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Curvature of the vapour pressure curve

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Abstract

This paper brings out the existence of the maximum in the curvature of the vapour pressure curve. It occurs in the reduced temperature range of 0.6–0.7 for all liquids and has a value of 3.8–4.8. A set of 17 working fluids consisting of several refrigerants, carbon dioxide, cryogenic liquids and water are taken as test fluids. There exists also a minimum close to the critical point which can be observed only when a thermodynamically consistent functional form of the vapour pressure equation is chosen. This feature, in addition to throwing some light on the behaviour of the vapour pressure curve, could provide some useful inputs to the choice of working fluids for vapour pressure thermometers and thermostatic expansion valves.

Keywords: Vapour–liquid equilibria; Vapour pressure; Pure liquids; Curvature

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1. Introduction

The shape of the vapour pressure curve of liquids has been a topic of investigation for several researchers. Numerous ways of representing it have been reported in the literature [1]. The vapour pressure curve is also the starting point for the choice of working fluids of heat engines, refrigeration systems and heat pumps. It is the basis for the choice of bulb fluids of vapour pressure thermometers and thermostatic expansion valves. In addition, several of these engineering systems require the slope and the second derivative of the vapour pressure curve. For example, the response of a thermostatic expansion valve or a vapour pressure thermometer or dynamic response of an evaporator in a refrigeration system require information on the derivatives of the vapour pressure curve. It is a balance among various criteria that guides the designers towards the choice of a particular fluid. In general, designers like to operate those systems in the linear portion of a property curve. However, since this is almost impossible in the case of the vapour pressure curve, the next alternative will be to operate at a point where the effects of non-linearity are the least. A description of the shape of the vapour pressure curve has been made through the value of acentric parameter ($\omega = -\log p_{\mathrm{r}} - 1$ at a reduced temperature of 0.7) and the Rieldel parameter ($\alpha = \mathrm{d}\ln p/\mathrm{d}\,\ln T$). On the other hand a better way of defining the shape of the curve could be the curvature itself. In this paper, it is brought out that most of the fluids exhibit a maximum in the reduced curvature of the vapour pressure curve, which occurs within a small spread of the reduced temperature. But, the value of the maximum reduced curvature shows an appreciable variation which is predominantly governed by the nature of the liquid. The existence of this maximum is yet another one further to the ones reported earlier [2–5]. The existence of a minimum in the curvature near the critical point, however, can not be predicted unless the functional form of the vapour pressure curve is appropriately chosen.

2. Curvature of the vapour pressure curve

The reduced curvature (inverse of the radius of curvature) of the vapour pressure curve at a given temperature is defined as

$$\rho_{\mathrm{r}} = \frac{\mathrm{d}^2 p_{\mathrm{r}}/\mathrm{d}T_{\mathrm{r}}^2}{[1 + (\mathrm{d}p_{\mathrm{r}}/\mathrm{d}T_{\mathrm{r}})^2]^{3/2}} \tag{1}$$

where p_{r} is the reduced pressure ($= p/p_{\mathrm{c}}$) and T_{r} the reduced temperature ($= T/T_{\mathrm{c}}$). The derivatives appearing in the above equation can be obtained if the functional form of the vapour pressure equation is known. There are several forms of this equation. Notable ones among them are (i) equation derived from the Clausius–Clapeyron equation with constant heats of vaporization

$$\ln p_{\mathrm{r}} = A_0 \left(1 - \frac{1}{T_{\mathrm{r}}}\right) \tag{2}$$

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(ii) due to Wagner [6]

$$\ln p_{\rm r} = \frac{[A_1(1-1/T_{\rm r})+A_2(1-1/T_{\rm r})^{1.5}+A_3(1-1/T_{\rm r})^2+\dots]}{T_{\rm r}} \qquad (3)$$

and (iii) Riedel [7]

$$\ln p_{\rm r} = A + \frac{B}{T_{\rm r}} + C\ln T_{\rm r} + DT_{\rm r}^6 \qquad (4)$$

Use of Eq. (2) in Eq. (1) yields

$$\rho_{\rm r} = A_0 p_{\rm r} T_{\rm r}^3 \frac{A_0/(T_{\rm r}-2)}{(T_{\rm r}^4 + A_0^2 p_{\rm r}^2)^{3/2}} \qquad (5)$$

Eqs. (3) and (4) yield more complicated albeit algebraic equations.

3. Results and discussion

A plot of reduced curvature for methane using Eq. (2) with $A_0 = 5.4$ which is evaluated based on the data over the entire liquid–vapour coexistence region measured by Kleinrahm and Wagner [8] and Eq. (3) is shown in Fig. 1. In that figure the variation of curvature derived from the modified Wagner equation for methane [9] is also shown. Both show the existence of the maximum at the same $T_{\rm r}$, but the value of the maximum with Eq. (2) is slightly larger than with Eq. (3). The value of $T_{\rm r}$ at the maximum can be found by solving the equation:

$$\frac{{\rm d}\rho_{\rm r}}{{\rm d}T_{\rm r}} = 0 \qquad (6)$$

which for Eq. (2) reduces to solution of

$$6T_{\rm r}^6 - 6A_0T_{\rm r}^5 + A_0^2T_{\rm r}^4 - 6A_0^2p_{\rm r}^2T_{\rm r}^2 + 6A_0^3p_{\rm r}^2T_{\rm r} - 2A_0^4p_{\rm r}^2 = 0 \qquad (7)$$

For methane, one of the roots of interest is $T_{\rm r} = 0.623$ which is the same as seen in Fig. 1. However, the value of the reduced curvature at this reduced temperature is 3.91 with Eq. (2) and 3.80 if Eq. (3) is used. Such a close agreement is not surprising because in the low pressure region validity of constancy of heat of vaporization, which is the basis for Eq. (2), is a fair approximation.

Although it appears, prima facie that Eqs. (2) and (3) virtually yield the same curvature over the whole saturation line, an expanded version of Fig. 1 near the critical point, shown in Fig. 2, indicates that Eq. (3) shows a minimum very near the critical point, which is not replicated by the Eq. (2). For this figure a value of $A_0 = 5.83$ based on data between 185 K and the critical point [8] is used. In Fig. 2, the variation of the Riedel parameter for methane near the critical temperature derived using Eq. (3) is also shown. The existence of a minimum for this parameter has been predicted by Planck and Riedel [10] and confirmed by several investigators [6,11]. Yet, it is apparent that the minima in curvature and the Rieldel parameter do not occur at the same reduced temperature.

As the critical point is an abrupt discontinuity in the liquid–vapour coexistence curve, the radius of curvature there should be zero implying that the curvature → ∞. This implies that ${\rm d}^2 p_{\rm r}/{\rm d}{T_{\rm r}}^2 \rightarrow \infty$ at the critical point. The Wagner equation through one of the $(1 - T_{\rm r})$ terms with $1 <$ power < 2, ensures that this criterion is satisfied. In the same vein, ${\rm d}\alpha/{\rm d}T \rightarrow \infty$ at the critical point. The main difference between the curvature and the Rieldel parameter is that the former rapidly rises from the point of minimum to ∞ whereas the latter increases a finite value (typically in the range of 5–7). From these arguments it can be deduced that the vapour pressure curve is the closest to being linear very near the critical point.

Table 1 shows the data on reduced maximum curvature, reduced pressures and temperatures at the point of maximum curvature for several fluids by extending the above analysis.

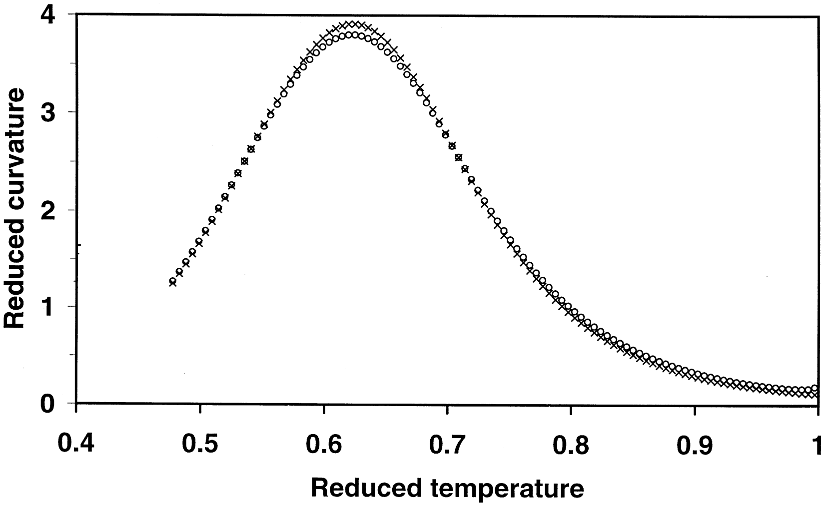

Fig. 1. Variation of reduced curvature of the vapour pressure curve for methane: (×) Eq. (2) with $A_0 = 5.4$; (○) Eq. (3).

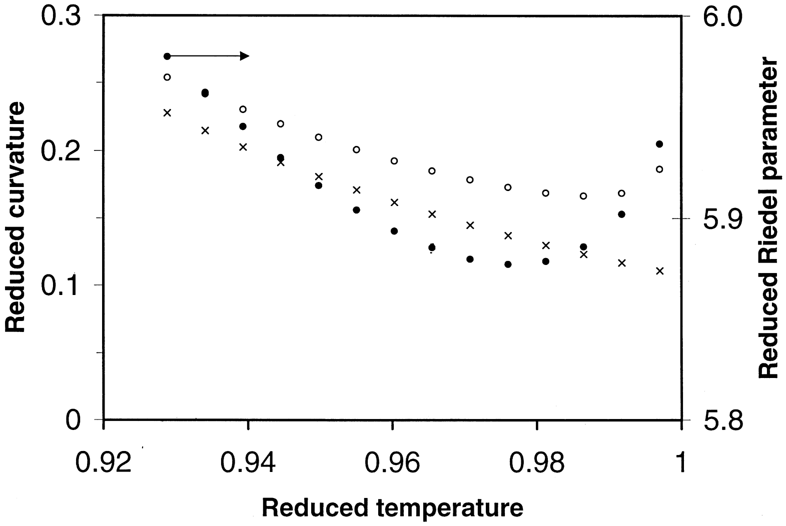

Fig. 2. Same as Fig. 1 but expanded near the critical point with the addition of reduced Riedel parameter: (×) Eq. (2) with $A_0 = 5.83$; (○) Eq. (3); (●) reduced Riedel parameter (right ordinate).

Fig. 3 shows the plot of reduced curvature versus reduced temperature for some of those fluids. The specimens investigated cover a wide range of fluids of interest, e.g. from non-polar cryogenic liquids to polar refrigerants. It can be seen that the reduced curvature goes through a maximum value at $0.6 < T_r < 0.7$ for most the fluids considered here. Carbon dioxide [27] does not depict this feature as its reduced triple point is > 0.7. There is a close analogy between several polar fluids. Cryogenic liquids and ethylene show a marked deviation. Firstly, the value of the maximum is smaller and it occurs at a lower temperature compared to the other fluids. The value of the reduced pressure (p_r) at the point of maximum curvature was found to be in the range of 0.033 (R-245fa) to 0.041 (C_6F_{14}).

Fig. 4 shows the expanded zone near the critical point. Here again, it can be observed that vapour pressure equations other than the ones of Wagner type, as in the case of R-245fa [23], or the Wagner type without a term having a power between 1 and 2, as in the case of C_6F_{14} [24], are unable to depict the existence of the minimum. From the thermodynamic point of view the need for defining an appropriate functional form of the vapour pressure equation need not be over emphasized.

The practical implications of this study are as follows: in the construction of vapour pressure thermometers, one likes to have a good dynamic response. Given that these temperature sensors are non-linear, it is expected that if the fluid has the maximum curvature in the zone of interest, the response will be large enough to allow stable manipulation. In the light of extremely precise pressure measurement techniques being available now, this could be a feature that can be used in the construction of these instruments. This zone of maximum dynamic response will be at pressures above but closer to atmospheric for the fluids that have the critical pressure higher than about 30 bar. For very high molecular weight organic compounds (e.g. propane family refrigerants) the critical pressures are smaller than this value.

On the other hand, in the case of thermostatic expansion valves, it will be preferable to operate away from the maximum curvature zone. Indeed, it is better to operate closer to the critical point where the curvature is the least. Incidentally, in this zone the gradient of the vapour pressure curve is so large that the valve could respond fast to the changes in the pressure at the outlet of evaporator.

For refrigeration systems with R-134a and other similar ozone friendly fluids, one could use cross-charged thermostatic expansion valves with the sensor bulb being filled with a refrigerant whose molecular weight is larger than that of R-134a. This necessitates adopting the propane family of refrigerants for which the critical pressures are low. The state of the bulb fluid can be closer to the critical, yet

Table 1
Sources of data and reduced properties for the fluids investigated

Fluid	Source	ρ_r max	p_r at ρ_r max	T_r at ρ_r max
Argon	[12]	3.78	0.037	0.617
Xenon	[13]	3.80	0.038	0.621
Methane	[9]	3.80	0.036	0.619
Nitrogen	[14]	3.90	0.036	0.626
Ethylene	[15]	4.04	0.036	0.637
R-32	[16]	4.47	0.035	0.672
R-123	[17]	4.55	0.035	0.672
R-125	[18]	4.61	0.034	0.675
R-134a	[19]	4.64	0.034	0.679
R-143a	[20]	4.45	0.036	0.671
R-152a	[21]	4.49	0.035	0.673
R-227ca	[22]	4.71	0.034	0.683
R-245fa	[23]	4.72	0.033	0.683
C_6F_{14}	[24]	4.64	0.041	0.701
HFE-245	[25]	4.93	0.033	0.680
Water	[26]	4.60	0.038	0.689

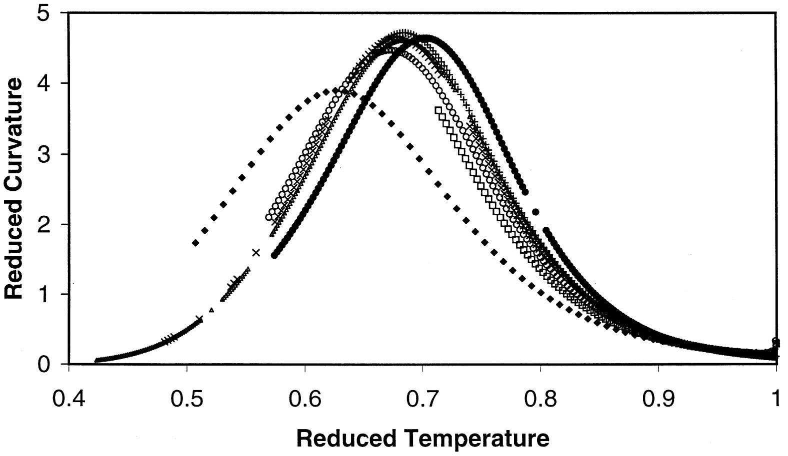

Fig. 3. Plot of reduced curvature of vapour pressure curve for several fluids: (◆) Nitrogen; (☐) CO_2; (△) water; (○) R-32; (×) R-134a; (+) R-245fa; (●) C_6F_{14}.

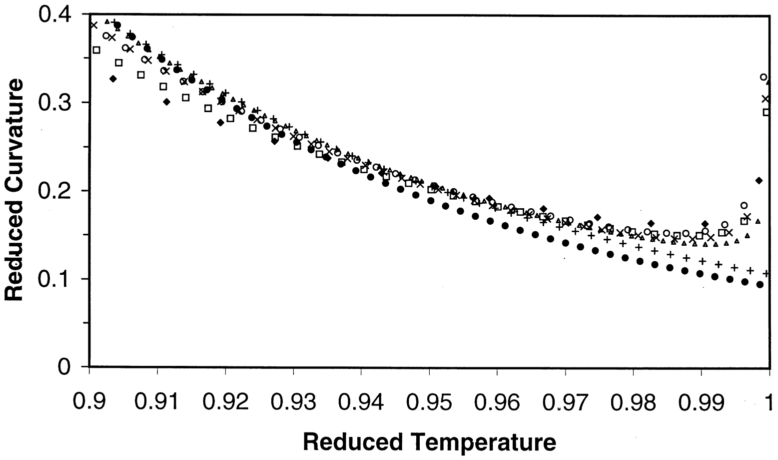

Fig. 4. Same as Fig. 3 but expanded near the critical point: (◆) Nitrogen; (☐) CO_2; (△) water; (○) R-32; (×) R-134a; (+) R-245fa; (●) C_6F_{14}.

the pressure could be no more than 20 bar. This obviates the need for using thick bulbs.

4. Conclusions

This article has brought out the existence of the maximum and the minimum in the curvature of the vapour pressure curve. The coordinates of the maximum are strong functions of the nature of the liquid. These features could provide additional inputs for the choice of a functional form for vapour pressure curves. The locations of the maximum could be used as a guiding factor for the choice of the fluid in vapour pressure thermometry and in sensor bulbs of the thermostatic expansion valves used in refrigeration systems.

References

[1] J. McGarry, Ind. Eng. Chem. Process Des. Dev. 22 (1983) 313–322.
[2] K. Srinivasan, M.V. Krishna Murthy, Int. J. Refrig. 8 (1985) 143–146.
[3] K. Srinivasan, Int. J. Refrig. 12 (1989) 194–197.
[4] K. Srinivasan, J. Phys. D: Appl. Phys. 26 (1993) 448–451.
[5] K. Srinivasan, in: Proceedings of the Australian Bicentinnial International Congress on Mechanical Engineering, Institution of Engineers, Australia, Conference Publication No. 88/6, 1988, pp. 79–83.
[6] W. Wagner, Report No. PC/T15, IUPAC Thermodynamic Tables Project Centre, Imperial College, London, 1977.
[7] L. Riedel, Chim. -Ing. Tech. 26 (1954) 83–89.
[8] R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. 18 (1986) 739–760.
[9] S. Khan, K. Srinivasan, High Temp. High Pressures 26 (1994) 427–438.
[10] R. Plank, L. Riedel, Ingenieur Arch. 16 (1948) 255–266.
[11] G.R. Somayajulu, J. Chem. Eng. Data 31 (1986) 438–447.
[12] Ch. Tegeler, R. Span, W. Wagner, J. Phys. Chem. Ref. Data 28 (1999) 779–850.
[13] O. Sifner, J. Klofmar, J. Phys. Chem. Ref. Data 23 (1994) 63–152.
[14] P. Novak, R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. 29 (1997) 1157–1174.
[15] P. Novak, R. Kleinrahm, W. Wagner, J. Chem. Thermodyn. 28 (1996) 1441–1460.
[16] F. Yi-Dong, H. Li-Zhong, Z. Ming-Shan, Fluid Phase Equilibria 111 (1995) 273–286.
[17] S. Khan, K. Srinivasan, High Temp. High Pressures 26 (1994) 519–530.

[18] C.-C. Piao, M. Noguchi, Fluid Phase Equilibria 125 (1996) 45–54.
[19] S. Khan, K. Srinivasan, J. Phys. D: Appl. Phys. 29 (1996) 3079–3088.
[20] K. Srinivasan, L.R. Oellrich, Int. J. Refrig. 20 (1997) 332–338.
[21] S.L. Outcalt, M.O. McLinden, J. Phys. Chem. Ref. Data 23 (1994) 605–636.
[22] L. Shi, Y.-Y. Duan, M.S. Zhu, L.-Z. Han, X. Lei, Fluid Phase Equilibria 163 (1999) 109–117.
[23] T. Sotani, H. Kubota, Fluid Phase Equilibria 161 (1999) 325–335.
[24] G. Ernst, J. Gürtner, H. Wirbser, J. Chem. Thermodyn. 29 (1997) 1125–1128.
[25] A.R.H. Goodwin, D.R. Defibaugh, L.A. Weber, J. Chem. Eng. Data 43 (1998) 846–848.
[26] W. Wagner, A. Pruß, J. Phys. Chem. Ref. Data 22 (1993) 783–787.
[27] R. Span, W. Wagner, J. Phys. Chem. Ref. Data 25 (1996) 1509–1596.