Understanding the Relative Volatility of Materials: A Comparison of Thermal Analysis, GC Analysis and Chamber Test Techniques.

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Introduction:

Many industries are becoming increasingly concerned about volatile materials which evaporate into the atmosphere during storage, use and disposal of the chemical products they use. In many areas, this tendency for evaporation is being quantified in terms of the VOC (volatile organic chemical) content. New government regulations designed to curb VOC emissions are rapidly appearing, and some of these new laws have created significant challenges in the area of VOC analysis. Before reliable enforcement of VOC regulations can occur, accurate and precise methods for the determination of the VOC content of commercial products must be developed. In addition, a clear definition of a VOC threshold needs to be set. This talk will summarize the benefits and issues associated with several currently used methods of VOC analysis; including thermal evaporation methods, GC analysis and Chamber Testing. The science of VOC is not trivial, and a full understanding of VOC requires attention to details.

Relative Volatility and the VOC Threshold:

The volatility of a material depends on ones definition and frame of reference. In general, not all organic compounds are considered volatile. All materials exhibit some vapor pressure at any given temperature above absolute zero, but this does not mean that all materials should be considered volatile. The vapor pressure exhibited at room temperature by high MW polymers, graphite, sodium salts of linear alkylbenzenesulfonates, many inorganic salts and numerous other ionic and/or high MW materials is negligible to the point where these materials are usually considered to be completely “non-volatile”. For intermediate MW materials including C18 fatty acid methyl esters, naphthenic base oils, higher MW N-alkylalkanolamines (MW > 150), higher MW polyols, glycerol and numerous other compounds, the vapor pressure at room temperature is very low but measurable. For volatile materials like hexane, ethanol, acetone and related solvents and other low MW compounds, the vapor pressure produced at room temperature is significant and easily measured. The vapor pressure produced by a material at a given temperature is a measure of the volatility of the material at that temperature, and the relative vapor pressure of two materials at a given temperature is a measure of the relative volatility of the two materials at that temperature. One obvious criterion for the determination of the VOC status of a material is the vapor pressure of the material at a given temperature. A certain maximum vapor pressure at a given temperature could be established as a threshold limit above which a compound is considered a VOC. To use this definition of VOC threshold in a regulatory setting, an accurate determination of vapor pressure at the set temperature must be available. More conveniently, a reference material can be chosen as the threshold determinant for VOC at all temperatures. With the reference compound definition of the VOC threshold, a standardized test for the relative volatility of a molecule under consideration as compared to the reference compound can be used for the determination of VOC status.

Vapor Pressure Measurement:

The vapor pressure of an organic material can be measured directly by carefully purifying the material, completely degassing it and placing it in an appropriately sized and completely evacuated container fitted with an accurate absolute pressure gauge. With this setup in place, one can equate the measured absolute pressure inside the container at a given temperature with the vapor pressure of the material at this temperature. A slightly less accurate measurement of vapor pressure at certain distinct temperatures (*i.e.*, the boiling temperatures) can be obtained by distilling the material at controlled absolute pressure (*i.e.*, controlled vacuum). Distillation techniques are, of course, only applicable to molecules which can be distilled without decomposition, and the specific VP/T data point pairs obtained are determined by the distillation pressure(s) available. The accuracy of the VP/T data obtained from a distillation obviously depends on the accuracy of the temperature and pressure measurement techniques employed.

Vapor Pressure as a Function of Temperature (Activated Process Derivation):

One can use experimentally determined VP/T data points to determine best-fit constants in equations relating vapor pressure to temperature. Obviously, an accurate equation relating VP to T is needed for sensible best-fit constants to be determined. An accurate VP/T equation employing accurately determined best-fit constants can be used to interpolate and/or extrapolate from measured VP/T points to arbitrary temperatures.

A simple derivation of the relationship of vapor pressure to temperature is given below:

Model boiling as an equilibrium process:

$$\mathrm{A(l)} \rightarrow \mathrm{A(g)} \qquad K \equiv \text{equilibrium constant} = \frac{\text{fugacity (activity) of gas}}{\text{activity of liquid}}$$

This model assumes we are distilling a pure liquid material into an atmosphere composed of the same material. This assumption is not significantly different from the real situation which occurs when distilling a **pure** high boiling material under vacuum. We make a few assumptions:

$$\text{fugacity of A} \approx \text{partial P of A} \approx \text{total P observed during vacuum distillation} \approx \text{vapor P of A @ T}$$

The activity of a pure liquid is unity by definition:

$$K = P = \text{vapor pressure of A @ T}$$

$$\Delta G(\text{vaporization}) = \Delta G^{\phi}(\text{vaporization}) + RT\ln(K) = \Delta G^{\phi}(\text{vaporization}) + RT\ln(P)$$

$$\text{At equilibrium,}\ \ \Delta G(\text{vaporization}) = 0$$

$$\Delta G^{\phi}(\text{vaporization}) = -RT\ln(K) = -RT\ln(P)$$

The ΔG^{ϕ} value is the free energy per mole change for the point where the gas has activity = 1. This is to say that the ΔG^{ϕ} value occurs wherein the P = 1 in the units being used to measure P.

$$\Delta H^{\phi} - T\Delta S^{\phi} = -RT\ln(P)$$

$$\ln(P) = -\Delta H^{\phi}/RT + \Delta S^{\phi}/R$$

$$\ln(P) = -A/T + B$$

$$\log(P) = 2.302585\ln(P)$$

The simplest theoretical dependence of the vapor pressure of a molecule on the temperature is a two parameter logarithmic function with T typically converted to absolute (K). The slope and intercept of a graph of log(P) versus 1/T can be directly converted to the standard enthalpy and standard entropy of vaporization. With T in Kelvin, the value of the slope (A) can be set equal to $\Delta H^{\phi}/R$ and the value of intercept (B) can be equated with $\Delta S(P)^{\phi}/R$ (R = universal gas constant, standard entropy depends on the units used to measure P). The enthalpy of vaporization is a constant in this model, and the value derived for the enthalpy of vaporization will be an average for the range of temperature used to derive the best fit equation. The value of B will depend on the units used to measure the pressure, as the entropy of vaporization is pressure dependent and the standard entropy change will be the one that occurs when P = 1 in the units of pressure used. Stated differently, the value of B multiplied by the universal gas constant (R) can be set equal to the entropy of vaporization for a pressure equal to one in the pressure units employed. For P = 1:

$$\ln(P) = \ln(1) = 0 = -A/T + B = -\Delta H^{\phi}/RT + \Delta S^{\phi}/R$$

$$\Delta S^{\phi} = \frac{\Delta H^{\varphi}_{\text{vaporization}}}{T} \quad \text{(for P = 1)}$$

The value of the entropy of vaporization can be determined at any pressure as $\Delta H^{\phi}/T_{BP}$ with T_{BP} = boiling temperature @ P.

Clausius-Clapeyron Derivation of VP as a function of T:

The Clausius-Clapeyron equation furnishes the same relationship between VP & T as is given by the above Activated Process (AP) derivation. In the above AP derivation, T is taken as the boiling temperature. In the Clausius-Clapeyron equation, T can be regarded more simply as a constant temperature at which vaporization is taking place. The Clausius-Clapeyron equation can be derived by starting from one of the thermodynamic state functions.

$$dG = VdP - SdT$$

$$dG_M = \mu = V_M dP - S_M dT = \text{chemical potential} = \text{molar free energy change}$$

$$\mu_l = \mu_g \text{ (isothermal phase change) (l = liquid, g = gas)}$$

$$V_l dP - S_l dT = V_g dP - S_g dT$$

$$dP/dT = (S_g - S_l)/(V_g - V_l) = \Delta S_{\text{vaporization}}/\Delta V_{\text{vaporization}}$$

$$dP/dT = \Delta S/\Delta V$$

$$\Delta S_{vaporization} = \Delta H_{vaporization}/T$$

$$dP/dT = \Delta H/T\Delta V$$

$$\text{Take } \Delta V_{vaporization} \approx V_{gas} \text{ with } V_{gas} = nRT/P \ (n = 1)$$

$$dP/dT = (\Delta H)P/RT^2$$

$$dP/P = (\Delta H /R)\ dT/T^2$$

$$\ln(P) = -\Delta H/R\ (1/T) + C \text{ (constant of integration)}$$

Referring to the activated process derivation above, with $A = \Delta H_{vaporization}/R$ and B = C (constant of integration), we have the same equation.

$$\ln(P) = -A/T + B$$

The Clausius-Clapeyron equation gets one to the same relationship with a little more work.

Expanded VP/T Correlations:

The two parameter logarithmic relationship of vapor pressure to temperature is oftentimes expanded by engineers into the Antoine Equation (wherein a third adjustable constant C is added):

$$\ln(P) = A/(T + C) + B$$

The parameter C is sometimes regarded as simply a means of converting a two parameter equation from the absolute temperature scale to the centigrade temperature scale. However, when the parameter C is adjusted to fit experimental data, it typically takes a value substantially lower than the 273.15 which would be expected if it were simply converting from absolute to centigrade temperature scales (Thomson, G. W.; "The Antoine Equation for Vapor Pressure Data" *Chemical Reviews* 1946, *38(1)*, 1 – 39). The Riedel equation is an even more complicated version of the VP/T relationship with 5 adjustable constants (A, B, C, D, E). The Riedel equation is preferred by physical chemists needing the greatest degree of accuracy.

$$\ln(P) = A/T + B + C\ln(T) + DT^E$$

Intuitive Correlation of Vapor Pressure @ T to the Normal Boiling Point:

Setting a volatility threshold requires defining the maximum vapor pressure at a given temperature for which a material can be considered a non-VOC. Perhaps the most intuitive way to assess the relative volatility of two molecules is via a comparison of their normal boiling points. The normal boiling point of a material is the temperature at which the material will boil at atmospheric pressure. Thus, the vapor pressure of a material at its normal boiling point is atmospheric pressure (≈760 Torr). For low boiling materials (normal BP < 100 ^{o}C) that are reasonably stable in air, the normal boiling point is determined directly via simple distillation at atmospheric pressure. For higher boiling compounds (BP > 200 ^{o}C), vacuum distillation is typically required in order to avoid significant degradation of the product. Pressure and temperature data from several vacuum distillations run at differing vacuum (*i.e.*, different absolute pressures) can be fit into one of the equations mentioned above to extrapolate to a theoretical normal boiling point. The accuracy of an extrapolation of vacuum distillation data to a normal boiling point depends on the accuracy of the vacuum distillation data collected and also on the accuracy of the equation used to carry out the extrapolation.

The Determination of the Normal Boiling Point for High Boiling Compounds:

The determination of the normal boiling point of materials that are thermally and oxidatively stable at the normal boiling temperature is straightforward. Heat the pure material in a distillation apparatus until it boils. Allow the boiling liquid system to attain a steady state wherein the movement of vaporized material has heated the neck of the apparatus to a constant temperature. Take this temperature at the proper point in the neck of the apparatus as the boiling point. A barometer should be used to establish the exact atmospheric pressure that prevails in the location where the distillation is carried out. True ambient atmospheric pressure distillations can only be carried out at an elevation close to sea level on a calm day. The repetition of simple distillation procedures by different people over time leads ultimately to an accurate and universally accepted normal boiling point for a given material.

The determination of the normal boiling point of materials that are thermally unstable at the normal boiling temperature requires vacuum distillation. Even if one decides to simply distill a high boiling material at ambient pressure with acceptance of the yield loss inherent from thermal decomposition, it will still be impossible to measure an accurate normal boiling point for the pure material. This is because co-distillation of the continuously produced impurities will alter the measured boiling temperature sufficiently to render it inaccurate as a measure of normal boiling point. If, for instance, the pure material continuously dehydrates at the temperature of the distillation, then a multi-component gradient of the original material and the dehydrated byproduct, along with water, will be set up within the distillation apparatus. This steady state gradient will result in a continuously changing temperature within the neck of the apparatus, and this temperature variation will make it impossible to determine an accurate normal boiling point for the pure material. The difficulty in distilling thermally unstable materials at atmospheric pressure is easily overcome by employing vacuum distillation. Carrying the distillation out under vacuum allows for the boiling point to be reduced to a point where the molecule is no longer unstable with an additional benefit being removal of most of the oxygen from the system.

Calculation of the Normal Boiling Point for a Material Distilled Under Vacuum:

The relationship between the vapor pressure of a pure material, taken as the absolute pressure at which a distillation is carried out, and the temperature, taken as the boiling temperature in the neck of the distillation apparatus, is usually modeled with a two parameter logarithmic fit. One measures the boiling temperature at as many different absolute pressures (*i.e.*, differing settings of controlled vacuum) as is practical and then fits the data to a log(P) versus 1/T plot by linear regression.

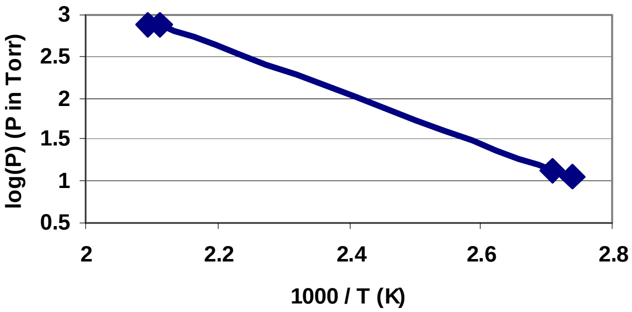
$$\ln(P) = -A/T + B$$

Note that the temperature should be converted to the absolute Kelvin scale. We can illustrate the calculation of a normal boiling point for butylaminoethanol (BAE, CAS RN 111-75-1, GMW = 117.19). Table 1 is a compilation of literature data for the boiling point of BAE versus absolute pressure for the limited number of distillations that have been reported.

BP (^{o}C)	BP (^{o}K)	P (torr)	P (KPa)	Reference
204	477.15	760	101.32	Sanui; Ogata; *J. Polym. Sci. Part A*, **1970**; *8*, 277-278.
200	473.15	756	100.79	Matthes; Justus Liebigs Ann. Chem., **1901**, *315*, 128.
96	369.15	13	1.733	Okada, M. *et al.*; *Chem. Pharm. Bull.*, **1978**, *26*, 3891-3896.
92	365.15	11	1.466	Cope; Hancock; *J. Amer. Chem. Soc.*, **1942**, *64*, 1503-1504.

Table 1: Literature data available for absolute pressure versus boiling temperature of BAE.

Graph 1 below shows a plot of the base ten log of the absolute pressure in Torr versus 1000/T, with T converted to Kelvin (absolute scale), for the four literature distillations shown above.



Graph 1: Plot of log(P) versus the inverse of absolute T for literature reported vacuum distillations of BAE.

The two parameter best-fit equation (in base 10 log and natural log) for BAE based on linear regression of the four P/T data pairs ($r^2 = 0.9996$) available is given below.

$$\log_{10}(\mathrm{P}) = \frac{-2909}{\mathrm{T}} + 9.0013 \quad \ln(\mathrm{P}) = \frac{-6698}{\mathrm{T}} + 20.7263$$

From the slope and intercept of the best fit equation, the following average enthalpy of vaporization, entropy of vaporization at the normal boiling point (BP ≈ 200 ^{o}C) and entropy of vaporization at unit measurement pressure (1 Torr) can be calculated:

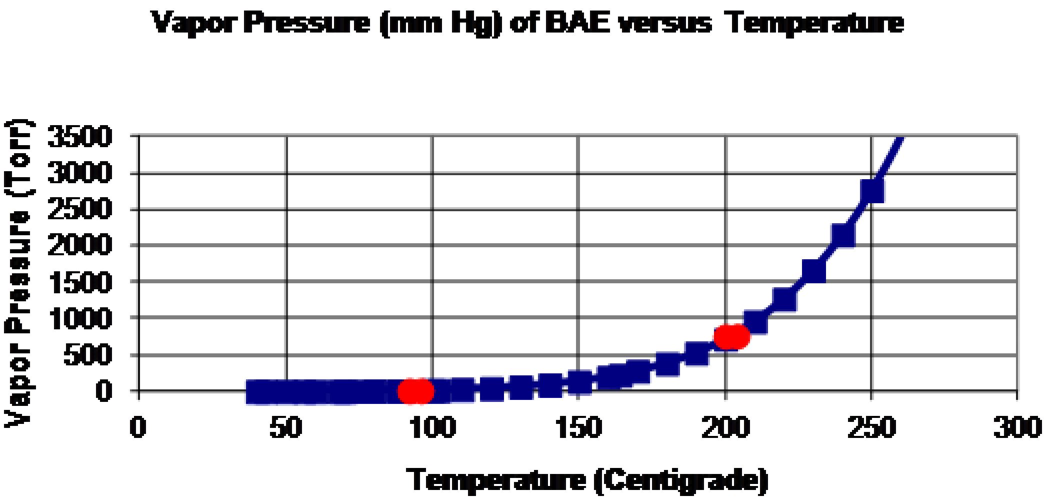
$6698 \times R = \Delta H$
$20.7263 \times R = \Delta S$ @ 1 Torr
R = universal gas constant = 8.31447 Joules/K-mol

$\Delta H_{vaporization} = 55.7$ kJ/mole

$\Delta S_{vaporization}$ @ 1 atm = $\Delta H_{vaporization} / T_{BP}$ = 55.7 kJ/mole ÷ 473 K = 117.7 J/mol-K

$\Delta S_{vaporization}$ @ 1 Torr = 172.3 J/mol-K

See the paper of Chickos, *et al.* (Chickos, J. S.; Acree, Jr., W. S.; *Journ. Phys. Chem. Ref. Data*, **2003**, *32(2)*, 519-878) for a compendium of enthalpies of vaporization. From the best fit equation, we can also calculate a normal boiling point of ≈ 202 ^{o}C for BAE. In this case, the material could be distilled reasonably well at atmospheric pressure, wherein there was observed a normal boiling point of 204 ^{o}C. Undoubtedly, this normal boiling point was slightly perturbed by continuous decomposition during the atmospheric pressure distillation. The calculated vapor pressure of BAE as a function of temperature, as determined by the equation derived above, is plotted in Graph 2 below.



Graph 2: The calculated vapor pressure in Torr of butylaminoethanol (BAE) versus temperature (^{o}C). Literature data is superimposed as red dots on the calculated vapor pressure curve.

The calculated values of the average enthalpy of vaporization, entropy of vaporization at the normal boiling point, entropy of vaporization @ 1 Torr and the normal boiling point for different combinations of arbitrarily set values of the best fit constants A & B are given in Table 2 below:

A ($\log_{10}$)	$\Delta H_{vaporization}$	B ($\log_{10}$)	$\Delta S_{vaporization}$ @ 1 Torr	$\Delta H_{vaporization}/T_{BP}$ @ 1 atm	T_{BP} @ 1 atm (^{o}C)
2500	47.86 kJ/mol	7	134.0 J/K-mol	78.86 J/K-mol	334
2500	47.86 kJ/mol	8	153.2 J/K-mol	98.01 J/K-mol	215
2500	47.86 kJ/mol	9	172.3 J/K-mol	117.15 J/K-mol	135
3000	57.43 kJ/mol	7	134.0 J/K-mol	78.86 J/K-mol	455
3000	57.43 kJ/mol	8	153.2 J/K-mol	98.01 J/K-mol	313
3000	57.43 kJ/mol	9	172.3 J/K-mol	117.15 J/K-mol	217
3500	67.01 kJ/mol	7	134.0 J/K-mol	78.86 J/K-mol	577
3500	67.01 kJ/mol	8	153.2 J/K-mol	98.01 J/K-mol	411
3500	67.01 kJ/mol	9	172.3 J/K-mol	117.15 J/K-mol	299

Table 2: Calculated values of the enthalpy of vaporization (A x R), entropy of vaporization at the normal boiling point ($\Delta H/T_{BP}$), unit pressure entropy of vaporization @ 1 Torr (B x R) and normal boiling point for arbitrarily selected values of the best fit constants A & B from a $\log_{10}$ plot of the two parameter fit: $\log(P) = -A/T + B$ with pressure measured in Torr.

The average molar entropy of vaporization @ 1 atm for most distillable molecules is on average ≈ 85 J/K-mol (Trouton's Rule; see Goodman, J. M.; Kirby, P. D.; Haustedt, L. O.; "Some calculations for organic chemists: boiling point variation, Boltzmann factors and the Eyring equation" *Tetrahedron Letters* **2000**, *41*, 9879 – 9882) with a range from 70 J/K-mol to about 130 J/K-mol encompassing almost all normally distilled materials. The molar enthalpy of vaporization varies over a wider range from less than 1 kJ/mol to over 300 kJ/mol (see Chickos, J. S.; Acree, Jr., W. S.; "Enthalpies of Vaporization of Organic and Organometallic Compounds, 1880–2002" *Journ. Phys. Chem. Ref. Data*, **2003**, *32(2)*, 519-878). The enthalpy of vaporization for most semi-volatile materials of interest in coatings will range from 30 kJ/mol to 80 kJ/mol.

Inaccuracies Associated with Calculated Normal Boiling Points:

There are several problems with using data from disparate literature sources for the calculation of a normal boiling point. Foremost among these problems is the assessment of validity for individually reported literature values. A wildly aberrant data point can be removed with Dixon's Q test, but, beyond the elimination of grossly unaligned data, most of the reported P/T pairs will need to be considered. The influence of errant data on a calculated normal boiling point can be significant. Table 3 below illustrates the influence that an inaccurate data point can have on a calculated normal boiling point derived from a limited set of data.

Measured BP (^{o}C)	Accurate P (Torr)	Measured P (Torr)	Accurate ΔH_{vap}	Calculated ΔH_{vap}	Accurate ΔS_{vap} (760 Torr)	Calculated ΔS_{vap} (760 Torr)	Accurate Normal BP (^{o}C)	Calculated Normal BP (^{o}C)
100	100	100	46.2 kJ/mol A = 5553	35.5 kJ/mol A = 4268	116.4 J/K-mol B = 16.882	87.8 J/K-mol B = 13.438	123	131
70	5	10						
180	90	100	34.7 kJ/mol A = 4175	53.2 kJ/mol A = 6392	68.9 J/K-mol B = 11.168	110 J/K-mol B = 16.105	230	210
150	20	10						
250	100	110	41.2 kJ/mol A = 4951	52.0 kJ/mol A = 6254	71.4 J/K-mol B = 11.463	92.4 J/K-mol B = 13.995	304	290
200	10	6						

Table 3: The influence of an inaccurate data point in a two data point set on the calculated normal boiling point determined by correlation with a "$\log(P) = -A/T + B$" plot.

The normal BP is proportional to the enthalpy of vaporization and inversely proportional to the entropy of vaporization. One slightly inaccurate pressure measurement at high vacuum can easily alter a calculated normal boiling point by over 25 ^{o}C. It is more typical for significant errors to occur in the measurement of the absolute pressure at high vacuum as opposed to the distillation temperature, but inaccurate temperature measurements (*e.g.*, incorrect placement of the thermometer in the stem of the distillation head) may also occur. Typically there is a limited amount of literature data available, and the different laboratories involved oftentimes exhibit different degrees of attention to accuracy. The influence of errors in literature data is difficult to assess unless one takes the time to independently check at least 5 P/T data pairs in a standardized setup (*i.e.*, run 5 different sets of vacuum distillation conditions yourself).

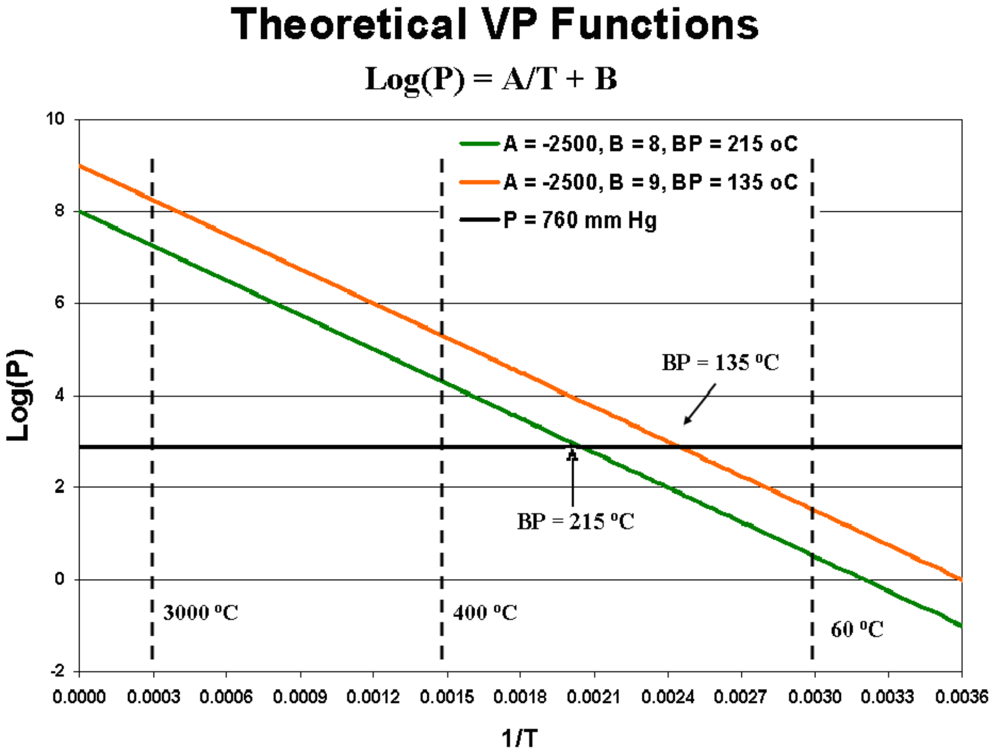
None of the "accurate" or the "calculated" values in Table 3 are outside the normal range. The hypothetical data listed in Table 3 implies materials with accurate entropy of vaporization values

(@ 1 Atm) at the outer limits of the normal range and thus the exclusion of erroneous data is not possible based on the calculated enthalpy of vaporization and entropy of vaporization values.

Changes in Relative Volatility with Temperature:

The use of a reference compound of known volatility can be used for the establishment of a VOC threshold. The reference material (marker compound) is judged to be at the threshold of VOC volatility. Materials that are more volatile than the marker compounds are considered VOC's and molecules that are less volatile than the marker compound are considered to be non-VOC's. The volatility of the marker compound can be benchmarked in several ways. The normal boiling point of the marker compound is oftentimes set as the threshold for a VOC. Molecules with higher normal boiling points than the marker compound are not VOC's while molecules with lower normal boiling points than the marker compound are VOC's. This system of VOC definition is in use within the EU. The EU threshold for definition as a VOC is a normal boiling point below 250 ^{o}C as defined within ISO 11890 documentation.

One subtlety in using the normal boiling point as a basis for a threshold definition of a VOC is the possibility of changes in the relative volatility of two different molecules at different temperatures. The assumption that differences in the normal boiling point of two materials accurately reflect the relative volatility of two molecules at all temperatures is based on the assumption of a vapor pressure versus temperature behavior as represented in Graph 3 below.



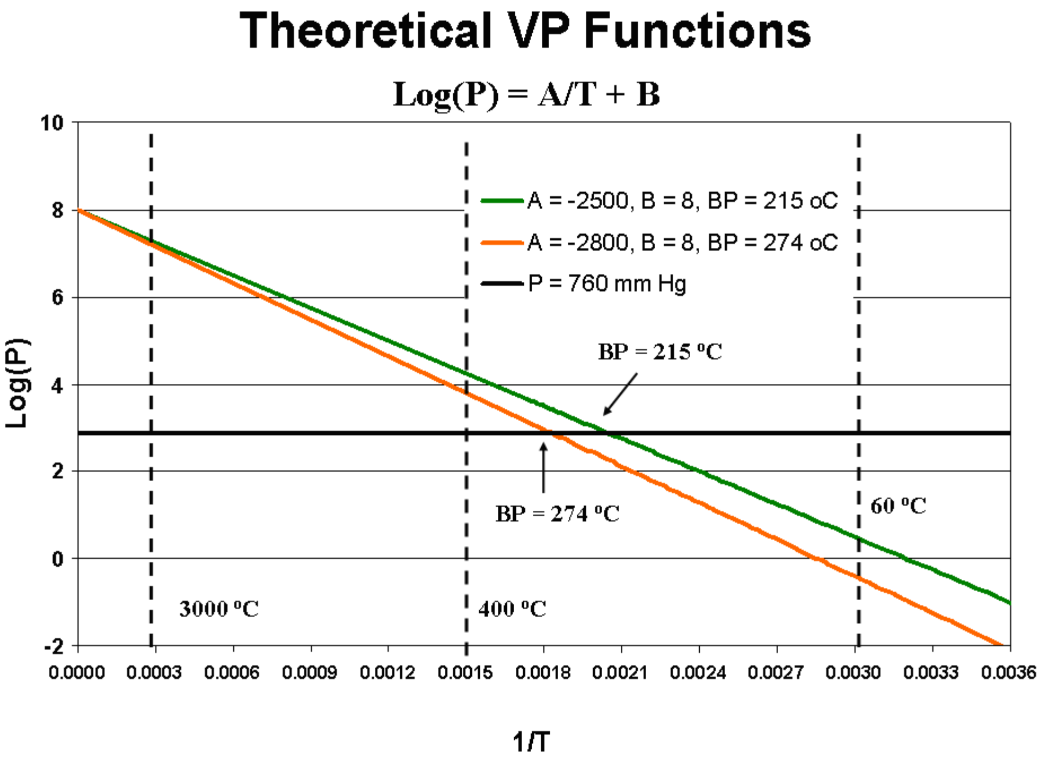
Graph 3: Two molecules with identical enthalpies of vaporization but different y-intercepts (entropy of vaporization at P = 1, nominal log of VP at infinite T). The relative volatility of these two materials remains constant with T.

The relative volatility of two molecules “M” & “N” can be defined as the ratio of their vapor pressures at a given T, and this ratio is constant at any given temperature when M (green line) & N (orange line) behave as shown Graph 3. In Graph 3, the quantity log(VP of M) minus log(VP of N) is a constant. Thus, the ratio of the vapor pressure of M to the vapor pressure of N is a constant at all temperatures.

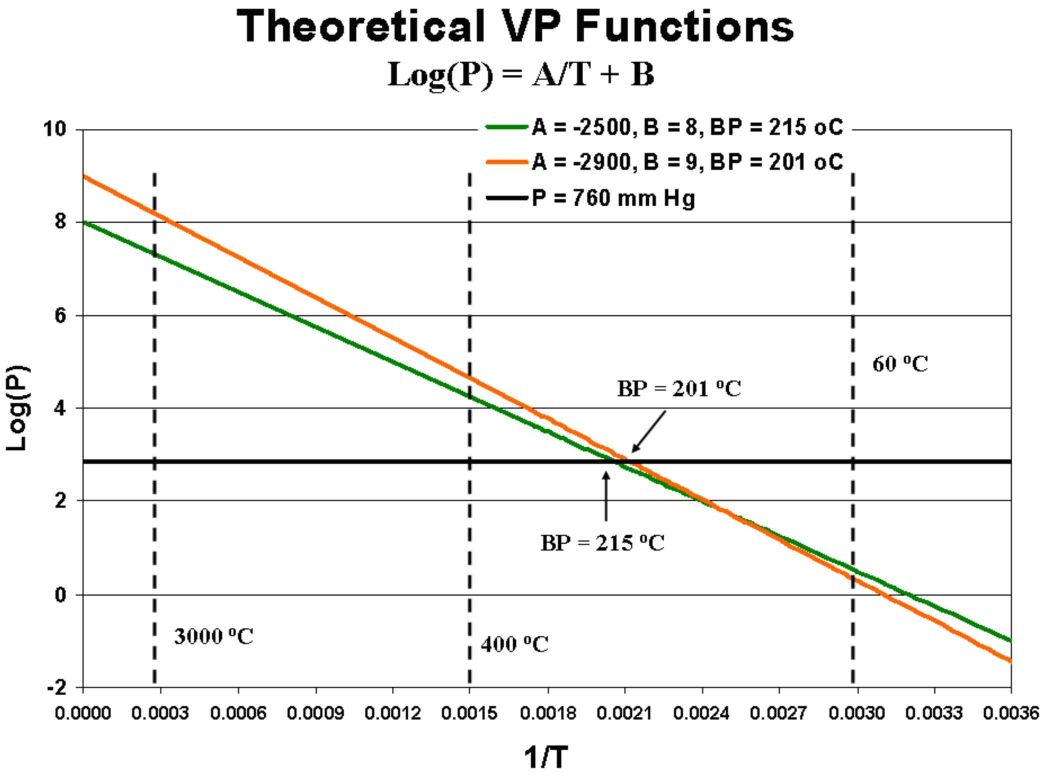
$$\log(\text{VP of N}) - \log(\text{VP of M}) = \text{constant}$$

$$\text{Ratio of VP of M/N} = 10^{\log(\text{VP of M})}/10^{\log(\text{VP of N})} = 10^{\{\log(\text{VP of N}) - \log(\text{VP of M})\}} = 10^{\text{constant}} = \text{constant}$$

However, it is likely that the ideal behavior shown in Graph 3 is not observed at all temperatures, and vapor pressure versus temperature profiles such as those shown in Graph 4 & Graph 5 below are equally likely to occur. In Graph 4, the difference in relative volatility (vapor pressure) of “M” (green line) and “N” (orange line) increases as the temperature is decreased (movement to the right on the 1/T axis). In Graph 5, the relative volatility (vapor pressure) of “M” (green line) and “N” (orange line) inverts at a temperature slightly lower than the normal boiling point. In general, the relative volatility of two pure materials will not remain the same at all temperatures, and relative volatility data (*e.g.*, ratio of vapor pressures) collected at high temperatures does not necessarily indicate the relative volatility of the materials at RT (room temperature).



Graph 4: The vapor pressure versus temperature profile for two molecules with identical y-intercepts (entropy of vaporization at P = 1) but different enthalpies of vaporization. The difference in volatility at the normal boiling point becomes more pronounced at lower temperatures.



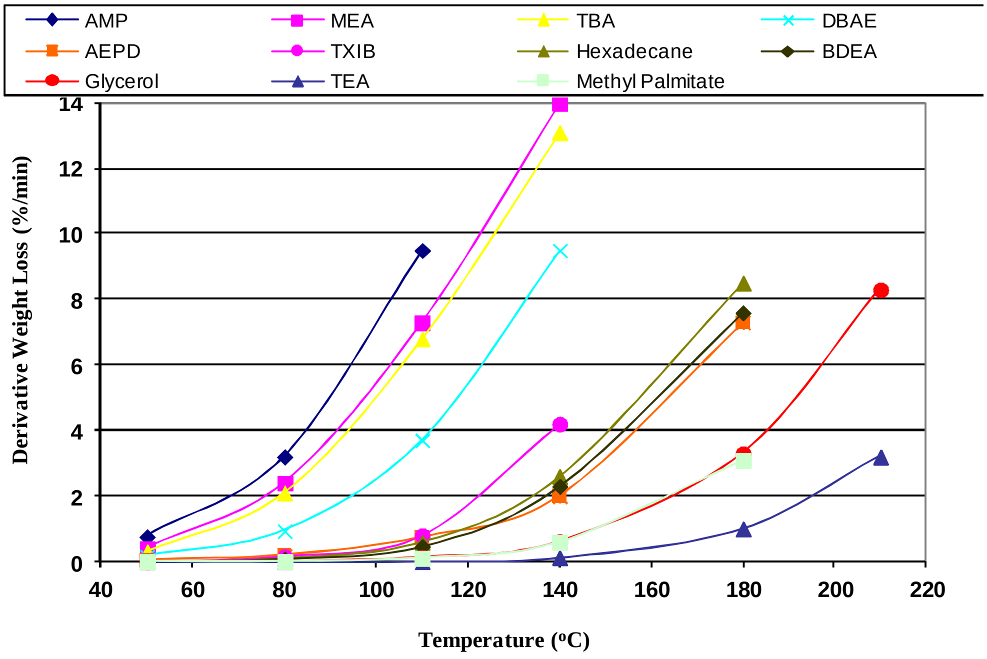
Graph 5: The vapor pressure versus temperature profile for two molecules with different y-intercepts (nominal log of vapor pressure @ infinite T) and different enthalpies of vaporization. The relative volatility at the normal boiling point can invert at lower temperatures.

Relative Volatility Measurements by Isothermal TGA:

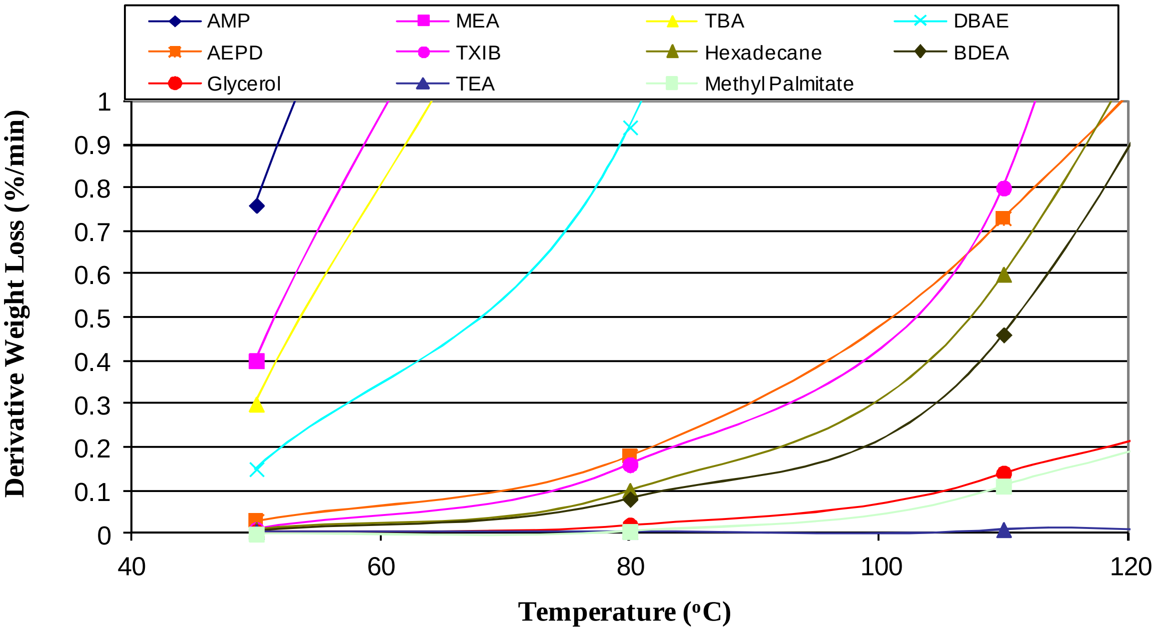
The effect of temperature on the relative volatility of materials can be demonstrated by experiment. Thermal gravimetric analysis is used to accurately and precisely determine the loss of weight from a given material at a given temperature under standard conditions of gas purge flow. Table 4 below presents derivative weight loss values for a number of pure materials of interest in coatings. The derivative weight loss values were determined as a function of temperature over the range from 50 °C – 210 °C. The derivative weight loss (dW/dt, taken as percent weight loss per minute) was recorded after 1.25% (≈ 0.5 mg from 40 mg) of the material had evaporated from the sample. The time it took to reach the point where the derivative weight loss was taken is given in minutes below the derivative weight loss value. Details are given in the experimental section. The derivative weight loss data as a function of temperature collated in Table 4 is also presented in Graph 6. The derivative weight loss curves generally array themselves in proportion to their normal boiling points. An expansion of Graph 6 is given in Graph 7. It can be seen in Graph 7 that a significant number of "inversions" in relative volatility occur between room temperature and the normal boiling point of high boiling liquids. An inversion is defined as a point where the relative volatility of two materials inverts; that is to say that the material which was less volatile at higher temperatures becomes more volatile at lower temperature.

Compound	dW/dt @ 50 °C	dW/dt @ 80 °C	dW/dt @ 110 °C	dW/dt @ 140 °C	dW/dt @ 180 °C	dW/dt @ 210 °C	Normal BP
Methyl Palmitate	ND	0.005 >180 min	0.11 (12 min)	0.6 2.2 min	3.1 0.4 min	-	330 °C
TEA	0.005 180 min	0.005 150 min	0.01 60 min	0.12 9 min	1.0 1 min	3.2 0.5 min	335 °C
Glycerol	0.005 180 min	0.02 37 min	0.14 6 min	0.62 2 min	3.3 0.4 min	8.3 0.1 min	290 °C
BDEA	0.005 180 min	0.08 14 min	0.46 2 min	2.3 0.5 min	7.6 0.1 min	-	285 °C
2-methylhexadecane	0.007 130 minutes	0.10 11.5 min	0.64 2 min	2.4 0.5 min	7.3 0.2 min	-	294 °C
Hexadecane	0.01 120 min	0.10 14 min	0.62 2 min	2.6 0.5 min	8.5 0.1 min	-	285 °C
TXIB	0.01 80 min	0.16 6 min	0.80 1 min	4.2 0.4 min	-	-	280 °C
AEPD	0.03 40 min	0.18 6 min	0.73 1.7 min	2.0 0.6 min	7.3 0.2 min	-	260 °C
DBAE	0.15 8 min	0.94 1.3 min	3.7 0.33 min	9.5 0.1 min	-	-	230 °C
TBA	0.3 3 min	2.1 0.6 min	6.8 0.2 min	13.1 0.1 min	-	-	215 °C
MEA	0.40 3 min	2.4 0.5 min	7.4 0.2 min	14 0.1 min	-	-	170 °C
AMP	0.76 1.6 min	3.2 0.4 min	9.5 0.1 min	-	-	-	165 °C

Table 4: The derivative weight loss (% weight loss per minute) of 12 compounds at different temperatures after 1.25% (≈ 40 mg total weight, 0.5 mg weight loss) of material evaporated with nitrogen purge. The time in minutes at which the derivative weight loss was taken is given below the weight loss value. A dash indicates evaporation occurred too quickly to measure, ND = "not detectable". The normal boiling point is rounded to the nearest 5 °C.

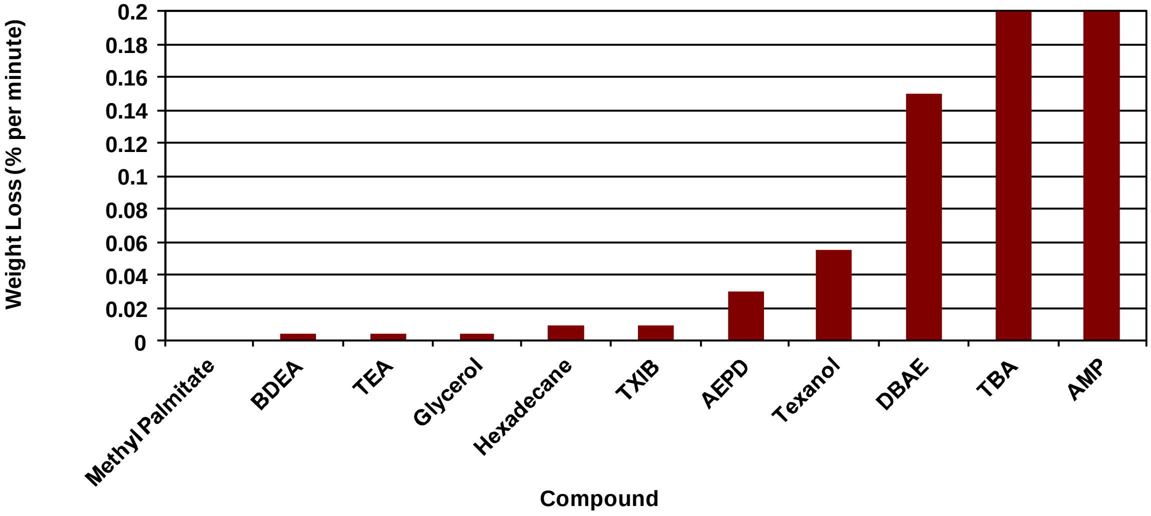


Graph 6: Derivative Weight Loss (DWL) as a function of temperature for some compounds of interest in coatings.



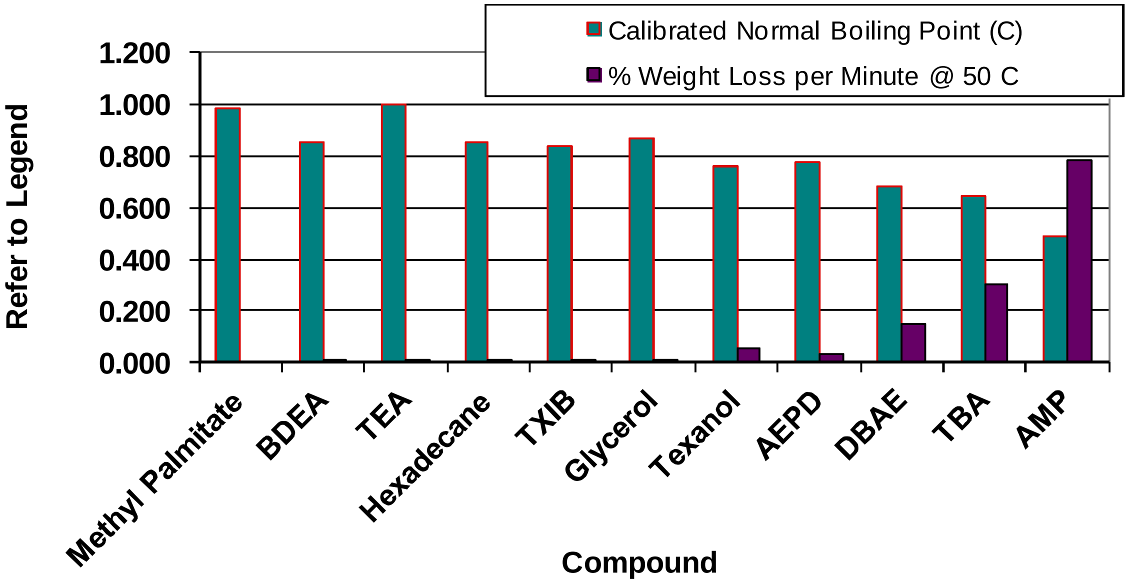
Graph 7: Expansion of Derivative Weight Loss (DWL) as a function of temperature graph for some compounds of interest in coatings. Inversions in relative volatility are evident.

The derivative weight loss at 50 ^{o}C is shown as a bar chart in Graph 8 below.



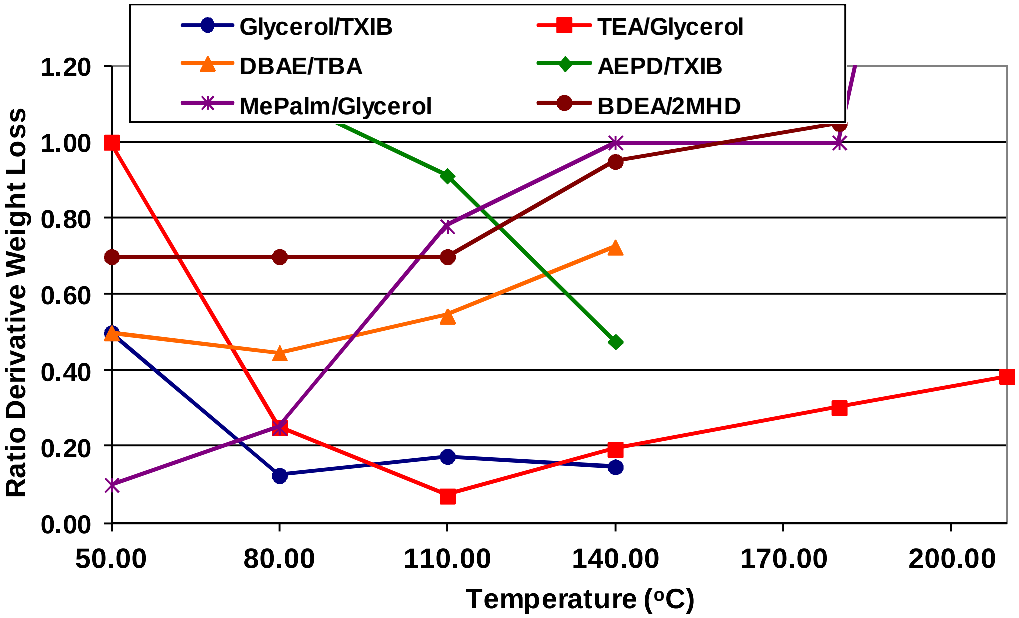
Graph 8: The derivative weight loss after 1.25% evaporation of 11 compounds of interest in coatings at 50 ^{o}C.

A bar plot showing the derivative weight loss at 50 ^{o}C alongside the calibrated normal boiling point (normal boiling point divided by the highest value in the set; 335 ^{o}C) is given below in Graph 10:



Graph 10: Derivative weight loss at 50 ^{o}C plotted alongside the calibrated normal point (normal boiling point divided by the highest value in the set; 335 ^{o}C).

It can be seen from Graph 10 that there is a rough correlation between normal boiling point and derivative weight loss at temperatures significantly lower than the boiling point, but the trend is not absolute. The relative volatility of two molecules at a given temperature can be defined as the ratio of their derivative weight loss under some set of standard TGA conditions at that temperature. By this definition, the relative volatility of some pairs of molecules chosen arbitrarily from Table 4 are presented in Graph 11 below.



Graph 11: Ratio of derivative weight loss (% weight per minute) versus T for six pairs of compounds from Table 3.

Note that lines which pass through a ratio value of 1.0 show inverted volatility. The summation of a large amount of data demonstrates that relative volatility comparisons should be carried out at a temperature as close to the use temperature of interest (*e.g.*, the temperature at which the coating is dried/cured; usually room temperature) as is experimentally possible. Note that discrepancies between high temperature assessments of volatility and vapor pressure at lower temperatures have been described previously: Nielsen, C.; Hogh, B.; Wallstrom, E.; "VOC or not: Determination of an Important Environmental Parameter" *Surface Coatings International (Journal of Oil & Colour Chemists Association)*, **1997**, *80(10)*, 467-472.

Use of Gas Chromatography as a Measurement of Volatility:

Given the difficulty associated with vapor pressure measurements at low temperature and the ubiquitous use of high T volatility (*e.g.*, normal boiling points) as a benchmark for volatility at RT, other methods of volatility assessment can be considered. Gas chromatography (GC) is a form of gas/liquid chromatography wherein a mixture is analyzed by injecting it as a gas into a column which is placed in a temperature controlled oven. The components of the mixture partition between a liquid stationary phase and the gas phase as they are pushed through the column by an inert carrier gas. An appropriate temperature program is applied to the oven based on the expected relative volatility of components of the mixture. The materials are quantified as they exit the column using a number of detection techniques (*e.g.*, FID, TCD, TEA, *etc.*). A schematic view of a gas chromatograph is given below in Figure 1:

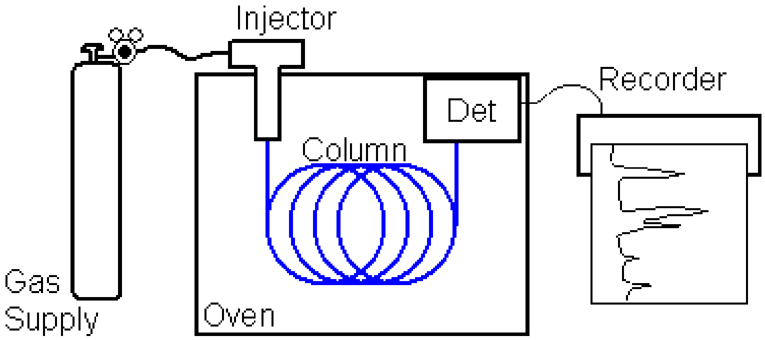
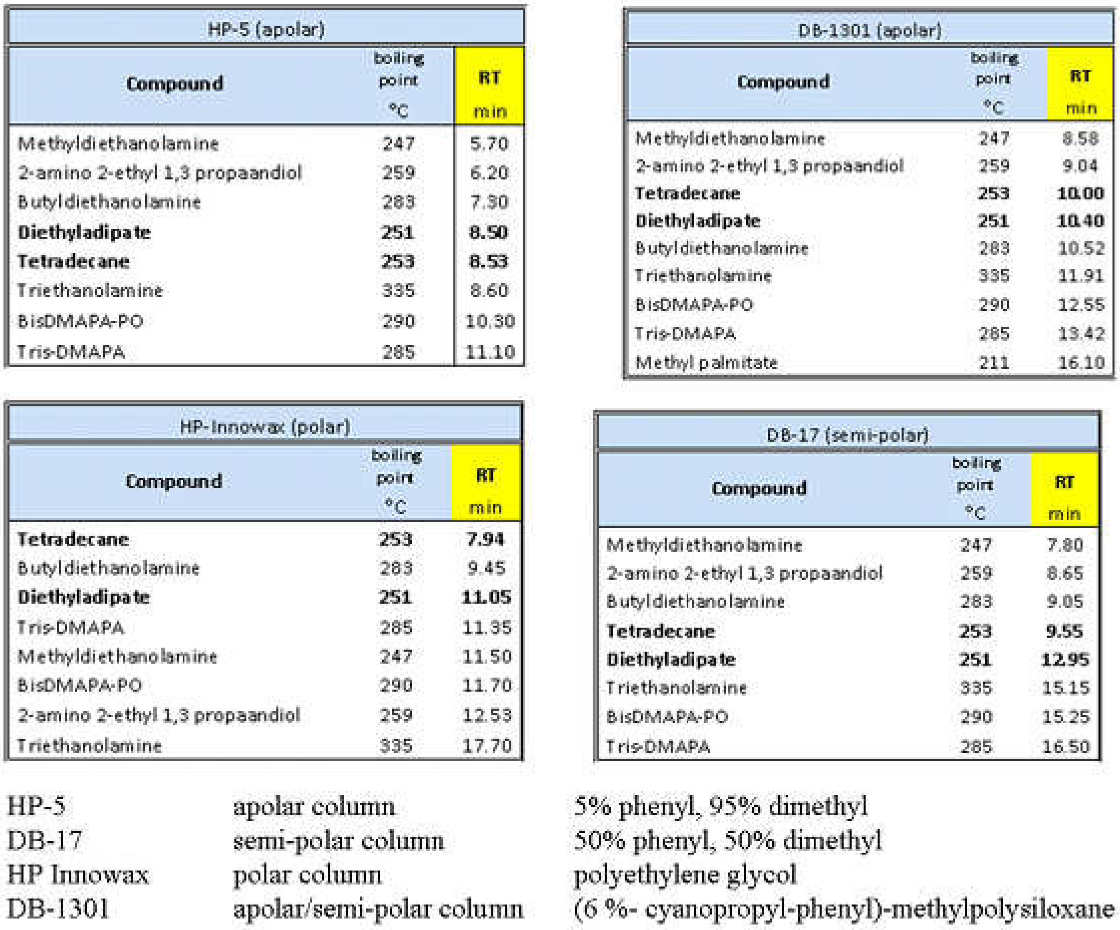


Figure 1: Schematic view of a gas chromatograph.

The inverse of the retention time (*i.e.*, time it takes for a material to pass through the column from injection to detection) of a material on a given column with a given temperature program can be roughly correlated with the volatility of the material. The GC technique is mostly used to separate and quantify the components of an unknown mixture, but the retention times of differing components within a mixture can be roughly correlated with their relative volatility for the average temperature at which the thermal program was run. See, for instance, US patent 5,808,180 wherein GC retention times measured with a standardized thermal program are used to correlate with the normal boiling points of a series of homologous hydrocarbons. GC is marginally useful for the determination of relative volatility in a series of related homologous compounds, but comparison of GC retention times for different types of compounds of differing polarity is not useful. The retention times observed for eight high boiling materials on four different columns are given below in Figure 2:



HP-5 (apolar)

Compound	boiling point °C	RT min
Methyldiethanolamine	247	5.70
2-amino 2-ethyl 1,3 propaandiol	259	6.20
Butyldiethanolamine	283	7.30
Diethyladipate	**251**	**8.50**
Tetradecane	**253**	**8.53**
Triethanolamine	335	8.60
BisDMAPA-PO	290	10.30
Tris-DMAPA	285	11.10

DB-1301 (apolar)

Compound	boiling point °C	RT min
Methyldiethanolamine	247	8.58
2-amino 2-ethyl 1,3 propaandiol	259	9.04
Tetradecane	**253**	**10.00**
Diethyladipate	**251**	**10.40**
Butyldiethanolamine	283	10.52
Triethanolamine	335	11.91
BisDMAPA-PO	290	12.55
Tris-DMAPA	285	13.42
Methyl palmitate	211	16.10

HP-Innowax (polar)

Compound	boiling point °C	RT min
Tetradecane	**253**	**7.94**
Butyldiethanolamine	283	9.45
Diethyladipate	**251**	**11.05**
Tris-DMAPA	285	11.35
Methyldiethanolamine	247	11.50
BisDMAPA-PO	290	11.70
2-amino 2-ethyl 1,3 propaandiol	259	12.53
Triethanolamine	335	17.70

DB-17 (semi-polar)

Compound	boiling point °C	RT min
Methyldiethanolamine	247	7.80
2-amino 2-ethyl 1,3 propaandiol	259	8.65
Butyldiethanolamine	283	9.05
Tetradecane	**253**	**9.55**
Diethyladipate	**251**	**12.95**
Triethanolamine	335	15.15
BisDMAPA-PO	290	15.25
Tris-DMAPA	285	16.50

HP-5	apolar column	5% phenyl, 95% dimethyl
DB-17	semi-polar column	50% phenyl, 50% dimethyl
HP Innowax	polar column	polyethylene glycol
DB-1301	apolar/semi-polar column	(6 %- cyanopropyl-phenyl)-methylpolysiloxane

Figure 2: The GC retention time in minutes for eight high boiling materials. Split injection; injector temperature = 250 ^{o}C; injection volume 0.2 µl; split ratio = 1/100; column as specified at 30 m length, 320 µm diameter and 0.25 µm film thickness; He carrier gas, column flow = 2 ml/min; oven program is 60 ^{o}C for 1 minute followed by 15 ^{o}C per minute to 325 ^{o}C followed by 20 minutes at 325 ^{o}C; FID T – 325 oC with 30 ml/min hydrogen and 300 ml/min air; make + column flow = 30 ml/minute.

One significant uncertainty in the use of GC retention time as a measure of volatility is the effect of poor GC peak shape. The GC peak for triethanolamine is given in Figure 3 below:

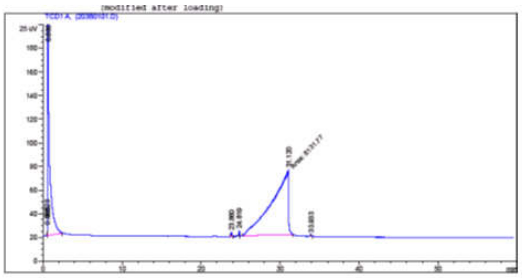
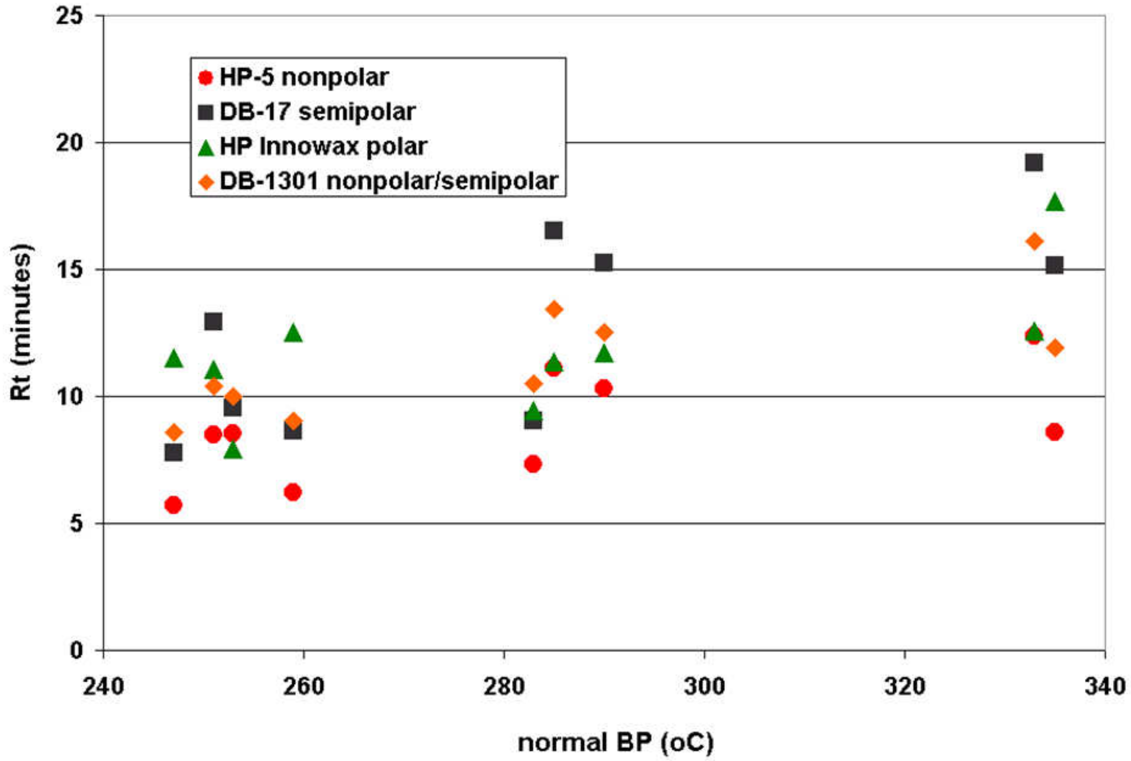


Figure 3: The GC peak shape for triethanolamine. There is a significant degree of uncertainty in setting an exact retention time when the GC peak has a poorly defined shape.

The retention times given in Figure 2 are plotted versus reported normal boiling point in Graph 12 below. It can be seen that disparate types of molecules display little universal correlation between measured GC retention time and normal boiling point.



Graph 12: The retention times of eight compounds on four different GC columns arrayed versus the reported normal boiling points of the compounds.

The Chamber Test Evaluation of Volatility:

The most direct measurement of the RT volatility of the components of a liquid thin film (*e.g.*, a freshly applied coating) is the Chamber Test. The Chamber Test employs GC analysis of the sorbent concentrated components present in the ambient atmosphere above a specified amount of a liquid coating applied as a thin film within a sealed chamber. The results of Chamber Tests are typically reported as emission factors with units of micrograms per square meter per hour. The emission factor is calculated from the chamber concentration at a given time according to the equation EF = (CC/L)ACR with CC = chamber concentration; L = loading; ACR = air change rate. The results of Chamber Testing are oftentimes used with emission decay models to predict the level of coatings components that will be present in the breathing atmosphere near a newly coated wall/surface at longer time intervals. The best aspect of the Chamber Test is that it quantifies the actual concentration of airborne components above a drying/curing coating at various time intervals. When run correctly, the Chamber Test is the most accurate assessment of true RT volatility. The Chamber Test can be used to assess the volatility profile of an individual additive. For the Chamber test to be used to assess individual component volatility, one simply quantifies the amount of the additive in question in the atmosphere above the paint at different appropriate time intervals. For example, the VOC status of a AAA (n-alkylalkanolamine) can be assessed by the Chamber Test. Table 6 and 7 below presents Chamber Test results for two paints, described in Table 5, which were subjected to Chamber Testing at 150 grams paint applied per square meter.

Component (Acrylic Resin Based paint)	**Pounds per 100 Gallons**	**Pounds per 100 Gallons**
R-746 TiO_2 (Dupont, pigment)	349.8	349.8
Tamol 731A (Dow; dispersant)	7.5	7.5
BYK 348 (Byk, silicone surfactant)	1.0	1.0
Tego Foamex 810 (Evonik; defoamer)	0.5	0.5
Kathon LX 1.5% (Dow, biocide)	1.6	1.6
Grind		
Water	20.9	20.9
RHOPLEX VSR 2015 (Dow; resin)	524.2	524.2
Vantex T (Taminco, AAA)	**2.0**	
DMAE (Taminco, AAA)		**2.0**
BYK 348 (as above)	1.0	1.0
Tego Foamex 810 (as above)	0.5	0.5
Acrysol RM 2020NPR (Dow; thickener)	30.5	30.5
Acrysol RM 8W (Dow; thickener)	4.3	4.3
Water	121.3	121.3
Total Weight	1065.1	1065.1
pH	8.9	9.4
Density, lbs. / gallon	10.6	10.6
PVC = 22.2%; VS = 36.0%; VOC = 0 g/L		

Component (VAE Resin Based Paint)	**Pounds per 100 Gallons**	**Pounds per 100 Gallons**
Water	250.0	250.0
Natrosol Plus 330 (Aqualon, thickener)	2.5	2.5
Vantex T (Taminco, AAA)	**6.0**	
DMAE (Taminco, AAA)		**6.0**
Acticide BW 20 (Thor; biocide)	1.1	1.1
FoamStar A-38 (Cognis; defoamer)	1.5	1.5
Tamol 1124 (Dow; dispersant)	3.0	3.0
Carbowet DC01 (APCI, surfactant)	2.0	2.0
Mix		
Tronox CR 826 (Tronox, TiO_2)	250.0	250.0
Camel White (pigment)	25.0	25.0
Burgess No. 28 (Burgess, pigment)	50.0	50.0
Grind		
Water	73.1	73.1
Eco VAE 401 (Celanese Resin)	408.0	408.0
Polyphobe TR 117 (Coatex, thickener)	25.0	25.0
FoamStar A-38 (above)	2.0	2.0
Total Weight	1099.2	1099.2
pH	8.4	9.3
Density, lbs. / gallon	11.0	11.0
PVC = 31.6%; VS = 36.4%; VOC < 2 g/L		

Table 5: Two low VOC paint formulas (one acrylic resin based and one VAE resin based) used for Chamber Testing of paint VOC content. The two paints differ with respect to their formulas and each was made up with two different pH neutralizing AAA's. DMAE is N,N-dimethylaminoethanol. Vantex-T is BDEA (butyldiethanolamine), a zero VOC AAA sold by Taminco.

EMISSION FACTORS OF INDIVIDUAL VOLATILE ORGANIC COMPOUNDS (μg/m²•hr)

CAS RN	Chemical ID	Vantex T - Acrylic	DMAE - Acrylic
Total	TVOC	254.1	270.5
119-61-9	Benzophenone	155.6	157
142-96-1	n-Butyl ether	33	28.1
112-34-5	Ethanol, 2-(2-butoxyethoxy)	16.5	18.6
141-62-8	Tetrasiloxane, decamethyl	8.5	9.4
141-63-9	Pentasiloxane, dodecamethyl	6.8	6.9
590-01-2	Butyl propionate	6.2	4.6
7299-91-4	2-Butenoic acid, butyl ester	4.6	4.8
25551-13-7	Trimethylbenzene (All Isomers)	4.2	5.2
100-52-7	Benzaldehyde	4	2.2
107-51-7	Trisiloxane, octamethyl	3.5	3.6
107-52-8	Hexasiloxane, tetradecamethyl	3.3	3.6
112-30-1	1-Decanol (N-Decyl alcohol)	3	3.3
112-31-2	Decanal	2.7	2.2
123-86-4	Acetate, butyl	2.2	-
108-01-0	DMAE	-	19.1
541-01-5	Heptasiloxane, hexadecamethyl-	-	1.9

Table 6: The results of Chamber Test analysis of the acrylic resin based paints described in Table 5; applied at 150 grams per square meter with the emission factor taken at 24 hours.

EMISSION FACTORS OF INDIVIDUAL VOLATILE ORGANIC COMPOUNDS (μg/m²•hr) (VAE Resin based Paint)

CAS NUMBER	**COMPOUND IDENTIFIED**	**ELAPSED EXPOSURE HOUR**			
		6	**24**	**72**	**168**
104-76-7	1-Hexanol, 2-ethyl†	120	13.2	3.4	1.2
1653-40-3	1-Heptanol, 6-methyl*	47.7	4.8	1.2	
57-55-6	1,2-Propanediol (Propylene glycol)†	22.8	2.1		
26952-21-6	Isooctanol*	15.8	1.4		
57803-73-3	(S)-(+)-5-Methyl-1-heptanol*	9.3			
1120-21-4	Undecane†	8.0	1.7		
110-49-6	Ethanol, 2-methoxy, acetate†	7.8			
71-36-3	1-Butanol (N-Butyl alcohol)†	7.3	3.0	1.7	1.0
556-67-2	Cyclotetrasiloxane, octamethyl†	6.1	1.6		
112-31-2	Decanal†	4.9	0.9		1.2
107-21-1	1,2-Ethanediol (Ethylene glycol)†	4.9			
541-02-6	Cyclopentasiloxane, decamethyl†	4.6	1.3		
821-98-7	4-Undecene, (Z)-*	4.5			
124-18-5	Decane†	4.3			
112-44-7	Undecanal*	4.0	1.1		
629-50-5	Tridecane†	3.8			
126-86-3	2,4,7,9-Tetramethyl-5-decyn-4,7-diol	3.6	8.3	9.5	7.9
55956-25-7	2-Propanol, 1-[1-methyl-2-(2-propenyloxy)ethoxy]*	3.6			
112-54-9	Dodecanal*	3.5	1.4		

CAS NUMBER	**COMPOUND IDENTIFIED**	**ELAPSED EXPOSURE HOUR**			
		6	**24**	**72**	**168**
124-19-6	Nonyl aldehyde (Nonanal)†	3.5	1.0		1.2
470-99-5	2-Cyclohexen-1-ol, 3,5,5-trimethyl*	2.9			
66-25-1	Hexanal†	2.8	1.9		
141-78-6	Acetate, ethyl	2.7			
111-87-5	1-Octanol	2.6			
112-40-3	Dodecane†	2.4			
109-02-4	Morpholine, 4-methyl*	2.3			
124-13-0	Octanal†	1.8			
112-70-9	1-Tridecanol	1.7	1.2		
112-30-1	1-Decanol (N-Decyl alcohol)	1.7			
143-08-8	1-Nonanol	1.6			
2311-46-8	Hexanoic acid, 1-methylethyl ester*	1.5			
112-41-4	1-Dodecene	1.4			
100-52-7	Benzaldehyde	1.3			
111-71-7	Heptanal (Heptaldehyde)†	1.3			
21460-36-6	2-Propanol, 1-(2-propenyloxy)-*	1.3			
6434-76-0	6-Tridecene, (E)-*	1.3			
142-82-5	Heptane	1.1			
6175-49-1	2-Dodecanone*	1.1			
821-95-4	1-Undecene	1.1			
61142-79-8	1-Decene, 8-methyl-*	1.0			
629-59-4	Tetradecane†	1.0			
629-62-9	Pentadecane	1.0			
3970-62-5	3-Pentanol, 2,2-dimethyl	0.9			

Table 7: The results of Chamber Test analysis of the VAE resin based paint containing vantex-T as described in Table 5 applied at 150 grams per square meter with the emission factors taken at 6, 24, 72 and 168 hours. *Indicates NIST/EPA/NIH best library match only based on retention time and mass spectral characteristics. †Denotes quantified using multipoint authentic standard curve. Other VOCs quantified relative to toluene. Quantifiable level is 0.02 µg based on a standard 18 L air collection volume.

A compliance summary for the VAE based paint as determined by Chamber Testing is given below in Table 8:

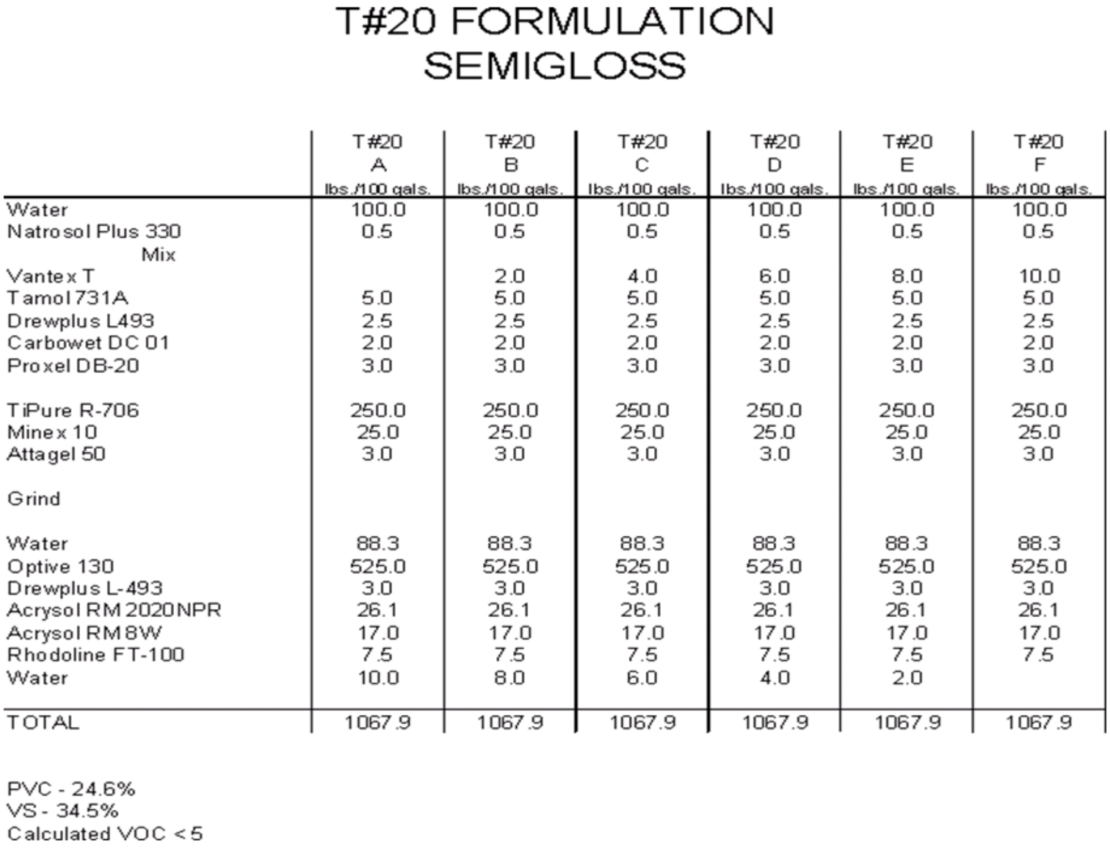
Analysis	AgBB Requirements	Measured Value	Complies? (Y/N)
TVOC	≤ 10 mg/m³ (3 days) ≤ 1.0 mg/m³ (7 days)	0.029 mg/m³ (3 days) 0.020 mg/m³ (7 days)	Y Y
Carcinogenic Compounds	Carcinogenic VOCs of EU cat. 1 and 2 ≤ 0.01 mg/m³ (3 days) Carcinogenic VOCs of EU cat. 1 and 2 ≤ 0.001 mg/m³ 7 days)	none (3 days) none (7 days)	Y Y
R Value	≤1 (7 days)	0.007	Y
TSVOC	≤ 0.1 mg/m³ (7 days)	< 0.002 mg/m³	Y

Table 8: Compliance summary for the VAE resin based paint listed in Table 5.

The results of Chamber Testing sometimes reveal unexpected compounds in the ambient atmosphere above paint. An unexpected finding is illustrated by the presence of significant amounts of benzophenone in the ambient atmosphere above the acrylic resin based paint listed in Table 5. In Table 6, the presence of DMAE and the absence of BDEA establishes the zero-VOC nature of Vantex®-T (BDEA). In Table 7, the absence of BDEA at all sample times further establishes the zero VOC nature of this AAA.

Controlled Evaporation in an Oven as an Assessment of Volatility:

Methods based on EPA Method 24 are, in fact, crude TGA based methods. The set temperature is a constant 110 °C. The purge is turbulent air flow as is set up in an ASTM 111 type fanned oven. Weight loss from a 0.5 gram sample after 1 hour is the TGA benchmark. The use of EPA Method 24 inspired VOC assessments can be problematic for the measurement of low VOC levels. The accuracy of oven evaporation based measurement is generally not sufficient for VOC levels less than ≈ 50 grams per liter. An alternative to a single Method 24 based VOC determination is the use of sequential additive dosing. In this technique, the additive of interest is added to the paint at levels of 0%, 50%, 100%, 150%, 200% and 250% of the normal level. An oven evaporation based determination of VOC is carried out on all six paints and a trendline is established. The results of two sequential addition assessments carried out on the series of paint formulas listed in Tables 9 & 10 is summarized in Table 11 below.

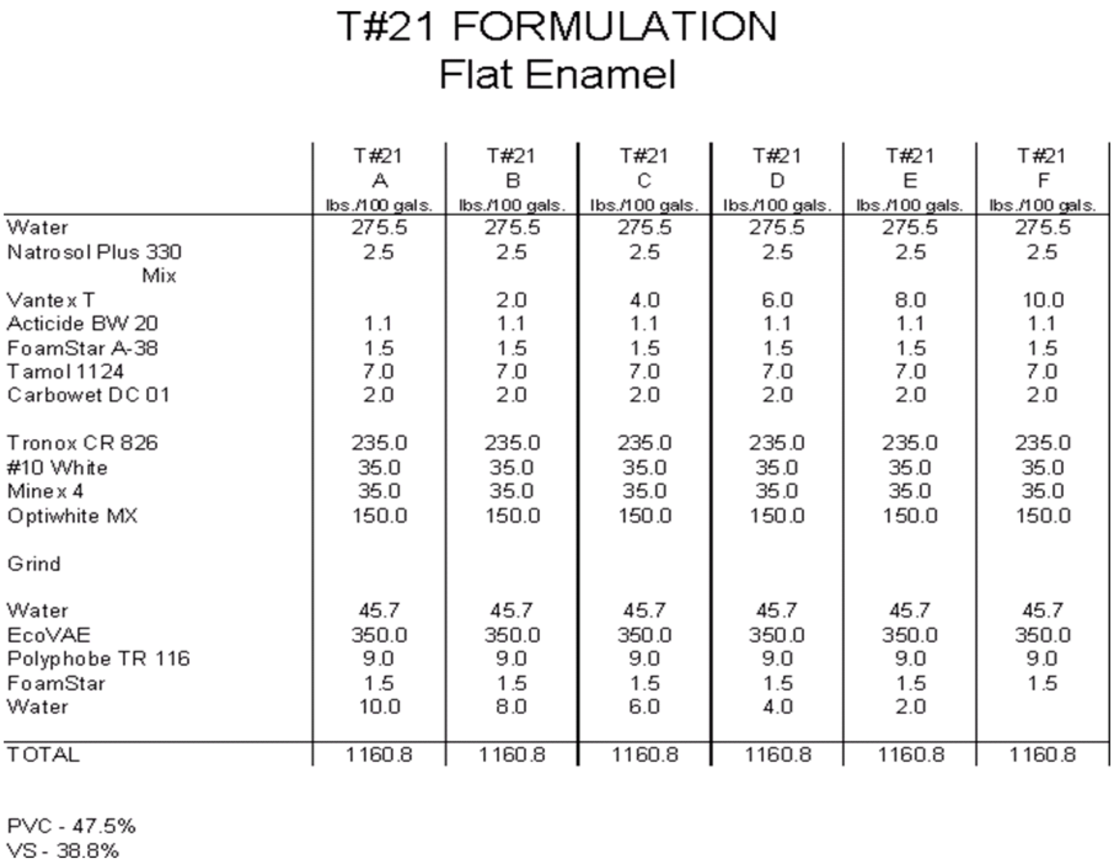


T#20 FORMULATION
SEMIGLOSS

	T#20 A lbs./100 gals.	T#20 B lbs./100 gals.	T#20 C lbs./100 gals.	T#20 D lbs./100 gals.	T#20 E lbs./100 gals.	T#20 F lbs./100 gals.
Water	100.0	100.0	100.0	100.0	100.0	100.0
Natrosol Plus 330	0.5	0.5	0.5	0.5	0.5	0.5
Mix						
Vantex T		2.0	4.0	6.0	8.0	10.0
Tamol 731A	5.0	5.0	5.0	5.0	5.0	5.0
Drewplus L493	2.5	2.5	2.5	2.5	2.5	2.5
Carbowet DC 01	2.0	2.0	2.0	2.0	2.0	2.0
Proxel DB-20	3.0	3.0	3.0	3.0	3.0	3.0
TiPure R-706	250.0	250.0	250.0	250.0	250.0	250.0
Minex 10	25.0	25.0	25.0	25.0	25.0	25.0
Attagel 50	3.0	3.0	3.0	3.0	3.0	3.0
Grind						
Water	88.3	88.3	88.3	88.3	88.3	88.3
Optive 130	525.0	525.0	525.0	525.0	525.0	525.0
Drewplus L-493	3.0	3.0	3.0	3.0	3.0	3.0
Acrysol RM 2020NPR	26.1	26.1	26.1	26.1	26.1	26.1
Acrysol RM 8W	17.0	17.0	17.0	17.0	17.0	17.0
Rhodoline FT-100	7.5	7.5	7.5	7.5	7.5	7.5
Water	10.0	8.0	6.0	4.0	2.0	
TOTAL	1067.9	1067.9	1067.9	1067.9	1067.9	1067.9

PVC - 24.6%
VS - 34.5%
Calculated VOC < 5

Table 9: Six sequential SA resin based paint formulas used for sequential addition VOC analysis by oven evaporation.

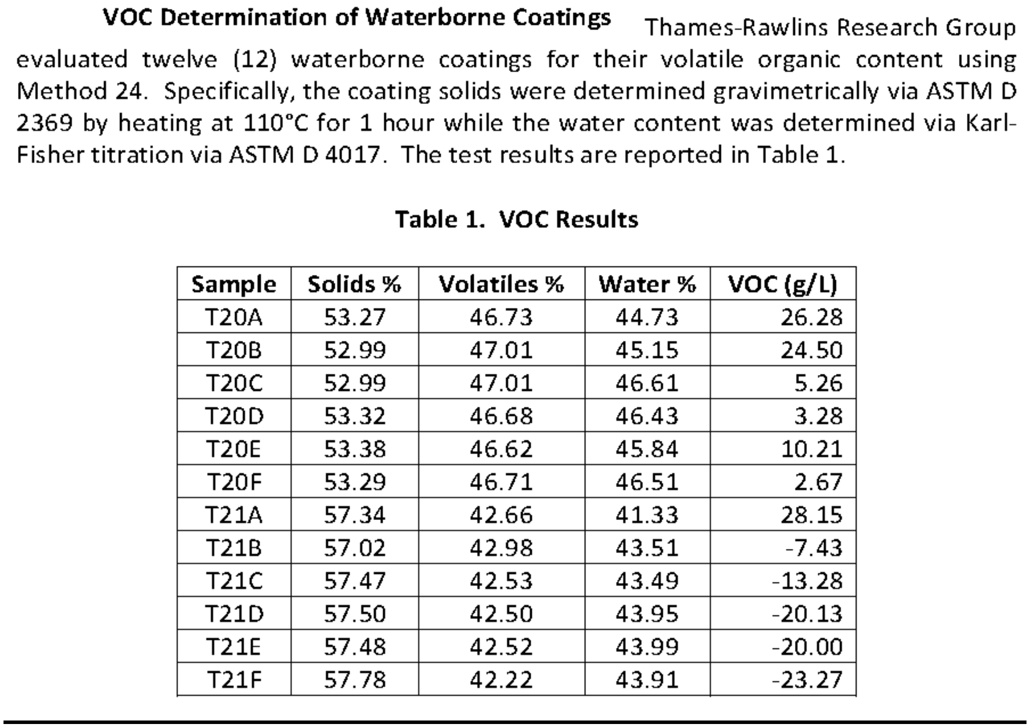


T#21 FORMULATION
Flat Enamel

	T#21 A lbs./100 gals.	T#21 B lbs./100 gals.	T#21 C lbs./100 gals.	T#21 D lbs./100 gals.	T#21 E lbs./100 gals.	T#21 F lbs./100 gals.
Water	275.5	275.5	275.5	275.5	275.5	275.5
Natrosol Plus 330	2.5	2.5	2.5	2.5	2.5	2.5
Mix						
Vantex T		2.0	4.0	6.0	8.0	10.0
Acticide BW 20	1.1	1.1	1.1	1.1	1.1	1.1
FoamStar A-38	1.5	1.5	1.5	1.5	1.5	1.5
Tamol 1124	7.0	7.0	7.0	7.0	7.0	7.0
Carbowet DC 01	2.0	2.0	2.0	2.0	2.0	2.0
Tronox CR 826	235.0	235.0	235.0	235.0	235.0	235.0
#10 White	35.0	35.0	35.0	35.0	35.0	35.0
Minex 4	35.0	35.0	35.0	35.0	35.0	35.0
Optiwhite MX	150.0	150.0	150.0	150.0	150.0	150.0
Grind						
Water	45.7	45.7	45.7	45.7	45.7	45.7
EcoVAE	350.0	350.0	350.0	350.0	350.0	350.0
Polyphobe TR 116	9.0	9.0	9.0	9.0	9.0	9.0
FoamStar	1.5	1.5	1.5	1.5	1.5	1.5
Water	10.0	8.0	6.0	4.0	2.0	
TOTAL	1160.8	1160.8	1160.8	1160.8	1160.8	1160.8

PVC - 47.5%
VS - 38.8%

Table 10: Six sequential VAE resin based paint formulas used for sequential addition VOC analysis by oven evaporation.



VOC Determination of Waterborne Coatings Thames-Rawlins Research Group evaluated twelve (12) waterborne coatings for their volatile organic content using Method 24. Specifically, the coating solids were determined gravimetrically via ASTM D 2369 by heating at 110°C for 1 hour while the water content was determined via Karl-Fisher titration via ASTM D 4017. The test results are reported in Table 1.

Table 1. VOC Results

Sample	Solids %	Volatiles %	Water %	VOC (g/L)
T20A	53.27	46.73	44.73	26.28
T20B	52.99	47.01	45.15	24.50
T20C	52.99	47.01	46.61	5.26
T20D	53.32	46.68	46.43	3.28
T20E	53.38	46.62	45.84	10.21
T20F	53.29	46.71	46.51	2.67
T21A	57.34	42.66	41.33	28.15
T21B	57.02	42.98	43.51	-7.43
T21C	57.47	42.53	43.49	-13.28
T21D	57.50	42.50	43.95	-20.13
T21E	57.48	42.52	43.99	-20.00
T21F	57.78	42.22	43.91	-23.27

Table 11: The results of oven evaporation analysis of VOC for the two sets of paint formulas given in Tables 8 & 9.

Whereas individual oven evaporation analyses are prone to significant error, the overall trendline is more reliable. The results summarized in Table 9 clearly show that the additive under investigation, Vantex-T, does not contribute to the VOC content of either of the two paints.

Conclusions:

Even with an accurate two parameter fit of vapor pressure versus temperature, the RT relative volatility of high boiling molecules can't be fully assessed. Comparisons of normal boiling points, GC retention times and/or other measures of vapor pressure taken at relatively high temperature are not reliable for the prediction of relative volatility at room temperature (RT). The only reliable means of comparing the volatility of two materials within a given temperature range is to use instrument based thermal analysis methods operated within this temperature range. The simplest approach is to use weight loss comparisons measured by isothermal thermogravimetric analysis (TGA) at a temperature as close to the temperature of interest as is possible. Normal boiling points are a good high temperature volatility benchmark, but the establishment of a consistent normal BP takes some work. Distillation of materials at relatively high T/P results in continuous decomposition during the distillation, and thus the distillation temperature measured actually represents the vapor pressure of a mixture of the compound with its thermal degradation products. The Chamber Test is the best option for volatility at RT.

Appendices:

Appendix I - Detailed Derivation of the Two Parameter Fit of Vapor Pressure and T:

Starting with an equation of state:

$$dG = VdP - SdT \qquad \text{assume the ideal gas law: } PV = nRT \textbf{ @ constant T}$$

$$dG = VdP = \frac{nRT}{P}dP$$

$$\Delta G = nRT\ln(P_f/P_i)$$

$$G \text{ @ } P_f = G \text{ @ } P_i + nRT\ln(P_f/P_i)$$

assume $n = 1$ & G^{ϕ} refers to $P = 1$ (standard state)

$$G = G^{\phi} + RT\ln(P)$$

The use of the partial pressure of a gas can be generalized to the activity of a species n:

$$G = G^{\phi} + RT\ln(\text{activity of } n) = G^{\phi} + \lim(\, n \to 0) \text{ of } RT\ln[n] \approx G^{\phi} + RT\ln[n]$$

$$[n] = \text{concentration of } n$$

$$dG = VdP - SdT + \sum(\Delta \text{ amount of component})(\Delta \text{ free energy per unit amount of component})$$

Define the chemical potential of a species as:

$$(\partial G/\partial n)_{P,T} = \mu \qquad (\partial G/\partial n)_{P,T,\, n = 1} = \mu^{\phi}$$

$$\mu = \mu^{\phi} + RT\ln(a)$$

At constant T & P :

$$dG = \sum\{\mu^{\phi} + RT\ln(a)\}dn$$

Combine all the chemical potentials for a given process into Q and assume concentration ≈ activity, and take ΔG^{ϕ} as the free energy change per mole when all species are at unit activity:

$$\Delta G = \Delta G^{\phi} + RT\ln Q \qquad \Delta G = 0 \text{ at equilibrium } (Q = K) \qquad \Delta G^{\phi} = -RT\ln K$$

The derivation of the equation $\Delta G^{\phi} = -RT\ln K$ assumes that T is a constant. The same derivation can be independently applied at different temperatures, but there is no fundamental reason to assume that the standard state free energy change will be the same at different temperatures. Thus, the use of a constant enthalpy of vaporization is an assumption. Looking at measured enthalpy of vaporization values for a number of molecules indicates that the constant enthalpy of vaporization assumption is reasonable over the range of temperatures normally used to determine the normal BP via correlation of P/T pairs from vacuum distillation data (*i.e.*, from vacuum up to 1 atmosphere or less). The assumption is not valid for pressures significantly above 1 atmosphere.

The derivation of the two parameter ln(P) versus 1/T (T in kelvin) fit for vapor pressure as a function of T incorporates three major assumptions:

1) Pressure = Fugacity
2) Enthalpy of vaporization is constant over temperature range considered
3) Vacuum distillation data can be used to approximate vapor pressure of pure material at T

With these assumptions noted, then

$$\Delta G^{\phi}(\text{vaporization}) = -RT\ \ln(K) \qquad K = \text{equilibrium constant}$$

Model boiling as an equilibrium process:

$$A(l) \rightarrow A(g) \qquad K \equiv \text{equilibrium constant} = \frac{\text{activity of gas}}{\text{activity of liquid}}$$

<u>Appendix II - Enthalpy and Entropy of Vaporization of Polar Alkanolamines and Glycerol:</u>

ΔH^{ϕ} (vaporization) α normal BP

ΔH^{ϕ} (vaporization) is fairly constant with changes of T & P over T range from RT to normal BP

ΔS^{ϕ} (vaporization) α 1/(normal BP)

The entropy of vaporization is a function of the pressure

ΔS^{ϕ} (vaporization) α 1/P (entropy change is greater at lower P)

Entropy drives the material into the more disordered gas state. Enthalpy drives material into the liquid state where intermolecular interactions are more favorable.

Below is a Table of correlation (lnP versus 1/T) determined values of enthalpy of vaporization and entropy of vaporization (entropy at 1 mm Hg and at 1 atmosphere) as determined by all available literature data found in the Beilstein database for a number of alkanolamines and water:

Molecule	Normal BP (^{o}C)	ΔH^{ϕ} (kJ/mol)	ΔS^{ϕ} (J/mol-K) (P = 1 atmosphere)	ΔS^{ϕ} (J/mol-K) (P = 1 Torr)
Water	100	43.27	116.0	171.37
AMP	164	54.48	124.6	179.9
MEA	170	56.05	126.5	181.54
IPAE	173	52.46	117.6	172.23
BAE	200	55.69	117.7	172.33
DGA	220	72.44	146.9	201.67
BDEA	283	69.90	125.7	184.90

Table 12: Calculated enthalpy of vaporization and entropy of vaporization for some polar alkanolamines and water.

The calculated entropy of vaporization values are unusually high. The measured value for water is usually quoted as ≈110 J/K-mol. Trouton's Rule predicts that the entropy of vaporization at 1 atmosphere for most normally distilled materials will average at 85 J/K-mol with variance from 70 J/K-mol to 110 J/K-mol possible. Entropy of vaporization @ 1 atm above 120 J/K-mol is unusual. The exact calculated values of the entropy of vaporization @ P are undoubtedly influenced by the limitations of the correlation method used, but the trend clearly indicates that there are important fundamental VP/T differences between alkanolamines and other highly polar molecules like glycerol as compared to less polar molecules.

Appendix III - The Influence of Composition on Volatility:

The volatility of a material depends on the composition of the solution/mixture within the material resides. This can be simply demonstrated by measuring the vapor pressure over pure ammonia (≈ 124 psi @ 20 ^{o}C; all ammonia) versus the vapor pressure over a 10% wt/wt aqueous solution of ammonia (< 3 psi at @ 20 ^{o}C; ≈ 85% ammonia, 15% water).

The effect of solvation on vapor pressure can be approximated by Raoult's law. Aqueous solutions of BAE will be used as a specific example (BAE and water are miscible). One first needs to have reasonably accurate equations for the vapor pressure of pure BAE and pure water as a function of temperature. These equations are given below. The two parameter equation ($\log_{10}$P)for the vapor pressure of BAE as a function of temperature is given below (derivation of equation given in calculation of normal BP section):

$$\log(P) = \frac{-2909}{T} + 9.0013 \qquad \text{BAE}$$

The corresponding equation for water is given below (see Appendix IV for data):

$$\log(\mathrm{P}) = \frac{-2260}{\mathrm{T}} + 8.9522 \qquad \text{Water}$$

Note that the normal boiling point of water as predicted by this equation is slightly over 99 ^{o}C, as opposed to the correct value of 100 ^{o}C exactly. More accurate equations for the vapor pressure of water as a function of T are available, but this equation was used so that the accuracy would be comparable to that inherent within the equation employed for BAE.

Some values of the correlation predicted vapor pressure of pure water and pure BAE over the temperature range from 0 ^{o}C – 200 ^{o}C are given in the Table below:

Temperature (^{o}C)	Temperature (K)	VP (Pure Water)	VP (Pure BAE)
0	273.15	4.768	0.022
10	283.15	9.345	0.053
20	293.15	17.492	0.120
40	313.15	54.351	0.515
60	333.15	147.390	1.860
80	353.15	356.988	5.808
100	373.15	786.420	16.051
120	393.15	1598.667	40.003
140	413.15	3034.113	91.259
160	433.15	5427.601	192.922
190	463.15	11818.745	525.288
200	473.15	14986.564	713.089

Table 13: The correlation predicted vapor pressure of pure water and pure BAE over a range of T.

We can use Raoult's law (total VP = sum of vapor pressures of individual components multiplied by mole fraction) to calculate the normal boiling point of binary solutions of BAE/water over the entire range of compositions by setting the sum of the partial pressures equal to 760 Torr and then numerically solving T. Representative values are given in Table 14 below.

Mole Fraction Water	Mole Fraction BAE	BP (Solution, K)	BP (Solution, ^{o}C)
1	0	372.2378792	99.08787917
0.90	0.1	375.0021465	101.8521465
0.80	0.2	378.1283771	104.9783771
0.70	0.3	381.7167242	108.5667242
0.60	0.4	385.9136881	112.7636881
0.50	0.5	390.9449623	117.7949623
0.40	0.6	397.1834079	124.0334079
0.30	0.7	405.3059143	132.1559143
0.20	0.8	416.7263931	143.5763931
0.00	1	475.2890344	202.1390344

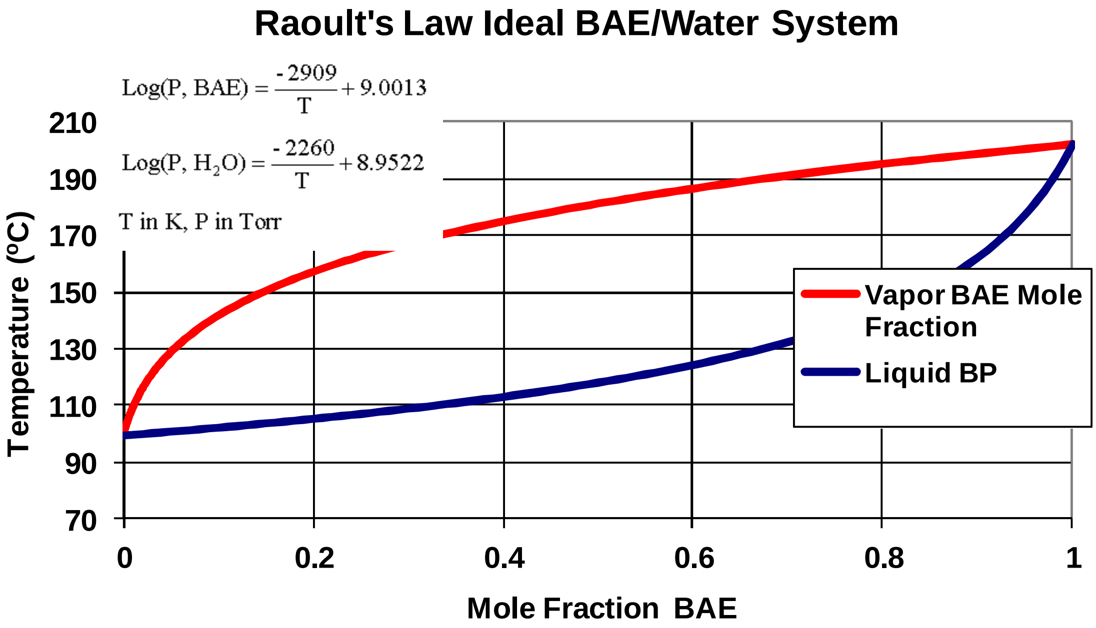
Table 14: BP calculated by setting $x_A P_A + x_B P_B = 1$ Atmosphere with P_A & P_B determined by correlation equation.

The composition of the vapor phase above the liquid at the normal boiling point can be determined by setting the vapor phase mole fractions of each component equal to the vapor pressure of the pure component at the normal boiling point multiplied by the liquid phase mole fraction for the given composition all divided by the total vapor pressure (760 Torr). Typically the pressure for the BP is set at P = 1 atmosphere, but this is not necessary. Some representative data for the BAE/water system is given in Table 15 below:

Mole Fraction Water	Mole Fraction BAE	BP (Solution, ^{o}C)	Vapor Mole Fraction Water	Vapor Mole Fraction BAE
1	0	99.08787917	1	0
0.90	0.1	101.8521465	0.997692205	0.002307795
0.80	0.2	104.9783771	0.994649899	0.005350101
0.70	0.3	108.5667242	0.990520769	0.009479231
0.60	0.4	112.7636881	0.984703536	0.015296464
0.50	0.5	117.7949623	0.976093758	0.023906242
0.40	0.6	124.0334079	0.962453855	0.037546145
0.30	0.7	132.1559143	0.938582836	0.061417164
0.20	0.8	143.5763931	0.88959798	0.11040202
0.10	0.9	162.0003405	0.754708208	0.245291792
0.08	0.92	167.3354365	0.697868038	0.302131962
0.06	0.94	173.6078478	0.617829741	0.382170259
0.04	0.96	181.1372115	0.499597279	0.500402721
0.02	0.98	190.403421	0.314075778	0.685924222
0.00	1	202.1390344	0	1

Table 15: Vapor phase composition above boiling solution of BAE/water at different compositions.

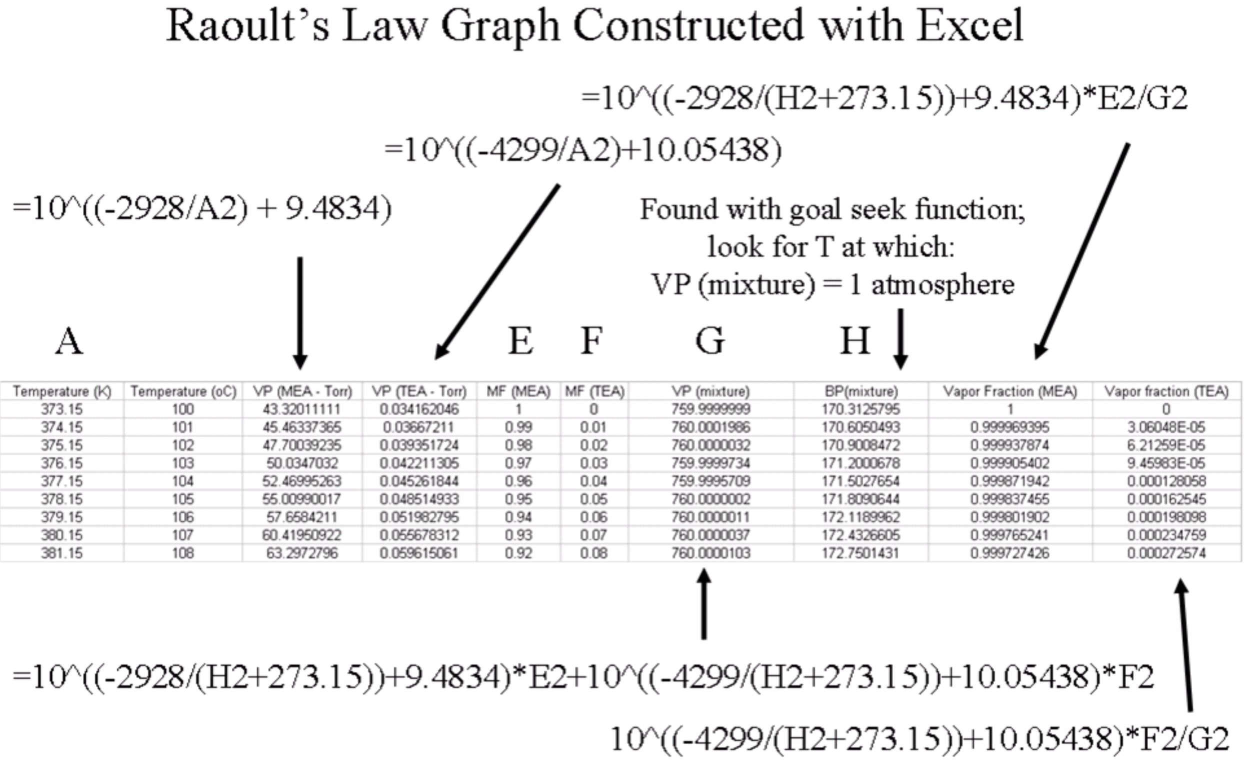
A phase diagram for the fractional distillation of an ideal water/BAE system at 1 atmosphere pressure based on the data calculated above is given in Graph 13 below.



Graph 13: A binary phase diagram for the BAE/water system at 1 atmosphere.

The blue line designates the normal BP of a given composition and the red line represents the vapor composition that distills from the binary mixture at a given composition. Note that the vapor phase composition for a given boiling liquid phase is traced horizontally from the blue line. Horizontal lines in the graph are isothermal. If one imagines distilling an ideal 5% wt/wt solution of water in BAE (mole fraction of BAE = 0.75, mole fraction of water = 0.25), then the BP should be approximately 135 °C with a vapor composition of approximately 40 % BAE wt/wt and 60% water wt/wt. This ideal approximation of the effect of solvation on vapor pressure is somewhat involved as is. The analysis becomes unwieldy when transient vapor phase structures (*i.e.,* azeotropes) are considered. Thus it is apparent that conclusions based on comparing the normal boiling points of pure compounds are not always relevant when assessing the volatility of the compounds in solution. The complications resulting from a non-ideal relationship of vapor pressure with temperature and/or from the complicating effects of solvation can be avoided through the use of thermal analysis methods at conditions/temperatures that are as close as possible to the conditions of interest. If the influence of a solvent (*e.g.,* water) must be considered, then thermal analysis of the material in solution can be carried out.

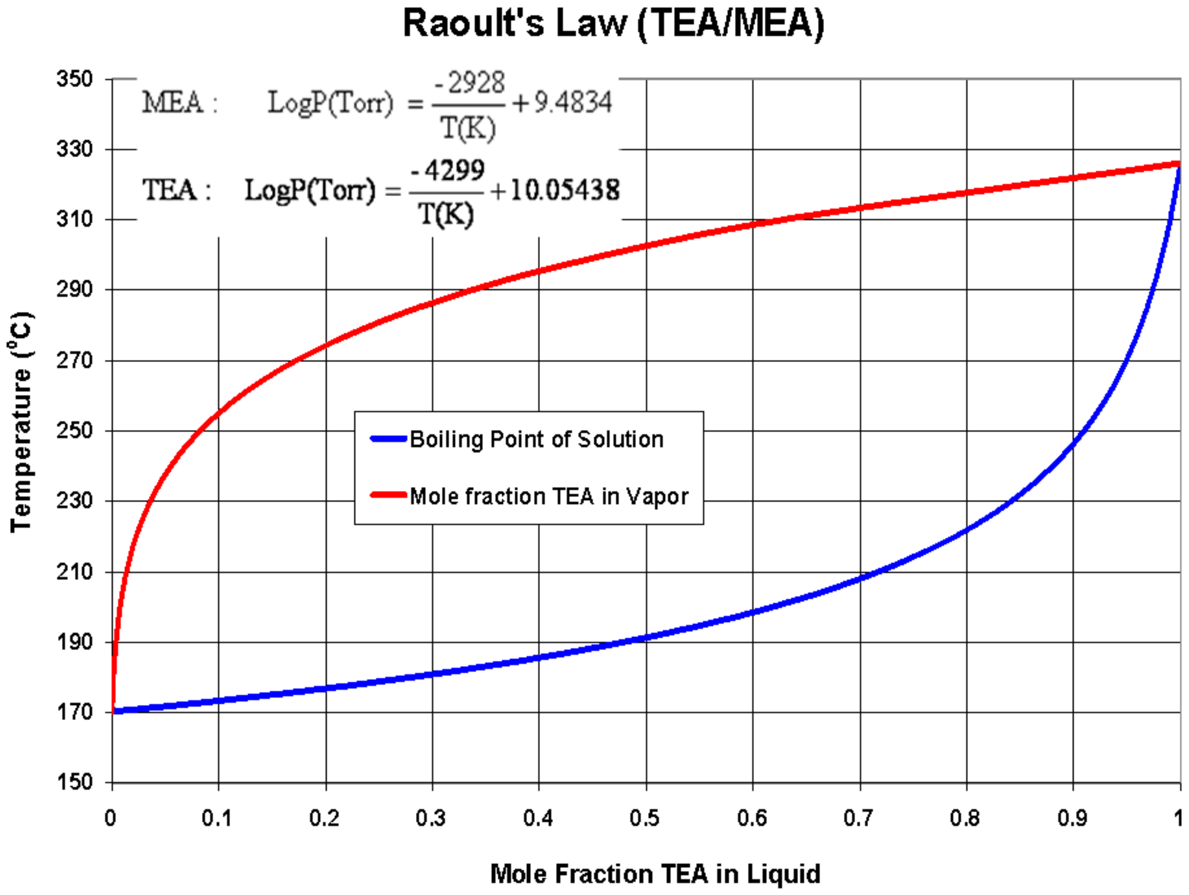
The use of Excel for the construction of a binary phase diagram is illustrated in Figure 4 below. One uses the goal seek function to find the boiling point of a given composition numerically. The correlation derived two parameter vapor pressure equations for MEA (monoethanolamine) and TEA (triethanolamine) are given in typical excel format. The combined equation used for numerical determination of the BP is the one in column G.



```
=10^((-2928/(H2+273.15))+9.4834)*E2/G2
=10^((-4299/A2)+10.05438)
=10^((-2928/A2) + 9.4834)
=10^((-2928/(H2+273.15))+9.4834)*E2+10^((-4299/(H2+273.15))+10.05438)*F2
10^((-4299/(H2+273.15))+10.05438)*F2/G2
```

Temperature (K)	Temperature (oC)	VP (MEA - Torr)	VP (TEA - Torr)	MF (MEA)	MF (TEA)	VP (mixture)	BP(mixture)	Vapor Fraction (MEA)	Vapor fraction (TEA)
373.15	100	43.32011111	0.034162046	1	0	759.9999999	170.3125795	1	0
374.15	101	45.46337365	0.03667211	0.99	0.01	760.0001986	170.6050493	0.999969395	3.06048E-05
375.15	102	47.70039235	0.039351724	0.98	0.02	760.0000032	170.9008472	0.999937874	6.21259E-05
376.15	103	50.0347032	0.042211305	0.97	0.03	759.9999734	171.2000678	0.999905402	9.45983E-05
377.15	104	52.46995263	0.045261844	0.96	0.04	759.9995709	171.5027654	0.999871942	0.000128058
378.15	105	55.00990017	0.048514933	0.95	0.05	760.0000002	171.8090644	0.999837455	0.000162545
379.15	106	57.6584211	0.051982795	0.94	0.06	760.0000011	172.1189962	0.999801902	0.000198098
380.15	107	60.41950922	0.055678312	0.93	0.07	760.0000037	172.4326605	0.999765241	0.000234759
381.15	108	63.2972796	0.059615061	0.92	0.08	760.0000103	172.7501431	0.999727426	0.000272574

Figure 4: The construction of a binary phase diagram for MEA and TEA using Excel.



Graph 14: A binary phase diagram for MEA and TEA at 1 atmosphere.

Appendix IV - Vapor Pressure of Water:

Vapor pressure data for water was available on the Oklahoma State University website (http://intro.chem.okstate.edu/1515SP01/Database/VPWater.html). Some representative data from the OSU website is given in Table 16 below (BP = boiling point, VP = vapor pressure).

BP (oC)	BP(K)	1000/BP(K)	VP (Torr)	log(VP)
0.00	273.15	3.66099	4.60	0.66276
1.00	274.15	3.64764	4.90	0.69020
20.00	293.15	3.41122	17.50	1.24304
40.00	313.15	3.19336	55.30	1.74273
75.00	348.15	2.87233	289.10	2.46105
80.00	353.15	2.83166	355.10	2.55035
96.00	369.15	2.70893	657.60	2.81796
98.00	371.15	2.69433	707.30	2.84960
99.00	372.15	2.68709	733.20	2.86522
100.00	373.15	2.67989	760.00	2.88081

Table 16: Vapor pressure of water as a function of temperature. One hundred values of VP from 0 °C to 100 °C were used to construct the two parameter correlation of VP versus T for water: $\log(P) = \frac{-2260}{T} + 8.9522$

The two parameter best fit correlation equation derived is given below ($r^2 = 0.9999$):

$$\log(P) = \frac{-2260}{T} + 8.9522$$

Apparent $\Delta H_{vaporization}$ = 43.27 kJ/mole & $\Delta S_{vaporization}$ @ 1 Torr = 171.37 J/(mole-^oK)

Note that far more accurate equations for the VP of water as a function of T are available. This equation was used so that the accuracy would be comparable to that available via the equation employed for BAE.

Some comparative data for the enthalpy of vaporization of water is given below in Table 17:

T (^oC)	Enthalpy Vaporization (kJ/mole)	T (^oC)	Enthalpy Vaporization (kJ/mole)
0	45.054	200	34.962
25	43.990	220	33.468
40	43.350	240	31.809
60	42.482	260	29.930
80	41.585	280	27.795
100	40.657	300	25.300
120	39.684	320	22.297
140	38.643	340	18.502
160	37.518	360	12.966
180	36.304	374	2.066

Table 17: Some literature values for the enthalpy of vaporization of water from: Marsh, K. N., Ed., *Recommended Reference Materials for the Realization of Physicochemical Properties*, Blackwell, Oxford, 1987.

The enthalpy of vaporization of water calculated from the parameter A of the two parameter best fit equation for the relationship of vapor pressure to temperature: $\log(P) = \frac{-2260}{T} + 8.9522$
The value of enthalpy of vaporization calculated is approximately equal to the measured enthalpy of vaporization at a temperature close to the middle of the range of the temperatures used to derive the best fit parameters A & B.

Appendix V - Normal BP of N-butyldiethanolamine (GMW = 161.3, CAS RN 102-79-4):

The normal boiling point (BP) of a high-boiling material can be determined by a number of techniques. One method is via correlation of carefully collected P/T data points taken from vacuum distillations of the material at different absolute pressures. Four P/T data point pairs for the distillation of N-butyldiethanolamine (BDEA) are given below in Table 18. The absolute pressure was measured with a calibrated Piezovac PV20 vacuum gauge (Leybold Vakuum GMBH, Koln, Germany). All four of these distillations were run in Taminco's laboratories with care taken to insure accurate and internally consistent results.

Boiling T (^oC)	Boiling T (K)	Absolute P (mbar)	ln(P)	1000/T(K)
82	355.15	0.6	-0.5108	2.8157
143	416.15	11	2.3979	2.4030
153	426.15	20	2.9957	2.3466
166	439.15	30	3.4012	2.2771
283.6	**556.8**	**1013.25**	**6.9209**	**1.7961**

Table 18: Carefully collected P/T data point pairs at different absolute pressures for the vacuum distillation of pure BDEA (N-butyldiethanolamine). Column 1 is the observed BP. Column 2 is BP converted to absolute (K) scale. Column 3 is the Absolute P of the distillation given in units of mbars. Column 4 is the natural log of the absolute pressure. Column 5 gives 1000/T(K), which is a more convenient unit than 1/T for use in the correlation. The fifth row is extrapolated from the data above it using the derived correlation equation (shown below).

The two parameter correlation equation derived from the above data is given below:

$$\ln(P) = \frac{-7298}{T} + 20.030 \qquad \text{BDEA}$$

$r^2 = 0.9981$

7298 x R = $\Delta H_{vaporization}$ = 60.7 kJ/mol

20.075 x R = $\Delta S_{vaporization}$ @ 1 mbar = 166.5 J/K-mol

R = universal gas constant = 8.31447 Joules/K-mol

Accurate Predicted Normal BP = 284 ^oC

$\Delta S_{vaporization}$ @ 1 Atmosphere = $\Delta H_{vaporization}$/(normal BP) = 109 J/K-mol

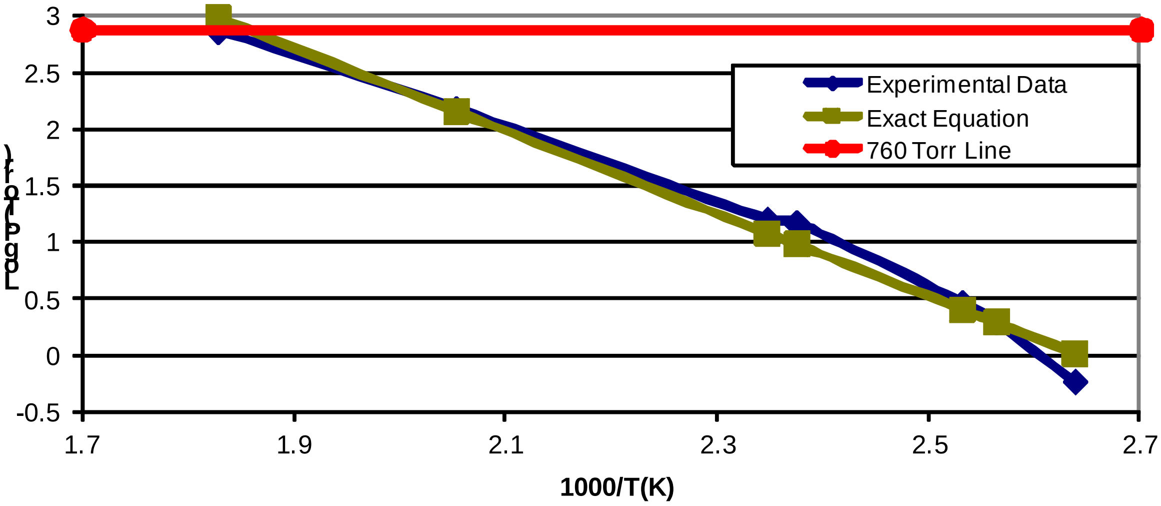
1 atmosphere = 1013.25 mbar

A similar analysis using all available literature data is given below. The data collected from the literature is summarized in Table 19.

BP (^oC)	BP (^oK)	P (Torr)	Reference
274	547.15	741	Matthes; Justus Liebigs Ann. Chem.; 315; 1901; 128.
214	487.15	150	Matthes; Justus Liebigs Ann. Chem.; 315; 1901; 128.
153	426.15	16	Ishiguro et al.; Yakugaku Zasshi; 74; 1954; 1162, 1164; Chem.Abstr.; 1955; 14767.
148	421.15	15	Fujiki; Collect. Scient. Pap. 5th Anniv. Shizuoka Coll. Pharm.; 1958; 147; Chem.Abstr.; 1959; 3050.
122	395.15	3	Shimanskii et al.; Sb. Tr. Ukr. Nauchn.; 6; 1960; 99; Chem.Abstr.; 58; 1963.
117	390.15	2	Yang, Qinzheng; Lin, Jimao; Li, Fangzheng; Synth.Commun.; EN; 31; 18; 2001; 2817-2822.
106	379.15	0.6	Szarvasi,E. et al.; EJMCA5; Eur. J. Med. Chem. Chim. Ther.; FR; 11; 1976; 115-124.

Table 19: All available literature data for the vacuum distillation of BDEA.

Below in Graph 15 is a correlation of the base ten log of the absolute pressure in Torr versus boiling point given as 1000/T with T in Kelvin (absolute scale) for the literature data points in Table 19.



Graph 15: Literature data and trendline for the data available in the literature concerning vacuum distillation of BDEA.

The best-fit literature data based equations for BDEA are:

$$\log(P) = \frac{-3652}{T} + 9.660638 \qquad \ln(P) = \frac{-8409}{T} + 22.244441$$

$r^2 = 0.9820$

8409 x R = $\Delta H_{vaporization}$ = 69.9 kJ/mol

22.244 x R = $\Delta S_{vaporization}$ @ 1 Torr = 184.9 J/K-mol

R = universal gas constant = 8.31447 Joules/K-mol

Inaccurate Predicted Normal BP ≈ 276 ^{o}C

$\Delta S_{vaporization}$ @ 1 atmosphere = $\Delta H_{vaporization}$/(normal BP) ≈ 127 J/K-mol

The use of diverse literature data can be problematic in that P/T data point pairs of differing accuracy must be used together. The various people who collected the literature data had different intentions for its use. Some individuals sought merely to report a value within +/- 25% of the actual value, while other workers endeavored to report the best values possible. It is difficult to judge the various authors' motivations, as people typically don't report parenthetically the degree to which they cared about accuracy. In the data correlations above, the values for r^2 and $\Delta S_{vaporization}$ @ 1 atmosphere are much more reasonable for the data set we collected with the intention of correlating to a normal BP than it is for the larger set of literature data derived from numerous papers with differing objectives.

The normal boiling point of BDEA can also be established by thermal analysis methods like DTA/TGA as shown in Figure 5 below:

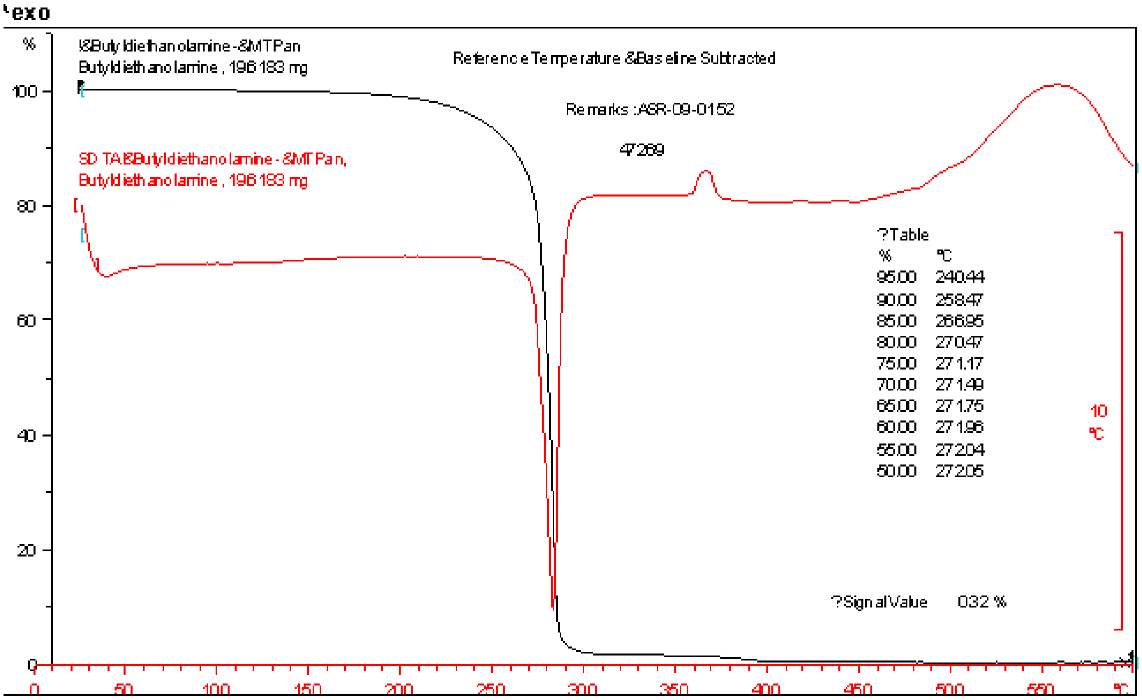


Figure 5: Ramp TGA with overlaid first derivative for BDEA. The indicated normal BP is 283 °C.

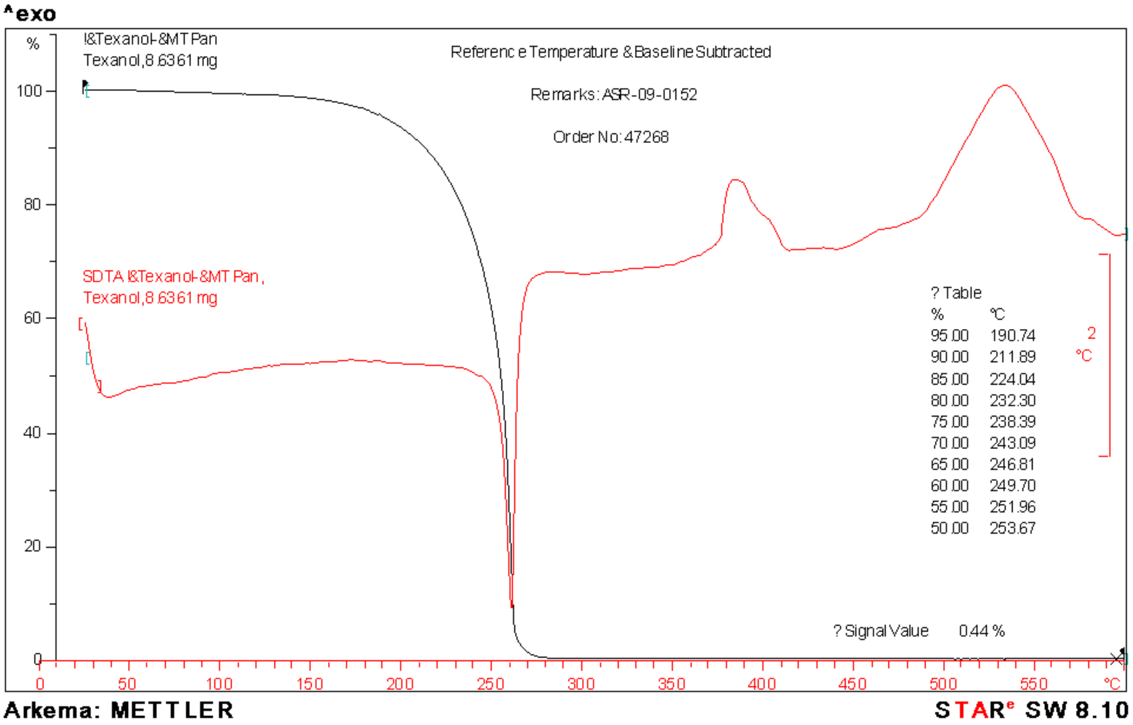


Figure 6: Ramp TGA with overlaid first derivative for Texanol (blend of isobutyrate esters). The indicated normal BP is 260 °C. The material is composed of monoisobutyrate esters with normal BP ≈ 255 °C and a diisobutyrate ester with normal BP ≈ 280 °C. The 260 °C value is a weighted average.

Appendix VI – Experimental Section:

The TGA work was carried out with a TA Instruments Q500 Thermal Gravimetric Analyzer (www.tainstruments.com). The derivative weight loss was calculated as the slope of the weight loss (%) curve at a given time. Linear regression was carried out on 24 data points (12 seconds) centered at the time of interest. Samples ranging from 38 mg to 44 mg (higher weights were sometimes used at temperatures where evaporation was so rapid that most of the sample evaporated before the equilibration time was complete) were run with a purge gas flow of 40 ml/min of nitrogen and a balance gas flow of 60 ml/min of nitrogen. The derivative weight loss values were taken after 0.5 mg (≈ 1.25 %) of material had evaporated relative to the point t = 0 minutes. Differing amounts of material evaporated during the thermal equilibration of the instrument. A compilation of representative initial sample weights along with the corresponding weight remaining at t = 0 is given in the Table below. The derivative weight loss was taken as an average over a sufficient time period centered on the time of interest to get good statistics (typically 10 data points).

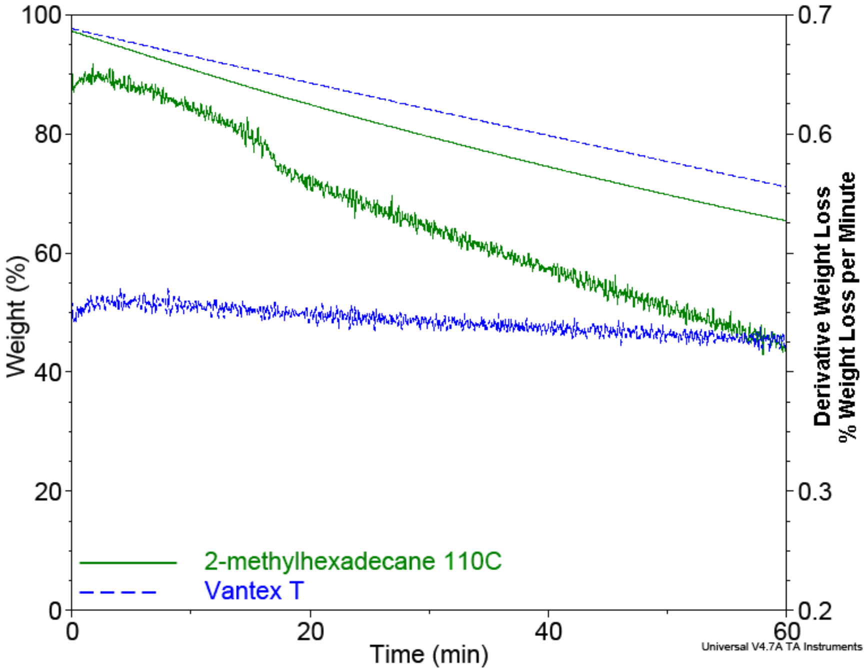
Sample (Temperature, ^oC)	Initial Weight of Sample	Weight of Sample at t = 0
MePalm (50 ^oC)	40.0 mg	40.0 mg
MePalm (110 ^oC)	39.2 mg	39.0 mg
MePalm (140 ^oC)	40.75 mg	39.75 mg
MePalm (180 ^oC)	40.1 mg	33.9 mg
TEA (50 ^oC)	39.37 mg	39.24 mg
TEA (110 ^oC)	40.69 mg	40.41 mg
TEA (140 ^oC)	40.83 mg	40.15 mg
TEA (180 ^oC)	41.06 mg	38.82 mg
Glycerol (140 ^oC)	40.09 mg	38.46 mg
Glycerol (180 ^oC)	40.94 mg	33.46 mg
BDEA (140 ^oC)	38.25 mg	34.05 mg
BDEA (180 ^oC)	47.21 mg	27.32 mg
2-methylhexadecane (140 ^oC)	40.62 mg	35.71 mg
2-methylhexadecane (180 ^oC)	40.77 mg	22.56 mg
AEPD (140 ^oC)	41.72 mg	36.70 mg
TXIB (140 ^oC)	67.54 mg	31.34 mg

Methyl Palmitate: Obtained from Aldrich, 99% pure, BP extrapolated from vacuum distillation
TEA: Triethanolamine, 99.5% purity obtained from Sigma-Aldrich (literature BP)
Glycerol: Anhydrous, 99% pure, obtained from Sigma-Aldrich (literature BP)
Vantex®-T: N-butyldiethanolamine (99.5% purity, BP determined by DTA & correlation, Appendix V)
2-Methylhexadecane: Obtained from Sigma-Aldrich, 99% pure (literature BP, Chenzhong, C.; Shusheng L.; Zhiliang, L.; "On Molecular Polarizability: 2. Relationship to the Boiling Point of Alkanes and Alcohols" *J. Chem. Inf. Comput. Sci.* **1999,** *39*, 1105-1111.)
Hexadecane: Obtained from Sigma-Aldrich, 99% pure (literature BP)
TXIB: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate ester (Eastman, BP from Eastman literature)
AEPD: 2-amino-2-ethyl-1,3-pentanediol (98%, Angus-Dow, BP from Angus literature)
DBAE: N,N-dibutylaminoethanol, 99% pure (Taminco, literature BP)
TBA: Tributylamine, 99% pure (Taminco, literature BP)
MEA: Monoethanolamine obtained from Sigma-Aldrich, 99% pure (literature BP)
AMP: 2-amino-2-methyl-1-propanol (90%, 5% water, Angus-Dow, BP from Angus literature)

A partial data set for TGA of 2-methylhexadecane (2MHD) and N-butyldiethanolamine (BDEA) at 110 ^{o}C is given below. The derivative weight loss (dW/dt) value after 0.5 mg (≈ 1.25%) weight loss from an initial weight of approximately 40 mg was found to be the most consistent initial weight loss point in the data sets.

Time (minutes)		Temperature (^{o}C)		Weight (mg)		dW/dt (%/min)	
2MHD	BDEA	2MHD	BDEA	2MHD	BDEA	2MHD	BDEA
time = 0 minutes							
.003866666	0.00386666	109.7643	109.7659	39.96028	44.34711	0.6623330	0.4623203
0.01250000	0.00833333	109.7701	109.7687	39.95618	44.34462	0.6538800	0.4616416
0.02916666	0.02500000	109.7750	109.7737	39.95180	44.34110	0.6507046	0.4585491
0.04583334	0.03750000	109.7802	109.7773	39.94705	44.33872	0.6471004	0.4566046
0.05416668	0.05000000	109.7810	109.7805	39.94472	44.33621	0.6471394	0.4544458
0.06250000	0.06250000	109.7842	109.7851	39.94260	44.33369	0.6455606	0.4516626
time to 0.5 mg weight loss							
1.879167	2.425000	110.0116	110.0230	39.46134	43.84724	0.6453386	0.4573902
1.887500	2.437500	110.0130	110.0231	39.45922	43.84442	0.6448798	0.4575980
time = 15 minutes							
14.99583	14.99583	110.0055	110.0054	36.08025	41.24192	0.5967906	0.4527250
15.00417	15.00833	110.0048	110.0044	36.07825	41.23928	0.5974456	0.4532470
15.01250	15.02083	110.0042	110.0050	36.07617	41.23675	0.5973576	0.4531350
time = 60 minutes							
60.00000	59.98750	110.0023	110.0012	26.87498	32.27976	0.4307953	0.4292217

A typical plot showing both overall weight loss (wt %) and derivative weight loss (weight % per minute) is presented below.



The derivative weight loss decreases as the sample evaporates throughout the experiment. The derivative weight loss is constant throughout approximately the first 5 mg (40 mg total weight) of weight loss and then decreases thereafter. The Table below shows the initial derivative weigh loss and the derivative weight loss after 50% of the sample has evaporated at 110 ^{o}C.

Compound	dW/dt (weight % per minute) @ 110 ^{o}C (initial t)	dW/dt (weight % per minute) @ 110 ^{o}C (after 50% weight loss)
Glycerol	0.14	≈ 0.10
BDEA	0.46	0.41
2-methylhexadecane	0.64	≈ 0.43
hexadecane	0.62	0.54
AEPD	0.73	≈ 0.55
TXIB	0.8	0.68
DBAE	3.7	3.4
TBA	6.8	6.5
MEA	7.4	6.9

A plot of BDEA versus methyl palmitate with nitrogen purge gas at 110 ^{o}C is given below: