

AN EMPIRICAL NUMERICAL RELATION BETWEEN EVAPORATION RATE AND FLASH POINT OF COMMON INDUSTRIAL LIQUID MATERIALS

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Abstract

It is a common occurrence that information on flash points [T_f] and/or relative evaporation rates [$r_{evap}(AcOBu=1)$] are not always included simultaneously in safety data sheets of biofuels, biosolvents and common liquid materials in general, as mandated by the newest requirements of the United Nations Globally Harmonised System of Classification and Labelling of Chemicals. Compliance with these requirements improve the safety and health of employees, by potentially bringing about cost savings through appropriate storage and handling conditions, as well as the use and disposal of chemicals. Improvement of this circumstance can be done by either include the missing experimental datum or by offering an estimated figure, based on a clear simple molecular rationale. The calculation of either property from the other is possible by means of the equation: $T_f/^{\circ}C = 22 - 38 \times \log r_{evap}(AcOBu = 1)$ empirically obtained by correlation of 81 T_f and $r_{evap}(AcOBu=1)$ data pairs ($p < 0,01$). The equation was assessed with the reported T_f of 32 additional test liquids and showed an average absolute deviation of 8 $^{\circ}C$.

Keywords: Evaporation rate, Flash point, Occupational safety.

1. Introduction

The search for “green” neoteric materials must obviously include not only the appropriate reactivity characteristics for the particular chemistry at hand (e. g. solvent compatibility with the reaction-mixture components), but also economic and regulatory issues, as well as the corresponding aspects of energy needs and waste disposal.

Manufacturers, distributors, and importers must make available safety data sheets (SDS) to users, as the way to communicate about hazards of chemical products handling.

This article deals with the physical properties *flash point* (T_f) and *evaporation rate* (r_{evap}), two important safety, health and environmental (SHE) issues. According to the Globally Harmonized System of Classification and Labelling of Chemicals [1], these two physical parameters are particularly mandatory amongst the minimum information pieces that should be included in SDS.

For the case of classic and neoteric raw materials, solvents or biofuels, consideration of their SHE properties is a major step toward a sustainable industrial future, but it is a common fact that one of the two above mentioned parameters is not always included in SDS of liquid materials. Thus, process chemists, engineers, laboratory personnel, safety professionals and operators of industrial equipment rely on SDS as the documents that register the relevant information on health and other occupational safety issues concerning the use of either pure substances or complex mixtures. SDS should also include information for their safe use and hazards associated with handling and storage of the particular materials in an occupational location. For the case of liquids and volatile solids (e.g., naphthalene, *para*-dichlorobenzene, or camphor), the SDS physico-chemical parameters should include vapour pressure (p_v) usually at 25 °C, r_{evap} at room temperature and T_f .

Unfortunately, very many SDS fail to include some values of important physical parameters, such as the three mentioned above.

The determination of T_f is a straightforward procedure, obviously when the proper equipment is available. Most cases comply by reporting this parameter. On the other hand, the volatility of liquids indicated by r_{evap} is not always reported. It is measured as indicated by procedures such as ASTM D3539. The equipment needed implies a higher monetary investment than for the case of T_f determinations, and this may be the cause of the quandary.

Vapour pressure is the pressure of a vapour in equilibrium with its condensed phase. For the case of a volatile solid, it is more properly called sublimation pressure [2].

The evaporation rate measures how fast a material becomes vapour. It is customary to report the value relative to the quantity corresponding to *n*-butyl acetate, represented by the symbol $r_{evap}(\text{AcOBu} = 1)$.

Fast evaporating liquids have $r_{evap}(\text{AcOBu} = 1) > 3,0$ such as acetone (5,3) or *n*-hexane (8,3). Medium speed evaporating liquids are in the range 0,8 – 3,0 as the case of 95% aqueous ethanol as example (1,4). Slow evaporating liquids are considered as those with $r_{evap}(\text{AcOBu} = 1) < 0,8$ as the case of water with 0,3.

T_f is the minimum temperature at which condensed materials form a vapour above its surface in concentration high enough that one can make it to kindle by the

effect of an ignition source. T_f is an empirical parameter rather than a fundamental physical property.

A method for T_f prediction has been proposed by Alibakhshi et al. [3] based on normal boiling points and molecular group contributions of pure organic liquids. The method offers predictions with average absolute deviation of 14% relative to experimentally observed values.

It is the impression of the author that workers in industrial fields relate r_{evap} more to health matters and T_f to fire and explosion hazards.

The utility of having $r_{evap}(\text{AcOBu}=1)$ and T_f values at hand does not come down to only fire/explosion risks, but also in the formulation and production of perfumery, cosmetic, and edible products. The evaluation of emissions of volatile solvents is mandatory for the design of pharmaceutical and food plants where organic solvents are used [4]. Joshi and Adhikari [5] offer an interesting comment on the usefulness of r_{evap} for first-aid procedures, as the case of contact of eyes with solvents or other irritant substances: "In case of chemical contact to eye, ... immediately flush with running water for at least 15 minutes, by keeping the eyelid open will allow proper air supply to the eye which will enhance fast evaporation of solvents from eye surface and decrease the furthermore risk".

As indicated above, $r_{evap}(\text{AcOBu} = 1)$ and T_f are not always given simultaneously in SDS, therefore it is useful to have an easy numerical procedure for the estimation of either of the missing datum, often $r_{evap}(\text{AcOBu} = 1)$.

A much broader discussion about chemical and SHE properties of neoteric materials can be found in the papers of Prat et al. [6], Diorazio et al. [7], and Clark et al. [8].

This communication gives an empirical equation that links T_f and $r_{evap}(\text{AcOBu} = 1)$ as aid for practical industrial and occupational-health personnel, and for companies that need to fulfil the GHS mandates.

2. Materials and Methods

A linear relation is expected to exist between T_f and $\log r_{evap}(\text{AcOBu}=1)$, as explained in the subsequent Results and Discussion section. The best regression parameters were obtained by least-squares fitting (*Excel*).

The T_f and $r_{evap}(\text{AcOBu} = 1)$ data set employed in this study consisted of 81 liquids obtained from reference sources such as the books of Smallwood [9], Wypych [10], and Li and Chemat [11].

The Pearson's correlation coefficient (R_p) was used as crude index of goodness of fit since there is an unknown degree of variation in the accuracy amongst the data pairs in all recorded data by the authors mentioned above.

3. Results and Discussion

The molecular concept of p_v is the measure of the tendency of molecules to escape from condensed surfaces to the vapour phase, and therefore both r_{evap} and T_f are dependent on the former thermodynamic equilibrium-phase property.

The Knudsen-Hertz equation gives the flux of evaporating molecules from a condensed surface on a molar base [12]:

$$\frac{-dn_{liq}/dt}{Area} = \kappa \frac{p_v(T)}{\sqrt{2\pi M RT}} \quad (1)$$

where κ is the transmission factor that gives the fraction of molecules that remain in the gaseous phase, $p_v(T)$ is the material vapour pressure at temperature T , M its molecular mass and RT has its usual meaning.

Mackay and Van Wesebeeck [13] have proposed a semi-empirical relationship between r_{evap} and $p_v(T)$, based on the Knudsen-Hertz equation, slightly modified from molar into ponderal terms:

$$-\frac{dm/dt}{Area} = constant \times p_v(T) \times M \quad (2)$$

The proportionality constant includes temperature and κ . It is known since more than half a century ago, that κ values depend on the specific properties of liquids and solids [14]. Nevertheless, the empirical observation of Mackay and Van Wesebeeck [13] indicates that the proportionality parameter varies within a relatively narrow range enough to provide acceptable estimations of r_{evap} . The average value of the constant obtained by those authors from the r_{evap} and $p_v(T)$ properties of 82 liquids at 25 °C is 1464, with a $p = 0,005$ uncertainty range of ± 180 (12%).

As indicated above, T_f is also a manifestation of $p_v(T)$. In fact, the empirical correlation $T_f = a + b \log p_v(T)$ is known between these properties [9], where the parameters a and b have appropriate values for different molecular families such as alcohols, esters, ethers, hydrocarbons, etc. [10]. Thus, one can expect on intuitive and merely mathematical grounds that a correlation should exist between T_f and $\log r_{evap}(\text{AcOBu} = 1)$. Such relationship is observed indeed in Fig. 1 for a training set of 81 liquids with data obtained from the compilations of Smallwood [9], Wypych [10] and Li and Chemat [11].

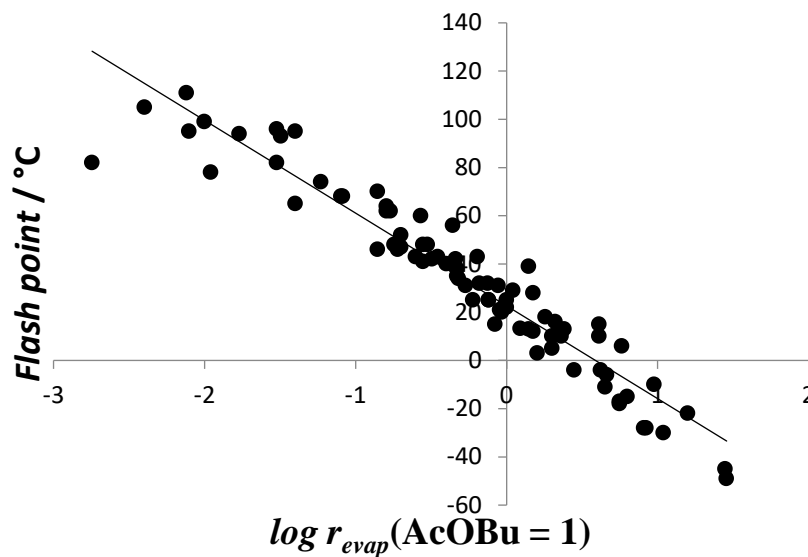


Fig. 1. Correlation between the flash point of various liquids and their rates of evaporation.

The regression equation obtained from linear least-squares fitting is:

$$T_f / ^\circ\text{C} = (22 \pm 1) - (38 \pm 1) \log r_{\text{evap}}(\text{AcOBu} = 1) \quad (3)$$

The Pearson's correlation coefficient $|R_p| = 0,95$ ($p < 0,01$) is acceptable, despite the large number of information sources that make up the tables in those reference compilations.

A set of 32 additional liquids was further subjected to testing by using the above regression equation; 8 were pure substances and 15 were complex solvent mixtures. They were chosen due to their more complex nature, relative to simple pure substances. Figure 2 shows the comparison of T_f values observed by direct report and the estimated values obtained from the use of Eq. (3).

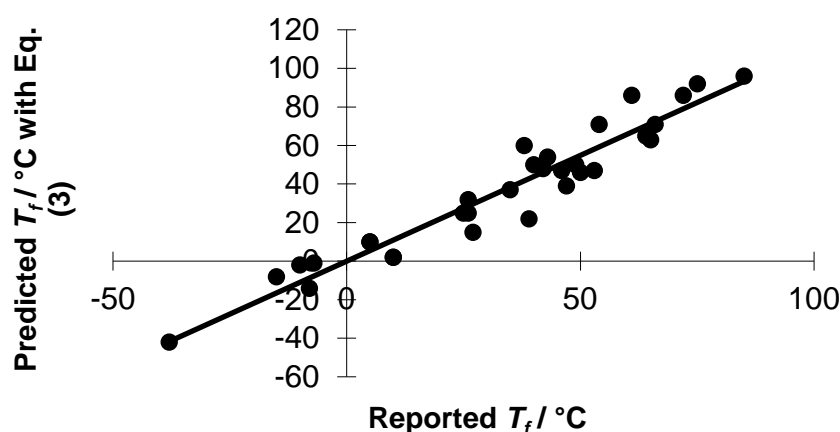


Fig. 2. Validation of equation (3).

The agreement between the calculated and observed values is acceptable ($R_p = 0,96$). The line in Fig. 2 is represented by the equation:

$$\text{Predicted } T_f / ^\circ\text{C} = (1,10 \pm 0,04) \text{ Reported } T_f / ^\circ\text{C} \quad (4)$$

This testing database shows an average absolute deviation of $8 ^\circ\text{C}$, but the result is adequate for the objective pursued in this work as shown in *Appendix B*. Inclusion of the additional 32 liquids in the training database has no significant numerical consequences on the parameters of Eq. (3).

The magnitude of $r_{\text{evap}}(\text{AcOBu} = 1)$ for a volatile material is a function of the chemical nature of the substance itself, the temperature of the liquid and the air around, the atmospheric pressure, and even also the relative humidity of the environment. Laboratory measurements of r_{evap} are frequently carried out *side by side* with *n*-butyl acetate. The initial rate of evaporation of a liquid is compared with that of the reference ester. This consideration opens the need to utilise a better evaporation kinetic parameter than initial rates for mixtures, because initial rates depend on their composition; as the more volatile components exit the condensed phase, and the remaining liquid becomes more concentrated with the less volatile

constituents. Thus, actual rate of evaporation of mixtures ($-dm/dt$) is not constant for liquid mixtures as predicted by the Hertz-Knudsen equation but decreases along the evaporation process. This endeavour is currently under study in our laboratory.

4. Conclusions

The following practical conclusions derived from the present study will surely contribute to comply with health and environmental issues required by the Globally Harmonised System of Classification and Labelling of Chemicals.

- An empirical relationship was found between flash point and the logarithm of the relative rate of evaporation of liquids with a high degree of statistical significance ($p < 0,01$).
- Equation (3) allows the calculation of the relative rate of evaporation of liquids from the more commonly reported flash-point data. The calculation of flash point is also possible when rate of evaporation is the known parameter.
- Performance of Eq. (3) is adequate since it gives an average absolute deviation of 8 °C in the calculated T_f values.
- The calculation of rates of evaporation of liquids is useful information for the evaluation of health risks because a substance with high r_{evap} implies it readily forms vapour which can be inhaled in relatively closed working spaces. Likewise, having an assessment for T_f is important for fire investigation and protection related to the use of a given material. Thus, the use of Eq. (3) when either flash point or the relative rate of evaporation is missing in SDS solves the difficulty.
- The use of the mathematical relation described in this work Eq. (3) is a way to fill blank spaces in SDS concerning mainly with rates of evaporation, since the estimations yielded by Eq. (3) are of sufficient accuracy; and can be taken as a sign of corporate responsibility from manufacturers and dealers of chemicals.
- The $r_{evap}(AcOBu = 1)$ of mixtures of components correspond to the observed initial rate of evaporation of the materials, relative to the constant rate of evaporation of *n*-butyl acetate. The values have physical meaning but, a more theoretically sound correlation would be between T_f and the fractional rate of evaporation of the multicomponent liquid (first-order kinetics for the evaporation process). This issue is now under study in our laboratory.

Nomenclatures

p_v	Vapour pressure, kPa
$r_{evap}(AcOBu = 1)$	Relative evaporation rate
T_f	Flash point, °C
n_{liq}	Moles of evaporating liquid at time t, mol
$-dm/dt$	Ponderal rate of evaporation, kg s ⁻¹
M	Molecular mass of evaporating liquid, kg mol ⁻¹
a, b	Fitting linear parameters
R_p	Pearson correlation coefficient

Abbreviations

SDS	Safety Data Sheet
SHE	Safety, Health and Environmental

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Appendix A

Database of liquids used for obtaining Eq. (3)

Liquid	$r_{\text{evap}}(\text{AcOBu} = 1)$	$T_f / ^\circ\text{C}$
Acetone	5.6	-18
Methyl acetate	9.5	-10
Ethanol	2.4	13
Isopropanol	1.5	12
1,4-Dioxane	2.2	12
s-Butyl acetate	2.1	16
Toluene	2	5
Isopropyl acetate	1.6	3

Liquid	$r_{\text{evap}}(\text{AcOBu} = 1)$	$T_f / ^\circ\text{C}$
<i>s</i> -Butanol	0.9	21
Diethyl carbonate	1.1	29
Turpentine	0.48	34
<i>n</i> -Butanol	0.47	35
Cellosolve®	0.35	43
Fusel	0.32	42
Butyl-cellosolve®	0.082	68
Ethyl acetate	4.2	-4
Methyl-ethyl ketone	4.6	-6
<i>n</i> -Pentane	28.6	-49
<i>n</i> -Hexane	15.8	-22
<i>n</i> -Heptane	2.8	-4
Methanol	4.1	15
<i>n</i>-Butyl acetate	1	22
Xylene mixture	0.76	25
<i>n</i> -Octane	1.23	13,3
Cyclohexane	5.6	-17
Benzene	4.5	-11
Ethylbenzene	0.84	15
<i>n</i> -Propanol	1	25
<i>i</i> -Butanol	0.6	25
<i>n</i> -Pentanol	0.3	48
Cyclohexanol	0.08	68
Propylene glycol	0.01	99
Propylene glycol methyl ether	0.66	32
Methyl-cellosolve®	0.47	38
Tetralin	0.059	74
<i>i</i> -Pentanol	0.19	46
Cyclohexanone	0.25	43
<i>N</i> -metil-2-pyrrolidone	0.04	95
Acetophenone	0.03	82
Diethyl ether	28	-45
Diisopropyl ether	8.1	-28
Methyl <i>tert</i> -butyl ether	8.4	-28
Tetrahydrofuran	6.3	-15
Cellosolve® acetate	0.2	52
Dimethylformamide	0.17	62
Dimethyl-acetamide	0.14	70
Carbon disulphide	10.9	-30
2-Nitropropane	1.5	28
Furaldehyde	0.16	62
Acetonitrile	5.8	6
Pyridine	0.93	20
Dimethyl sulfoxide	0.0079	95
Ethylene glycol	0.0076	111
Methyl-isobutyl ketone	1.4	13
Limonene	0.28	48
<i>i</i> -Butyl acetate	1.8	18
<i>n</i> -Amyl acetate	0.4	40
Methyl-cellosolve® acetate	0.44	56
Diethylene glycol monomethyl ether	0.032	93
Diacetone alcohol	0.16	64
Methyl-isoamyl ketone	0.64	43
Di-isobutyl-ketone	0.27	60
Isophorone	0.03	96
Nitromethane	1.4	39
Pine oil	0.011	78
Cumene	0.14	46
Styrene	0.536	31
Xylene	0.76	25
Methanol	4.1	10

Liquid	$r_{\text{evap}}(\text{AcOBu} = 1)$	$T_f / ^\circ\text{C}$
Methyl-isobutyl-carbinol	0.28	41
2-Ethyl-hexanol	0.0018	82
Furfuryl alcohol	0.04	65
Methyl-propyl ketone	2.3	10
Methyl-butyl ketone	0.98	23
Di-isobutyl ketone	0.2	47
Methyl-cyclohexanone	0.18	48
Mesityl oxide	0.88	31
<i>n</i> -Propyl acetate	2	10
Ethyl-diglycol	0.017	94
Butyl-diglycol	0.004	105
1-Methoxy-2-propanol	0.75	32
Ethoxy-propanol	0.46	42
Isobutyl isobutyrate	0.48	34
Diethylene glycol monobutyl ether	0.00285	98
Diethylene glycol monoethyl ether	0.00941	92
Nitroethane	1.28	30
1-Nitropropane	0.85	35

Appendix B

Database of liquids used for assessment of Eq. (3)

Material	T_f calculated ($^\circ\text{C}$)	T_f observed ($^\circ\text{C}$)
SBP 140/165 (Shell) M = 128	26	32
White spirit (Spiridane)	47	39
White spirit (Spiridane)	26	25
White spirit (Spiridane)	25	25
Kerosene (total)	72	86
Kerosene (total)	75	92
Kerosene (total)	85	96
Solvarex 10 A	65	63
Solvarex 10 LN	64	65
Exxol	-15	-8
SBP 80/110 LNH (Shell) M 100	-10	-2
Laquer diluent	-7	-0,9
VM&P naphtas type I	5	10
VM&P naphtas type II	27	15
VM&P naphtas type III	5	10
Deodorised kerosene	61	86
High flash aromatic naphtas, Type I Aromatic 100	42	48
High flash aromatic naphtas, type II Aromatic 150	66	71
Wood turpentine	35	37
Dipentene	49	50
Pine oil	54	71
Varsol 3139 Solvent	43	54
Esso, M 143	40	50
Solvent 3040	38	60
Ethyl acrylate	10	2
Methyl methacrylate	10	2
Vinyl acetate	-8	-14
Acetic acid	39	22
Propionic acid	50	46
Acetaldehyde	-38	-42
2-Ethyl-butyl acetate	53	47
Ethyl lactate	46	47