Study of Odor Qualification of Solvents Used In Coating Compositions

Patrick D. Ziemer†, James Woo, and Taki Anagnostou—Eastern Michigan University*

A review of the literature regarding human odor perception reveals significant variation in the threshold limit value. This is especially true with solvents used in coating compositions. Therefore, in order to more accurately determine threshold concentrations, a series of experiments were run using the Devlin olfactometer. Nineteen solvents were evaluated. Solvents were rated using Steven's Law parameters K, which gives an indication of odor magnitude potential, and n, which characterizes the effects of dilution. In addition, equations were established from which the minimum solvent concentration for human odor detection could be calculated.

INTRODUCTION

Odor control has become a critical but often ignored part of coating technology. Kenson,[1] for example, has described various techniques to control the emission of compounds that create odor. This article is but one example describing the magnitude of the problem of controlling odor. Confusion also exists as to the minimum concentration of solvents necessary to induce odor perception.[2] Researchers tend to agree on the odor potential of some solvents, but have published wide ranges for other solvents. For example, published results for cyclohexanone range from 1.0 to 1.2 ppm, while results for methyl ethyl ketone range from 1 to 8 ppm, and xylene from 2.2 to 8.0 ppm.

In the coatings industry, solvents from industrial finishes are a major source of odor problems. The drive toward lower VOCs has only worsened the situation. The industry has found itself in a position where less solvent can smell like more. Solvents that have been introduced to allow lower VOCs often have very intense odors, which can cause concern to the public and to regulatory agencies. A better understanding of exactly which solvents can be expected to be problematic as well as of which are not highly odorous is of great interest to many formulators. One goal of this work is to provide a more accurate threshold concentration for human odor detection.

There is a great deal of speculation as to the mechanism in human detection. Many different theories exist as to what triggers neural impulses that produce the sensation of odor. Although the mechanism of excitation is not understood, the physiology of olfaction is fairly well understood.[3] Unlike taste, there are many different receptors for different types of odors, and different combinations of signals from these different receptors give us our different sensations of smell.

Whitfield[4] identifies several proposed methods of odor stimulation based on the size of a molecule, its shape, or its stereochemistry. The molecule could tear a hole through the cell membrane causing a signal, or fit into a receptor like a lock and key, thereby initiating a signal to the brain. In our investigation, we also attempted to determine if chemical properties of a molecule such as polarity, hydrogen bonding, or water solubility trigger an odor response. Other theories suggest that a reaction involving the odorant when it dissolves into the outer surface of the receptor cells stimulates smell, or even that the frequency of electron vibrations may trigger odor response. The theory that has the most current support is that molecular stereochemistry determines odor.

Each of these properties was compared with odor responses for the various solvents tested. As work progressed, other properties were identified for analysis and these included vapor pressure, evaporation rate, dielectric strength, resistivity, water solubility, and surface tension. The properties are summarized in *Table* 1. When these values were graphed versus the results shown in *Table* 2, it is evident that there is no good

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*Emission Evaluation Center, Room 201, Sill Hall, Ypsilanti, MI 48197.
† CCP, Kansas City, MO.

Table 1—Summary of Data

Solvent	MW	VP(20) mm Hg	VP(25) mm Hg	Evaporation Rate nBuOAc=1	H-bond Solubility Parameter	Dielectric Constant	Dipole Moment	Water Solubility	Surface Tension (dynes/cm²)	Electric Resistance Megohms
Amyl (pentyl) acetate (AmAc)	130.19	4	5.19	0.487	2.78	4.75	1.91	0.20%	28.5	16
Amyl (pentyl) alcohol (AmOH)	88.15	2	2.33	0.1795	6.97	13.9	1.8	1.70%	23.8	0.2
Amyl (pentyl) propionate (AmPr)	144.21	—	—	—	—	—	—	—	—	—
Butanol, normal (nBu)	74.12	4.39	6.46	0.4573	7.55	17.5	1.66	7.90%	24.6	<.2
Butanol, secondary (sBu)	74.12	12	17.63	1.2469	7.23	16.6	—	20.60%	24	<.2
Butanol, tertiary (tBu)	74.12	40	—	—	—	10.9	—	—	—	—
Butyl acetate (BA)	116.16	7.8	11.28	0.9994	3.3	5.01	1.84	0.50%	25.1	>20
Butyl lactate (BL)	146.18	0.3	0.3	0.03	6.03	—	—	—	—	—
Cyclohexanone (CH)	98.14	3.4	2.75	0.2239	5.39	18.3	3.01	2.33%	27.7	<.1
Ethyl ethoxy propionate (EEP)	146.19	1.11	1.11	0.1099	3.89	—	—	2.90%	27	20
Ethyl acetate (EA)	88.11	76	96.82	7.4677	4.35	6.02	1.78	2.90%	23.9	20
Isophorone (IP)	138.21	0.18	0.21	0.0205	1.55	—	—	1.20%	32.3	<.1
Methyl amyl (Pentyl) Ketone (MAK)	114.2	1	3.17	0.2781	3.51	15.4	—	0.50%	26.1	0.4
Methyl ethyl ketone (MEK)	72.1	85	90.39	6.3064	4.63	12.51	2.75	27.10%	24.6	0.2
Methyl isobutyl ketone (MIBK)	100.16	16	19.92	1.6379	2.87	—	—	2.00%	23.6	0.4
Propylene glycol Methyl ether acetate (PMA)	132.2	3.7	—	0.4	4.8	—	—	20.00%	26.4	5
Propylene glycol n-Butyl ether (PnB)	132.2	0.6	0.84	0.0797	5.63	—	—	6.40%	27.4	0.4
Texanol (Tex)	216.3	<.01	<.01	0.002	4.8	—	—	0%	28.9	>20
Xylene (Xyl)	106.17	9.5	7.36	0.67	0.71	2.4	0.45	0%	28.7	>20

correlation of odor versus any one of the colligative properties.

METHODOLOGY

The odor of a particular solvent was evaluated via a panel of 10 people using the Devlin olfactometer. The Devlin olfactometer is built into a controlled environment room. The room has been designed with considerations for humidity and temperature along with room air handling. The room has 16 air exchanges per hour with balanced make-up and exhaust vents near the ceiling and floor levels.

Table 2—Odor Response Constants

Solvent	K	n	R^2 of Equation
Amyl (pentyl) acetate	41	0.43	0.475
Amyl (pentyl) alcohol	30	0.18	0.998
Amyl (pentyl) propionate	25	0.19	0.205
Butanol, normal	20	0.41	0.899
Butanol, secondary	21	0.42	0.899
Butanol, tertiary	3.0	0.37	0.912
Butyl acetate	42	0.55	0.854
Butyl lactate	68	0.07	0.599
Cyclohexanone	4.9	0.84	0.254
Ethyl ethoxy propionate (EEP)	250	0.45	0.938
Ethyl acetate	13	0.12	0.951
Isophorone	68	0.24	0.627
Methyl amyl (pentyl) ketone	43	0.47	0.363
Methyl ethyl ketone	18	0.35	0.962
Methyl isobutyl ketone	8.5	0.52	0.747
Propylene glycol Methyl ether acetate (PMA)	63	0.40	0.951
Propylene glycol n-Butyl ether (PnB)	1.4	1.70	0.946
Texanol	18	0.38	0.228
Xylene	28	0.58	0.578

In brief, the Devlin olfactometer is a system where a controlled dilution of a source (air with solvent dissolved in it, in this case) can be presented to one of three possible sources. The instrument is mostly computer controlled with an operator controlling valves to determine which of three ports receives a diluted sample of the source. The other two ports receive the same flow, but only air filtered through activated charcoal is present. The olfactometer also provides a system where the panelist can press a button corresponding to the port where they believe they detect some odor. This signal is read by the computer and data from all the panelists is combined to determine an odor level. Dilution of the sample stream is accomplished by using Unit Inc.'s mass flow controllers to monitor and control dilution. The system, as designed, has the capability to deliver a sample in a range of dilutions from 1:6 to 1:3000. In this testing, the factor of dilution is referred to as the Odor Units of a sample. A 1:6 dilution is a value of 6 Odor Units (OU) and a 1:3000 dilution gives a value of 3000 OU.

The Devlin olfactometer looks like a small computer station with some manual valves flanked by 10 cubicles or study carols. Each cubicle contains three ports, each port color coded red, green, or white and three buttons, also red, green, and white. During testing, each port has a continuous flow of approximately three liters per minute. The entire system is balanced for uniform airflow through each of the 30 ports on a regular basis, generally weekly. In order to minimize contamination, all surfaces in contact with the samples and air streams were of Teflon or stainless steel. When a test is run, a panelist sits in each of the 10 cubicles and upon receiving a signal from the operator sniffs each of the three ports. The panelists are given approximately 30 seconds to determine if they detect an odor from one of the ports. If an odor is detected, the panelist presses the button the same color as the port where the odor was detected. The

panelists then wait for the next signal; they sniff again and determine if an odor is detected. No effort is made to identify the odor or to judge an odor as pleasant or offensive. Only the absence or presence of odor is evaluated. A block diagram of this instrument is given in *Figure* 1. A more detailed explanation of the Devlin olfactometer is given in reference (5).

Samples are prepared for testing in the following manner. First, a specific volume of pure solvent is injected into a Tedlar bag, which is then diluted to a known concentration with filtered air. This bag is then used as the sample in a triplicate set of measurements. The Tedlar bags were fabricated, flushed with filtered air, and checked for leaks prior to use. Sample bags were tested within 24 hr of collecting the sample. Bags were used only once and then discarded. In order to insure that condensation on the bag's surface did not occur, the saturation concentration of solvent was calculated in *Appendix* 1. This allowed us to calculate the maximum volume of solvent injection. However, in all cases we found that the odor threshold was far below the condensation concentration.

The tests were run in triplicate and each test was run beginning at a high dilution (low concentration) and ending with a low dilution (high concentration). A range of dilutions was identified where no one was expected to detect the odor at the highest dilution and everyone was expected to detect it at the lowest dilution. Dilutions were decreased in a logarithmic type progression until 12 tests had been run, or until all panelists had identified the odor. This procedure was then repeated twice more for each sample and the results averaged.

The Devlin olfactometer is computer controlled to collect and record panelist responses, and to minimize operator variability. The odor data was collected and tabulated by a computer program, which reported the ED_{50}. The ED_{50} is defined as the odor concentration where 50% of the panelists are able to detect the odor. This value was calculated using the standard best fit least square technique proposed by Dravinek.[6] The Devlin olfactometer was designed to accurately reduce the concentration of the odorant in very small increments, thus overcoming the deficiency of other reported olfactometers.

In order to determine a critical odor concentration, this standard procedure for the Devlin olfactometer had to be modified. In this study, several changes were made from a previous work.[5] One significant change that was made was to move from a forced choice method to a non-forced choice method. This change was made to minimize errors in the data caused by panelists who do not detect an odor and are simply guessing randomly as to which port contains the odor. The way in which calculations were made was also changed to improve the quality of the data. One change was that actual solvent concentrations where detection occurred were used in the calculations as opposed to an interpolation between the last non-detected concentration and the next detected concentration. Also, two rather than three consecutive correct identifications of odor were determined to be a positive detection, and thirdly, two consecutive incorrect identifications at higher concentrations nullified positive detection at a lower concentration. These changes helped to minimize the effect of a logarithmic progression of dilutions. Odor unit values were shifted slightly higher, but the greater benefit was the minimization of the polarization effect caused by a single high odor value from a single panelist.

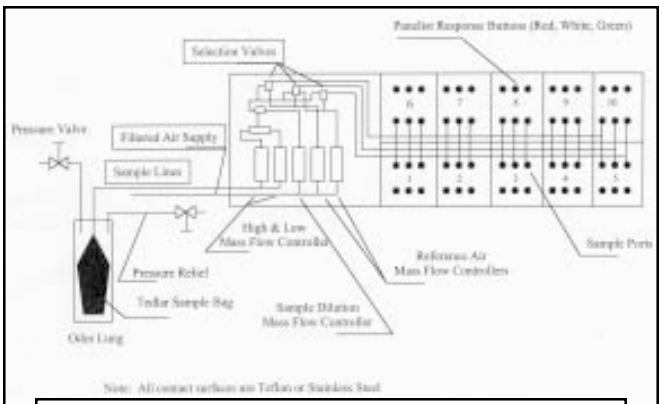

Figure 1—Devlin olfactometer

Initial work focused on the point at which only 50% of the panelists were able to detect the odor, which was then termed as the critical odor concentration or ED_{50}. This method was useful for finding a cutoff point below which an odor was no longer detected, but had limitations in determining an odor response curve. It also increased error, as some of the panelists could no longer detect the odor. Since we were looking for the relationship between concentration and odor response, the point of focus was changed to be the lowest concentration where all panelists were still able to detect an odor. This greatly reduced the noise that had existed in the initial data, and helped to reduce data variability. However, in some cases, variability still existed. This was not surprising since identical panelists were not used in all cases, and different solvents might be expected to act differently. Since there was no way to eliminate this variability, and there was no way to prove that it was not due to the nature of the solvent, the best fit relationship was still used to determine the odor values.

RESULTS AND DISCUSSION

Steven's law[10] explains the relationship between concentration and perceived odor intensity. It states that the intensity of sensation, S, increases with the concentration of the odorant, C, according to the function:

$$S = K*(C)^n$$

In this function, K and n are constants for a particular odorant. If the log is taken of both sides of this equation and the result simplified, the following relation is obtained:

$$\text{Log}(S) = n*\log(C) + K$$

From this equation, it is shown that the value of the constants in Steven's law can be obtained by graphing the log of the concentration against the log of the odor intensity. The slope of the line determines n, and the y-intercept determines the value for K. An alternative ap-

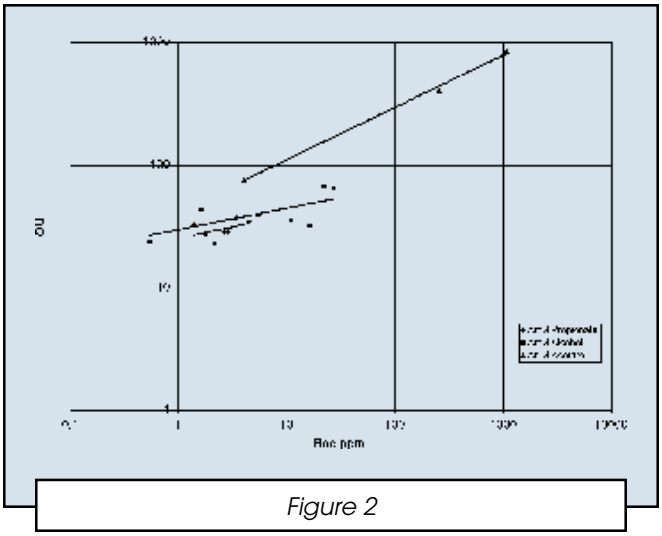

Figure 2

proach would be to graph the power equation and use the values from the power function that is the best fit to the data. This second option was used to obtain the values of the constants for solvents examined in this study.

Steven's law proved to yield excellent results in the solvent concentration ranges that were examined. The relationship was not valid when non-detection occurred with several panelists or at high concentrations where saturation quickly becomes a major factor. Despite these limitations, this relation fits very well for the concentrations of solvents we identified for study.

The main objective of this work was to devise a relationship that could be used with any solvent to give results that were both meaningful and easily understood. The variables that were identified for use in this equation were the concentration in ppm (v/v) and odor units (OU), a unitless number. These terms are further defined in *Appendix* 2. We found that a straightforward way to examine the data was demonstrated by Steven's law. The log of concentration (log (C)) was plotted against the log of the odor intensity (log (OU)). Using a spreadsheet on a computer, the values of C and OU were simply plotted on a logarithmic scale rather than plotting the logs of these values. Either method gave equivalent plots. A best fit to the data using a power relationship was calculated, and the values for K and n were obtained from the equation for this curve. The graphs attained in this manner gave positive values for both K and n with the K value giving indication of the odor magnitude potential of the solvent. The higher the K value the greater the odor potential. The n value defines the dilution effect with a large n showing a large change in odor intensity with concentration changes, and a small n demonstrating a lesser effect.

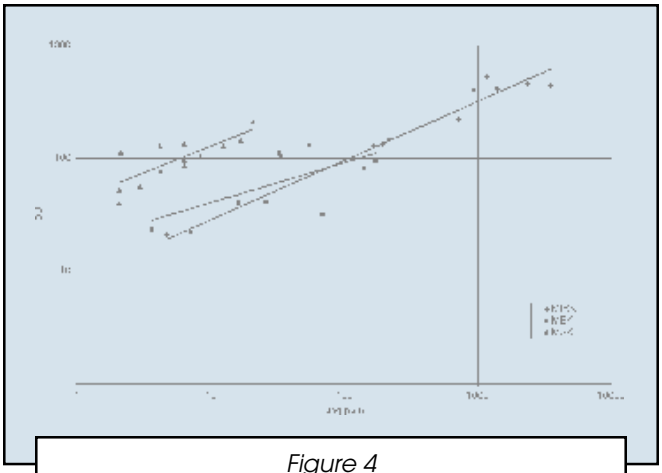

Figure 4

Figures 2-6 present odor versus concentration data for the 19 solvents studied. The equation for each solvent was generated using regression analysis of the data points. In this model, K was the y-intercept where C has a value of 1.0 ppm. (This value predicts the odor units for a sample bag with a concentration of 1 ppm.) Solvents could be compared under these conditions, but to look at different sample concentrations in the bag, the value of K was not enough. Additional information was needed to determine the odor response to a sample that was at a significantly different initial concentration than 1.0 ppm. Each solvent in the study was tested at various sample concentrations. Each concentration was run in triplicate. The majority of samples were run with a panel of 10 people although results of tests with as few as eight panelists were deemed acceptable. Responses from the

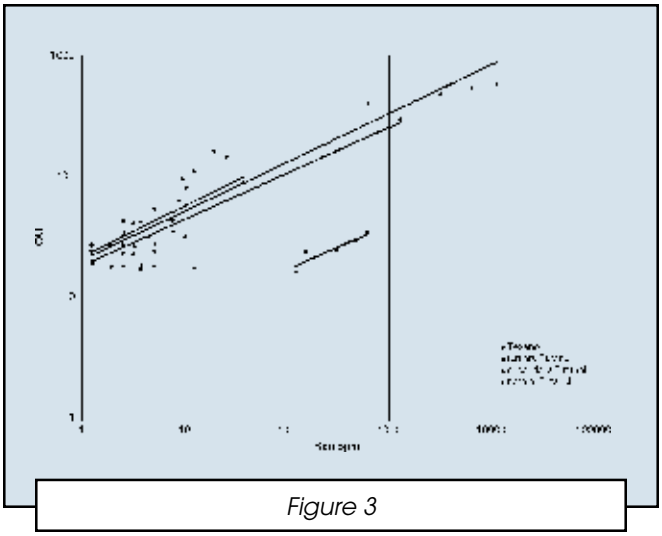

Figure 3

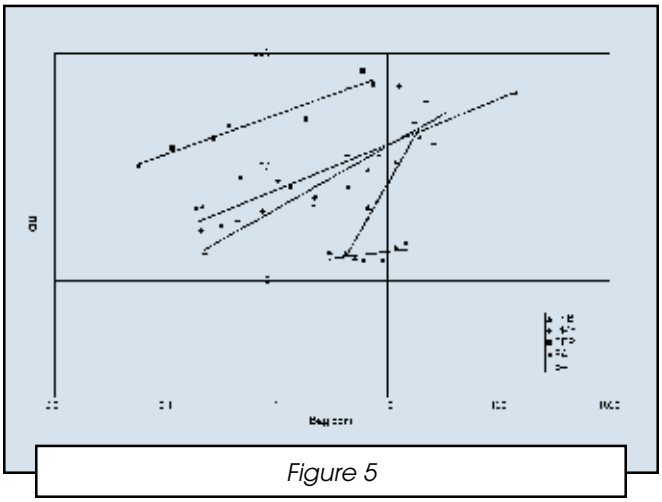

Figure 5

panelists were compiled and odor unit values calculated for each initial concentration of a solvent.

As can be seen in the various graphs, some solvents had as few as three data points where other solvents had 20 or more data points. The reason for this variability in the number of data points was the availability of the panelists and scheduling of the olfactometer. Also, some solvents were run by the same procedure as part of other studies, and this data was analyzed and incorporated into this study as well. In order to have some understanding of the quality of the data for the different solvents, an R^2 value was calculated for each solvent and the equation fit to the data for that solvent. This gave an indication of how well the curve fit the actual data gathered. As can be seen from *Table* 2, some solvents gave very good values for R^2 indicating a very good fit while some gave low values suggesting poor data.

Values for the constants K and n were obtained from the graphs, and are reported in *Table* 2. One solvent, ethyl ethoxy propionate (EEP), had a value of K that was extremely high. It has been shown many times in the emissions center that EEP containing coating compositions possessed high odor values, and were identified as very highly odiferous formulations. For EEP, the K value is 290 and the n value is 0.35. For PnB (Propylene glycol, n-butyl ether) the K value is 1.4 and the n value is 1.7. The elimination of EEP from formulations significantly reduced odor. On the other hand, PnB has unusually low odor stimulation in human responses, suggesting that it could be used to create paint formulations with little to no odor.

In order to have a number that is meaningful in trying to eliminate an odor, the values of K and n were used to calculate the degree of odor at various low concentrations. Due to the limitations of the olfactometer, the maximum dilution that could be made and tested accurately was to an OU value of approximately 20. The maximum flow rate of the meter for the sample air and the volume of the sample bag created this limitation. An extremely high flow rate would empty the bag before the test could be completed. Due to this limitation, the point at which an odor is said to be undetectable is when the value for odor units is 20 or less. Solvent concentrations were calculated that would give 20 odor units using Steven's law and the constants found for that solvent. This data is tabulated in *Table* 3.

The diluted bag concentrations were used to calculate the actual concentration at the nose when the value of 20 odor units is reached. This gives a factual number for solvent concentration in between panelist detection and non-detection. These values ranged from around 0.2 ppb (parts per billion) for a very odorous solvent like EEP, to 5-8 ppm for low odor solvents like tertiary butanol. The majority of the solvents tested ranged between 10 and 250 ppb for detection limits at the nose. This data is also summarized in *Table* 3.

These results are revealing when relating compound structure and chemistry and their relation to human odor response. Many of the more intense odors are esters. Esters are commonly used as fragrances and flavors, and it is no surprise that their odors prove to be more intense than other classes of chemicals. Alcohols

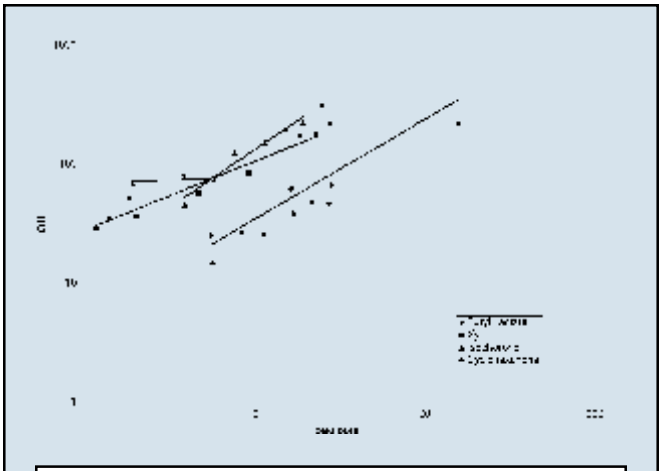

Figure 6

have fairly weak odors. As the length of the main carbon chain increases from four to five carbon atoms, odor intensity goes up significantly. This trend seems to generally hold with other classes of compounds including acetates and ketones. Ethers and esters together in the same molecule give much stronger odors than either group alone. Molecules that have six to eight atoms (carbon or oxygen) tend to have the most intense odors. Molecules with much longer or shorter chains seem to have much reduced odor.

These trends do not give absolutely clear indications of what causes odor or how easily one can predict the odor of an unknown solvent, but they do give a starting point. A hypothesis was made that additional information could be learned by looking at the physical properties of these solvents. Solvent properties were taken from various reference sources. Much of the solvent data came from technical literature from Eastman[7] and Lange's *Handbook of Chemistry, 13th Edition*. Solubility parameters, evaporation rates, and vapor pressures were taken

Table 3—Concentrations to Give 20 Odor Units

Solvent	Bag ppm Calculated for OU=20	ppb @ nose 20 OU
Butanol, tertiary	159.717	7986
Ethyl acetate	25.373	1269
Cyclohexanone	5.358	267.9
Methyl isobutyl ketone	5.139	256.9
Propylene glycol n-Butyl Ether (PnB)	4.787	239.3
Methyl ethyl ketone	1.396	69.76
Texanol	1.310	65.51
Butanol, normal	0.988	49.42
Butanol, secondary	0.848	42.38
Xylene	0.574	28.68
Amyl (pentyl) propionate	0.289	14.44
Butyl acetate	0.256	12.82
Methyl amyl (pentyl) ketone	0.194	9.69
Amyl (pentyl) acetate	0.184	9.21
Amyl (pentyl) alcohol	0.109	5.43
Propylene glycol Methyl ether acetate (PMA)	0.057	2.87
Isophorone	0.006	0.30
Ethyl ethoxy propionate (EEP)	0.003598	0.180
Butyl lactate	9.81E-09	4.90E-07

from material published by Hoy.[8] Water solubility data was also gathered from *The Merck Index*.[9] Properties which were examined included dielectric constant, dipole moment, evaporation rate, hydrogen bonding solubility parameter, molecular weight, resistivity, surface tension, vapor pressure, and water solubility. Unfortunately, upon comparison between values of each of these properties and values for the constants K and n, no significant correlation was observed. Although disappointing, this work was valuable in demonstrating that there is no simple correlation in odor based on any single property that was examined.

CONCLUSIONS

As a result of this study, a methodology for measuring and comparing odors of solvents was established. An equation was identified based on Steven's law that allows odor levels and dilution responses to be compared between different solvents. Also, a material with an unknown odor character can quickly and easily be compared to the odor response of a number of common solvents using the Devlin olfactometer. Some general conclusions regarding the relationship between structure and odor response can be made from the data, but no single property of the solvents has a significant correlation to the odor response.

References

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Appendix 1—Calculations for Solvent Condensation Concentration

Aromatic 150 has a vapor pressure of 0.62 mm Hg at 68°F (20°C)

What amount of this solvent will saturate 40 liters of air at 68°F before starting to condense on the walls of the Tedlar bag?

$$PV = nRT$$

0.62 mm Hg (1 atm/760 mm Hg) 40 Liters = n .082054 Liters - atm $mole^{-1}K^{-1}$293.15 K

$(.62)(40)/760 = n(.082054)mole^{-1}(293.15)$

n = .0014 moles (142 g/mole) = 0.19 g

Maximum Bag Concentration Volume = (.9*)(x)=.19

x = .21cm^3 or 210 microliters

*specific gravity of Aromatic 150 is 0.9

Appendix 2—Definition of Odor Units

The definition of odor units is as follows:

$$OU = \frac{F}{Vs}$$

$$Cn = Cb * \frac{Vs}{F + Vs}$$

$$Cb = Cn * \frac{(F + Vs)}{Vs}$$

$$\frac{OU}{Cb} = \frac{\frac{F}{Vs}}{Cn * \frac{(F + Vs)}{Vs}}$$

Or simplified:

$$\frac{OU}{Cb} = \frac{F}{F + Vs} * \frac{1}{Cn}$$

OU = Odor units
F = Flow of dilution air
Cn = Concentration at nose (for detection)
Cb = Concentration in the bag (referred to in ppm)
Vs = Volume of sample air in total air stream