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An equation for the estimation of alcohol-air diffusion coefficients for modelling evaporation losses in fuel systems

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HIGHLIGHTS

- Diffusion coefficients are needed for predicting evaporation losses in fuel systems.
- Nine equations were applied to the binary gaseous alcohol-air mixtures.
- Experimental results were obtained at temperatures 25–50 °C for C1 to C5 alcohols.
- Results were compared with data from literature and from equations predictions.
- A new four-parameter equation is proposed showing good agreement with experiments.

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ABSTRACT

Alcohols (not only ethanol but also methanol, propanol, butanol and pentanol) are receiving increasing attention as components for blending with conventional fuels (gasoline and diesel or biodiesel fuels) because they can be an efficient means to increase the renewable fraction of fuels and to reduce emissions. Mathematical models for predicting evaporation losses in storage and fuel distribution systems require information about diffusion coefficients, among other characteristic parameters of the alcohols and of the alcohol-air gaseous mixtures. Nine equations in the literature have been described and applied to the binary gaseous mixtures alcohol-air to estimate the diffusion coefficient. Other equations were discarded because they are not applicable to alcohol-air systems. The resulting diffusion coefficients were plotted against temperature for the five mentioned alcohols, and the results were compared with experimental data obtained from measurements with capillary glass tubes immersed in a controlled temperature glycerine bath at 25 °C, 30 °C, 40 °C and 50 °C. The diffusion coefficients were determined from the variation of the height of the liquid column and the vapour pressure. From comparing the standard deviations with respect to the experimental data, although the best fit for all alcohols was reached with the Arnold equation (0.0247 cm^2/s), it was concluded that there is not a unique optimal formula for all alcohols. Additionally, all the revised equations underestimate the effect of temperature for methanol, ethanol and propanol. Specific logarithmic equations were proposed in this work for estimating the diffusion coefficient for each alcohol, and finally, a four-parameter equation was also proposed for the five alcohols studied, which provided excellent agreement (standard deviation 0.0045 cm^2/s).

1. Introduction

Alcohols are receiving increasing interest as fuels for various reasons. On the one hand, new processes are being developed for the production of alcohols from renewable feedstocks [1]. Therefore, blends of gasolines or diesel fuels (or even diesel biodiesel blends) with alcohols are becoming one of the most efficient means to introduce a renewable fraction in the fuel, to improve its sustainability, to reduce its viscosity [1,2] and to provide some oxygen content, which will be essential to reduce soot emissions from spark ignition [3,4] or diesel engines [5–7]. However, different challenges will have to be faced for the future extension to the large-scale use of these alcohols as fuel components. One of these challenges is to address the fuel storage and handling difficulties

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derived from the high volatility of alcohols. Previous experiences with ethanol blends with either gasoline or diesel fuels have proved that different technical modifications in the fuelling system are necessary, such as the installation of seals for fuel tanks, flame arresters, security valves on both vehicle fuel tanks and fuel station tanks, special systems to recover fuel vapours on vehicles and fuel stations and to avoid vapour locks, etc. [8,9]. These restrictions constitute a barrier for the massive use of these blends in private vehicles, and have limited their practical use to captive fleets, such as those of urban buses or public construction vehicles and civil machinery.

The design of the most adequate storage and fuelling systems for each blend requires detailed knowledge about the evaporation losses from the liquid phase and the diffusion along the gas phase. Diffusion models often assume constant values for the diffusion coefficient neglecting the effect of temperature and pressure [10], or use polynomial fits as a function of temperature [11]. One of the most challenging points in this modelling process is the selection of the equation for estimating the diffusion coefficient alcohol-air. This work reviews the equations reported in the literature and proposes their application to different alcohol-air mixtures, the alcohols ranging from methanol to pentanol. This is a first step for the modelling of the evaporation losses from alcohols in tanks, lines and nozzles and their diffusion into habitable spaces.

The first approach for the estimation of the diffusion coefficient was proposed by Maxwell and Stefan [12] who used previous classical works by Meyer [13] and Jeans [14]. One of the key studies is the theory proposed by Chapman and Enskog, as cited in [12], who solved the Bolztmann equation. Based on this theory, different approaches have been proposed to solve the diffusion coefficient. Among these, the methods proposed by Chapman and Enskog [12] and Wilke and Lee [15] make use of the collision integral, whereas other equations do not include this parameter, either because they neglect the molecular interactions between the mixed gases or because they have an empirical origin. The equations reported in the literature for the determination of the diffusion coefficient were fitted to a variety of blends of inorganic and organic compounds [15–32], none of them being specific for a family of substances. Additionally, there is a wide dispersion among the experimental values reported in the literature for the diffusion coefficient of C1 to C5 alcohols with air, which may be attributed to differences in the experimental methods [33]. Moreover, these results are scarce for temperatures above 25 °C and for alcohols other than n-butanol y ethanol [18,19].

This motivated the present study, where the equations proposed in the literature are compared with experimental data for diffusion coefficients reported for C1 to C5 linear alcohols, and with experimental results obtained in this work from the variation of the liquid height and the vapour pressure of the alcohols in a capillary glass tube subjected to different temperatures. The final objective of this study is the selection of an existing equation or the proposal of a new one for the determination of the diffusion coefficient, with the aim to be applied to the estimation of alcohol evaporation losses in fuel systems operating under atmospheric conditions.

2. Diffusion of alcohols in air

The diffusion coefficient is defined as the ratio between the mass (or molar) flux of a component in a gaseous mixture and its concentration gradient, in absence of mechanical or convective forces. This coefficient is necessary to mathematically formulate the Fick's law, which expresses the linear relationship between diffusion flux and concentration gradient [34,35]. If this is applied to an alcohol (A) in a mixture of alcohol vapour (coming from evaporation) and air (AIR), inside a vessel with no circulation of air, the Fick's law can be expressed as:

$$\dot{m}_A'' = Y_A \cdot \dot{m}_A'' - \rho \cdot D_{A-\mathrm{AIR}} \frac{\mathrm{d}Y_A}{\mathrm{d}x} \tag{1}$$

with $\dot{m}_A''$ being the mass flow rate per unit area (with units kg/s m^2) of alcohol in the vertical direction, x, and Y_A being the alcohol mass fraction in the vapor phase. The first term in Eq. (1) represents the convective transport whereas the second represents the diffusion transport, with $D_{A-\mathrm{AIR}}$ being the binary diffusion coefficient (in m^2/s).

Diffusion transports alcohol mass from the interface towards the open section of the fuel tank or the security valve. Right after the tank filling or after any increase in temperature, diffusion is enhanced because there is no alcohol content in the vessel, the gradient of concentration being maximal. When the quasi-steady regime is finally reached, the mass of alcohol transported from the interface almost stabilizes providing steady alcohol concentration profiles, which permit to estimate the evaporation loss rate. To build up a mathematical model for predicting the alcohol vapor transportation, information about the mass fraction of alcohol at the liquid–vapor interface is needed, for which properties of the alcohol (vapor pressures) and of the binary gaseous mixture (activity coefficients) are also needed. Especially in the case of alcohol-diesel (or biodiesel) blends, vapor pressure of the latter component can be neglected as a consequence of its low volatility. After the boundary conditions at the interface being determined, diffusion can be calculated.

For the determination of the diffusion coefficients of alcohols in their binary alcohol-air gaseous mixtures different approaches have been proposed, which are revised below. Some of them include the collision integral.

3. The collision integral

The collision integral (Ω_D) accounts for the interactions between molecules of the gases being mixed and it depends on temperature. To simulate the intermolecular forces, molecular potential energies must be modelled, either following the Lennard-Jones potential function [36] or the Stockmayer one [37]. From the potential function, an expression can be derived for the collision integral. This would be equal to unity when molecules are considered as rigid spheres.

The use of the mentioned potential functions led to the proposal by Hirschfelder et al. [38] of a table relating the non-dimensional ratio between the product of the Boltzmann constant and the temperature, and the maximum attraction energy, $kT/\varepsilon_{A-\mathrm{AIR}}$, with a function associated with the intermolecular forces, Hirschfelder function, which can be identified as half of the collision integral. Later on, Neufeld proposed the following equation [39,40] to estimate the collision integral, Ω_D. This equation accurately fitted the data listed in Hirschfelder's table, multiplied by two:

$$\Omega_D = \frac{1.06036}{\left(\frac{kT}{\varepsilon_{A-\mathrm{AIR}}}\right)^{0.1561}} + \frac{0.193}{\exp\left(0.47635\frac{kT}{\varepsilon_{A-\mathrm{AIR}}}\right)} + \frac{1.03587}{\exp\left(1.52996\frac{kT}{\varepsilon_{A-\mathrm{AIR}}}\right)} + \frac{1.76474}{\exp\left(3.89411\frac{kT}{\varepsilon_{A-\mathrm{AIR}}}\right)} \tag{2}$$

For the determination of ε/k, Eq. (3) was used for each component, with T_b being the normal boiling temperature in K. These results are then used for obtaining the average value for each