A corresponding states treatment of the liquid–vapor saturation line

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\textbf{A B S T R A C T}

In this work we analyze correlations for the maxima of products of some liquid–vapor saturation properties. These points define new characteristic properties of each fluid that are shown to exhibit linear correlations with the critical properties. We also demonstrate that some of these properties are well correlated with the acentric factor. An application is made to predict the properties of two new low global warming potential (GWP) refrigerants.

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1. Introduction

The liquid–vapor phase transition continues to enthrall the science and engineering communities. Several features of scientific interest are being unraveled and saturation properties are also the first to be considered in the design of engineering systems such as vapor compression based refrigeration, heat pumping devices and Rankine cycle based power generating units. A number of interesting features have already been brought forth by several researchers [1–3]. Among them are the saturated liquid density \[\rho_l\] [4], the enthalpy of vaporization \[\Delta h_f\] [5–8], the vapor pressure curve \[p(T)\] also proposed a polynomial relation between the two points along the vapor pressure curve. Srinivasan also observed that the reduced temperatures \(T_{sp1r}\) and \(T_{sp2r}\), at which \(\phi_{1r}\) and \(\phi_{2r}\), respectively, attain the maximum, showed a linear correlation. Later on, Velasco et al. [15] covered 1214 fluids and established that the linear relation between the two Srinivasan’s points generally holds good except at extreme cases. They also proposed a polynomial relation between the two points along the vapor pressure curve. Tian et al. [16] also report that the criterion of a maximum \(p/(1 - T)\) can be used to optimize the coefficients in cubic equations of state. These two points on the vapor pressure curve set the limits of operation of several practical thermodynamic cycles. The objective of this paper is to derive some generalized correlations related to several other saturation properties. They are the relation between the temperature at which the maximum in the product of saturation temperature and liquid density exists vs the critical temperature, and the temperature at which the saturated vapor enthalpy is a maximum [17].

The NIST Chemistry WebBook [18] database has been used in assessing various entities described in this paper because it is able to meet the current needs of scientific accuracy and industrial relevance. We have considered the 75 fluids available in this database. A list of these fluids together with their critical parameters and other quantities defined in this work is presented in tables S1 and S2 of...
It is expected that the present article would be of use in the first order estimate of properties of newer fluids being synthesized (such as hydrofluoro-olefins and hydrofluoroalkanes like R-1234yf) for meeting the exigencies of low global warming working fluid requirements. However, this paper does not address other issues of application such as toxicity and flammability that are seldom described from an analysis of saturation properties.

2. First formulation: salient points obtained from the coexistence curve

Srinivasan and Krishna Murthy [4] reported that all fluids have a maximum in the product \( \psi \equiv T \rho_f \) of saturation temperature and liquid density, and that the reduced temperature at this point has a value around 0.82, which is weakly dependent on the complexity of the liquid molecule. As depicted in figure 1, we find that the temperature \( T^* \) where \( \psi_{\text{max}} \) occurs bears the following linear relationship with the critical temperature \( T_c \):

\[
T^*/K = 0.8862 + 0.8109(T_c/K).
\] (1)

This expression gives a better picture of the correlation between \( T^* \) and \( T_c \) than the observation of constancy of \( \psi \) across a variety of fluids. However, this paper does not address other issues of application such as toxicity and flammability that are seldom described from an analysis of saturation properties.

The inset of figure 1 shows the percent relative deviation (100 \( \times \) absolute relative deviation) is obtained for Helium with a value around 0.82, which is weakly dependent on the complexity of the liquid molecule. As depicted in figure 1, we find that the temperature \( T^* \) where \( \psi_{\text{max}} \) occurs bears the following linear relationship with the critical temperature \( T_c \):

\[
A(\sigma, \rho_f) \equiv 1 - \frac{f_{\text{correlation}}}{f_{\text{tabulated}}},
\] (2)

The inset of figure 1 shows the percent relative deviation (100 \( \times \) absolute relative deviation) of \( T^* \) for the fluids considered in this work. The average absolute relative deviation for all fluids is \( A_{\text{av}} = 0.61 \% \). The maximum absolute relative deviation is obtained for helium with a value \( A_{\text{max}} = 12.22 \% \). The average absolute relative deviation is defined as

\[
A_{\text{av}} \equiv \frac{1}{n} \sum_{i=1}^{n} |A_{ij}| = \frac{1}{n} \sum_{i=1}^{n} \left| 1 - \frac{f_{\text{correlation},i}}{f_{\text{tabulated},i}} \right|. \] (3)

while the maximum absolute relative deviation is

\[
A_{\text{max}} \equiv \max_{i} |A_{ij}| = \max_{i} \left| 1 - \frac{f_{\text{correlation},i}}{f_{\text{tabulated},i}} \right|. \] (4)

We also have determined the coefficient of determination for this correlation, obtaining a value \( R^2 = 0.9997 \). We note that this coefficient is defined as

\[
R^2 \equiv 1 - \frac{\sum(f_{\text{tabulated}} - f_{\text{correlation}})^2}{\sum(f_{\text{tabulated}})^2}. \] (5)

where

\[
f_{\text{tabulated}} \equiv \frac{1}{n} \sum_{i=1}^{n} f_{\text{tabulated},i}. \] (6)

is the average value of the tabulated data.

The symbols are the values obtained for the 75 fluids included in the NIST Chemistry WebBook [18] (see table S1 of the supplementary data). The solid line represents equation (1). The inset shows the percent relative deviations of \( T^* \).

3. Second formulation: maxima along the vapor pressure curve

As mentioned in the introduction, the existence of a maximum in \( \phi_{1i} = T_i(1 - p_i) \) and \( \phi_{2i} = p_i(1 - T_i) \) along the vapor pressure

\[
N \sigma^2 = 0.317V_c. \] (8)

This is shown in figure 2, where we also plot the linear fit \( \sigma_{\text{fit}}/\text{nm} = 0.02049 + 0.9530(\sigma_c/\text{nm}) \).

with \( R^2 = 0.9956 \), \( \lambda_{\text{av}} = 1.07 \% \), and \( A_{\text{max}} = 7.13 \% \) for Helium.

This is equivalent to a plot of \( \rho_f / \rho_0 \) vs. \( \rho_f \) and is shown in figure 3. It is evident that a good linear correlation exists:

\[
\rho_f / \rho_0 = 18.216 + 2.209 \rho_f (\text{kg} \cdot \text{m}^{-3}), \] (9)

with \( R^2 = 0.9924 \). We also obtain \( \lambda_{\text{av}} = 5.217 \% \), and \( A_{\text{av}} = 47.59 \% \) for Hydrogen.

At the point where \( \psi = T \rho_f \) attains its maximum value one has

\[
\sigma_0 \equiv - \frac{1}{\rho_f} \frac{\partial \rho_f}{\partial T} \bigg|_{T^*} = \frac{1}{T^*}, \] (11)

where we note that \( \sigma_0 \) cannot be construed to be the thermal expansion coefficient (\( \chi \)) because it is not obtained at constant pressure. Yet, the difference in temperatures between points where each of them is equal to the inverse of temperatures is not significantly different for most fluids.
and (13). The inset shows the percent relative deviations of maximum and the maximum values.

The curve has been brought out in recent years [11,15]. The reduced temperatures \( T_{sp1r} \) and \( T_{sp2r} \), at which these functions attain the maximum and the maximum values \( \phi_{sp1r} \) and \( \phi_{sp2r} \), themselves can be well correlated. We further observe (figure 4) that there are also linear correlations between the critical temperature \( T_c \) and the temperatures \( T_{sp1r} = T_{sp1}T_c \) and \( T_{sp2r} = T_{sp2}T_c \) at which those maxima occur. We obtain:

\[
T_{sp1}/K = 0.7609(T_c/K) - 6.0155, \tag{12}
\]

with \( R^2 = 0.9989, A_{av} = 3.78\% \), and \( A_{max} = 160.02\% \) for Helium.

\[
T_{sp2}/K = 0.8951(T_c/K) - 4.5368. \tag{13}
\]

with \( R^2 = 0.9996, A_{av} = 2.30\% \), and \( A_{max} = 97.26\% \) for Helium.

Analogously, \( \rho_{sp1r} = \rho(T_{sp1}) = \phi_{sp1r} \rho_c/(1 - T_{sp1}/T_c) \) and \( \rho_{sp2r} = \rho(T_{sp2}) = (1 - \phi_{sp2r}/T_{sp2}) \rho_c \) also hold similar linear relationships with \( \rho_c \) as shown in figure 5 and the correlations are given below:

\[
\rho_{sp1r}/MPa = 0.05500(\rho_c/MPa) + 0.03353. \tag{14}
\]

with \( R^2 = 0.9819, A_{av} = 9.09\% \), and \( A_{max} = 37.05\% \) for Dodecane.

\[
\rho_{sp2r}/MPa = 0.4032(\rho_c/MPa) + 0.01567. \tag{15}
\]

with \( R^2 = 0.9998, A_{av} = 1.03\% \), and \( A_{max} = 14.02\% \) for Helium.

Traditionally, the acentric factor \( (\omega \equiv -\log_{10}(\rho_c) - 1 \text{ at } T = 0.7) \) has been used as a parameter characterizing the saturation vapor pressure. It is worthwhile examining its relation with the three maxima discussed above. Figure 6 shows a summary of the behavior. It is apparent that \( \omega \) correlates very well with \( T_{sp1r}(1 - \rho_{sp1r}) = \phi_{sp1r} \rho_c T_c \), and reasonably with \( \psi_{max} = T_c \rho_b^* \). Evidently, these relations are not linear. The noise in the correlation in the last one can be ascribed in most cases to equations of state that are not accurate enough whereas in other cases it rises due to compounding of molecular complexities that affect \( T_c \) and \( \rho_b^* \). We obtain the following quadratic correlations:

\[
T_{sp1r}(1 - \rho_{sp1r}) = -0.1055\omega^2 + 0.1892\omega + 0.6297, \tag{16}
\]

with \( R^2 = 0.9981, A_{av} = 1.28\% \), and \( A_{max} = 6.95\% \) for Ammonia.

\[
\rho_{sp2r}(1 - T_{sp2r}) = 0.03274\omega^2 - 0.04874\omega + 0.05763, \tag{17}
\]

with \( R^2 = 0.9959, A_{av} = 0.13\% \), and \( A_{max} = 1.12\% \) for Helium.

\[
T_c \rho_b^* = -0.2688\omega^2 + 0.5528\omega + 1.7317. \tag{18}
\]

with \( R^2 = 0.8388, A_{av} = 0.60\% \), and \( A_{max} = 2.54\% \) for Methanol.
with $R^2 = 0.9905$, $A_{64} = 4.81\%$, and $A_{\text{max}} = 29.88\%$ for H$_2$O. A few fluids that do not strictly follow the above generalised correlation are H$_2$O, D$_2$O and Methanol. This correlation also generally implies that $T_{\text{hmax}} > T_c$.

However, the linear correlation between $\sigma$ and $T_{\text{hmax}}$ proposed by Srinivasan [17] fails to be satisfied when extended to the whole range of fluids as seen in figure 8. A correlation that best describes the data is

$$T_{\text{hmax}}/T_c = -2.0282(\sigma/\text{nm})^2 + 2.8175(\sigma/\text{nm}) + 0.2577.$$  \hspace{1cm} (20)

with $R^2 = 0.9427$, $A_{64} = 2.18\%$, and $A_{\text{max}} = 16.46\%$ for Xenon. We note that Hydrogen, Parahydrogen, Helium, Argon, Krypton, Xenon and Methanol show a large deviation in figure 8 and have not been considered in the correlation.

The engineering implications of the above findings are as follows. Seldom practical thermodynamic cycles operate at temperatures higher than $T_{\text{hmax}}$. An exception to this is the transcritical carbon dioxide ($T_{\text{hmax}} = -24.5^\circ\text{C}$) refrigeration cycle when operating for medium temperature supermarket refrigeration or air conditioning. Between $T_{\text{hmax}}$ and $T_c$, the isentropes and the saturated vapor line diverge implying that a large desuperheating zone would be required for condensation of vapors. Ideally, one would like to have the compression isentropes to be close to the saturation curve in the superheated vapor region on the pressure-enthalpy plane, which happens for refrigerants such as propane. This is possible only when condensation temperatures are below $T_{\text{hmax}}$. The flattening of the curve in figure 8 at high values of the molecular length parameter implies that $T_{\text{hmax}} \rightarrow T_c$ and hence the critical region of the saturated vapor enthalpy curve has a plateau.

5. Predictions

One of the main goals of the correlations presented in this work is to demonstrate their usefulness for performing predictions of saturated properties of emerging refrigerants. As a check of the predictions given by the above correlations we have considered two new low GWP refrigerants HFO 1234yf and HFO 1234ze (E) for which recent results are available [20–24]. In the case of HFO 1234yf, $T_c = 367.85\text{K}$, $p_c = 3.382\text{MPa}$ and $\rho_c = 477\text{kg/m}^3$ [20–22] and for HFO 1234 ze(E), $T_c = 382.52\text{K}$, $p_c = 3.632\text{MPa}$ and $\rho_c = 486\text{kg/m}^3$ [23]. Our predictions for HFO 1234yf and HFO 1234ze (E) are presented in table 1 where we compare with data obtained from published results [20–24]. By and large the data corresponding to the maxima are in good agreement. However, there is a moderately large difference in the acentric factors, which is not surprising since the acentric factors are obtained from the correlation presented in equation (17), which itself requires data from the correlations given by equations (13) and (15). An alternative way of obtaining the acentric factors is via equation (16) that in turn requires data from equations (12) and (14). This alternative way yields even worse results because of the scatter in the data for $\rho_{p_{c2}}$ as shown in figure 5.

6. Summary

To summarize, the occurrence of maxima in products of a few liquid–vapor saturation properties has been revisited and a few interesting linear empirical relations have been derived between the critical properties and properties at the temperatures of the maxima. More concretely, we have found that the temperature $T^*$ where the $T\rho_f$ attains a maximum value shows a nice linear correlation with the critical temperature $T_c$, and also the molecular length parameter $\sigma$ and the density $\rho_c$ at this point are linearly related to their corresponding critical properties $\sigma_c$ and $\rho_c$, respectively. Furthermore, the temperatures and pressures of the maxima of
Tr(1 − pc) and pc(1 − Tr) have been shown to present linear correlations with Tr and pc. In addition, we have shown that the maximum values of the considered products are well correlated with the acentric factor. Finally, the temperature T h max where the saturated vapor enthalpy has a maximum has been shown to correlate well with T⁄ and the ratio of these two temperatures shows a quadratic correlation with σ. As a practical application of our results we have predicted the properties of two of the new low GWP refrigerants HFO 1234yf and HFO 1234ze (E) with good success.

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Appendix A. Supplementary data

Tables S1 and S2 of the critical parameters and other quantities obtained from the 75 fluids available in the NIST Chemistry WebBook [18] can be found in the online version. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2011.08.005.

References