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NEW SATURATED VAPOUR PRESSURE–TEMPERATURE RELATION

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ABSTRACT

Using the dimensionless coordinates

$$T^* = \left(\frac{T_C}{T} - 1\right) \Big/ \left(\frac{T_C}{T_{NB}} - 1\right)$$

$$P^* = \left(\frac{P_C}{P} - 1\right) \Big/ \left(\frac{P_C}{P_{NB}} - 1\right)$$

an empirical vapour pressure–temperature relation of the form

$$P^* = T^{*[m+n(T^*)^a]}$$

has been established along the two-phase saturation equilibrium curve over the entire liquid range up to the critical point. Comparison with experimental values for a series of selected organic, inorganic and quantal fluids produced average percentage deviations ranging from 0 0054% to 0 8098% with an overall average percentage deviation of 0 4065% (340 data point pairs) The proposed relation compares excellently with other vapour pressure–temperature calculation methods

INTRODUCTION AND THE PROPOSED METHOD

In a univariant thermodynamic system, the one component, two-phase equilibrium is determined by the Clausius–Clapeyron differential equation which for the saturated vapour–liquid equilibrium is given as

$$\left(\frac{dP}{dT}\right)_S = \frac{\Delta H_V}{T(V_g - V_l)} \tag{1}$$

where ΔH_V is the molar heat of vaporization, and the term $(V_g - V_l)$ is the associated molar volume change of the system between gaseous (g) and liquid (l) phases along the liquid–vapour pressure saturation curve. The subscript S refers to this liquid–vapour pressure equilibrium state. The univariance of this thermodynamic system assures us of the continued coexistence of a vapour–liquid phase pair along the saturation curve so that the vapour pressure becomes solely a single-valued function of temperature. Consequently, within the limits of this equilibrium restriction, the vapour pressure may be considered to be a unique function of temperature over the complete liquid–vapour two-phase equilibrium range, from the triple point

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to the critical point of the given substance. In fact, since eqn. (1) is an exact thermodynamic relation, it can be integrated provided that complete knowledge of all parameters involved is available.

While we already know that ΔH_V is a unique function of temperature, the volume difference $(V_g - V_l)$ depends in a complex manner on both state parameters, temperature and pressure. If we plot the involved phase coexistence states with temperature and volume as coordinates, then the resulting plot will occupy not merely a two-phase coexistence curve but rather a complete two-phase region. The existence of such a volume–temperature two-phase region has deterred an analytic solution of eqn. (1). Despite these difficulties, an array of theoretical and semi-empirical pressure–temperature relations has been found [1–12]. Yet is has been also indicated [7,13] that in order to obtain a sufficiently accurate predictive expression for the vapour pressure of liquids from the triple point to the critical point, an equation of at least four terms is necessary.

This work develops a semi-empirical relation between the saturation pressure and temperature for pure compounds applicable from the triple point to the critical point. To establish this relation, the previously proposed reduced dimensionless temperature, T^*, and pressure, P^* (see Fish and Lielmezs [14], Lielmezs [15], and Santrach and Lielmezs [16]), defined as

$$T^* = \left(\frac{T_C}{T} - 1\right) \Big/ \left(\frac{T_C}{T_{NB}} - 1\right) \tag{2}$$

$$P^* = \left(\frac{P_C}{P} - 1\right) \Big/ \left(\frac{P_C}{P_{NB}} - 1\right) \tag{3}$$

where T, T_C, T_{NB} are the temperatures, (K), and P, P_C, P_{NB} are the pressures (atm) of the given state, the critical point and the normal boiling point, respectively, were used.

In order to combine the proposed dimensionless coordinates, T^* and P^* [eqns. (2) and (3)], into a single functional form taken along the saturation curve, we write

$$P_s^* = \mathrm{f}(T) \tag{4}$$

where s is the saturated vapour pressure–temperature equilibrium state; note a probable empirical relation between these parameters [eqn. (4)] as revealed by Figs. 1 and 2. Indeed, Fig. 1 shows a non-linear $P_s^* - T_s^*$ relation for a series of pure inorganic and organic compounds, while Fig. 2 amplifies this observation more specifically giving a plot of log P_s^*/log T_s^* vs. T_s^* for the simple fluids Ar, Kr, Xe.

In view of the shown empirical correlations (Figs. 1 and 2), it was felt advantageous to write the following relation

$$P_s^* = T_s^{*[m+n(T^*)^a]} \tag{5}$$

or, equivalently

$$\frac{\ln P_s^*}{\ln T_s^*} = m + n(T_s^*)^a \tag{6}$$

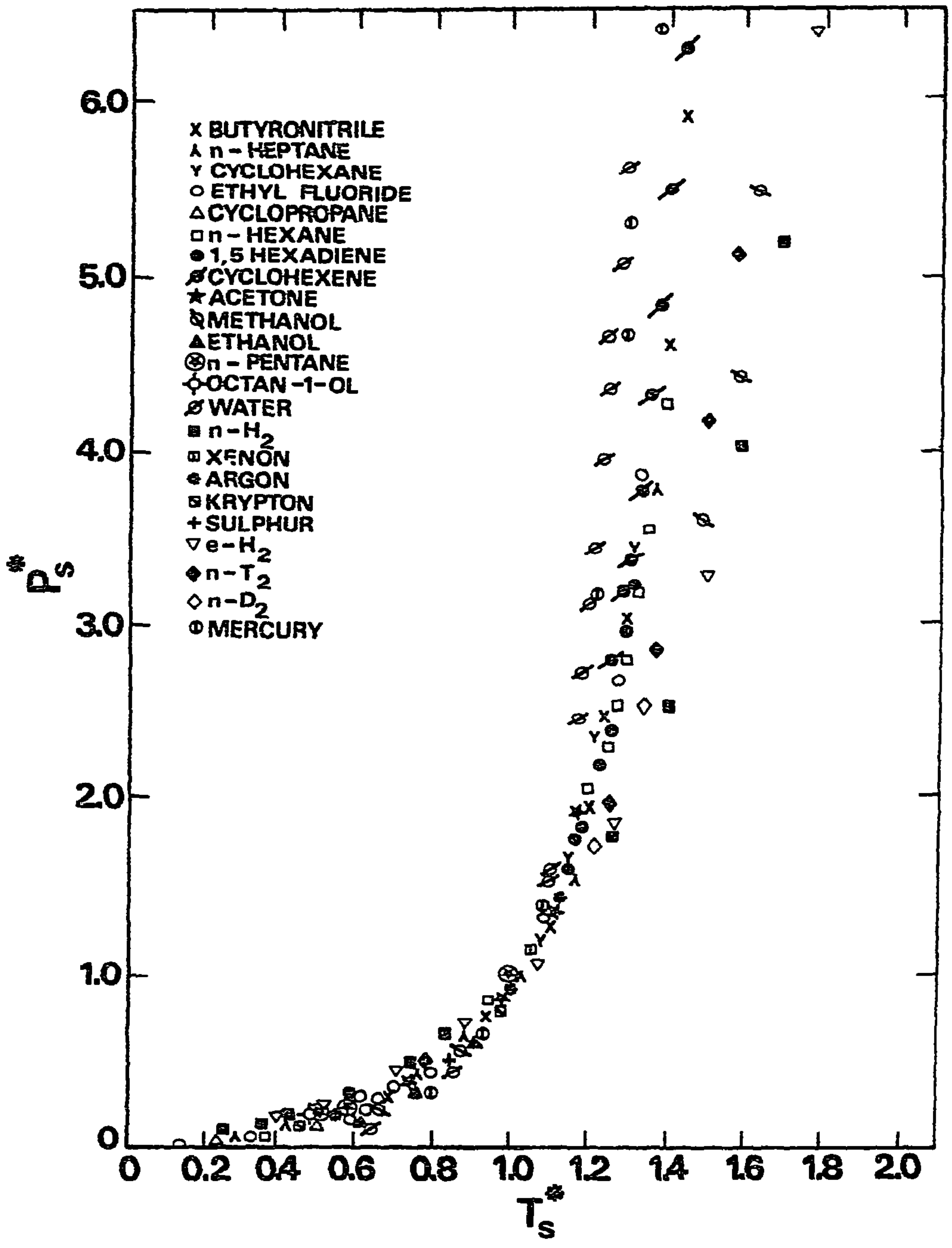

Fig 1 $P_s^*-T_s^*$ relation for a series of organic and inorganic compounds

where *m*, *n* and *a* are characteristic constants of given single compounds. The values of these three constants *m*, *n* and *a* (Table 1) are determined from the available, selected, experimental data sets (Tables 1–4) for each compound separately in such a

TABLE 1

Summary of data

Fluid	Coefficient of eqn (5)			Saturated temp range (K)	Refs for vapour pressure data	Temp (K)				Ave. percentage deviation[c]
	m	*n*	*a*			Triple point, (K)	Ref	Critical point[b] (K)	Normal boiling point[b] (K)	
Methane	1.54902	2.3847	0.7766	92–190	4,5[a]	90.65	30	191.0	111.7	0.636
Ethane	1.62007	2.41207	0.8150	155–288	24			305.4	185.4	0.498
Propane	1.44695	2.3705	0.6900	231–370	25			369.8	231.1	0.445
n-Heptane	1.54731	2.01297	0.8825	271–537	4,5[a]			540.2	371.6	0.7559
n-Octane	1.56119	1.91675	0.900	292–563	4,5[a]			569.4	398.8	0.8098
Argon	1.63986	2.29529	0.800	93–124	27	83.78	27	150.8	87.3	0.082
Krypton	1.52802	2.53347	0.7667	127–175	28	115.95	27	209.4	119.8	0.1398
Xenon	1.56648	2.52865	0.7400	162–289	27	161.3	27	289.7	165.0	0.334
n-Hydrogen	1.35167	1.16035	0.775	14–33	26,29	13.96	26	33.2	20.4	0.7287
HD	1.35715	1.31682	0.7500	17–35	26	16.60	26	35.9	22.1	0.3001
e-D_2	1.40995	1.37736	0.7750	20–38	26	18.69	26	38.3	23.6	0.1700
Water	2.02476	3.64085	0.8500	273–550	20	273.16	31	647.3	373.2	0.1279
n-Propanol	1.23102	3.19786	0.775	292–371	21			536.7	370.4	0.3768
n-Butanol	2.04584	2.26234	1.05	296–391	21			562.9	390.9	0.6273
Acetic acid	2.12606	2.04202	1.000	304–415	22			594.4	391.1	0.0963
Acetone	1.83862	2.20816	0.9375	325–372	23			508.1	392.2	0.0054
Benzene	1.60584	2.54574	0.8250	303–562	4,5[a]	278.68	30	562.2	353.3	0.7781

[a] The data used were taken from Thodos and co-workers data sets (refs 4 and 5)

[b] All values listed were taken from Reid et al [1]

[c] Average percentage deviation defined in footnote p 16

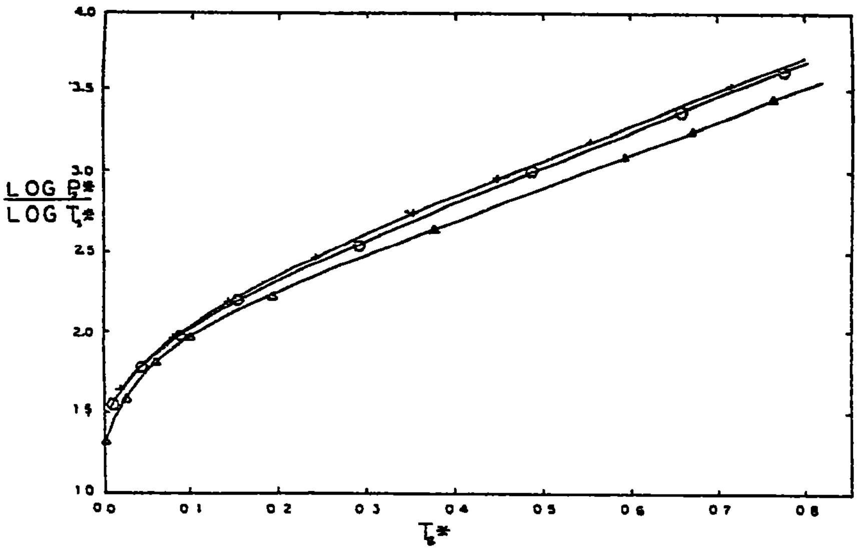

Fig 2 Relation of log P_s^*/logT_s^* vs T_s^* for simple fluids ▲, Argon ○, krypton. ⊛, xenon

way as to minimize the following error function (EF)

$$\mathrm{EF} = \min \sum_{i}^{N} \left[\frac{P_{\mathrm{s(calc,}i)} - P_{\mathrm{s(exp,}i)}}{P_{\mathrm{s(exp,}i)}} \right]^2 \tag{7}$$

where EF is the error function, $P_{\mathrm{s(exp,}i)}$ is the experimental saturated state vapour pressure at the corresponding temperature T_{s_i}, $P_{\mathrm{s(calc,}i)}$ is the calculated saturated state vapour pressure at the same temperature T_i, predicted by using eqn. (5) if there is a given set of substances characterizing coefficients *m*, *n* and *a*, and *N* is the number of experimental data point pairs used. Comparison of the calculated and experimental data indicates (Tables 1–4, Figs. 3–5) that eqn. (5) and the three calculated constants, *m*, *n* and *a* (Table 1), are valid within the specified accuracy limits (Tables 1–4) over the entire liquid range from the triple point to the critical point. Indirectly the use of reduced coordinates, T_s^* and P_s^* [eqns. (2 and 3)], is

TABLE 2

Comparison of the accuracy of using eqn (5) (this work) and Antoine's equation [19]

Liquid	Temp range (K)	Eqn (5), this work [a]				Antoine's equation [19]		
		N	*N*>2%	Ave %	Max %	*N*>2%	Ave %	Max %
Water	273–550	30	0	0.1279	0.5603	3	0.4432	2.8758
n-Propanol	292–371	12	0	0.3768	1.0148	3	1.6927	5.6912
n-Butanol	296–391	13	0	0.6273	1.7499	8	3.4881	7.8188
Acetic acid	304–415	27	0	0.0963	0.2225	0	0.4492	1.5842
Acetone	325–372	11	0	0.0054	0.0190	0	0.6378	0.7953

[a] *N* = number of data points, *N*>2% = number of data points exceeding 2% deviation, ave % = average percentage deviation, see footnote p. 16, max. % = maximum percentage deviation

TABLE 3

Comparison of the accuracy of using eqn (5) (this work) and eqn by Zia and Thodos [5]

Liquid	Temp. range (K)	Eqn (5), this work [a]				Zia and Thodos [5]		
		N	$N>2\%$	Ave %	Max %	$N>2\%$	Ave %	Max %
Methane	92–190	18	2	0 6361	2 1636	0	0.3243	0 6997
Ethane	155–288	14	0	0 4977	0.9902	0	0 4350	0 7843
Propane	231–370	26	0	0 4448	1.0850	0	0.2229	0.5308
n-Heptane	271–537	20	2	0 7555	2 6840	0	0 3625	1 1934
n-Octane	292–563	17	1	0 8098	3 1582	1	0 3786	2 2051
HD	17– 35	13	0	0 3001	0 9435	0	0 3953	1 0610
e-HD_2	20– 38	13	0	0 1700	0 6056	0	0 5290	1 4229

[a] N = number of data points, $N>2\%$ = number of data points exceeding 2% deviation, ave % = average percentage deviation see footnote p 16, max % = maximum percentage deviation

validated by the already noted finding of Fish and Lielmezs [14], Lielmezs [15], and Santrach and Lielmezs [16] that there exists a unique relation between the dimensionless temperature T_s^* [eqn. (2)] and the reduced entropy of vaporization, S^*, defined as

$$S^* = \left(\frac{\Delta H_V}{T_s}\right) / \left(\frac{\Delta H_{VB}}{T_B}\right) \tag{8}$$

where ΔH_V is the heat of vaporization at a given temperature, T_s, while ΔH_{VB} is the heat of vaporization at the normal boiling point, T_B.

EXPERIMENTAL DATA USED AND COMPUTER PROGRAMMING

The summary of experimental data used is found in Table 1. It should be noted that all of the listed experimental data were considered to be of sufficient accuracy

TABLE 4

Comparison of the accuracy of using eqn (5) (this work) and eqn by Gomez-Nieto and Thodos [4]

Liquid	Temp range (K)	Eqn (5), this work [a]				Gomez-Nieto and Thodos [4]		
		N	$N>2\%$	Ave %	Max %	$N>2\%$	Ave %	Max %
Argon	93–124	12	0	0 0819	0 1945	0	0.7505	0 8935
Krypton	127–175	18	0	0 1398	0 3556	4	1 2466	3 3988
Xenon	162–289	34	1	0 3341	2 0122	0	0 2944	1 5902
n-Hydrogen	14– 33	21	3	0 7287	2 8328	6	1 5145	2.4720
Benzene	303–562	21	1	0 778	2 7519	0	0 2673	1 2064

[a] N = number of data points; $N>2\%$ = number of data points exceeding 2% deviation, ave % = average percentage deviation, see footnote p 16, max % = maximum percentage deviation

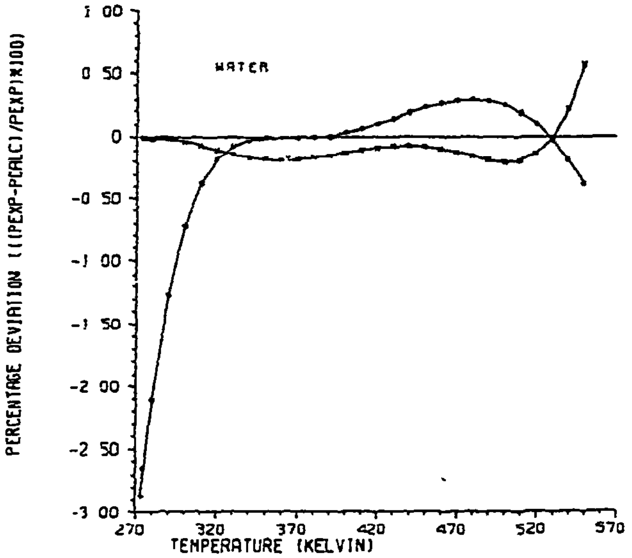

Fig 3 Comparison of the accuracy of eqn (5), this work (×), and the Antoine equation [19] (◇) Data for H_2O

for this work (for a critical assessment of input data used, see the references cited, Table 1), and hence were not further re-evaluated. To obtain the three substance characterizing constants, *m*, *n* and *a* [eqns. (5) and (7); Table 1], a non-linear function optimization programme was written [17,18].

Since results of this work [eqn. (5) Tables 1–4] were compared, first, with values obtained from Antoine's [19] equation, and second, with the more recent vapour

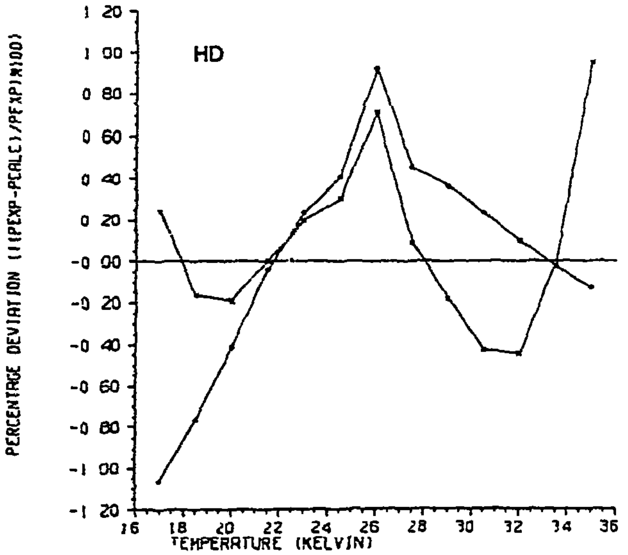

Fig 4 Comparison of the accuracy of eqn (5), this work (×), and the Zia and Thodos equation [5] (◇) Data for HD.

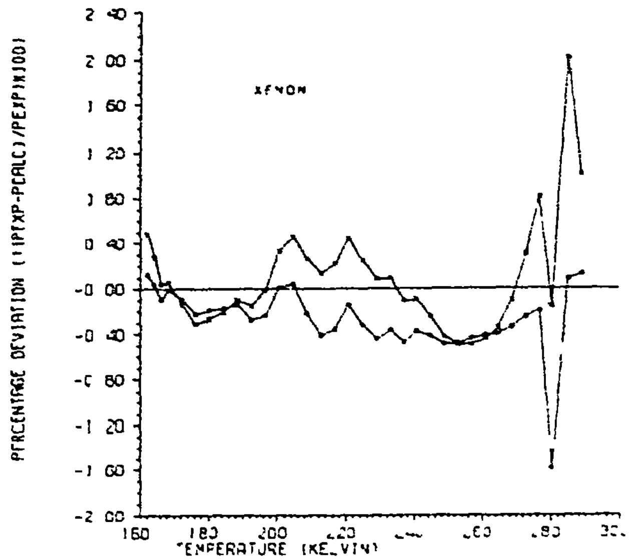

Fig 5 Comparison of the accuracy of eqn (5), this work (×), and the Gomez-Nieto and Thodos equation [4] (◇) Data for Xe

pressure–temperature relations as proposed by Thodos and co-workers [4,5] *, additional computer programmes for these equations were also established.

RESULTS AND DISCUSSION

Table 1 summarizes the experimental input data and the calculated compound-characterizing constants *m*, *n* and *a* for a series of pure organic and inorganic substances. The average percentage deviation (A.P.D.) ** for the given 340 data point pairs is 0.4065%. Table 1 also shows that the smallest average percentage deviation of 0.0054% is for acetone while the largest of 0.8098% is for *n*-octane. Table 2 compares the results obtained by means of eqn. (5), this work, to those of Antoine's equation [19] for five, strongly polar, hydrogen bonded compounds. It is seen that for these listed compounds, the proposed relation [eqn (5)] is superior to Antoine's method [19]. The best results for this test case have been obtained for acetone, the worst for *n*-butanol. Figure 3 showing the percentage deviation vs.

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* The percentage deviation defined as

$$\mathrm{P.D.} = \left[\frac{P_{s(\mathrm{calc},i)} - P_{s(\mathrm{exp},i)}}{P_{s(\mathrm{exp},i)}}\right] \times 100$$

was used as a basis of comparison, see Tables 1–4

** The average percentage deviation is defined as

$$\mathrm{A.P.D.} = \frac{1}{N}\sum_{i=1}^{N} |P.D._i|$$

where N = total number of data point pairs 'i'.

temperature plot for water, from the triple point of 273.16–550 K, accentuates this observation. Table 3 compares the results obtained by means of eqn. (5), this work, to those of a generalized vapour pressure equation specifically set-up for non-polar hydrocarbons by Zia and Thodos [5]. It is seen that for all hydrocarbons listed, the vapour pressure equation of Zia and Thodos [5] is somewhat (0.2–0.3 percentage points lower) more accurate than the proposed relation [eqn. (5)], this work. However, for quantum fluids, HD (Fig. 4) and e-D_2, eqn. (5) yields more accurate predictions. Even if this difference in accuracy is not important, the vapour pressure equation of Zia and Thodos [5] warrants to be considered as the equation of choice when working with non-polar hydrocarbons. The reason for this is that although the vapour pressure equation of Zia and Thodos [5] is given through a complex functional relation between the reduced pressure P_r and the reduced temperature T_r; it essentially requires that only values for T_C and P_C be known. On the other hand, eqn. (5), this work, requires values for T_C, P_C, T_{NB} and additionally, the calculated values of the substance characterizing constants m, n and a. Table 4 compares the results obtained by means of eqn. (5), this work, to those of a generalized vapour pressure equation for non-polar substances by Gomez-Nieto and Thodos [4]. The test compounds were the simple fluid series argon, krypton, xenon, and additionally, the quantum fluid n-hydrogen and an aromatic substance, benzene. It appears that in terms of data used (Tables 1 and 4) the application of eqn. (5) for the simple fluid series with the exception of xenon, resulted in considerably lower percentage deviation values than when the generalized equation of Gomez-Nieto and Thodos [4] was used. In the case of xenon over the complete liquid range form the triple point to the critical point (Tables 1 and 4; Fig. 5) both equations performed nearly equally well in the average percentage deviation value changes. For calculating vapour pressure values for n-hydrogen eqn. (5) seemed to be more accurate than the equation of Gomez-Nieto and Thodos [4] while the reverse appeared to be true for benzene.

In compounds for which we have available saturated vapour-liquid equilibrium data over the whole liquid region from the triple points to the critical point (Table 1), we note that eqn. (5) predicts more accurately at the triple point region than in the vicinity of the critical point (Figures 3–5). As a matter of fact the average percentage deviation at the triple point region is below 0.5%, while at the critical point the average percentage deviation within the framework of compounds studied in this work may approach 3% value (for instance, n-octane, n-H_2; see Tables 1–4, Figs. 4 and 5). In terms of general accuracy eqn. (5) was found to be superior to Antoine's equation [19] (Fig. 3, Table 2); comparable to Zia's and Thodos [5] hydrocarbon equation for non-polar hydrocarbons (Fig. 4, Table 3); and at least as accurate as the general vapour pressure equation of Gomez-Nieto and Thodos [4] (Fig. 5, Table 4). The results of this comparison (Figures 3–5, Tables 1–4) indicate that the proposed saturated vapour pressure–temperature relation [eqn. (5)] may be thought to be of general validity. Further extension of this equation to include binary saturated vapour–liquid equilibrium systems, is suggested.

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