Thermochimica Acta 511 (2010) 107–111

Contents lists available at ScienceDirect

Thermochimica Acta

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

Estimation of normal boiling points of trialkyl phosphates using retention indices by gas chromatography

K. Panneerselvam, M.P. Antony, T.G. Srinivasan*, P.R. Vasudeva Rao

Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu 603 102, India

ARTICLE INFO

Article history:
Received 16 June 2010
Received in revised form 28 July 2010
Accepted 29 July 2010
Available online 6 August 2010

Keywords:
Trialkyl phosphates
Retention index
Normal boiling point
Topological indices
Regression analysis

ABSTRACT

Retention indices of several homologous trialkyl phosphates have been determined by gas chromatography on different polar stationary phases namely, Apiezon L, SE-30 and XE-60. Normal boiling points of these trialkyl phosphates have been evaluated and compared with available literature values. Topological indices such as *Xu* index, atom type index and steric effect index are derived for these phosphates and have been correlated with the normal boiling points using multiple regression analysis. The influences of alkyl chain length, relative position of alkyl branching and steric factors on retention index are investigated and also the effect of polarity of the stationary phase on retention indices is discussed.

1. Introduction

Trialkyl phosphates such as tri n-butyl phosphate (TBP) are important extractants in nuclear fuel reprocessing. PUREX (Plutonium Uranium Reduction EXtraction) is a well known aqueous reprocessing process where TBP [1–6] diluted in aliphatic hydrocarbons is employed to recover uranium and plutonium from irradiated nuclear fuel solution. Though TBP has been successfully employed for thermal reactor fuels over the past five decades, it has several shortcomings for fast reactor fuel reprocessing such as, third phase formation during the extraction of tetravalent metal ions, unacceptable aqueous solubility [7,8], hydrolytic and radiolytic degradation, and poor U (VI)/Th (IV) separation. Alternatives to TBP, such as tri-sec-butyl phosphate (TsBP), tri n-amyl phosphate (TAP), and triisoamyl phosphate (TiAP), which do not have the shortcomings of TBP but at the same time retain its merits have been developed and extensively studied in our laboratory. TsBP [9] and TiAP [10] have been found to be better candidates for THOREX (THORium uranium EXtraction) and PUREX process respectively. Trimethyl phosphate and triethyl phosphate find applications as fire retardant additives for rubber and plastic [11–14], plasticizers, insecticides, curing agents, stabilizers, anti-wear additives, lubricants etc.

Normal boiling point is an indispensable parameter for synthesis and is an important input for computing critical temperature, flash point, enthalpy of vaporization, etc. Normal boiling points have not been reported in the literature for several synthesized trialkyl phosphates, except triisobutyl phosphate. The direct measurement of boiling point for trialkyl phosphates is an extremely laborious, time-consuming and expensive process as it requires pure compounds. Also high molecular weight phosphates decompose prior to reaching their normal boiling points and necessitate measurements under reduced pressure and later corrections to ambient pressure leading to errors. In view of these shortcomings, development of reliable methods for estimating normal boiling points of these compounds is essential.

Gas chromatographic retention indices have been used in the present study for determining normal boiling point of trialkyl phosphates. This technique tolerates some impurities and enables estimation with high accuracy and precision. It is possible to obtain retention times of phosphates with widely ranging volatilities in a single temperature-programmed experimental run. Gas chromatographic retention mainly depends on the solute–stationary phase interactions resulting from the chemical, structural and electronic features of the compound of interest. The variation in the retention behaviour is due to the macrocosmic reflection of the molecular structures of the injected compounds and the stationary phase [15,16]. The retention index (RI) is usually determined by injecting the compound along with two n-alkanes whose retention times lie on either side under suitable temperature-programmed conditions

* Corresponding author. Tel.: +91 44 27480286; fax: +91 44 27480065.
E-mail address: tgs@igcar.gov.in (T.G. Srinivasan).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.07.032

and is given by the following equation [17,18]:

$$RI = 100N\left[\frac{t_{R(c)} - t_{R(z)}}{t_{R(z+n)} - t_{R(z)}}\right] + 100_z \quad (1)$$

where N is the difference in carbon number between the two n-alkanes that elute before and after trialkyl phosphate, t_R is the retention time for the trialkyl phosphate and Z is the carbon number of the n-alkane eluting immediately prior to trialkyl phosphate. Molecules of trialkyl phosphates with higher electron density than corresponding number of carbon atoms of alkanes have higher retention.

A major part of the current research in the computational chemistry, graph theory and Quantitative Structure–Property Relationship (QSPR)/Quantitative Structure–Activity Relationship (QSAR) involves topological indices. QSPR/QSAR is important complementary tools in computational chemistry to represent explain and, most importantly, predict a variety of physicochemical [19–21], biomedical [22] and toxicological properties [23]. QSPR can give insight into the aspects of the molecular structure which in turn influences various properties and has been used extensively to explain separation mechanisms, physicochemical properties of solutes in thin-layer [24] and gas chromatographic [18,25] techniques.

Topological indices are numerical graph invariants that quantitatively parameterize molecular structure and can be directly derived from the structure of the molecule on the basis of graph theory without any experimental effort. They can easily be computed and used to predict many physicochemical properties. Nevertheless choice of an appropriate index is very essential for obtaining good correlation and hence an error free prediction. For example most of the conventional topological indices such as, Wiener index [26], Balaban index [27], Randic index [28], Hosoya index [29] and Schluze index [30] are found unsuccessful for compounds with multiple bonds and heteroatoms, since these indices do not take into account the contribution of each of the individual atom types or groups. Most of the physicochemical properties depend on individual atoms or groups, polarizability of the molecule, length of carbon backbone, shape and branching of the molecule and their contribution to the structural environment in the molecule. Structural parameters that represent the size and bulkiness of alkyl groups would be expected to largely contribute to physicochemical properties. Thus the atom type index "*AI*", representing structural features, *Xu* index "X_U" which reflects size and composition of the molecule and the steric effect index "SV_{ij}" which reflects bulkiness of the molecules have been derived for all the trialkyl phosphates studied and a correlation has been attempted to predict the normal boiling point [31–34] of these phosphates with these indices using a multiple linear regression analysis.

2. Experiments

2.1. Materials

A homologous series of n-alkanes ranging from n-heptane to n-heptacosane (TCI) which served as standards for determining retention index and trimethyl phosphate (TMP) (Merck), triethyl phosphate (TEP) (Merck), tri n-butyl phosphate (TBP) (Alfa aesar) were of commercial origin and used as received without any additional pre-treatment. Triisobutyl phosphate (TiBP), tri-sec-butyl phosphate (TsBP), triisoamyl phosphate (TiAP), tri-2-methyl butyl phosphate (T2MBP), tri-sec-amyl phosphate (TsAP) and trihexyl phosphate (THP) were synthesized according to the described method [35,36] by using corresponding alcohol with phosphoryl chloride and were further purified by distillation under reduced pressure after extensive washings with distilled water and characterization using FTIR spectrophotometry.

Table 1
Characteristics of chromatographic column, 10% of stationary phases are coated on chromosorb W (HP), 80/100 mesh.

Notation	Stationary phase	Polarity
Apiezon L	Higher molecular weight hydrocarbon grease	143
SE-30	Dimethylpolysiloxane	229
XE-60	Cyanoethyl methyl siloxane	1785

2.2. Methods

The retention times of trialkyl phosphate reference standards (TEP, TMP, TiBP and TBP) and unknowns (TsBP, TsAP, T2MBP, TiAP and TAP) were determined by injecting along with n-alkane standards by a temperature-programmed method on different polar stationary phases. A Shimadzu GC–9A gas chromatograph equipped with flame ionization detector (FID) incorporating a packed stainless steel column (3.2 mm OD × 4 m length) was used for retention time measurements. Splitless injector was used for sample introduction. Injection port and FID were set at 225 °C for vaporization and detection of eluted compounds. Argon was used as mobile phase at a constant flow rate of 50 mL/min. Hydrogen (50 mL/min) and air (500 mL/min) were fed into FID to aid the ignition of the eluted compounds. The characteristics of stationary phase used in the chromatographic column are summarized in Table 1. The temperature of the column oven was programmed from 100 °C to 225 °C at 1.5 °C/min, and held at 100 °C for 2 min and 225 °C for 25 min, as initial and final temperature, respectively. Data handling was carried out by ASHCO® software. Using the retention time of the phosphates and alkane standards the retention indices were evaluated.

2.3. Topological indices

2.3.1. Xu and atom type indices

Xu index, novel atom type index (*AI*) defined and described elsewhere [37–43], encode the molecular connectivity, charge information and individual contributions from atoms or groups in the molecules to the physicochemical properties were derived using the vertex-adjacency matrix, $A = [a_{ij}]_{nxn}$ and distance matrix, $D = [d_{ij}]_{nxn}$. For example, a_{ij} is 1, if vertices "*i*" and "*j*" are adjacent and if they are separated by more than one carbon in between a_{ij} will be zero. Similarly d_{ij} is the length of shortest path between vertex "*i*" and vertex "*j*" in molecular graph *G*, $G = [V, E]$, Where "*V*" represents the atoms of the molecule and "*E*" symbolizes bonds between pairs of atoms.

Fig. 1 depicts the molecular graph of a typical trialkyl phosphate, T2MBP, where each vertex is represented by a number as per the

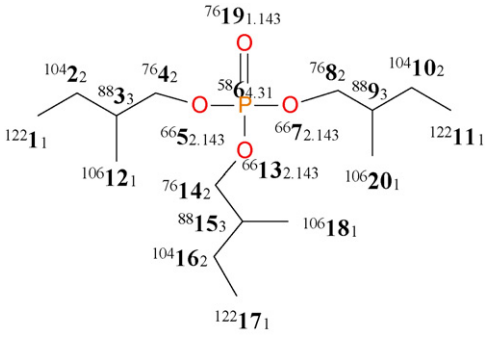

Fig. 1. Labeled molecular graph of T2MBP.