Fluid Phase Equilibria 427 (2016) 488–497

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

A method to estimate the thermal conductivity of organic alcohols in the liquid phase at atmospheric pressure or along the saturation line

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ARTICLE INFO

Article history:
Received 9 June 2016
Received in revised form
28 July 2016
Accepted 8 August 2016
Available online 9 August 2016

Keywords:
Thermal conductivity
Golden ratio
Alcohols

ABSTRACT

This work proposes an equation useful for engineering purposes and requiring the critical temperature T_c, the molecular weight M and three parameters: the "golden ratio" Φ, a factor *h* characteristic of the organic family and an exponent *a* linked with the number of carbon atoms. The investigation is based on the available experimental or experimental&predicted thermal conductivity data of alcohols from the database due to "The DIPPR Information and Data Evaluation Manager". The important family of alcohols represents the first example of the method, which is compared with other existing methods. The method was developed for 26 alcohols in the reduced temperature ranging from 0.30 to 0.90, the average absolute deviations between calculated and DIPPR thermal conductivity data are generally very low, being less than 5% and the maximum absolute ones less than 8%, for most of the alcohols.

1. Introduction

Knowledge of the thermal conductivity of liquids is required in the analysis of many phenomena, and its experimental value is often not available with acceptable reliability or sometimes not available at all; theoretical or semi-theoretical models of the liquid state (the so-called "gas-like" or "solid-like" models) are useless or of poor practical use, either for the errors they finally lead to, or for the excessive mathematical complication they involve.

What distinguishes solids, gases, and liquids on a microscopic scale is the intermolecular force and, subsequently, the energy transfer mechanisms. This interaction is usually represented by a potential function ψ, but the different models proposed in the scientific literature for the liquids do not allow to easily find a reliable value for thermal conductivity so that empirical or semi-empirical correlations are often necessary for several practical applications. In any case, in these correlations attention has to be paid in achieving a good balance between the values of the properties required to use the formula and the accuracy.

Thermal conductivity, λ, is defined by Fourier's law [1] which, assuming a mono-dimensional heat flow through a section of infinitesimal area dA normal to the direction x of the flow, can be written as follows:

$$dq = -\lambda dA \frac{dT}{dx} \quad (1)$$

where T is the temperature. The SI units, unless differently stated, are used in this paper.

equation (1) allows defining (or allows researchers to define) the thermal conductivity as a relation among the heat crossing a body of surface dA, thickness dx and the temperature gradient across it.

Reliable experimental liquid thermal conductivity values available in the literature are limited; for this reason, in the absence of a rigorous physical theory, empirical or semi-empirical models or estimation methods are necessary to obtain values of thermal conductivity of liquids useful for engineering purposes.

The thermal conductivity of liquids usually decreases with the increase of temperature, even if there are some exceptions to this behavior, for example water and some aqueous solutions. From the normal melting point to the normal boiling point and over, the thermal conductivity dependence on the temperature is usually almost linear, but this behavior near the critical point dramatically ceases and the critical point represents a singularity.

Following Assael et al. [2,3], the thermal conductivity of liquids is expressed as a function of temperature and density by three contributions representing the "dilute gas contribution", the "excess contribution" and the "critical enhancement contribution"; since the density data are not always available, the density is

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http://dx.doi.org/10.1016/j.fluid.2016.08.010
0378-3812/

usually substituted by pressure, whose variations are negligible up to values of 3, 4 MPa and most estimation methods neglect this dependency and express thermal conductivity as a function only of the temperature. In this work, a suitable equation for the liquid phase is proposed avoiding the presence of different contributions and linking the thermal conductivity with the temperature. Among the different organic families, alcohols have been chosen as a test to propose a consistent and complete estimation method whose results are compared with ten of the best empirical or semi-empirical equations proposed in the scientific and technical literature.

2. Family under investigation

An alcohol is an organic compound in which the hydroxyl functional group (-OH) is bound to a carbon atom. Due to the presence of the hydroxyl functional group, alcohols are characterized by the so-called "hydrogen bond"; moreover, because of the difference in electronegativity between oxygen and carbon, the alcohols are polar, and therefore hydrophilic, showing the ability of dissolving both polar and non-polar substances. For this reason, among the several uses of alcohols, of particular interest are the fields of solvents and reagents. Other important uses are in fuels, antifreeze, preservative and beverages. In organic synthesis alcohols behave as versatile intermediates.

A reliable and updated source of thermal conductivity values can be found in the DIPPR801 database [4], where experimental, predicted and smoothed data are reported. Furthermore, the DIPPR 801database collects data from a wide range of sources and considers them critical, giving quality codes for all data points.

The fluids containing the alcohol functional group were taken into account and, as presented in DIPPR801 database, they are divided into the sub-families of n-alcohols, aromatic alcohols (phenols), cycloaliphatic alcohols and other aliphatic alcohols (2-alkanols and methyl alkanols). Although phenols, whose hydroxyl group is attached to an unsaturated aromatic ring system, are more reactive than alcohols and act more like acids, they were still considered in the data treatment.

The DIPPR801 database was chosen because of its accuracy and extension: only for the alcohols, 110 compounds are reported and a deep analysis is developed in order to present experimental and predicted data with their accuracy and the different sources of the thermal conductivity data.

In this paper, the thermal conductivity data (experimental, smoothed and predicted) available from DIPPR801 database for the alcohols are analyzed. During the data collection, a fluid by fluid analysis was performed and only experimental or experimental&predicted data with claimed accuracy less than 10% were taken into account for the check of the proposed method and for the comparison with the other investigated methods.

3. The existing formulas

As before stated, because of the poor availability of reliable experimental thermal conductivity data, prediction methods are necessary. Existing methods can be divided into different categories. In many cases, they are classified on the basis of the original expressions they have been derived from: in fact there is a limited number of equations on which many others are based.

Since new expressions are continuously developed, a general classification is useful: in particular the following four categories have been considered in the recent past by Govender et al. [5]:

- general correlation methods: methods based on one or more component properties; usually the proposed equation is valid in the same form for all molecules independently of the chemical family;
- family methods: the formulas contain parameters that vary moving from family to family;
- group contribution methods: model parameters are fitted based on the different chemical groups that are present in the molecule;
- corresponding state methods: these methods are based on the Van der Waals assumption that all fluids deviate from the ideal gas behavior to about the same degree when compared at the same reduced temperature and reduced pressure.

A very useful collection of several equations is also due to Horvath [6]; the classical book of Poling, Prausnitz and O'Connell [7] was also taken into account. In particular, it is important to select methods evidencing acceptable accuracy together with easiness in handling; this condition implies that the number of necessary properties and parameters has to be limited; moreover the properties required must be easy to be found. In this paper, an equation containing parameters that vary moving from family to family is proposed.

4. The proposed equation

Starting from the 70's, Latini [8,9] and his group tested some empirical or semi-empirical estimation methods for several organic liquids belonging to different families in order to verify how they performed. Some considerations were derived:

- empirical formulas are usually more accurate than those based on simplified theories;
- the most reliable equations contain explicitly the temperature;
- the average absolute deviations between calculated and experimental data are usually greater than 15%;
- the accuracy of the formulas usually worsens as the temperature raises from 20 °C; moreover in some cases the dependence on the temperature is not correct.

In a later paper [10], the following equation was proposed:

$$\lambda = A\frac{(1-T_r)^{0.38}}{T_r^{\frac{1}{6}}} \tag{2}$$

where $Tr = T/T_c$ is the reduced temperature and the factor A is the value of the thermal conductivity at the reduced temperature $Tr \approx 0.55$ (only one experimental point is needed to determine A). The factor A moreover can be calculated by the knowledge of the molecular weight M, the critical temperature T_c, the normal freezing point T_f and the normal boiling point T_b. The reliability of Eq. (2) was confirmed by average absolute and absolute maximum deviations between calculated and experimental thermal conductivity data, respectively less than 8% and 15% [11] in the reduced temperature range 0.3–0.8 for about 150 different organic substances belonging to several organic families (saturated hydrocarbons, olefins, cycloparaffins, aromatics, alcohols, organic acids, ketones, esters, ethers and refrigerants). For its simplicity and accuracy, equation (2) has become a reference, reported in the classical work [11] by Poling, Prausnitz and O'Connel, but some problems had to be faced:

1) the exponent 0.38 is simply a mean value accepted on the basis of a wide investigation on the available experimental thermal conductivity data and is not physically grounded;