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A METHOD FOR PREDICTING VAPOR PRESSURES OF NONPOLAR LIQUIDS

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ABSTRACT

A new empirical relation involving vapor pressure, internal energy of vaporization and temperature is proposed. The development assumes the validity of the Hildebrand rule and utilizes the Clausius–Clapeyron equation. Equations are developed for predicting vapor pressure at any temperature from either the vapor pressure or internal energy of vaporization at a single reference temperature (25°C). Calculations are given, and compared with experimental results, for numerous nonpolar organic compounds.

INTRODUCTION

Recently we observed that the vapor pressures at 25°C of numerous nonpolar liquids can be related to their energies of vaporization by the empirical expression

$$\log_{10} p_{298} = 4.889 - 1.038 \times 10^{-4} \Delta \bar{E}_{\mathrm{vap},298}^{1.15} \tag{1}$$

where p_{298} is the equilibrium vapor pressure in torr and $\Delta \bar{E}_{\mathrm{vap},298}$ is the molar internal energy of vaporization of the liquid at 25°C[1]. This relation, used in conjunction with heat of dilution data and various theories of nonpolar liquid mixtures, has been valuable in predicting free energies of transfer of solutes (both polar and nonpolar) from dilute solution in nonpolar solvents to the vapor phase.

Considering the simple form of Eqn. (1), we thought it would be worthwhile to examine its applicability (with modified empirical constants) to liquids at temperatures other than 25°C. The present communication outlines the development of an equation which can be used to predict vapor pressures of a nonpolar liquid, throughout a range of temperatures, from knowledge of the energy of vaporization of the liquid at only one temperature (or, alternatively, from the known vapor pressure at a single temperature).

DEVELOPMENT OF THE VAPOR PRESSURE EQUATION

Eqn. (1) may be changed into a form which expresses the molar entropy of vaporization of a nonpolar liquid ($\Delta \bar{S}_{\mathrm{vap}}$) as a function of the molar volume of the vapor in equilibrium with the liquid ($\bar{V}_{\text{vap}}$). Hence, it is related to the familiar Hildebrand rule[2], which states that the entropies of vaporization of all normal liquids will be approximately the same if the liquids are compared at equal molar volumes of saturated vapor. Assuming that p_{298} may be related to $\bar{V}_{\text{vap}}$ by the ideal gas equation, and neglecting the volume of the liquid in comparison with that of the vapor, we may convert Eqn. (1) into

$$(\Delta\bar{S}_{\text{vap}}-R)^{1.15} = 8.52+13.74\log_{10}\bar{V}_{\text{vap}} \tag{2}$$

where $\Delta\bar{S}_{\text{vap}}$ is expressed in entropy units per mole and $\bar{V}_{\text{vap}}$ is in liters/mole. In deriving Eqn. (2), the reasonable assumption is made that $\Delta\bar{E}_{\text{vap}} = T\Delta\bar{S}_{\text{vap}}-RT$. An immediate test of Eqn. (2) is provided by substituting into it the value $\bar{V}_{\text{vap}} = 49.5$ l/mole, from which $\Delta\bar{S}_{\text{vap}}$ is calculated to be 22.2 e.u./mole; this result agrees well with the observation by Hermsen and Prausnitz[3] that the entropy of vaporization equals 22.4 ± 0.4 e.u./mole for some 20 nonpolar liquids at $\bar{V}_{\text{vap}} = 49.5$ l/mole. However, the significant result here is that, to the extent that both Eqn. (1) and the Hildebrand Rule apply, the numerical constants in Eqn. (2) should not depend upon temperature. Therefore, it should be possible to predict $\bar{V}_{\text{vap}}$ (and hence the vapor pressure) from $\Delta\bar{S}_{\text{vap}}$ alone, or alternatively, from $\Delta\bar{E}_{\text{vap}}$ at the given temperature. In many cases, of course, the entropy and energy of vaporization will not be known accurately at temperatures of interest; thus, the utility of Eqn. (2) for predicting equilibrium vapor volumes and vapor pressures will be somewhat limited.

Use of the Clapeyron equation together with Eqn. (2) leads to a vapor pressure equation which can be applied even when information about the temperature dependence of the energy or entropy of vaporization is lacking. Eqn. (2) may be written

$$(\Delta\bar{E}_{\text{vap}}/T)^{1.15} = 8.52+13.74\log_{10}\bar{V}_{\text{vap}} = 8.52+13.74\log_{10}(RT/p) \tag{3}$$

and differentiated to give

$$\mathrm{d}\,[(\Delta\bar{E}_{\text{vap}}/T)^{1.15}] = 13.74\,\mathrm{d}\log_{10}(T/p) \tag{4}$$

But one form of the Clausius–Clapeyron equation is

$$2.303\,\mathrm{d}\log_{10}p/\mathrm{d}T = \Delta\bar{E}_{\text{vap}}/RT^2+1/T$$

or

$$2.303\,\mathrm{d}\log_{10}(T/p) = -(\Delta\bar{E}_{\text{vap}}/RT^2)\mathrm{d}T \tag{5}$$

where it is again assumed that the vapor is ideal and that the liquid volume is negligible. Combining Eqns. (4) and (5), we have

$$\frac{\mathrm{d}(\Delta\bar{E}_{\text{vap}}/T)^{1.15}}{(\Delta\bar{E}_{\text{vap}}/T)} = -(13.74/2.303\,RT)\mathrm{d}T$$

which upon integration, and with substitution of numerical constants, becomes

$$(\Delta\bar{E}_{\text{vap}}/T)^{0.15} = -0.902\log_{10}T+\text{const.}$$

or

$$(\Delta\bar{E}_{\mathrm{vap}}/T)^{0.15} = (\Delta\bar{E}_{\mathrm{vap}}/T)_{\mathrm{ref}}^{0.15} - 0.902\log_{10}(T/T_{\mathrm{ref}}). \tag{6}$$

Eqn. (6) permits calculation of $\Delta\bar{E}_{\mathrm{vap}}$ as a function of the absolute temperature, T, given the value of $\Delta\bar{E}_{\mathrm{vap}}$ at a single reference temperature. Using 25 °C as the reference temperature, Eqns. (6) and (3) may be combined to give

$$[(\Delta\bar{E}_{\mathrm{vap},298}/298.16)^{0.15} - 0.902\log_{10}(T/298.16)]^{7.67} = 8.52 + 13.74\log_{10}(RT/p) \tag{7}$$

Eqn. (7) can be used to predict vapor pressures of a nonpolar liquid at various temperatures, given only $\Delta\bar{E}_{\mathrm{vap},298}$. Moreover, since Eqn. (1) provides a way to calculate $\Delta\bar{E}_{\mathrm{vap},298}$ from p_{298}, Eqn. (7) can be used to predict $p(T)$ from the measured vapor pressure at a single temperature.

APPLICATIONS AND OPTIMIZATION OF EMPIRICAL CONSTANTS

Table I includes experimental values of the vapor pressure and temperature for 25 nonpolar liquids, obtained from Ref. (4). Column 5 lists calculated values of vapor pressure, p^{calc}, obtained using Eqn. (7), with values of $\Delta\bar{E}_{\mathrm{vap},298}$ calculated using Eqn. (1) and experimental values of p_{298}. Values in parentheses in column 5 are percent deviations of calculated from experimental pressures. The root mean square deviation of the logarithm of the calculated pressures is 0.0449, compared to a deviation of 0.0412 in the logarithm of vapor pressures for the same liquids at 25 °C, calculated using Eqn. (1).

TABLE I

EXPERIMENTAL AND CALCULATED VALUES OF VAPOR PRESSURE AND TEMPERATURE FOR NONPOLAR LIQUIDS

Compound	T (°K)	p_{298}^{exp} (*torr*)	$p_{\mathrm{T}}^{\mathrm{exp}}$ (*torr*)	*Method I*[a] $p_{\mathrm{T}}^{\mathrm{calc}}$ (*torr*)	*Method II*[b] $p_{\mathrm{T}}^{\mathrm{calc}}$ (*torr*)
Benzene	353.26	95.135	760	711.8 (−6.3%)	719.8 (−5.3%)
	299.24		100	99.9 (−0.1%)	99.9 (−0.1%)
Toluene	383.78	28.44	760	721.6 (−5.1%)	731.2 (−3.8%)
	325.10		100	99.1 (−0.9%)	99.4 (−0.6%)
Ethyl benzene	409.34	9.50	760	715.8 (−5.8%)	725.6 (−4.5%)
	347.27		100	98.1 (−1.9%)	98.5 (−1.5%)
o-Xylene	417.57	6.60	760	713.8 (−6.1%)	723.5 (−4.8%)
	354.47		100	97.9 (−2.1%)	98.3 (−1.7%)
m-Xylene	412.26	8.29	760	711.8 (−6.4%)	721.5 (−5.1%)
	349.98		100	98.0 (−2.0%)	98.4 (−1.6%)
p-Xylene	411.51	8.76	760	721.3 (−5.1%)	731.2 (−3.8%)
	349.09		100	98.8 (−1.2%)	99.2 (−0.8%)
Propyl benzene	432.38	3.37	760	708.8 (−6.7%)	718.1 (−5.5%)
	367.20		100	96.6 (−3.4%)	96.9 (−3.1%)
Mesitylene	437.85	2.683	760	716.6 (−5.7%)	726.0 (−4.8%)
	372.05		100	98.3 (−1.7%)	98.7 (−1.3%)
Styrene	418.35	5.983	760	688.0 (−9.5%)	697.1 (−8.3%)
	355.53		100	94.7 (−5.3%)	95.1 (−4.9%)

TABLE I (cont'd)

Compound	*T (°K)*	p_{298}^{exp} *(torr)*	p_T^{exp} *(torr)*	*Method I*[a] p_T^{calc} *(torr)*	*Method II*[b] p_T^{calc} *(torr)*
Pentane	309.23	512.50	760	748.5 (−1.5%)	751.0 (−1.2%)
	260.66		100	104.4 (+4.4%)	103.2 (+3.2%)
Isopentane	301.01	688.0	760	757.6 (−0.3%)	758.3 (−0.22%)
	253.00		100	103.0 (+3.0%)	101.5 (+1.5%)
Neopentane	282.66	1286.0	760	774.6 (+1.9%)	770.0 (+1.3%)
	236.85		100	104.3 (−4.3%)	101.7 (+1.7%)
Hexane	341.90	151.25	760	727.0 (−4.3%)	734.1 (−3.4%)
	288.97		100	100.7 (+0.7%)	100.5 (+0.5%)
Heptane	371.58	45.72	760	709.6 (−6.6%)	718.6 (−5.4%)
	317.93		100	111.9 (+11.9%)	112.3 (+12.3%)
Octane	398.82	14.03	760	688.4 (−9.4%)	697.6 (−8.2%)
	338.86		100	95.9 (−4.1%)	96.3 (−3.7%)
Isooctane	372.39	49.37	760	765.7 (+0.75%)	775.8 (+2.1%)
	313.82		100	100.9 (+0.9%)	101.1 (+1.1%)
Cyclopentane	322.42	317.44	760	740.2 (−2.6%)	745.0 (−2.0%)
	271.85		100	101.8 (+1.8%)	101.1 (+1.1%)
Cyclohexane	353.89	97.58	760	739.2 (−2.7%)	747.7 (−1.6%)
	298.70		100	100.0 (0%)	100.0 (0%)
Methylcyclohexane	374.09	46.33	760	768.2 (+1.1%)	778.3 (+2.4%)
	315.23		100	101.1 (+1.1%)	101.3 (+1.3%)
Methylcyclopentane	345.00	137.50	760	740.0 (−2.6%)	747.5 (−1.6%)
	291.02		100	100.1 (+0.1%)	100.0 (0%)
1-Hexene	336.64	186.0	760	732.3 (−3.6%)	739.0 (−2.8%)
	284.26		100	101.0 (+1.0%)	100.6 (+0.6%)
1-Octene	394.44	17.38	760	700.3 (−7.9%)	709.8 (−6.6%)
	334.78		100	97.0 (−3.0%)	97.4 (−2.6%)
Propane	231.08	7096.0	760	1064.3 (+40%)	1017.8 (+34%)
	193.52		100	170.1 (+70.1%)	157.1 (+57.1%)
Butane	272.66	1823.0	760	806.6 (+6.1%)	797.9 (+5.0%)
	228.98		100	114.7 (+14.7%)	111.1 (+11.1%)
Carbontetrachloride	349.70	115.25	760	741.7 (−2.4%)	749.8 (−1.3%)
	295.04		100	100.3 (+0.3%)	100.3 (+0.3%)
RMSD in $\log_{10} p_T^{calc}$				0.04487	0.03815

[a] In Method I the unmodified constants $a = 4.889$ and $b = 1.038 \times 10^{-4}$ were used to calculate p_T.
[b] In Method II the modified values $a = 4.940$ and $b = 1.051 \times 10^{-4}$ were employed.

A slight improvement in fitting the vapor pressure data in Table I can be achieved by treating the numerical constants in Eqn. (1) as variable parameters. Thus, if Eqn. (1) is generalized to

$$\log_{10} p_{298} = a - b(\Delta\bar{E}_{vap,298})^{1.15} \qquad (1a)$$

Eqn. (2) becomes

$$(\Delta\bar{S}_{vap} - R)^{1.15} = \frac{a - \log_{10}(298.16\,R)}{298.16^{1.15}\,b} + \frac{\log_{10}\bar{V}_{vap}}{298.16^{1.15}\,b} \qquad (2a)$$

and Eqn. (7) becomes

$$\left[(\Delta\bar{E}_{\text{vap},298}/298.16)^{0.15} - \frac{0.15\log_{10}\dfrac{T}{298.16}}{1.15\,R\,(298.16)^{1.15}\,b}\right]^{(1.15/0.15)}$$

$$= \frac{a-\log_{10}(298.16\,R)}{298.16^{1.15}\,b} + \frac{\log_{10}(RT/p)}{298.16^{1.15}\,b} \qquad (7a)$$

Solving Eqn. (1a) for $\Delta\bar{E}_{\text{vap},298}$, and substituting into Eqn. (7a) gives the result

$$\log_{10} p = a + \log_{10}(T/298.16) - \left[(a-\log_{10} p_{298})^{(0.15/1.15)} - (0.15/1.15)\,\frac{\log_{10}(T/298.16)}{Rb^{(1/1.15)}298.16}\right]^{(1.15/0.15)} \qquad (8)$$

where R equals 1.987 cal mole^{-1} deg^{-1}. Least-squares values of the constants a and b were obtained by minimizing the combined sum of squares of deviations of calculated from experimental values of $\log_{10} p$, including both the points represented in Table I and the vapor pressure data at 25°C. The calculated values of p_{298} were obtained from Eqn. (1a), using experimental $\Delta\bar{E}_{\text{vap},298}$ values [4,5] and chosen values of the parameters a and b; vapor pressures at other temperatures (exhibited in Table I) were calculated from Eqn. (8). The vapor pressure at 25°C were assigned statistical weights of 2 (relative to values of vapor pressures at other temperatures) in generating the combined sum of squares of residuals. An absolute minimum in the sum of squares of residuals was located by nonlinear least-squares analysis; the least-squares values of the parameters are $a = 4.940$ and $b = 1.051 \times 10^{-4}$. The calculated vapor pressure (and % deviation) values in column 6 in Table I were computed using these constants. The root mean square deviation in the logarithm of the p^{calc} values given in Table I (obtained with the refined constants a and b) has been reduced to 0.0382 (or 8.8% in p) and the corresponding root mean square deviation in the log of the calculated vapor pressures at 25°C is 0.0444, only slightly greater than that obtained from the unmodified Eqn. (1). Some of the largest relative errors occur for systems like propane and butane, for which the ideal gas approximation is relatively poor. Omitting these systems from the analysis does not materially change the least-squares values of a and b, although it does decrease the root mean square deviations. It may be worthwhile ultimately to extend the present treatment by using fugacity in place of pressure and correcting for the volume of the liquid in the thermodynamic relations applied to vaporization. However, the equations given here are simple in form and require a minimum of experimental information in their application; it is doubtful that the anticipated improvement in predicted vapor pressures will be sufficient to warrant introducing correction terms to account for vapor phase nonideality and the liquid volume.

It should also be mentioned that the exponent in Eqns. (1) and (1a) and related expressions may be varied over a considerable range (1.15 ± 0.10) without significantly modifying values of the predicted vapor pressures. The least-squares constants a and b are, of course, changed when a different exponent is used, but this results in only a slightly worsened-fit to the equations.

CONCLUSION

The vapor pressure equations presented here are useful for a wide variety of nonpolar liquids. They are simple to apply, requiring only knowledge of the vapor pressure or the energy of vaporization at a single temperature. It will be interesting to compare the range of applicability of these equations with that of correlations given previously[6].

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