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Correlation of normal boiling points of dialkylalkyl phosphonates with topological indices on the gas chromatographic retention data

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ABSTRACT

The normal boiling point of twelve dialkylalkyl phosphonates has been determined using gas chromatographic technique. Dibutylhydrogen phosphonate has been used as reference for computing normal boiling point of dialkylalkyl phosphonates. Retention times of dialkylalkyl phosphonates have been measured by using temperature programmed technique. The topological indices namely, odd–even index, atom type index and steric effect index have been designed to capture surface interaction parameters. It was found to exhibit excellent correlation of the topological indices to the normal boiling point of dialkylalkyl phosphonates. Multiple linear regression analysis has been performed for development of quantitative structure property relationships discipline. It exhibited good predictive power ($R^2 = 0.998$).

1. Introduction

Solvent extraction technique has been widely utilized for reprocessing irradiated nuclear fuels for the recovery of actinides from the resultant waste solution. PUREX (plutonium uranium reduction extraction) process is a well known solvent extraction technique where tri-*n*-butyl phosphate $(n\text{-BuO})_3PO$ diluted with aliphatic hydrocarbon has been used as extractant for more than five decades [1–4]. Several organophosphorous based extractants such as homologue of trialkyl phosphates $(RO)_3PO$ [5,6], dialkylalkyl phosphonates $(RO)_2[R]$ PO [7,8] and alkyldialkyl phosphinates (RO) $[R]_2PO$, where R is alkyl group, have been developed and studied extensively for the extraction of actinides at our laboratory. In the structural formula of the above mentioned compounds, the enclosure of R, alkyl groups, in brackets indicates that the alkyl groups are attached to the phosphorus by CP bonds because of which the basicity of the P=O increases in contrast to COP bonds of R groups which are not enclosed by brackets. Trialkyl phosphates exhibit least basic P=O behavior in the above series of organophosphorus based extractants. The desired actinide extraction behavior can be achieved by varying steric and inductive effects of alkyl substituents and varying type and mode of bonding (i.e., COP or CP bonds) of alkyl organic groups in the neutral phosphorus-based compounds. Therefore, chemical structure of several neutral phosphorous-based extractants with different carbon chain length and position of methyl substituents on different carbon of the alkyl skeleton is a key contributor to the varying nature of extraction behavior towards actinides and lanthanides. The structure also plays an important role in assessing the radiochemical stabilities and physicochemical properties of the compounds. The structural parameters which influence physicochemical properties of the compounds are of great importance for the development of techniques for the separation and purification of actinide elements.

The normal boiling point (nbp) is an important property used to characterize and identify a new compound, and to estimate other physicochemical properties, such as critical temperature, vapor pressure, enthalpy of vaporization and flash point. It is intuitively evident that boiling point of compound is critically influenced by molecular weight and tendency to adhere with each together. The stronger the intermolecular forces are, the more strongly the molecules are held together and, hence, the higher the boiling point. The intermolecular interactions can be divided into the following types: dipole–dipole, dipole-induced dipole, induced dipole–induced dipole or dispersion forces and hydrogen bonding. The dipole interactions are related to the dipole moment of a whole molecule or of a part of a molecule, such as a functional group, e.g., phosphonate moiety. The dispersion forces are function of the molecule's polarizability, while hydrogen bonding can be facilitated by the presence of —OH, —NH, or —SH groups etc. Experimental normal boiling point data of several dialkylalkyl phosphonate have not been measured or estimated, and,

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moreover, determination of normal boiling point for a series of such compounds is extremely difficult because of its tedious and expensive procedure. The development of reliable method for estimating normal boiling point is required when a chemical procedure is unavailable, yet unknown, or hazardous to handle in the toxic environment.

Gas chromatographic (GC) retention times (t_R) has been used in the present study for computing normal boiling point of dialkylalkyl phosphonates. GC retention is mainly dependent on the interaction between solute and stationary phase resulting from topological, geometrical and electronic features of solute. GC retention data has often been used for identification of solute [9–11] when pure standards are non-existent. Retention index is the measure of retention behavior of solute relative to normal paraffin hydrocarbons used as reference set. This technique tolerates some impurities and enables estimation with high accuracy and precision. It is possible to measure the retention time of dialkylalkyl phosphonates with widely ranging volatilities and labile at higher temperature in a single temperature-programmed experimental run. The variation in the retention behavior is due to the macroscopic reflection of the molecular structures of the injected compounds and the stationary phase [12,13]. Gas chromatographic retention times (t_R) has been utilized for computing retention indices [14,15] and normal boiling point of compounds [16–18]. The retention time (t_R) is measured by injecting the dialkylalkyl phosphonates along with two normal paraffin hydrocarbons whose retention times lie on either side of the dialkylalkyl phosphonates under suitable temperature-programmed condition and is utilized for computation of normal boiling point of dialkylalkyl phosphonates by the following equation:

$$\mathrm{nbp}_c = \mathrm{nbp}_n + (\mathrm{nbp}_{n+1} - \mathrm{nbp}_n) \times \left[\frac{t_{R(c)} - t_{R(n)}}{t_{R(n+1)} - t_{R(n)}}\right] \quad (1)$$

where nbp_c is normal boiling point of dialkylalkyl phosphonates, nbp_n and nbp_{n+1} are normal boiling point of normal paraffin hydrocarbons with carbon number n and $n+1$ that elute before and after dialkylalkyl phosphonates. Retention time, $t_{R\ (c)}$, $t_{R\ (n)}$ and $t_{R(n+1)}$ are retention time for the dialkylalkyl phosphonates, normal paraffin hydrocarbons with carbon number n and $n+1$, respectively. Dibutylhydrogen phosphonate (DBHP) for which normal boiling point data is reported elsewhere [17] is used as reference to validate the experimental method.

Topological indices are numerical representation of the chemical structure derived on the basis of molecular graph by using distance, vertex-adjacency, reciprocal distance matrix etc. Topological indices can be easily designed for structural parameters and give good correlation with many physicochemical properties. Quantitative structure property relationships (QSPR) discipline is important complementary tools in computational chemistry that has been applied in the development of chemicals with specific properties and prediction of many physicochemical [19–22], biomedical [23] and toxicological properties [24]. The QSPR discipline provides a promising tool for estimation of many physicochemical properties based on topological indices derived solely from the molecular structure to fit experimental data. The advantages of QSPR discipline lie in the fact that it needs only the knowledge of chemical structure and is not dependant on any experimental efforts. Predicted properties are interpreted in terms of structurally related concept. Moreover, the QSPR discipline has been used as a tool for faster detection of favorable compounds and avoidance of synthesis of compounds with same property. In this article, the QSPR discipline that involves multiple linear regressions (MLR) analysis has been performed to correlate normal boiling point of dialkylalkyl phosphonates against structural parameters. Multiple linear regression analysis assumes that there is a linear relationship between the topological indices and its target properties.

2. Experimental

2.1. Materials

The precursor for Dibutylpropyl phosphonate (DBPP), Dibutylbutyl phosphonate (DBBP), Dibutylamyl phosphonate (DBAP), Dibutylhexyl phosphonate (DBHeP) and Dibutyloctyl phosphonate (DBOP) is dibutylhydrogen phosphonate (DBHP). Dibutylhydrogen phosphonate (DBHP) was prepared by treating 0.33 mol of PCl_3 with 1 mol of n-butanol under a purge of argon atmosphere over a period of 60–90 min at 273 K [25]. The reactants were stirred continuously under reduced pressure to remove the byproducts. Dibutylalkyl phosphonates (DBalP) was prepared according to the Michaelis Becker Reaction [26] by using sodium with dibutylhydrogen phosphonate in hexane. The Reaction steps are:

$$2(C_4H_9O)_2P(O)H + 2\ Na \rightarrow 2(C_4H_9O)_2P(O)Na + H_2$$

$$(C_4H_9O)_2P(O)Na + RBr \rightarrow (C_4H_9O)_2P(O)R + NaBr$$

(where R: proyl, butyl, amyl, hexyl and octyl).

Fig. 1 depicts the molecular structure dibutylalkyl phosphonates (DBalP). The detailed description of characterization of dibutylalkyl phosphonates is reported elsewhere [27]. Diamylhydrogen phosphonate (DAHP) and diisoamylhydrogen phosphonate (DiAHP) used as precursors for preparation of diamylalkyl phosphonates (DABP, DAAP, DAHeP) and diisoamylalkyl phosphonate (DiABP, DiAAP, DiAHeP). The preparation procedure and detailed description of characterization [28–31] of diamylalkyl phosphonates and diisoamylalkyl phosphonate were confirmed to be >99% by using IR, ^{31}P NMR and elemental analysis methods. Phosphorus trichloride (Fluka), sodium, n-butanol (Merck), n-pentanol (Merck), isopentanol (Merck), 1-bromopropane (Fluka), 1-bromobutane (Fluka), 1-bromopentane (Fluka), 1-bromohexane (Lancaster), 1-bromooctane (Lancaster), hexane (Merck), were used as received. The normal paraffin hydrocarbons ranging from n-decane to n-heneicosane (TCI) were of commercial origin and used as received without any additional pre-treatment.

2.2. Equipments

The measurement of retention times of two mixtures containing dialkylalkyl phosphonates and normal paraffin hydrocarbons was performed using a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector (FID). Two sets of mixtures of dialkylalkyl phosphonates along with normal paraffin hydrocarbons were prepared for avoiding the co elution of the

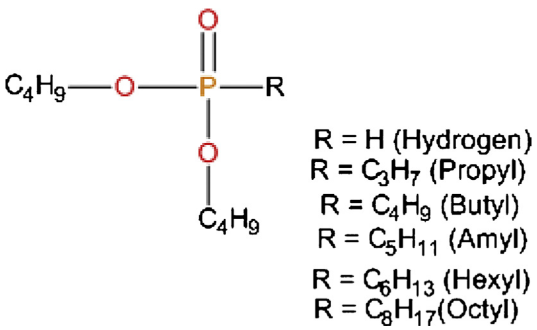

Fig. 1. Structure of dibutylalkyl phosphonates.