Temperature Dependence of the Lower Explosion Limits of pure Components and Mixtures

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Introduction

The knowledge of the temperature dependence of the Lower Explosion Limits (LEL) is a very helpful tool in explosion prevention, e.g. for drying processes at elevated temperatures. With increasing temperature the LEL decreases. So the use of the LEL at ambient temperature is not safe enough at elevated temperatures. It is however possible to approximate this decay linear till temperatures near to the autoignition temperature. The temperature dependence of the LEL of flammable liquids depends on the respective liquid and is influenced by the diameter of the vessel. Even if the LEL of a pure flammable substance is known for elevated temperatures, this is not sufficient if mixtures of chemicals are involved.

Fundamental Issues

S(LEL) = 100 $*$ (LEL_{100}-LEL_{20})/$LEL_{20,}$ which is the relative decrease of the lower explosion limit with increasing temperature, was reported by Zabetakis (1965) in a magnitude of about -7% of LEL_{20} per 100 K. From the experimental results from Schrödter (1986) and from our own experiments with the apparatus according to DIN 51649 (1986) a value of about -14% of LEL_{20} per 100 K can be derived. Values determined in an explosion vessel having a diameter of 80 mm may result in up to -23 % of LEL_{20} per 100 K (see Table 1). This difference is first of all due to the fact that the lower explosion limits at higher temperatures (> 150°C) decrease with increasing diameter of the explosion vessel (see Table 1).

Recent Experimental Progress

Experiments have been carried out with flammable mixtures to clarify whether

- the lower explosion limits, LEL(T), of flammable mixtures at elevated temperatures, T, can be calculated using LeChatelier's mixing rule (1891)

$$1/LEL_{mix}(T)=\sum_{i=1}^{n}\frac{x_i}{LEL_i(T)} \text{ ,} \qquad x_i\text{: molar amount of component i}$$

  and consequently via linear regression their temperature dependence
- the calculation of a mean relative temperature decrease $S(LEL)_{mean}$ of the lower explosion limit of the pure compounds

$$S(LEL)_{mean}=\sum_{i=1}^{n}x_i\cdot S(LEL)_i \text{ ,} \qquad \mathbf{/1/} \qquad x_i\text{: molar amount of component i}$$

results in safe figures.

These recent experiments have been carried out according to EN 1839 (2004) Method T (vertical glass tube: inner diameter 80 mm; height 600 mm respectively 800 mm, closed at both ends; spark ignition 0,5 Ws at the bottom; criterion: flame travelling upward at least 50 mm). The explosion vessel and the equipment for mixing the vapour/air mixtures have been arranged in a heating chamber. The respective test temperatures have been chosen in order to avoid any condensation of the mixture or its components. The liquids have been totally evaporated (see EN 1839 (2004)). More data see CHEMSAFE. The LEL have been measured at temperatures up to 200°C, examples see Fig. 1.

Table 1. Relative decrease of the LEL with increasing temperature in % per 100 K (rounded to 0,5 % per 100 K)

Substance	$\varnothing_{\text{vessel}}$: **25 mm Zabetakis (1965)**	$\varnothing_{\text{vessel}}$: **60 mm (DIN 51649)**	$\varnothing_{\text{vessel}}$: **80 mm (EN 1839 method T)**
Butyl propionate	(-7,0)*	-17,0	-17,0
Ethyl acetate	(-7,0)*	-14,0	-19,0
Pentyl acetate	(-7,0)*	-14,0	-17,0
Octyl octanoate	(-7,0)*		-23,0
Methanol	(-7,0)*	-13,0	-13,0
n-Butanol	(-7,0)*	-15,0	-17,0
n-Octanol	(-7,0)*	-13,0	-13,5
n-Hexane	-7,0	-14,0	-16,5
n-Heptene	(-7,0)*	-19,5	-20,0
m-Xylene	-7,0	-11,5	-19,0

*assumed by Zabetekis

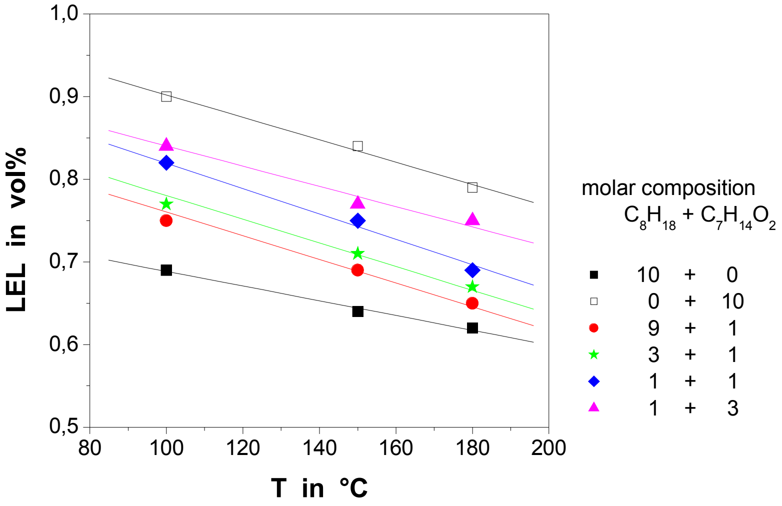

Figure 1. Temperature dependence of the LEL for n-octanol/n-pentylacetate mixtures

Table 2 summarises examples of $S(LEL)_{exp}$ for pure components and mixtures derived from the experimental data, the $S(LEL)_{mean}$ according to equ. /**1**/ for the mixtures, and the $S(LEL)_{LeChat}$ for the mixtures derived from LEL calculated according to LeChateliers rule using LEL of the pure compounds measured at different temperatures. The uncertainties for the different S(LEL) are roughly estimated as follows:

- $S(LEL)_{exp.}$: 1,5 times the uncertainty as given in EN 1839 (the uncertainty of the linear regression is taken into account)
- $S(LEL)_{mean}$: 2 times the uncertainty as given in EN 1839
- $S(LEL)_{LeChat}$: 2 times the uncertainty as given in EN 1839, slightly more for some mixtures with halogenated compounds, see Fig. 2

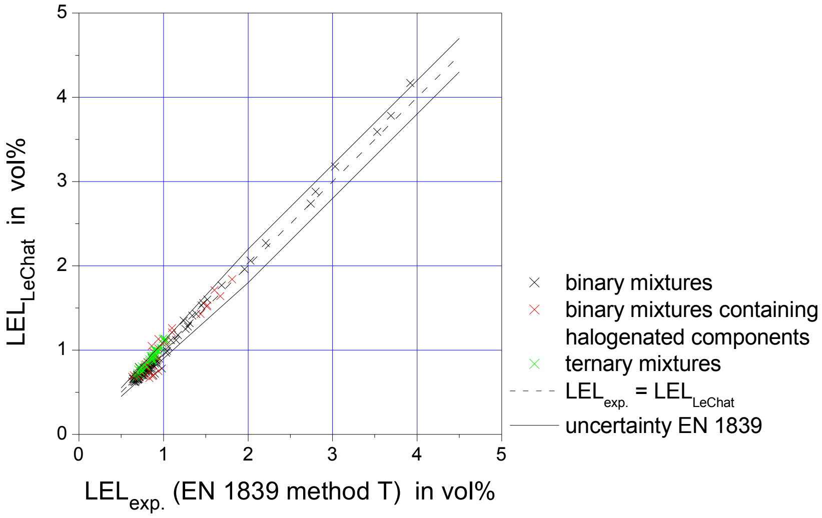

Figure 2. Measured LEL versus LEL calculated according to LeChatelier's rule (examples)

Table 2. Examples for $S(LEL)_{exp}$, $S(LEL)_{mean}$ and $S(LEL)_{LeChat}$ (rounded to 0,5 % per 100 K)

Pure substance or Mixture	$x_1/\sum_{i=1}^{n} x_i$ **mol/mol**	**$S(LEL)_{exp}$ % per 100K**	**$S(LEL)_{mean}$ % per 100K**	**$S(LEL)_{LeChat}$ % per 100K**
n-Octanol	1	-13,5 ± 2,0		
n-Pentylacetate	1	-13,0 ± 2,0		
n-Octanol + Pentylacetate	0,9	-14,0 ± 2,1	-13,5 ± 2,7	-13,5± 2,7
1,2-Dichloroethene	1	-16,0 ± 2,4		
n-Octanol + 1,2-Dichloroethene	0,7	-18,0 ± 2,7	-14,5 ± 2,9	-16,0 ± 3,2
n-Butylpropionat	1	-17,0 ± 2,5		
n-Octanol + n-Butylpropionat	0,8	-14,5 ± 2,2	-12,5 ± 2,5	-12,0 ± 2,4
n-Octanol + n-Butylpropionat	0,67	-11,0 ± 1,6	-11,5 ± 2,3	-10,5 ± 2,1
Methanol	1	-11,5 ± 1,7		
n-Octanol + Methanol	0,9	-11,5 ± 1,7	-12,0 ± 2,4	-12,0 ± 2,4
m-Xylene	1	-17,0 ± 2,5		
n-Octanol + m-Xylene	0,9	-11,5 ± 1,7	-14,0 ± 2,8	-11,5 ± 2,3

Conclusions

The values of $S(LEL)_{exp}$ of the pure components and of the mixtures investigated vary over a wide range from about -9 % to -23 % of LEL_{20} per 100 K.

The $S(LEL)_{exp}$ for mixtures are not in all cases between the values of the respective single components. They may be lower or higher. Therefore the $S(LEL)_{mean}$ calculated by linear interpolation as well as the values calculated using LeChatelier's mixing rule $S(LEL)_{LeChat}$ do not reflect in every case the experimental results. However taking into account the uncertainty given by – 20% (relative), see above, the calculated results become safe enough (Fig. 3) for many technical purposes. In all cases these calculated results provide a larger safety margin than the value of -14% per 100 K given in EN 1539 (2000) for dryers and ovens. If more precise results are required, experimental determination of the LEL at the respective conditions is necessary. Taking S as -25% of LEL_{20} per 100 K – although not in every case necessary – gives safe results under all known conditions without measurements.

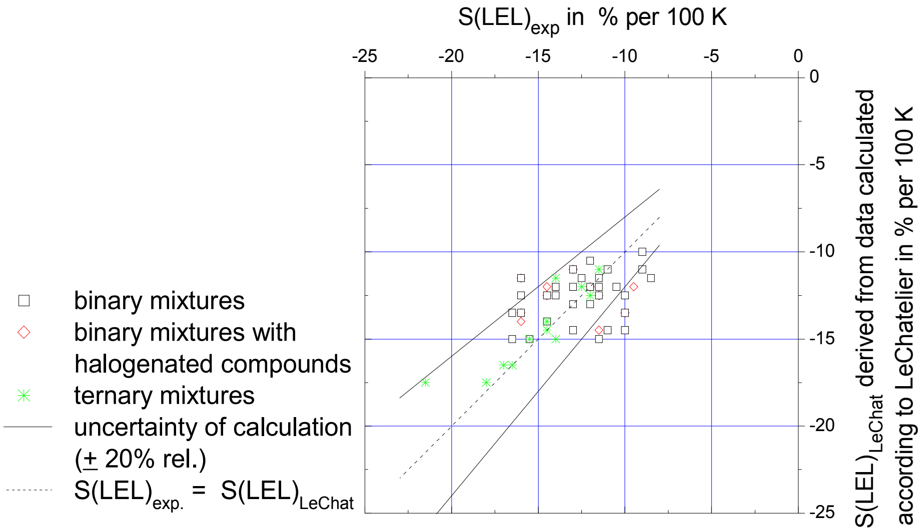

Figure 3. $S(LEL)_{exp}$ versus $S(LEL)_{LeChat}$

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