On the Temperature Dependence of Vaporization Enthalpy
and its Correlation with Surface Tension

Amin Alibakhshi[1], Bernd Hartke[1]

Theoretical Chemistry, Institute for Physical Chemistry, Christian-Albrechts-University,
Olshausenstr. 40, 24118 Kiel, Germany

Abstract

Temperature dependence of vaporization enthalpy is one of the most important thermophysical properties of compounds. In the present study, we theoretically developed relationships applicable to evaluation of vaporization enthalpy of compounds from diverse chemical families for a wide temperature range from melting point to the critical temperature. One outcome of the proposed approach is a relationship describing the correlation between the surface tension and vaporization enthalpy which outperforms the extensively applied Kabo method proposed for the same purpose.

1- Introduction

Temperature dependence of vaporization enthalpy is one of the key properties of chemicals with numerous important applications in chemistry and chemical engineering, including but not limited to estimation of saturation vapor pressure (highly required in major chemical processes such as distillation, evaporation, drying, humidification and dehumidification[1]), calculation of Hildebrand solubility parameter (required for evaluation of liquid-liquid equilibriums as well as evaluation of the solubility of solids, gases and other liquids [2-4]), evaluation of fire hazards [5], prediction of miscibility of polymer blends as a function of temperature and calculations of liquid-liquid separation processes such as leaching [6,7].

Experimental measurement of vaporization enthalpy for a wide temperature range is not always feasible, e.g., due to safety concerns or operational limitations. This has been the motivation of numerous scientific works in the past decades aiming at predicting vaporization enthalpy at various temperatures in silico. Although various approaches such as molecular dynamics [] or Monte Carlo simulation [], group contributions and QSPR based methods [] or machine learning [] have been exploited for this purpose, still the most straightforward and successful models are correlations which predict vaporization enthalpy as a function of temperature and usually some additional more readily available thermophysical properties.

Some of the most successful previously proposed correlations and a comparison of their performances are reported in table 1 (Details of individual correlations are provided as supplementary information).

Despite almost a century of research on this specific topic, almost all of the successful correlations applicable for predicting vaporization enthalpy of diverse compounds at wide temperature ranges have been developed empirically.

In the previous study, a correlation was derived for this purpose entirely on a theoretical basis, and it was demonstrated that its accuracy is comparable to that of empirically derived models for a limited temperature range [1]. The main aim of the present study is to provide an update on our theoretically derived correlation resulting in a substantial improvement in its accuracy for a much wider temperature range.

2- Theory

In the previous study, it was shown that the temperature dependence of vaporization enthalpy follows [1]:

$$\Delta h_{vap} = \Delta\varepsilon_{bs} - \frac{k_B}{2} T.\ln(T) - T\int \frac{\Delta\varepsilon_{bs}}{T^2} dT + CT, \tag{1}$$

where C is a constant and $\Delta\varepsilon_{bs}$ is the energy required for moving one molecule from the bulk of the liquid to the surface. Via the fundamental thermodynamics relationships between energy (ε), Helmholtz free energy (f) and entropy (s), which for our problem imply [1]:

$$\Delta\varepsilon_{bs} = \Delta f_{bs} + T\Delta s_{bs}, \tag{2}$$

$$\Delta s_{bs} = -\frac{d(\Delta f_{bs})}{dT}, \tag{3}$$

and exploiting the thermodynamics relationship among the free energy change for moving one molecule from the bulk of liquid to the surface (Δf_{bs}), surface tension (γ) and contribution of each molecule into the interfacial surface (a_s) which is defined as[1]:

$$\Delta f_{bs} = a_s\gamma, \tag{4}$$

we get:

$$\Delta\varepsilon_{bs} = a_s(\gamma - T\frac{d\gamma}{dT}). \tag{5}$$

By substituting (5) in (1) and using $\frac{d(\frac{\gamma}{T})}{dT} = \frac{T\frac{d\gamma}{dT}-\gamma}{T^2}$ and multiplying both sides by Avogadro's number, the correlation between the surface tension and molar vaporization enthalpy (ΔH_{vap}) is obtained as :

$$\Delta H_{vap} = a\left(2\,\gamma - T\,\frac{d\gamma}{dT}\right) - \frac{R}{2}\,T.ln(T) + \beta T, \tag{6}$$

in which a and β are constants.

For a constant temperature, (6) reduces to the Kabo's method which describes correlation between vaporization enthalpy and surface tension as:

$$\Delta H_{vap} = \mathcal{A}\left(N_A^{\frac{1}{3}}V^{\frac{2}{3}}\gamma\right) + \mathcal{B}, \tag{7}$$

and has already been extensively applied in numerous works specially in studying ionic liquids [8].

In the previous study, the constant α in eq.(6) was approximated via the liquid molar volume and assuming liquid phase molecules as true spheres, while the constant β was determined using a single item of reference data. Despite all these simplifying approximations, for a limited temperature range (between 50K below the normal boiling point up to 100 K below the critical temperature) the derived correlation yielded accuracies comparable with those of the most successful empirically developed models. Nevertheless, we noticed remarkable inaccuracies for the previously derived correlation when applied for wider temperature ranges, especially close to the critical temperature, which is mainly attributed to the assumption of true spheres for liquid molecules [1].

To overcome the above-mentioned shortcomings, in the present study and in contrast to the previous work, we calculate the constant α using reference data while the constant β is determined analytically and using the boundary condition at critical temperature. Accordingly, knowing that at critical temperature both vaporization enthalpy and surface tension approach zero, and due to continuity of the surface tension the $\frac{d\gamma}{dT}$ term also approaches zero, the constant β is found as:

$$\beta = \frac{R}{2} \ln(T_c), \tag{8}$$

which by substitution into eq.(6) results in:

$$\Delta H_{vap} = \alpha \left(2\,\gamma - T\,\frac{d\gamma}{dT}\right) - \frac{R}{2}\,T.\,ln(T) + \frac{R}{2}\,T \ln(T_c), \tag{9}$$

The constant α in eq.(9) as the only remaining unknown constant can be determined using a single reference data.

To obtain a more straightforward relationship describing temperature dependence of vaporization enthalpy, we also exploit the Guggenheim–Katayama relationship stated as [9]:

$$\gamma = \gamma^{\circ}\left(1 - \frac{T}{T_c}\right)^{11/9}, \tag{10}$$

which after substitution in eq.(9) results in:

$$\Delta H_{vap} = \alpha \left(2\,\left(1 - \frac{T}{T_c}\right)^{11/9} + \frac{11}{9}\frac{T}{T_c}\,\left(1 - \frac{T}{T_c}\right)^{2/9}\right) - \frac{R}{2}\,T.\,ln(T) + \frac{R}{2}\,T \ln(T_c). \tag{11}$$

3- Computational details

To benchmark the new model, we use thermophysical data of the DIPPR801 database [10]. Screening the dataset and selecting only the compounds with maximum uncertainty of 5% results in 767 compounds from diverse chemical families. The names of these compounds are provided as supplementary material.

For each compound, the experimentally determined data of vaporization enthalpies for 25 points linearly distributed between the melting point and the critical temperature were evaluated using the provided relationships in the DIPPR database.

Although the performance of vaporization enthalpy predictive correlations is commonly reported as average absolute relative error, in the present study we use Average Absolute Deviation (AAD) defined as

$$AAD = \frac{1}{N}\sum\left(\left|y_i^{exp} - y_i^{pred}\right|\right). \tag{12}$$

as a more appropriate parameter to evaluate the performance of the models. It is because at temperatures close to the critical point, the vaporization enthalpy approaches zero and as a result, small deviations in predicted data yield a very large relative error, resulting in an inappropriate inference about the performance of the studied models.

4- Result and discussion

In describing the correlation between the vaporization enthalpy and surface tension, the most obvious difference between the proposed relationship in eq.(6) and the widely accepted Kabo method is the existence of the $T\frac{d\gamma}{dT}$ term in our newly derived relationship. To evaluate the significance of this term on improving predictability of the vaporization enthalpy via surface tension, we calculated the constants of eq.(6) by regression using vaporization enthalpy data of the whole temperature range for two cases: once with and once without the $T\frac{d\gamma}{dT}$ term included.

According to the results, while for eq.(6) in its original form, estimating the constants by regression results in an AAD of 905.7 Joule/mol, removing the $T\frac{d\gamma}{dT}$ term and recalculating these constants yields an AAD of 2672.2 Joule/mol. This confirms the importance of the $T\frac{d\gamma}{dT}$ term in substantially improving predictability of the vaporization enthalpy. Similarly, calculating the constants without the $\frac{R}{2}\,T.ln(T)$ term also results in increasing the AAD by 19.34 Joule/mol. All these findings imply the veracity of the developed method

For eq.(9), estimating α using the enthalpy of vaporization at normal boiling point ($\Delta H_{vap,nbp}$) as the only reference point yielded an AAD of 1077.1 Joule/mol, while for the same compounds and temperature range, finding the two constants of the Kabo method (eq. 7) by regression using all data points of the whole temperature range yielded an AAD of 1714.8 joule/mol.

These results show that our newly derived relationship between vaporization enthalpy and surface tension (eq. 9) clearly outperforms the Kabo method as it requires only one adjustable parameter, does not require data of liquid molar volume and for the constant determined using only a single reference datum yields much higher accuracy at other temperatures compared to the Kabo method for which the constants are determined using reference data at all temperatures.

For direct evaluation of vaporization enthalpy without requiring surface tension data, we examined the performance of the proposed relationship eq. (11). Accordingly, for the constant α calculated via experimentally determined data of vaporization enthalpy at normal boiling point, an AAD of 1150.7 Joule/mol for the whole temperature range was achieved.

Although experimental data at any temperature can be used to determine the constant α, using vaporization enthalpy at normal boiling point would be more advantageous due to convenience of its experimental measurement on one hand and existence of several accurate and straightforward to implement correlations for predicting $\Delta H_{vap,nbp}$ on the other hand. In the present study we used and compared three such predictive correlations proposed by Chen [11], Vetere[12] and LIU[13] which provide accurate prediction of $\Delta H_{vap,nbp}$ using critical temperature and critical pressure and normal boiling point as the only required data. Accordingly, calculating α in eq.(11) via $\Delta H_{vap,nbp}$ predicted via these correlations yielded vaporization enthalpies predicted for the whole temperature rage with AADs of 1321.8, 1351.7 and 1470.2 Joule/mol, respectively. These results are compared with those obtained for the same dataset via the most successful empirical models in table 1.

As can be seen in table 1, the theoretically derived relationship proposed in the present study yields an accuracy comparable to those of the most successful empirically developed models. Nevertheless, it should be noted that as for the experimentally determined data, inaccuracies up to 5 percent are expected as reported by DIPPR, slight differences in accuracies of different models do not allow judgments about their performances. Specifically, most of the empirically developed models are parameterized to reproduce DIPPR data, which might result in higher accuracies for those models. For example, the higher accuracy of the model developed by Morgan compared to other empirical models might be due to employing the same relationship as the one provided by the DIPPR database to provide reference data at various temperatures, which was used in the present study to get reference data as well.

The distribution of AAD among some major chemical families is depicted in figure 1 and shows a rather smooth variability for the AAD which is not so dramatically influenced by the chemical families. In our previous study we reported an obvious increasing pattern between the observed average absolute relative errors (AARE%) and molecular weights, especially in 1-alkenes, n-alkanes, methyl alkanes and dimethyl alkanes, which was attributed to a proportional increase in deviation from the true sphere assumption used in calculating the constant α[1] with increasing molecular weight. Nevertheless, as depicted in figure 2, the alternative parameterization approach used in the present study to overcome inaccuracies due to the true sphere assumption clearly results in an almost uniform distribution of AARE% over molecular weight for the same groups, as expected.

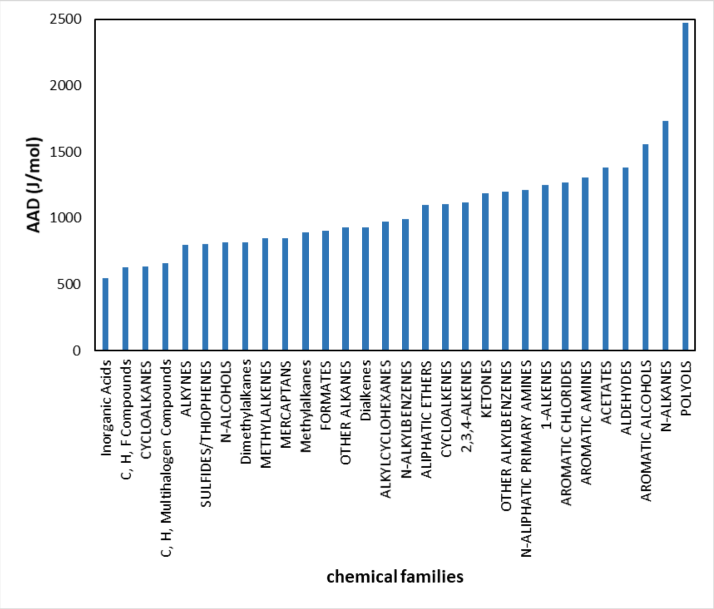

Figure 1- distribution of AAD among various chemical families

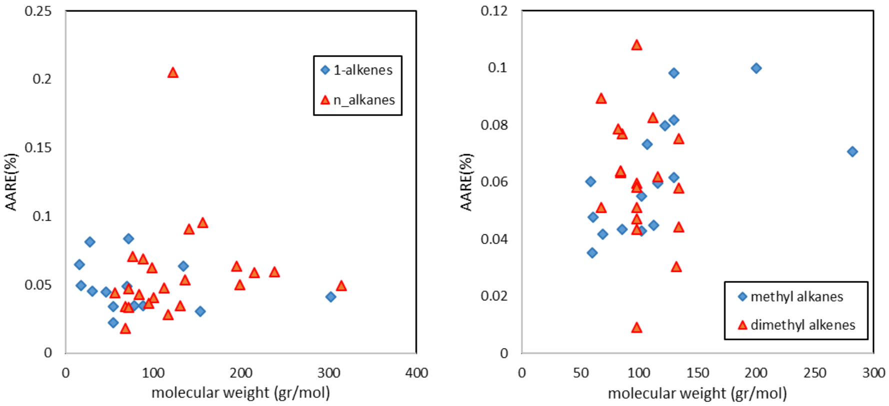

Figure 2- distribution of AARE(%) over molecular weights

Table 1- comparison of the results predicted via various models

	Model inputs	AAD (Joule/mol)
New relationship (eq. 11) $(\alpha\ determined\ via\ experimentally\ determined\ data)$	$T_{nbp}, T_c, \Delta H_{nbp}$	1158.99
New relationship (eq. 11) $(\alpha\ determined\ via\ the\ Chen\ model^{11})$	T_{nbp}, T_c, P_c	1321.8
New relationship (eq. 11) $(\alpha\ determined\ via\ the\ Vetere\ model^{12})$	T_{nbp}, T_c, P_c	1351.7
New relationship (eq. 11) $(\alpha\ determined\ via\ the\ Liu\ model^{13})$	T_{nbp}, T_c, P_c	1470.2
Fish-Lielmezs[14]	$T_{nbp}, T_c, \Delta H_{nbp}$	1085.4
Morgan[15]	T_c, ω	1021
Morgan-Kobayashi[16]	T_c, ω	1217.3
Sivaraman et. al. [17]	T_c, ω	1218.6
Carruth-Kobayashi [18]	T_c, ω	1350.1
Meyra et al. [19]	$T_{nbp}, T_c, \Delta H_{nbp}$	1959.3

5- References:

1 Alibakhshi, A. Enthalpy of vaporization, its temperature dependence and correlation with surface tension: a theoretical approach. *Fluid Phase Equilibria* **432**, 62-69 (2017).

2 Albahri, T. A. Accurate prediction of the solubility parameter of pure compounds from their molecular structures. *Fluid Phase Equilibria* **379**, 96-103 (2014).

3 Weerachanchai, P., Chen, Z., Leong, S. S. J., Chang, M. W. & Lee, J.-M. Hildebrand solubility parameters of ionic liquids: Effects of ionic liquid type, temperature and DMA fraction in ionic liquid. *Chemical engineering journal* **213**, 356-362 (2012).

4 Rai, N., Wagner, A. J., Ross, R. B. & Siepmann, J. I. Application of the TraPPE force field for predicting the Hildebrand solubility parameters of organic solvents and monomer units. *Journal of Chemical Theory and Computation* **4**, 136-144 (2008).

5 Alibakhshi, A., Mirshahvalad, H. & Alibakhshi, S. A modified group contribution method for accurate prediction of flash points of pure organic compounds. *Industrial & Engineering Chemistry Research* **54**, 11230-11235 (2015).

6 Genheden, S. & Essex, J. W. A simple and transferable all-atom/coarse-grained hybrid model to study membrane processes. *Journal of chemical theory and computation* **11**, 4749-4759 (2015).

7 Yang, L., Adam, C. & Cockroft, S. L. Quantifying solvophobic effects in nonpolar cohesive interactions. *Journal of the American Chemical Society* **137**, 10084-10087 (2015).

8 Zaitsau, D. H. *et al.* Experimental vapor pressures of 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imides and a correlation scheme for estimation of vaporization enthalpies of ionic liquids. *The Journal of Physical Chemistry A* **110**, 7303-7306 (2006).

9 Adam, N. (London, 1941).

10 Wilding, W. V., Rowley, R. L. & Oscarson, J. L. DIPPR® Project 801 evaluated process design data. *Fluid phase equilibria* **150**, 413-420 (1998).

11 Chen, N. Generalized Correlation for Latent Heat of Vaporization. *Journal of Chemical and Engineering Data* **10**, 207-210 (1965).

12 Vetere, A. New Generalized Correlations for Enthalpy of Vaporization of Pure Compounds. *Laboratori Ricerche Chimica Industriale, San Donato Milanese* (1973).

13 LIU, Z.-Y. Estimation of heat of vaporization of pure liquid at its normal boiling temperature. *Chemical Engineering Communications* **184**, 221-228 (2001).

14 Fish, L. W. & Lielmezs, J. General method for predicting the latent heat of vaporization. *Industrial & Engineering Chemistry Fundamentals* **14**, 248-256 (1975).

15 Morgan, D. L. Use of transformed correlations to help screen and populate properties within databanks. *Fluid phase equilibria* **256**, 54-61 (2007).

16 Morgan, D. L. & Kobayashi, R. Extension of Pitzer CSP models for vapor pressures and heats of vaporization to long-chain hydrocarbons. *Fluid Phase Equilibria* **94**, 51-87 (1994).

17 Sivaraman, A., Magee, J. W. & Kobayashi, R. Generalized correlation of latent heats of vaporization of coal-liquid model compounds between their freezing points and critical points. *Industrial & engineering chemistry fundamentals* **23**, 97-100 (1984).

18 Carruth, G. F. & Kobayashi, R. Extension to low reduced temperatures of three-parameter corresponding states: vapor pressures, enthalpies and entropies of vaporization, and liquid fugacity coefficients. *Industrial & Engineering Chemistry Fundamentals* **11**, 509-517 (1972).

19 Meyra, A. G., Kuz, V. A. & Zarragoicoechea, G. J. Universal behavior of the enthalpy of vaporization: an empirical equation. *Fluid Phase Equilibria* **218**, 205-207 (2004).