

STUDY REGARDING THE METHOD TO CALCULATE THE VAPOUR PRESSURE OF HYDROCARBON SOLVENTS FROM SIMPLE PHYSICO-CHEMICAL PROPERTIES

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ABSTRACT: It is important to note that hydrocarbon solvents, in spite of their complex composition, are regarded as substances and there fore have one vapor pressure value, just as they have ore flash point value.

The objective of this work was to develop arid validate a calculation tool, applicable for the determination of the vapor pressure of hydrocarbon solvents based on readily available physic-chemical properties of the substances.

At vapor pressures below 0.1 kPa, many of the measurement techniques, inch as ASTM D323 [3], are not applicable, for suitable methods, sample preparation and handling, and actual measurement are extremely time-consuming hence, in practice, such methods cannot be applied routinely.

KEYWORDS: adhesive, emissions, organic compounds, polymers, solvents, monitoring methods, hydrocarbon, and properties.

1. INTRODUCTION

The Solvent Emissions Directive [1] (EU Directive 1999/13/EC) limits emissions of Volatile Organic Compounds (VOCs) in many industrial processes. This directive defines a VOC as any organic compound having a vapor pressure of 0.01 kPa or more at 293.15°K(200 °C) or having a corresponding volatility under the particular conditions of use. The directive, however, does not specify any reference method to be used to determine the vapor pressure of organic substances.

2. MATERIALS AND METHODS

In OECD Guideline 104 (adopted on 1995) [2] for the testing of chemicals, seven methods to measure vapor pressure are included. Each method has its own range of applicability and variability (Figure 1). The gas saturation method is interesting since it covers a wide range including the cut-off value of the directive.

Another difficulty stems from the fact that most commercial hydrocarbons solvents are complex mixtures of hydrocarbons with up to 50 or more individual components. Furthermore, compositions can vary slightly from batch to batch.

The issues associated with measurement could be overcome if a user-friendly calculation tool was available. However, no standard method is available to calculate vapor pressures of higher boiling hydrocarbon so, vents (typically above 150°C] without a detailed breakdown of the com position. This has led most hydrocarbon solvents producers: o develop their own calculation tools. This resulted in the need to develop a simple and

consistent calculation method to determine whether a hydrocarbon solvent is a VOC under the Solvent Emissions Directive.

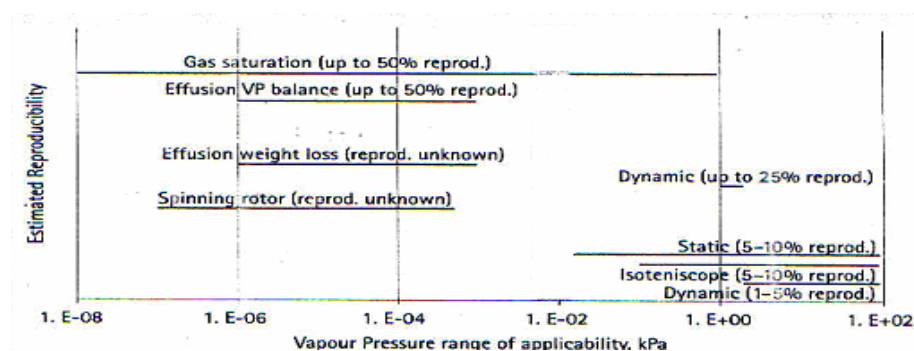


Fig. 1 Overview of methods to measure vapor pressures according to OECD Guideline 104

2.1 Calculation of vapor pressures from the physico-chemical properties

In the petrochemical industry, it is well recognized that petroleum fractions (and therefore hydrocarbon solvents) can be characterized with two parameters: (1) a "size" parameter such as the distillation range and (2) a "structure" parameter such as the ratio of aromatics to non-aromatics. The distillation characteristics (according to ASTM D 86 [6]) and the aromatics content are usually part of the specifications of commercial hydrocarbon solvents. ASTM D 86 measures the boiling point temperature as a function of the volume of the test substance distilled in a standard apparatus at atmospheric pressure. An example of a distillation curve is shown in Figure no.2.

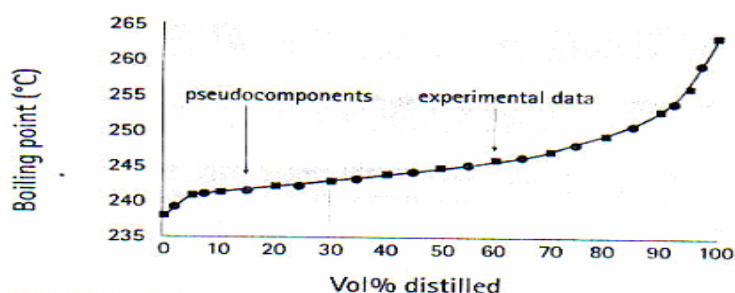


Fig. 2 Typical distillation curve and selection of pseudo-components

The distillation curve obtained using ASTM D 86 can be divided into a number of intervals with the volume intervals recorded. Subsequently, each fraction is regarded as a "pseudo-component". Taken together, these pseudo-components mimic the distillation properties of the actual sample. The boiling point of each pseudo-component is the average of the boiling points at the beginning and at the end of the volume interval concerned. (Figure no.2).

For the VPTool, thirteen points were chosen to describe the distillation curve, in line with the reporting format of ASTM D 86. This corresponds to twelve pseudo-components.

The vapor pressure of each pseudo-component can be determined using a regression of vapor pressures versus boiling points (Figure no. 3).

The regression was obtained from boiling point and vapor pressure data available for pure hydrocarbons in the DIPPR database [7]. For hydrocarbon compounds, it is widely accepted that mixtures can be regarded as ideal and that their vapors behave as perfect gases. The total pressure of a mixture of ideal gases is the sum of the partial pressures p_i of the individual gas components (Raoult's law):

$$P_{\text{mixture}} = \sum p_i = \sum x_i * P_i$$

where:

P_{mixture} = pressure of hydrocarbon solvent

p_i = partial pressure of pseudo-component i

x_i = molar fraction of pseudo-component i

P_i = vapour pressure of pseudo-component i

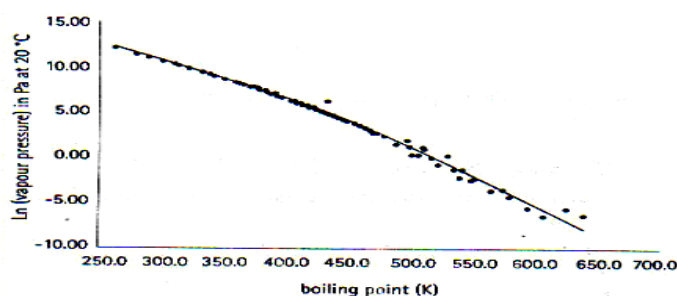


Fig. 3 Relationship between vapor pressure and boiling point for pure hydrocarbons

In order to calculate the total vapor pressure according to equation, the molar fractions of the pseudo-components have to be derived from volume % using the liquid molar densities. A plot of the molar densities of various hydrocarbon families versus their normal boiling points is shown in Figure no. 3 To simplify the calculation, only aromatic and paraffin regression curves from Figure 6 were used.

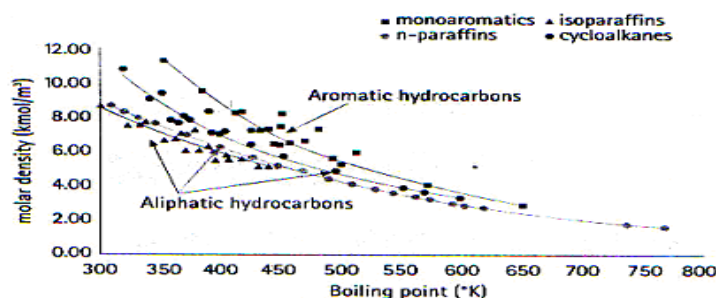


Fig. 4: Relationship between liquid molar density and boiling point for various pure hydrocarbon types (data from OIPPR.1998)

From the distillation temperature data and the aromatics content (ASTM D 1319 [8]) the molar density of each pseudo-component can be calculated using). The regression curve of mono-aromatics for the aromatic fraction and the regression curve of n-paraffin's for the non-aromatic part.

3. RESULTS AND DISCUSSIONS

Six mixtures of hydrocarbon compounds of known composition were prepared. Five of those mixtures were made of various amounts of n-paraffin in the C11-C15 range. The sixth mixture contained approximately 18% of 1,4-diisopropylbenzene, in addition to n-paraffin's.

The new VP Fool program, based on the aforementioned methodology, was used to calculate the vapor pressures of the six test samples of known composition (samples A to F). A comparison was made with the calculated results obtained with the Subtcc program [9] and with the vapor pressure measurements using the gas saturation method (Table no.1).

Table no. 1

Sample	A	B	C	D	E	F
VP Toll calculation	6,3	2,8	2,4	6,4	6,5	8,9
SUBTEC calculation	4,7	2,6	2,2	4,7	4,9	12,1
Gas saturation Measurement	3,8	2,2	2,0	4,1	4,3	10,0

Vapor pressures calculated with the VP Tool tended to be higher than vapor pressures obtained by measurement or with the SUB-TEC software, except for sample F that contains about 18% of an aromatic compound. The bias between the measured and the calculated vapors pressures using the VP Tool ranges from 0.4 to 2.5 Pa with an average of 1.5 Pa (about 30%). These discrepancies are considered acceptable ice they fall well within the variability found from actual measurements by various methods at these vapors pressure levels (Figure no. 1).

4. CONCLUSIONS

Taking into account the unavoidable sources of error Inherent to vapor pressure determination for low volatility products and the assumptions that needed to be made to keep the tool simple, the VP Tool is believed to be suitable as a standard tool to calculate vapor pressures of commercial hydrocarbon solvents. Since the VP Tool was not validated over a broad range of vapor pressures, it is proposed to limit its application range to products with initial boiling points higher than 20CTC by ASTM D 86 method (corresponding to vapor pressures lower than approx. 0.1 kPa).

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