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Estimation of pure component properties
Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions

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ABSTRACT

A group contribution method for the estimation of the normal boiling point of non-electrolyte organic compounds, which was published earlier, has been the basis for development of subsequent physical property methods. In this work, the model was extended to enable the prediction of vapor pressure data with special attention to the low-pressure region. The molecular structure of the compound and a reference point, usually the normal boiling point, are the only required inputs and enables the estimation of vapor pressure at other temperatures by group contribution. The structural group definitions are similar to those proposed earlier for the normal boiling point, with minor modifications having been made to improve the predictions. Structural groups were defined in a standardized form and fragmentation of the molecular structures was performed by an automatic procedure to eliminate any arbitrary assumptions. The new method is based on vapor pressure data for more than 1600 components. The results of the new method are compared to the Antoine correlative equation using parameters stored in the Dortmund Data Bank, as well as, the DIPPR vapor pressure correlations. The group contribution method has proven to be a good predictor, with accuracies comparable to the correlations. Moreover, because the regression of group contributions was performed for a large number of compounds, the results can in several cases be considered more reliable than those of the correlative models that were regressed to individual components only. The range of the method is usually from about the triple or melting point to a reduced temperature of 0.75–0.8.

1. Introduction

The correlation and prediction of vapor pressures has for long been a very important problem in engineering thermodynamics and has consequently been addressed by many researchers. In early studies, work was usually focused on the pressure region between a few kilopascal and the critical pressure, which is of primary importance for distillation. The description of the temperature dependence of the vapor pressure between a reduced temperature of 0.8 and 1.0 is not trivial.

Correlation or estimation of vapor pressures up to the critical point usually follows either the approach based on the work of Ambrose [1] at the UK. National Physical Laboratory (NPL) based on a Wagner equation form [2] or the Riedel model based on the Planck–Riedel equation [3,4]. Both models require knowledge of the critical temperature and pressure and reduce the number of coefficients, as well as, their numeric range using physically meaningful constraints. While both models are adequate to correlate experimental vapor pressure data, extrapolation into the low-pressure range is usually unsatisfactory.

Nowadays, a large amount of experimental data for common industrial components is available together with tabulated correlation parameters from different sources, e.g. DIPPR [5], DDB [6], PPDS [7], and there is usually no need to estimate the vapor pressure curve of key components in distillation. Due to the predominant influence of the vapor pressure on the vapor–liquid separation factor, one would also not rely on estimated data for this purpose. In addition, group contribution methods and similar correlations are usually of limited value for small molecules which represent the first members of a homologous series and show the largest deviation from the general trend in the series. Larger molecules in most cases have a low volatility and are less likely purified by distillation. Therefore, the estimation require-

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ments are more for low and medium pressures for fairly complex molecules.

Low and medium vapor pressure estimations for complex large molecules are of great importance:

- in process simulation when it comes to by-products and impurities;
- in environmental protection for the estimation of water–air, soil–air, and the various other compartment distribution coefficients [8];
- in supercritical fluid extraction of solids where these data serve as hypothetical sub-cooled liquid vapor pressures for the estimation of sublimation pressures and
- in various instances where knowledge of the vapor pressure is integral to accurately describe a system or process.

In this work, the focus is on the estimation of vapor pressures below a few atmospheres, in order to avoid the complex dependence on temperature near the critical point. As in our previous work on normal boiling temperatures [9,10] and critical data [11], the resulting larger deviations in the case of small molecules are accepted, as these are difficult anyway to handle by group contribution.

2. General behavior and available methods

The dependence of the logarithm of vapor pressure on reciprocal temperature is given by the well known Clausius–Clapeyron equation

$$\frac{\mathrm{d}\ \ln(P^{\mathrm{S}}/1\,\mathrm{atm})}{\mathrm{d}(1/T)} = \frac{-\Delta_{\mathrm{vap}}H}{R\Delta_{\mathrm{vap}}z} \tag{1}$$

When approaching the critical temperature, both $\Delta_{\mathrm{vap}}H$ and $\Delta_{\mathrm{vap}}z$ exhibit a very non-linear and strong change with temperature, which even modern volume translated equations of state find difficult to describe. As discussed in the previous paper [10], the normal boiling point and the critical point are governed by very different physical phenomena. At the normal boiling point the gain in (translational) entropy from vaporization is balanced out by the heat required to overcome the intermolecular interactions in the dense and cool (moderately structured) liquid phase, however, the critical point is determined by the equilibrium between repulsive and attractive forces in a moderately dense unstructured fluid ($\mathrm{d}P/\mathrm{d}V = 0$).Estimation of the critical temperature T_{c} based on the normal boiling temperature T_{b} and vice versa is often of limited accuracy as the ratio $T_{\mathrm{c}}/T_{\mathrm{b}}$ depends strongly on the size and chemical nature of the molecule. As an additional complication, between T_{b} and T_{c} the slope $\mathrm{d}\ln P^{\mathrm{S}}/\mathrm{d}(1/T)$ shows a point of inflection due to a minimum in $\Delta_{\mathrm{vap}}H/\Delta_{\mathrm{vap}}z$.

For this reason, corresponding states methods are usually not able to yield a reasonable estimate, unless information on the vapor pressure in the vicinity of the normal boiling temperature is utilized, usually using the acentric factor ω.

Even then they require critical temperature and pressure as a point of reference. Knowledge about the critical point is limited to a few hundred, mostly small molecules. Estimation or correlation techniques requiring the knowledge of the critical point, although very commonly used, will not be considered in this work to avoid unnecessary complications.

Several group contribution methods have been published for the estimation of vapor pressures without requiring knowledge about the critical point [12,13]. Many more can be constructed by combining estimation methods, for example for the normal boiling temperature, virial coefficient and liquid density, the heat of vaporization, and the difference in heat capacity of the two phases. Several approaches were published to calculate the vapor pressure directly from molecular properties without employing group contribution [14,15].

Another approach uses the UNIFAC method for the prediction of vapor pressures [16,17]. A disadvantage of this method is the requirement for additional data like virial coefficients and the limited range of applicability.

3. Development of the new method and results

The new method employs a slightly improved fragmentation scheme compared to the method for the estimation of normal boiling temperature published earlier [10]. The list of structural groups for the new method, second-order corrections and interacting groups are given in Tables 1–3 respectively, and the group parameter values for vapor pressure estimation are given in Tables 4–6 . Structural groups were defined in a standardized form and fragmentation of the molecular structures was performed by an automatic procedure to eliminate any arbitrary assumptions [18].

For a number of groups listed in Table 1, no parameters are available and vapor pressure estimation is not possible. The groups are nevertheless reported. In case data or reasonable estimates for other components containing these groups are available to the user, it is possible to calculate or regress the missing contribution. If the groups would have been discarded from the method, it might still have been possible to perform property estimation using simpler (lower priority) groups, but it would have led to large errors. For interacting groups, not every interaction is of similar importance. Ignoring specific group interactions will lead to similar errors, as demonstrated in the case of the normal boiling point estimation [10].

3.1. Development of the model equation

Assuming an ideal vapor phase and neglecting the small liquid phase volume it follows that

$$\frac{\mathrm{d}\ln(P^{\mathrm{S}}/1\,\mathrm{atm})}{\mathrm{d}(1/T)} = -\frac{\Delta_{\mathrm{vap}}H(T_0) + \int_{T_0}^{T}(C_{\mathrm{coex}}^{\mathrm{V}} - C_{\mathrm{coex}}^{\mathrm{L}})\,\mathrm{d}T}{R} \tag{2}$$

where

$C_{\mathrm{coex}}^{\mathrm{V}} - C_{\mathrm{coex}}^{\mathrm{L}}$ is the difference between the molar heat capacity of the vapor and liquid phase along the vapor–liquid saturation curve.

Assuming that

$$\Delta C_{\mathrm{coex}} = C_{\mathrm{coex}}^{\mathrm{V}} - C_{\mathrm{coex}}^{\mathrm{L}} = \mathrm{constant} \tag{3}$$

leads to the well known vapor pressure equation (Kirchhoff):

$$\ln\left(\frac{P^{\mathrm{S}}}{1\,\mathrm{atm}}\right) = A + \frac{B}{T} + C\ \ln\left(\frac{1}{T}\right) \tag{4}$$

Unfortunately, this equation cannot be written in temperature-explicit form. To avoid this, it was decided to use the Antoine equation, which is mathematically simpler, but is able to describe a similar curvature at not too high pressures (HPs) and usually extrapolates more reliably to low pressures:

$$\log\left(\frac{P^{\mathrm{S}}}{1\,\mathrm{atm}}\right) = A - \frac{B}{T - C} \tag{5}$$

The disadvantage of the Antoine equation, however, is its discontinuity at $T = C$ and a physically unrealistic increase in the slope of the vapor pressure curve at very low pressures. The value of C was examined by correlating vapor pressure data against the normal boiling point for several hundred components and it was found