1 = l_2 + g$, and $x^*_{NP,t}$ is the x^*_{NP}-value at which tricriticality occurs. Close to the tricritical point, the first term of Eq. (1) is sufficient to take into account, i.e. a plot of $\Delta T^{2/3}$ versus x^*_{NP} gives a linear relationship. This is shown in Figure 7. From this figure it can be seen that, for a linear extrapolation of the two lines to lower $\Delta T^{2/3}$, the two lines are likely to intersect the axis $\Delta T^{2/3} = 0$. Two TCPs appear at $x^*_{NP} = 0.4$ and $x^*_{NP} = 0.53$, approximately. However, a further invetigation of this x^*_{NP}-region might reveal that the TCPs lie closer to each other or do not occur at all.

Furthermore, in this ternary system the DCEP shifts to a lower mole fraction ($x^*_{NP} = 0.05$), and touches almost the axis $x^*_{NP} = 0$.

The binary system (carbon dioxide + pentanol) shows type-II fluid phase behavior (Lam et al., 1990). Type-II fluid phase behavior is characterized by a critical endpoint of the nature $l_1 = l_2 + g$. Therefore, in the ternary system (carbon dioxide + o-nitrophenol + pentanol), a transition from type-II into type-V fluid phase behavior takes place with increasing mole fraction x^*_{NP} (Figures 8 and 9). The two critical endpoint lines of different character ($l_1 = g + l_2$ and $l_1 = l_2 + g$), originating on the axis $x^*_{NP} = 1$, join each other in a TCP at about 320 K and $x^*_{NP} = 0.58$ in a temperature maximum (Figure 8).

From the axis $x^*_{NP} = 0$ (Figure 8) a critical endpoint line $l_1 = l_2 + g$ extends to lower

temperatures until it is hidden by the occurrence of solid o-nitrophenol.

For comparison, the systems (carbon dioxide + tetradecane + 1-alkanol) containing octanol to pentanol are presented in Figure 10. Two main differences can be seen between the two series of ternary systems. First of all, the type of phase behavior of the two binary subsystems is different. The binary mixture (carbon dioxide + tetradecane) has type-III fluid phase behavior, whereas the binary subsystem (carbon dioxide + o-nitrophenol) has type-V. Compared to the systems with tetradecane as one of the solutes, the difference with the systems containing o-nitrophenol is that the closed loop two-phase region is partially lacking in the latter system because the axis $x^*_{NP} = 1$ intersects the closed loop. However, the relationship between both series of ternary systems is obvious.

Another difference between both series of ternary systems is that in the systems with o-nitrophenol this component solidifies and, consequently, to lower temperatures the critical endpoint locus cannot be followed any more.

4 CONCLUSIONS AND RECOMMENDATIONS

A comparison of the three-phase behavior l_1l_2g of the two series of ternary systems (carbon dioxide + o-nitrophenol + 1-alkanol) and (carbon dioxide + tetradecane + 1-alkanol) shows that, in principle, the occurrence of closed loop two-phase regions (lg) in three-phase surfaces (l_1l_2g) is a general phenomenon. Regardless a Tx^*_{NP}- or a p,x^*_{NP}-diagram is considered, the general structure of these diagrams is characterized by the presence of a continuous critical endpoint locus of the nature $l_1 = g + l_2$ and a closed loop critical endpoint locus of the nature $l_1 = l_2 + g$. Depending of the size and/or location of this two-phase “hole”, all modifications shown in our previous work (Peters et al., 1995, 1996 and Gauter et al., 1996) and those shown in the present study can be derived from this basic

structure. For instance, a big “hole” may intersect the continuous critical endpoint locus of the nature $l_1 = g + l_2$, leading to the occurrence of tricriticality at the points of intersection. This phenomenon was found for example in the ternary system (carbon dioxide + tetradecane + hexanol). Although the phase behavior of the system (carbon dioxide + o-nitrophenol + pentanol) does not show the general behavior, as pointed out in the foregoing, a closer look makes clear that the basic structure also holds for this system. In this system both axis $x^*_{NP} = 0$ and $x^*_{NP} = 1$ partially cut off the left- and right-hand side respectively of the closed loop two-phase region (lg). Moreover, also due to the size of the “hole”, intersection with the continuous critical endpoint locus of the nature $l_1 = g + l_2$ occurs, causing tricriticality, whereas the low-temperature or low-pressure part of the “hole” (Figures 8 and 9 respectively) is hidden by the solid o-nitrophenol phase.

The general conclusion that can be drawn from this analysis is that if the basic structure of all systems investigated is correct, in all cases the following sequence of transformations of fluid phase behavior is related to this general behavior:

type-III ÷ type-IV ÷ type-III

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Table 1 Suppliers and purities of the substances used

substance	supplier	purity in mole%
carbon dioxide	Air products	99.95
o-nitrophenol	Fluka	>99
octanol	Fluka	>99
heptanol	Fluka	>99.5
hexanol	Fluka	>99
pentanol	Fluka	>99.0

Table 2 Critical endpoints of the ternary system (carbon dioxide + o-nitrophenol + octanol) * mean value

x^*_{NP}	lower $l_1 = l_2 + g$		higher $l_1 = l_2 + g$		$l_1 = g + l_2$	
	T [K]	p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]
0.00					309.12	7.97
0.24					313.27	8.56
0.335	279.66	3.95	299.25	6.25	314.32	8.69
0.342	278.98	3.92	298.95	6.26	314.43	8.75
0.35	278.32	3.82	300.48*	6.42*	314.48	8.71
0.36	275.11	3.51	302.21	6.70	314.61	8.73
0.40	270.12	3.06	307.16	7.40	314.88	8.77
0.43			308.76	7.64	315.25	8.86
0.51			311.58	8.12	316.01	8.96
0.60			313.66	8.76	316.52	9.04
0.72			313.31	8.38	316.58	9.01
0.76			312.43	8.22	316.29	8.98
0.85			309.15	7.69	315.47	8.85
0.93			304.65	6.99	314.28	8.70
1.00			298.88	6.18	312.91	8.52

Table 3 Critical endpoints of the ternary system (carbon dioxide + o-nitrophenol + heptanol)

x^*_{NP}	lower $l_1 = l_2 + g$		higher $l_1 = l_2 + g$		$l_1 = g + l_2$	
	T [K]	p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]
0.00					310.56	8.11
0.20	282.93	4.30	300.20	6.40	314.25	8.66
0.26	273.56	3.38	307.23	7.40	315.20	8.76
0.28	269.90	3.07	308.84	7.66	315.51	8.84
0.31			310.67	7.95	315.93	8.90
0.42			314.19	8.56	316.85	9.08
0.51			316.50	8.94	317.83	9.21
0.57			316.82	8.99	318.07	9.24
0.62			316.66	8.95	318.05	9.24
0.72			315.71	8.78	317.80	9.21
0.85			309.45	7.73	315.69	8.89
0.93			303.78	6.87	314.14	8.67
1.00			298.88	6.18	312.91	8.52

Table 4 Critical endpoints of the ternary system (carbon dioxide + o-nitrophenol + hexanol)

x^*_{NP}	lower $l_1 = l_2 + g$		higher $l_1 = l_2 + g$		$l_1 = g + l_2$	
	T [K]	p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]
0.00					312.93	8.41
0.07	283.10	4.33	304.28	6.97	314.31	8.61
0.14	271.70	3.24	312.19	8.16	316.01	8.85
0.19	264.24	2.62	315.17	8.63	317.10	9.00
0.23	260.77	2.37	316.32	8.88	317.53	9.12
0.30			318.39	9.21	318.83	9.29
0.61			318.72	9.24	319.46	9.40
0.66			317.14	9.00	318.63	9.31
0.71			315.71	8.72	318.13	9.20
0.82			311.01	7.94	316.46	8.97
1.00			298.88	6.18	312.91	8.52

Table 5 Critical endpoints of the ternary system (carbon dioxide + o-nitrophenol + pentanol)

x^*_{NP}	lower $l_1 = l_2 + g$		higher $l_1 = l_2 + g$		$l_1 = g + l_2$	
	T [K]	p [MPa]	T [K]	p [MPa]	T [K]	p [MPa]
0.00	273.60	3.42				
0.09	262.50	2.51				
0.13	258.00	2.21				
0.59			319.43	9.34	320.07	9.49
0.61			319.30	9.30	320.03	9.46
0.66			317.52	9.02	319.09	9.35
0.71			316.44	8.80	318.47	9.28
0.75			314.31	8.49	317.72	9.17
0.80			311.04	7.95	316.50	8.99
0.88			306.98	7.31	315.27	8.80
1.00			298.88	6.18	312.91	8.52

FIGURE CAPTIONS

Fig. 1 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + octanol), T,x^*_{NP}-diagram

Fig. 2 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + octanol), p,x^*_{NP}-diagram

Fig. 3 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + heptanol), T,x^*_{NP}-diagram

Fig. 4 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + heptanol), p,x^*_{NP}-diagram

Fig. 5 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + hexanol), T,x^*_{NP}-diagram

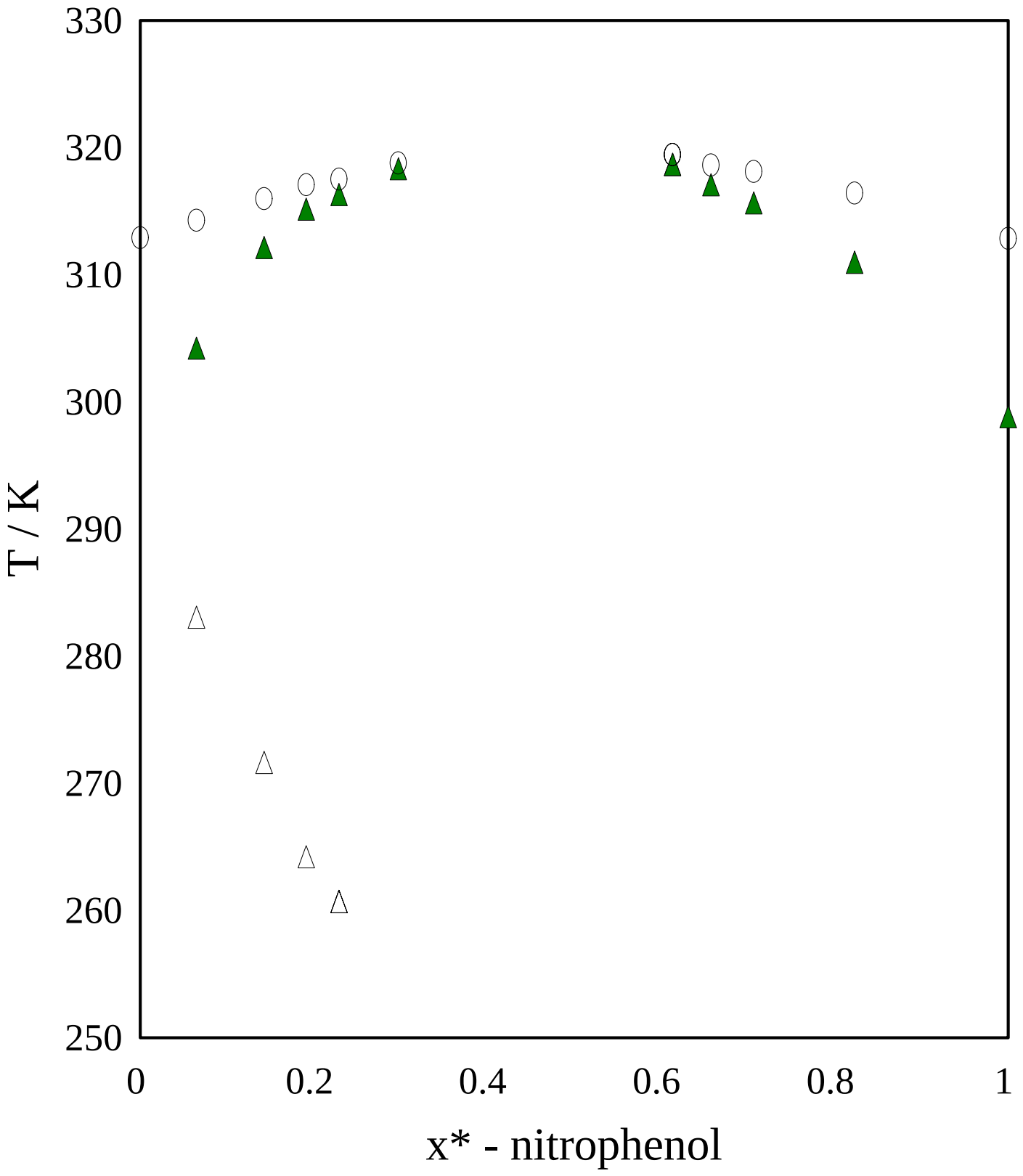
Fig. 6 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + hexanol), p,x^*_{NP}-diagram

Fig. 7 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + hexanol), $\Delta T^{2/3}$,x^*_{NP}-diagram

Fig. 8 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + pentanol), T,x^*_{NP}-diagram

Fig. 9 Critical endpoints for the ternary system (carbon dioxide + o-nitrophenol + pentanol), p,x^*_{NP}-diagram

Fig. 10 Critical endpoints for the ternary system (carbon dioxide + tetradecane + 1-alkanol), T,x^*_{C14}-diagram; triangles: octanol, circles: heptanol, squares: hexanol, crosses: pentanol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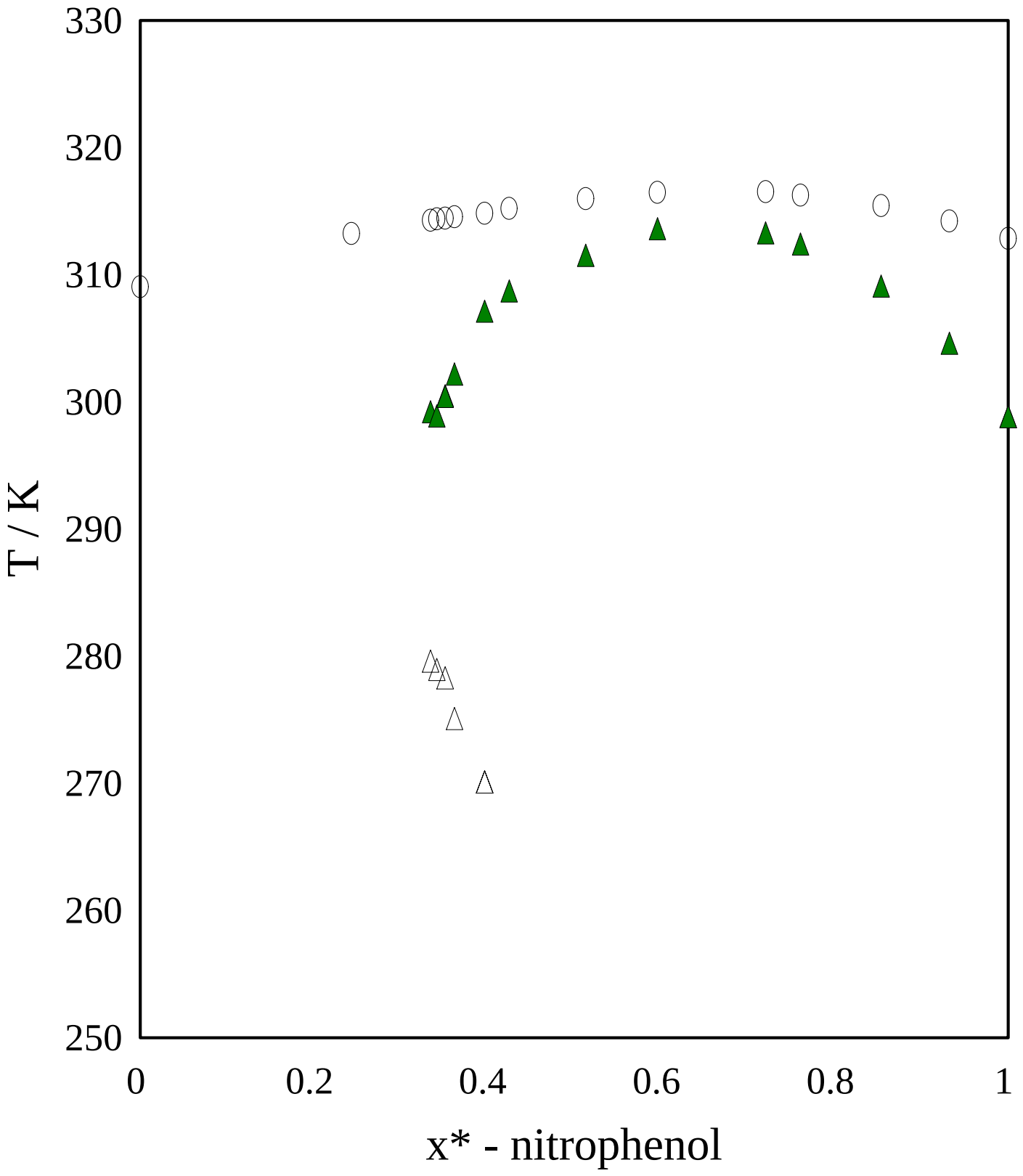
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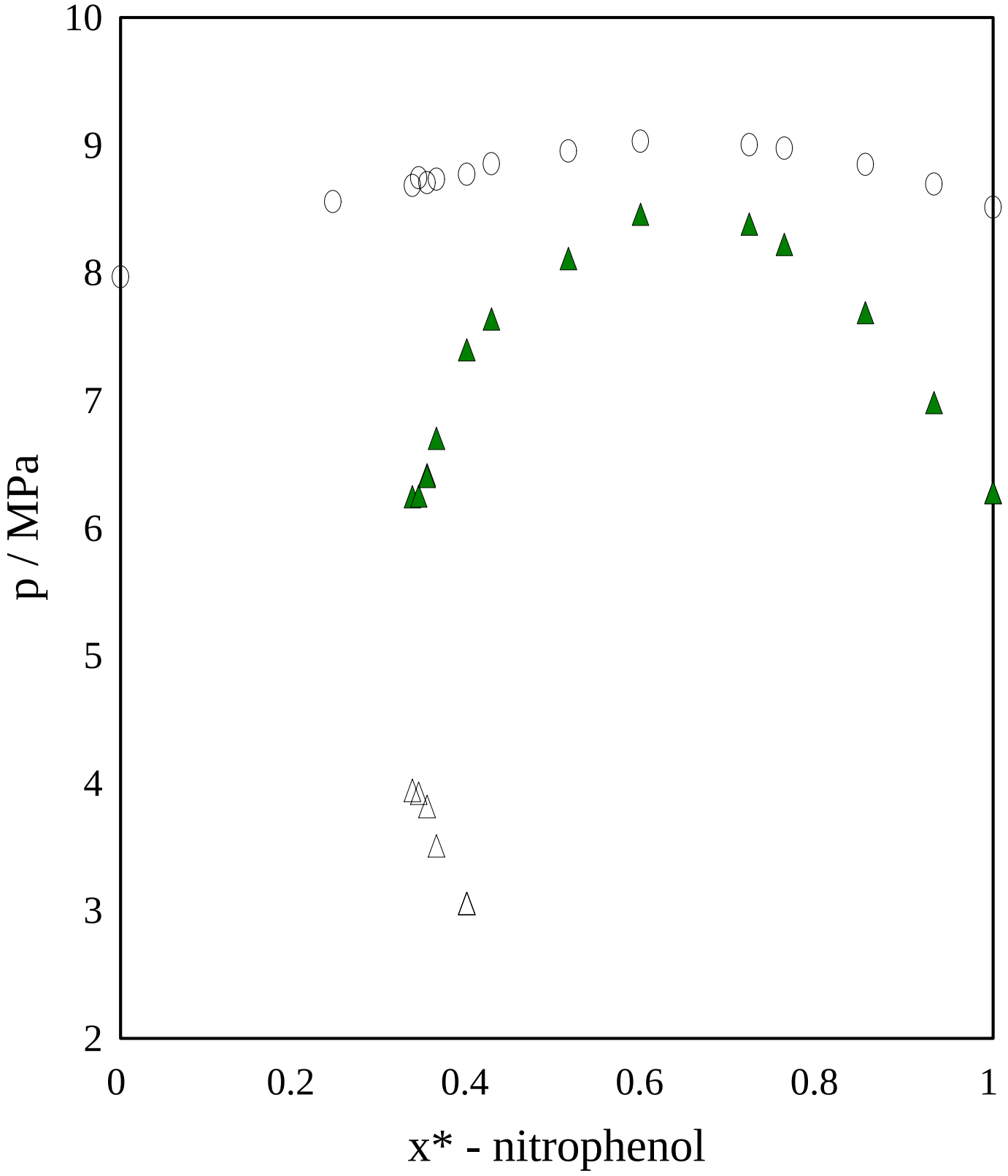
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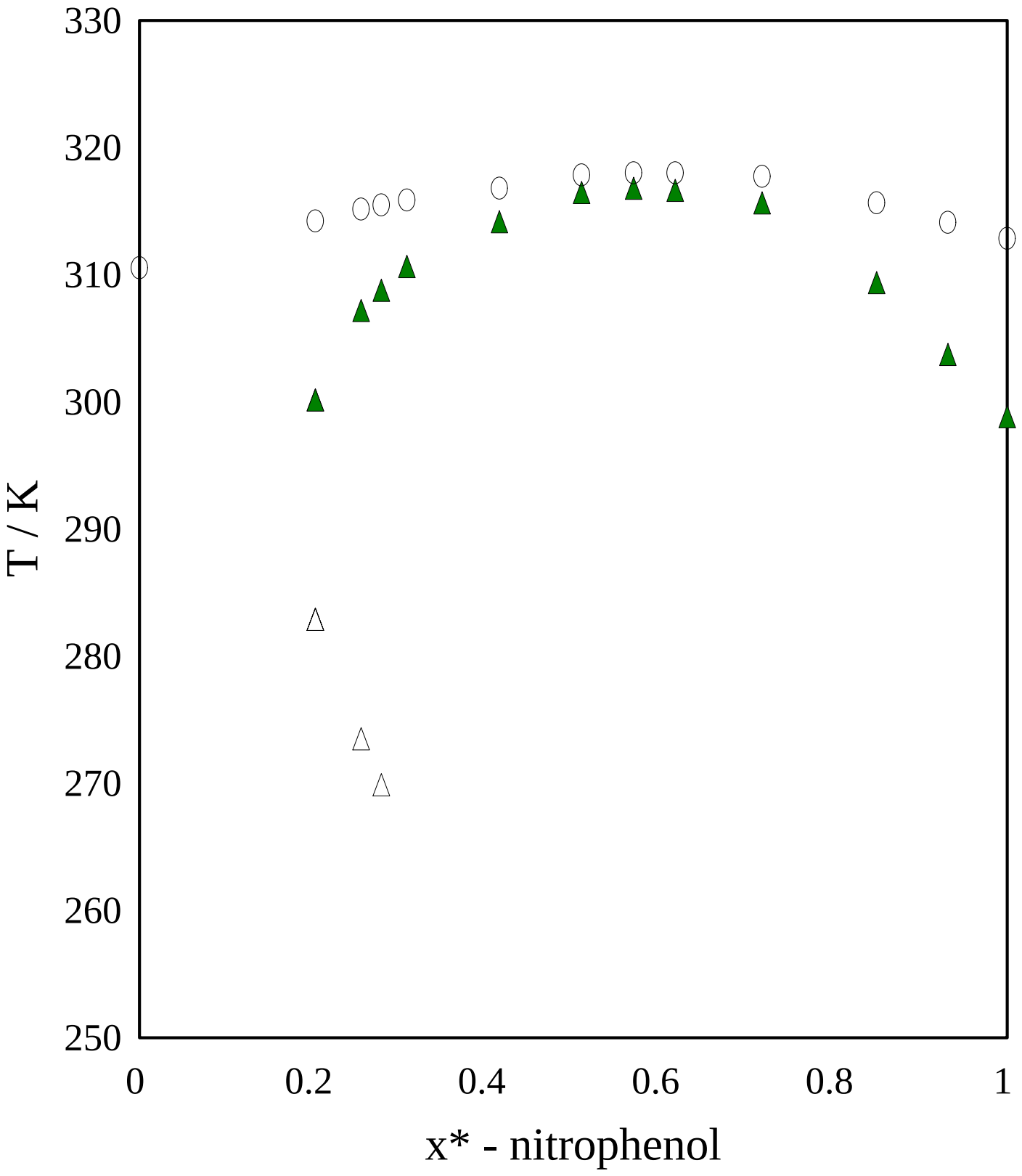
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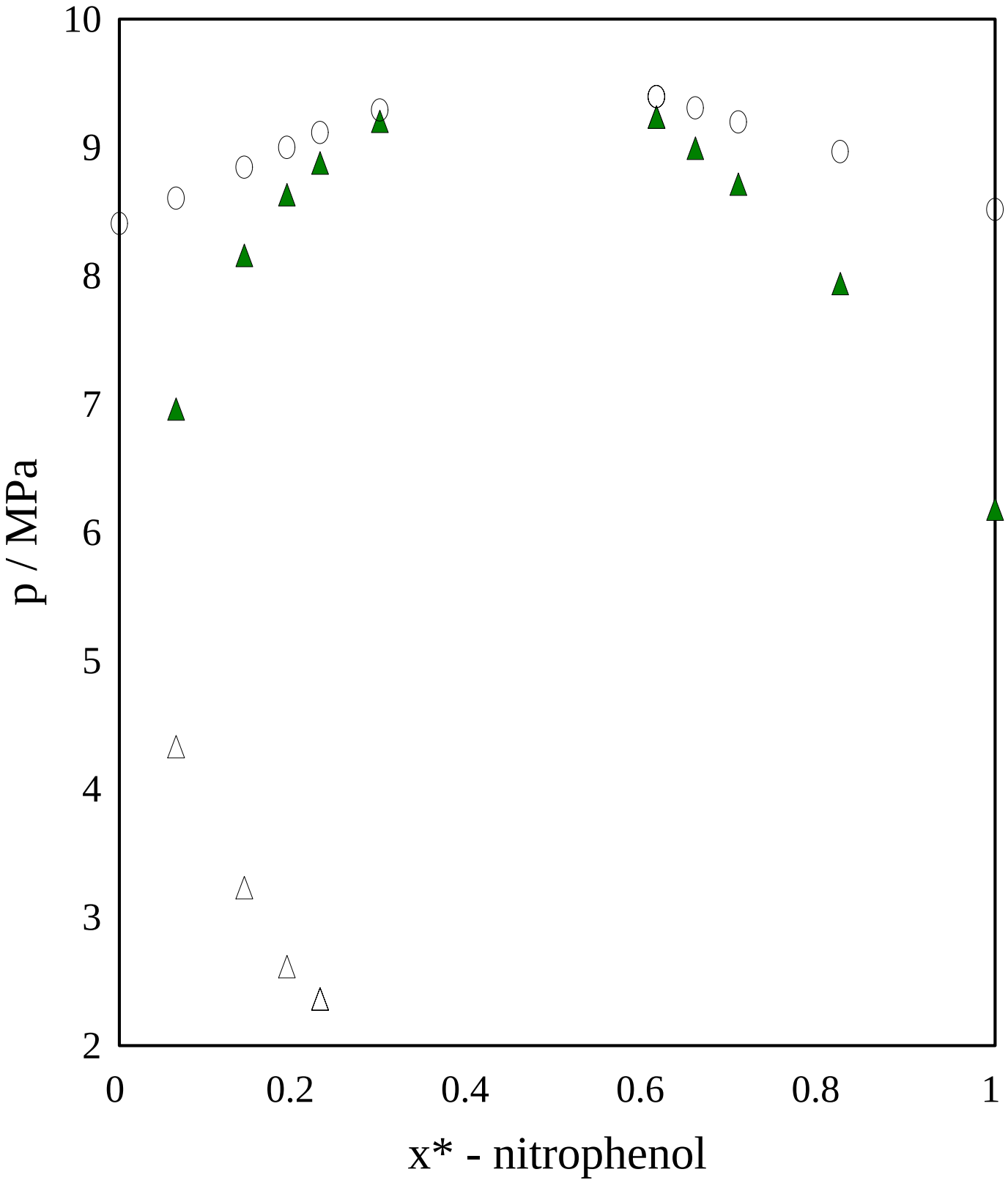
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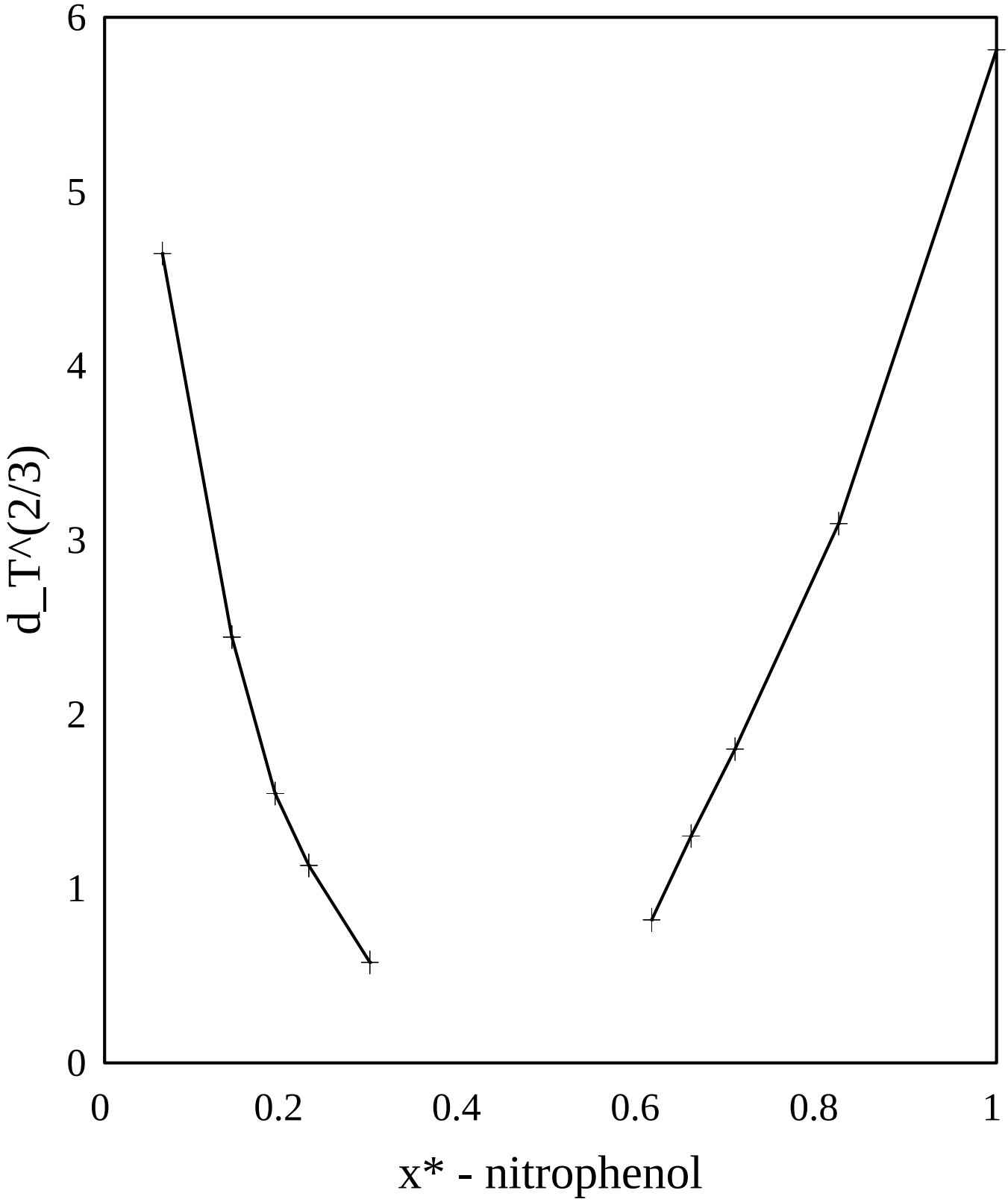
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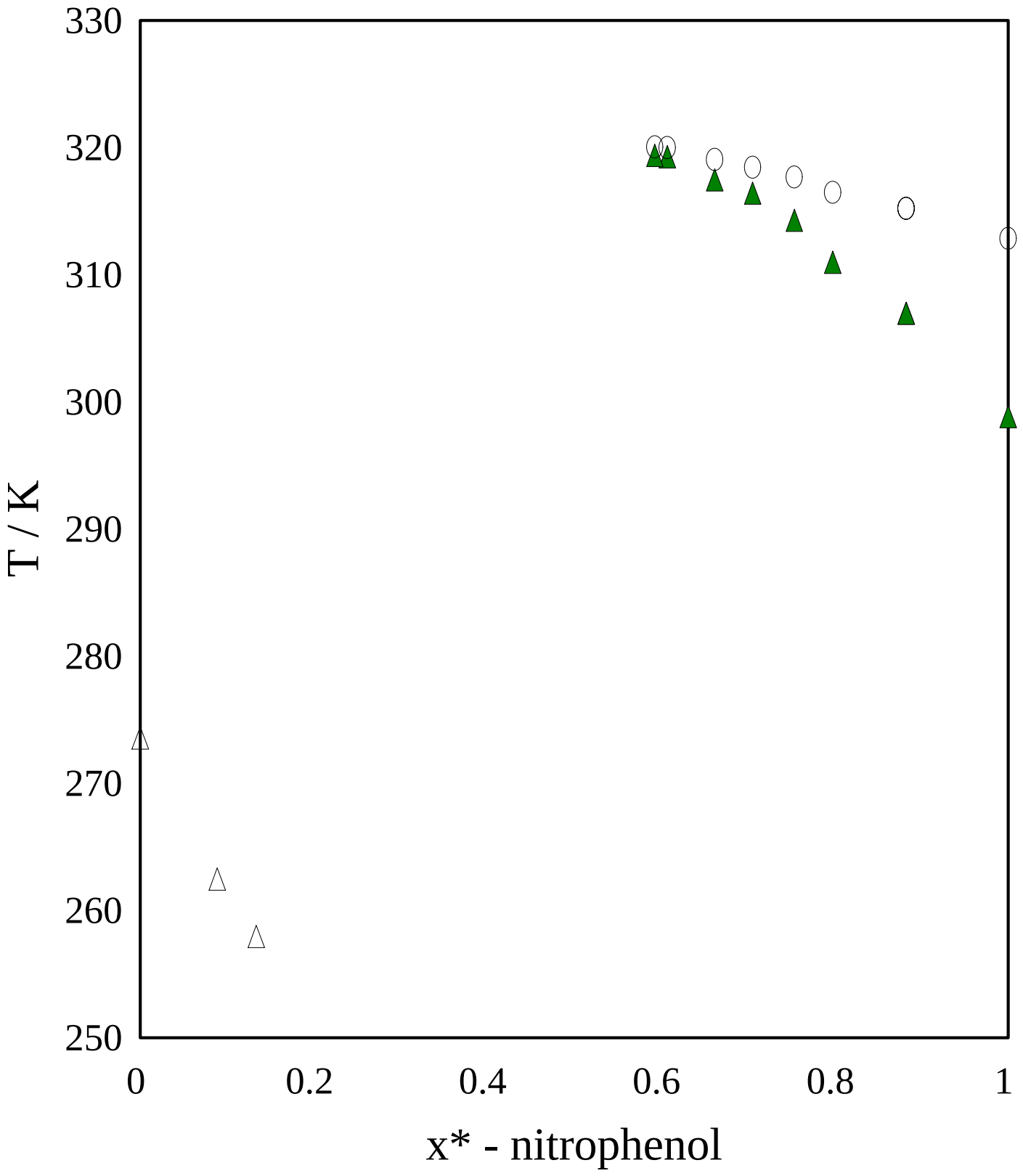
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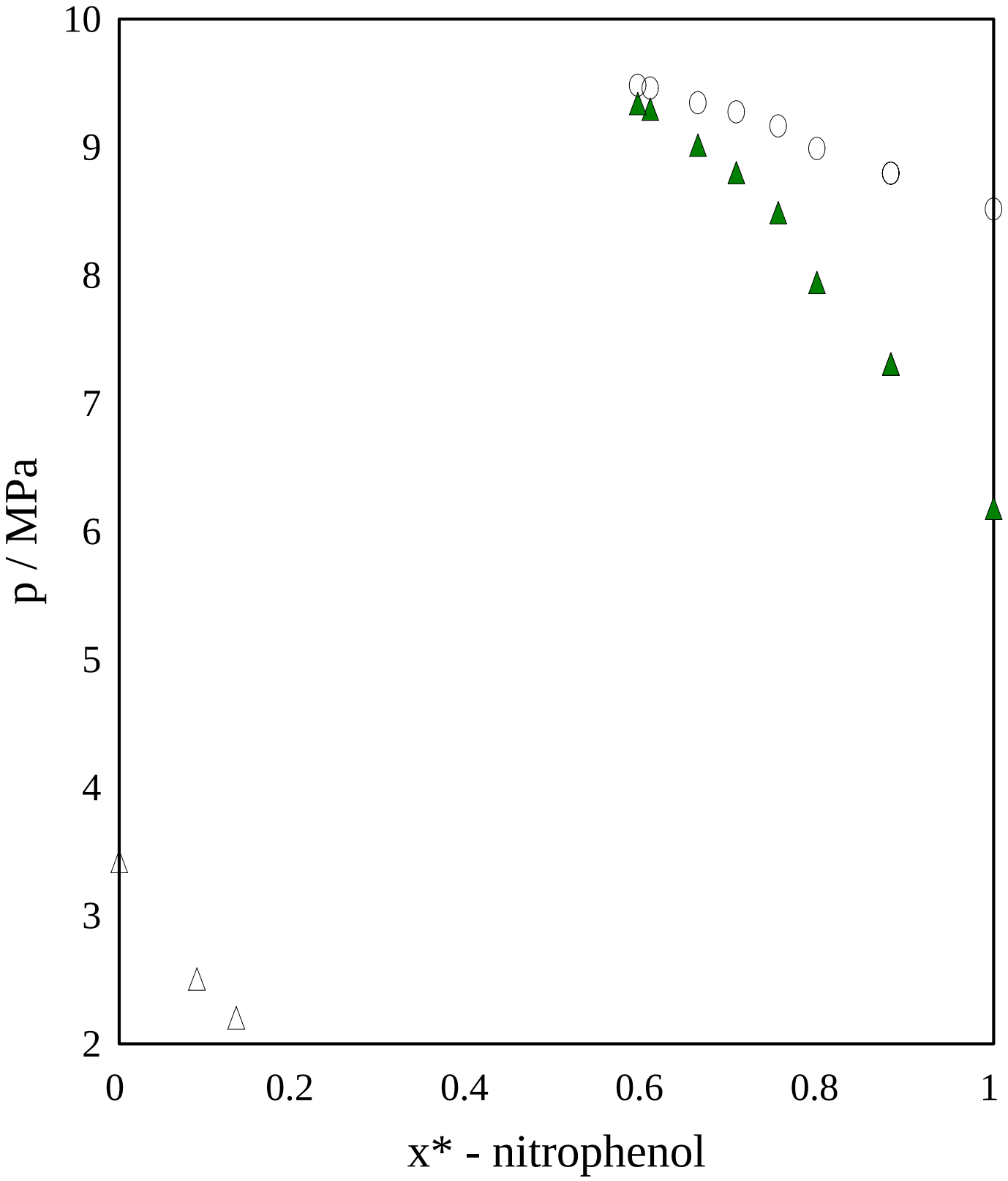
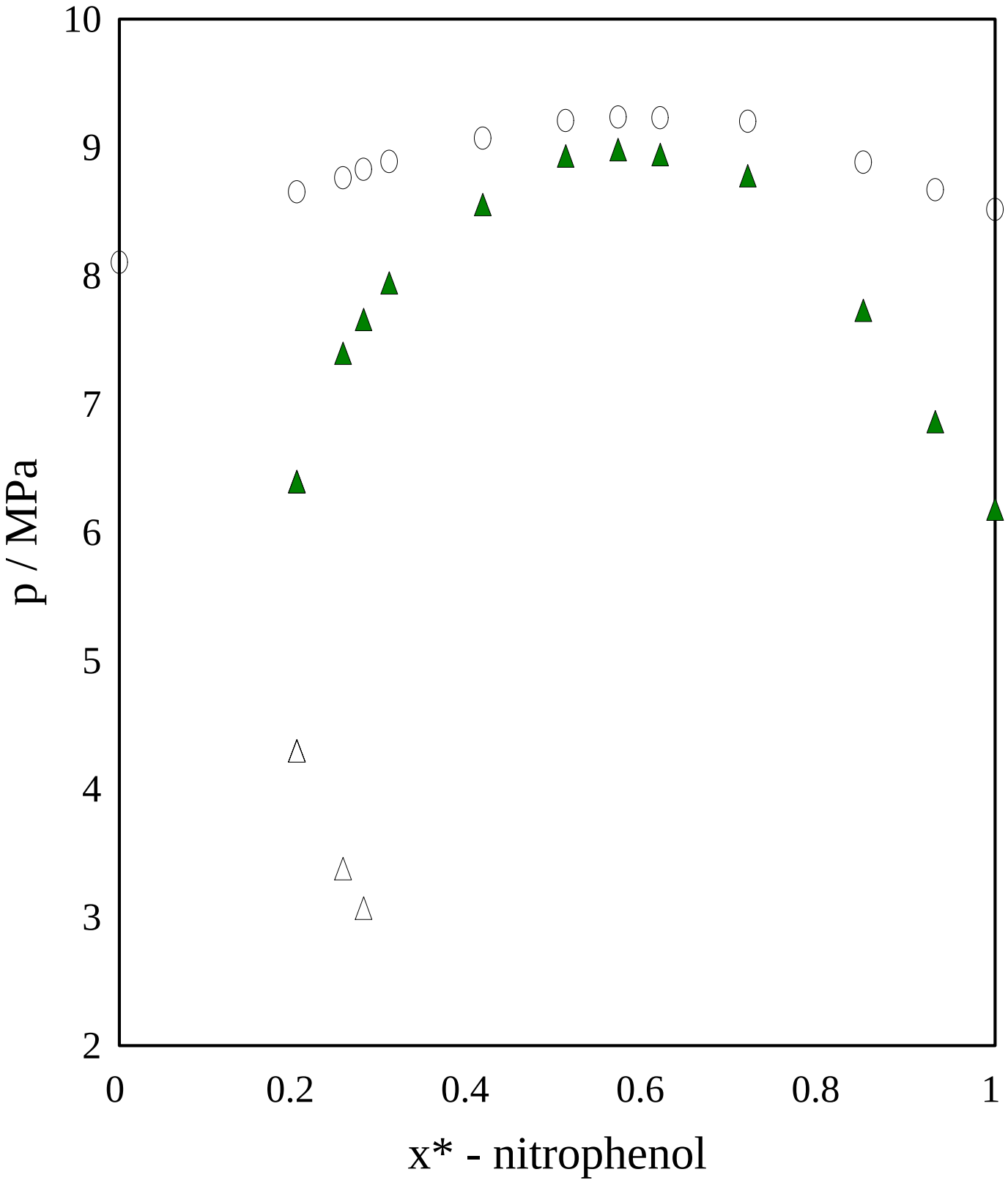
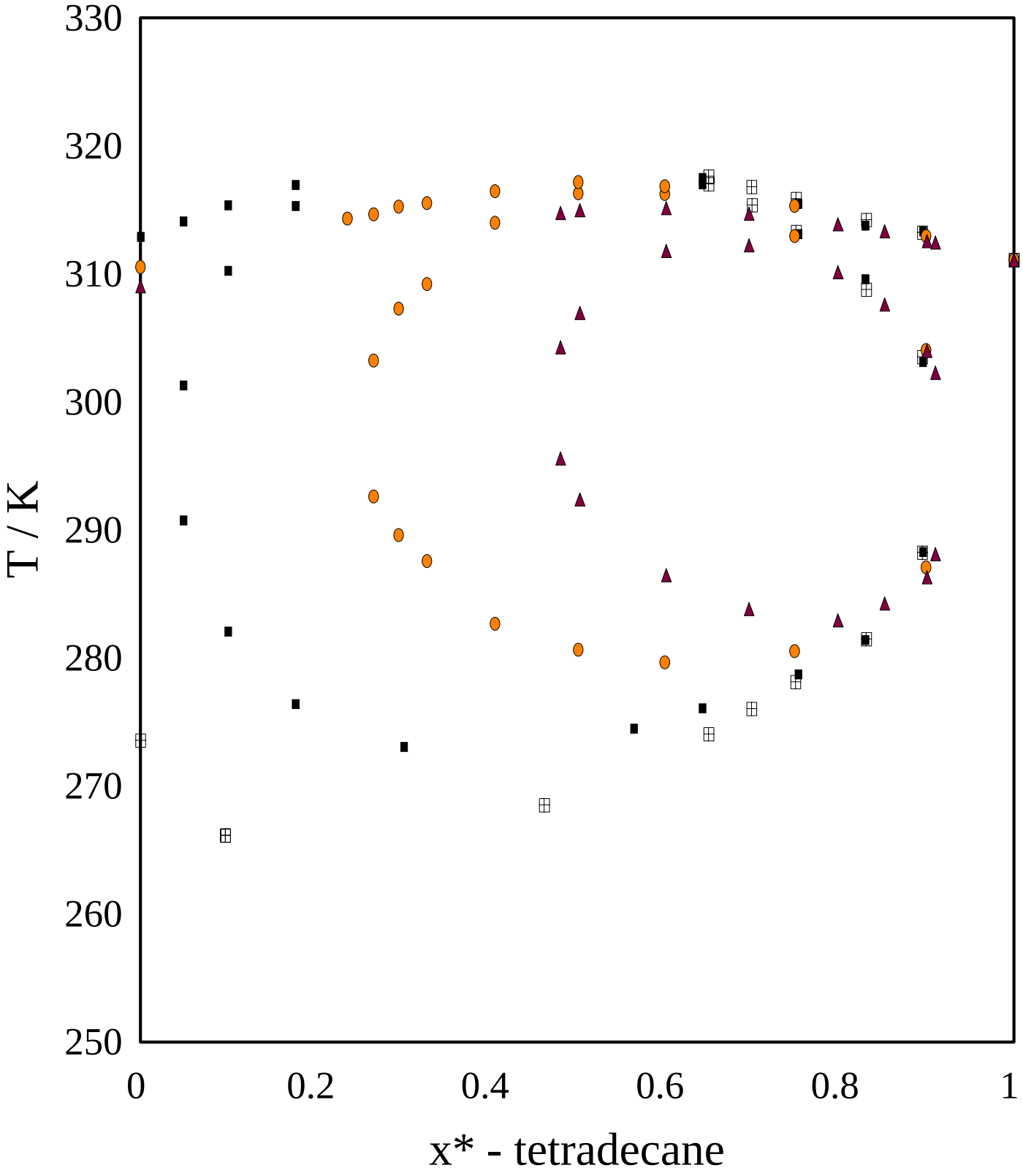
1
x* - nitrophenol


10
9
8
7
6
5
4
3
2
p / MPa
0
0.2
0.4
0.6
0.8
1
x* - nitrophenol


10
9
8
7
6
5
4
3
2
p / MPa
0
0.2
0.4
0.6
0.8
1
x* - nitrophenol


330
320
310
300
290
280
270
260
250
T / K
0
0.2
0.4
0.6
0.8
1
x* - tetradecane