

Measurement of enthalpies of vaporization of trialkyl phosphates using correlation gas chromatography

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

Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu 603102 India

Received 4 September 2007; received in revised form 11 October 2007; accepted 15 October 2007

Available online 23 October 2007

Abstract

The enthalpies of vaporization of several trialkyl phosphates such as, tri-*n*-butyl phosphate (TBP), triisobutyl phosphate (TiBP), tri-secondary butyl phosphate (TsBP), tri-*n*-amyl phosphate (TAP), triisoamyl phosphate (TiAP), Tri-2-methyl butyl phosphate (T2MBP), tri-secondary amyl phosphate (TsAP), and trihexyl phosphate (THP) have been measured for the first time using correlation gas-chromatographic technique. Normal paraffin hydrocarbons have been used as references after demonstrating the suitability of them by determining the enthalpies of vaporization of trimethyl phosphate (TMP) and triethyl phosphate (TEP) for which data is available in the literature. The vaporization enthalpies were correlated to structural parameters characterizing the compounds studied. Solvent accessible surface area (SAS), among the parameters, was found to exhibit excellent correlation to the enthalpies of vaporization of trialkyl phosphates as well as the normal paraffin hydrocarbons used as the reference. The Hildebrand's solubility parameters for the trialkyl phosphates were derived from the values of enthalpy of vaporization at 298.15 K.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Enthalpy of vaporization; Trialkyl phosphates; Retention time; Solvent accessible surface area; Quantitative structure property relationship; Hildebrand's solubility parameter

1. Introduction

Tri-*n*-butyl phosphate diluted in normal paraffins such as *n*-dodecane is used as an extractant for the separation of actinides from the spent fuel in the PUREX process for the past 50 years [1]. This is mainly due to the attractive properties of TBP such as economics, commercial availability, selectivity to actinides, good physical properties and fairly good stability towards chemical, thermal and radiolytic degradation. However, problems posed by TBP such as formation of a third phase during high loading conditions of tetravalent actinides, formation of deleterious degradation products and high aqueous solubility have induced researchers to look for alternatives which are devoid of these drawbacks. Alternative extractants such as, triisobutyl phosphate, tri-secondary butyl phosphate, tri-*n*-amyl phosphate, triisoamyl phosphate, etc., have been synthesized and extensively studied in our laboratory for applications in U/Th separation, thermal and fast reactor fuel reprocessing [2].

The physical and chemical properties of these solvents comprising the extractant and the diluent influence the hydrodynamic behavior and the extraction of the metal ions. The enthalpy of vaporization of a liquid is a useful thermodynamic parameter, because it allows the evaluation of important properties such as, the vapor pressure of the liquid at a given temperature, the solubility parameter [3,4] and standard molar enthalpy of formation [5,6]. Usually the enthalpy of vaporization is measured directly by calorimetry or derived from Clausius–Clapeyron equation by measuring the vapor pressure of the substance as a function of temperature. Both these methods have the drawback of requirement of highly pure starting materials (>99%) or materials with negligible high volatile impurities. Gas chromatography has been used to measure various thermodynamic properties of compounds [7–13]. Correlation gas chromatography (CGC) is an attractive technique for enthalpy of vaporization measurements [14,15]. The advantages of this technique are that it is fast, tolerates impurities, only a few micro-liters of the sample are needed and the enthalpy of vaporization of more than one substance can be measured in a single experimental run. It is an excellent technique and successful in providing enthalpy of vaporization of homologues [16,17] and isomeric series of

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

simple organic molecules. In this technique some reference solutes of similar structure with known enthalpy of vaporization are mixed with the compounds of interest and injected into the gas-chromatographic column, maintained in isothermal conditions, to determine the retention times which in turn are used to evaluate the enthalpies of vaporization at 298.15 K as well as at their respective boiling points. Tertiary amines [18] have been used as correlating references for hydrocarbons.

The enthalpy of vaporization of trimethyl phosphate (TMP) and triethyl phosphate (TEP) have been determined by vapor pressure measurement [19–21]. In the present study, the enthalpy of vaporization of TMP and TEP has been determined by the correlation gas-chromatographic technique using normal paraffin hydrocarbons as references. The values are in agreement with the results reported [19–21]. It is demonstrated by the above-mentioned experiment that normal paraffin hydrocarbons can be used for the measurement of enthalpy of vaporization of trialkyl phosphates. The enthalpies of vaporization of tri-*n*-butyl phosphate (TBP) and several homologues such as, triisobutyl phosphate (TiBP), tri-secondary butyl phosphate (TsBP), tri-*n*-amyl phosphate (TAP), triisooamyl phosphate (TiAP), Tri-2-methyl butyl phosphate (T2MBP), tri-secondary amyl phosphate (TsAP), and trihexyl phosphate (THP) have been determined using the correlation gas-chromatographic technique using normal paraffin hydrocarbons, TMP and TEP as references and attempts were made to correlate the measured enthalpies with several molecular parameters. Of the parameters attempted, good correlation could be obtained with solvent accessible surface area (SAS). The Hildebrand's solubility parameters for the trialkyl phosphates have also been derived from the values of enthalpies of vaporization at 298.15 K.

2. Experimental

2.1. Materials

Trimethyl phosphate, triethyl phosphate and all other chemicals were procured from Merck. Triethylamine and normal paraffin hydrocarbons were procured from Tokyo Chemical Industries. All the chemicals were used as received. The other trialkyl phosphates were synthesized by the reaction of POCl_3 with corresponding alcohol and were further purified by distillation under reduced pressure after extensive washing with distilled water [22,23].

2.2. Instruments

Shimadzu GC-9A Gas chromatograph, equipped with a flame ionization detector (FID) was used for chromatographic experiments. Argon was used as the carrier gas with a flow rate 55 mL/min. Hydrogen and air were fed into the FID with flow rates of 50 mL/min and 500 L/min, respectively, for aiding the combustion of the eluted compounds. ASHCO[®] software was used for data acquisition, analysis and report creation of chromatograms, etc.

2.3. Measurement of retention time

A 4 m × 3 mm of 10% Apiezon L packed column was used in the gas chromatograph. Splitless injection mode was used for sample introduction. Temperature-dependent retention time was obtained for all compounds. Isothermal chromatograms were obtained over a 50 K range at 10 K intervals of column temperature. A selected few *n*-hydrocarbons and triethylamine were chosen as reference, because of the availability and reliability of their enthalpy of vaporization as reference data for obtaining the correlation equation to calculate enthalpy of vaporization of trialkyl phosphate compounds. Methanol was used as an unretained compound and 5 μL of methanol was injected at all experimental temperatures as the non-retained reference to get the true retention time of the solute, i.e., the amount of time the solute molecule spends in the stationary phase, t'_R ($t'_R = t_R - t_M$, where t_R is the time elapsed from the instant of injection to the maximum of a chromatographic peak, and t_M is the required time for an unretained gas molecule to traverse the column). Each phosphate was mixed with different combinations of reference standards to ensure reproducibility of the computed values. Fig. 1 depicts a typical chromatogram obtained for the mixture 7 indicated in Table 1.

2.4. Evaluation of enthalpy of vaporization

Enthalpies of transfer from solution to vapor, $\Delta_{\text{sol}}^{\text{g}}H_m$, were evaluated by measuring temperature-dependent true retention time, t'_R , of a mixture consisting of both reference compounds and trialkyl phosphates. A plot of $\ln(t_0/t'_R)$ versus $(1/(T/K))$, where $t_0 = 1$ min, similar to the Clausius–Clapeyron plot of $\ln(p)$ versus $(1/(T/K))$, [24], results a straight line, whose slope is, by analogy, $-(\Delta_{\text{sol}}^{\text{g}}H_m)/R$, where R is the gas constant. The enthalpy of transfer, $\Delta_{\text{sol}}^{\text{g}}H_m$, is then correlated with the vaporization enthalpy of the references at 298.15 K [25] and at the respective boiling point [25]. The resulting linear equations were used to calculate vaporization enthalpy of the trialkyl phosphates at 298.15 K and at their boiling points. The evaluated enthalpies for the individual experimental conditions adopted are presented in Table 1. The average enthalpies of vaporization are presented in Table 2.

2.5. Evaluation of solubility parameter

Solubility parameter (δ) is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the enthalpy of vaporization.

$$\begin{aligned} \text{Solubility parameter}(\delta) &= \sqrt{c} = \left[\frac{(\Delta H - RT)}{V_m} \right]^{1/2} \\ &= \left[\frac{\Delta E}{V_m} \right]^{1/2} \end{aligned} \quad (1)$$

where c is the cohesive energy density, ΔH is the enthalpy of vaporization, R is the gas constant, V_m is the molar volume (molecular weight divided by density at 298.15 K) and ΔE is the

Table 1
Enthalpy of vaporization at 298.15 K and at the boiling point

Compound	$\Delta_{\text{sol}}^{\text{e}}H_{\text{m}}$ (kJ mol ⁻¹)	$\Delta_{\text{l}}^{\text{e}}H_{\text{vap}}$ at 298.15 K (kJ mol ⁻¹)			$\Delta_{\text{l}}^{\text{e}}H_{\text{vap}}$ at boiling point (kJ mol ⁻¹)		
		Literature [25]	Calculated	Difference (%)	Literature [25]	Calculated	Difference (%)
Mixture 1: experimental conditions: temperature range, 393.15–433.15 K; injector temperature, 448.15 K; FID temperature, 473.15 K; sample volume, 0.1 μL . All compounds are reference							
<i>n</i> -Octane	30.47	41.49	41.33	-0.38	34.41	34.80	1.12
<i>n</i> -Decane	39.86	51.42	51.71	0.56	39.58	39.49	-0.22
<i>n</i> -Undecane	44.29	56.58	56.60	0.03	41.91	41.86	-0.11
<i>n</i> -Dodecane	48.57	61.52	61.34	-0.29	44.09	44.16	0.15
Mixture 2: experimental conditions: temperature range, 453.15–493.15 K; injector temperature, 523.15 K; FID temperature, 523.15 K; sample size, 0.5 μL . All compounds are reference							
<i>n</i> -Tridecane	47.73	66.68	67.10	0.62	46.20	46.43	0.49
<i>n</i> -Tetradecane	50.67	71.73	70.94	-1.11	48.16	47.84	-0.66
<i>n</i> -Pentadecane	55.34	76.77	76.78	0.01	50.08	50.08	0.00
<i>n</i> -Hexadecane	59.13	81.35	81.53	0.22	51.84	51.91	0.13
Mixture 3: experimental conditions: temperature range, 408.15–438.15 K; injector temperature, 448.15 K; FID temperature, 448.15 K; sample size, 1 μL . All compounds are reference							
<i>n</i> -Undecane	43.42	56.58	56.22	-0.63	41.91	41.93	0.04
<i>n</i> -Dodecane	47.47	61.52	61.52	0.00	44.09	44.06	-0.06
<i>n</i> -Tridecane	51.46	66.68	66.73	0.07	46.20	46.16	-0.08
<i>n</i> -Tetradecane	55.32	71.73	71.79	0.08	48.16	48.18	0.04
TMP	36.75	47.31 ^d	47.50	0.42	NA	38.43	-
Mixture 4: experimental conditions: temperature range, 413.15–453.15 K; injector temperature, 458.15 K; FID temperature, 458.15 K; sample size, 1 μL ; sample is TsBP. Other compounds are reference							
Triethylamine	24.68	34.84	35.27	1.23	31.01	31.01	0.00
<i>n</i> -Dodecane	52.65	61.52	62.41	1.45	44.09	44.05	-0.09
<i>n</i> -Tridecane	57.30	66.68	66.92	0.35	46.20	46.22	-0.04
TEP	45.77	57.31 ^d	55.73	-2.73	NA	40.84	-
TsBP	60.01	NA	69.55	-	NA	47.48	-
Mixture 5: experimental conditions: temperature range, 443.15–483.15 K; injector temperature, 498.15 K; FID temperature, 498.15 K; sample size, 1 μL ; sample is TBP and TiBP. Other compounds are reference							
Triethylamine	15.39	34.84	35.67	2.38	31.01	31.16	0.48
<i>n</i> -Dodecane	43.13	61.52	62.85	2.16	44.09	43.86	-0.52
<i>n</i> -Pentadecane	56.05	76.77	76.43	-0.44	50.08	49.77	-0.62
<i>n</i> -Heptadecane	65.17	86.47	86.00	-0.54	53.58	53.94	0.66
TBP	60.68	NA	81.29	-	NA	51.89	-
TiBP	52.76	NA	72.97	-	NA	48.26	-
Mixture 6: experimental conditions: temperature range, 443.15–473.15 K; injector temperature, 498.15 K; FID temperature, 498.15 K; sample size, 1 μL ; sample is TiBP and TAP. Other compounds are reference							
Triethylamine	20.88	34.84	34.23	-1.75	31.01	31.16	0.48
<i>n</i> -Dodecane	45.06	61.52	62.94	2.30	44.09	43.82	-0.61
<i>n</i> -Pentadecane	56.59	76.77	76.63	-0.18	50.08	49.86	-0.44
<i>n</i> -Heptadecane	64.30	86.47	85.78	-0.79	53.58	53.89	0.57
TiBP	56.34	NA	76.33	-	NA	49.73	-
TAP	69.79	NA	92.30	-	NA	56.77	-
Mixture 7: experimental conditions: temperature range, 443.15–483.15 K; injector temperature, 498.15 K; FID temperature, 498.15 K; sample size, 3 μL ; sample is TAP and TsBP. Other compounds are reference							
Triethylamine	17.65	34.84	33.77	-3.07	31.01	30.92	-0.29
<i>n</i> -Dodecane	45.37	61.52	64.12	4.22	44.09	44.34	0.56
<i>n</i> -Pentadecane	56.98	76.77	76.84	0.09	50.08	49.96	-0.24
<i>n</i> -Heptadecane	64.30	86.47	84.85	-1.87	53.58	53.51	-0.13
TAP	69.59	NA	90.65	-	NA	56.07	-
TsBP	51.21	NA	70.52	-	NA	47.17	-

Table 1 (Continued)

Mixture 8: experimental conditions: temperature range, 423.15–463.15 K; injector temperature, 498.15 K; FID temperature, 498.15 K; sample size, 3 μ L; sample is TsBP and TBP. Other compounds are reference							
Triethylamine	25.06	34.84	34.55	−0.83	31.01	31.32	0.98
<i>n</i> -Dodecane	47.46	61.52	62.21	1.12	44.09	43.50	−1.35
<i>n</i> -Pentadecane	59.11	76.77	76.59	0.23	50.08	49.83	−0.50
<i>n</i> -Heptadecane	66.92	86.47	86.24	−0.26	53.58	54.08	0.92
TsBP	52.91	NA	68.94	–	NA	46.46	–
TBP	60.87	NA	78.77	–	NA	50.84	–
Mixture 9: experimental conditions: temperature range, 453.15–493.15 K; injector temperature, 498.15 K; FID temperature, 498.15 K; sample size, 1 μ L; sample is TBP. Other compounds are reference							
Butyl acetate	22.77	43.86	42.55	−2.91	36.28	36.01	−0.75
<i>n</i> -Dodecane	42.40	61.52	63.48	3.11	44.09	44.66	1.27
<i>n</i> -Tetradecane	50.75	71.73	72.96	1.70	48.16	48.34	0.37
<i>n</i> -Hexadecane	56.81	81.35	79.54	−2.20	51.54	51.00	−1.05
<i>n</i> -Heptadecane	62.73	86.47	85.99	−0.51	53.58	53.61	0.05
TBP	58.75	NA	81.65	–	NA	51.86	–
Mixture 10: experimental conditions: temperature range, 463.15–493.15 K; injector temperature, 533.15 K; FID temperature, 533.15 K; sample size, 1 μ L; sample is TsAP and T2MBP. Other compounds are reference							
Triethylamine	22.91	34.84	34.65	−0.55	31.01	31.26	0.79
<i>n</i> -Pentadecane	56.67	76.77	77.15	0.49	50.08	49.41	−1.35
<i>n</i> -Hexadecane	60.34	81.35	81.76	0.50	51.84	51.38	−0.89
<i>n</i> -Heptadecane	64.05	86.47	86.43	−0.04	53.58	53.38	−0.37
<i>n</i> -Octadecane	67.78	91.44	91.13	−0.34	55.23	55.38	0.27
<i>n</i> -Nonadecane	71.76	96.40	96.13	−0.28	56.93	57.52	1.02
TsAP	59.49	NA	80.69	–	NA	50.93	–
T2MBP	63.82	NA	86.14	–	NA	53.25	–
Mixture 11: experimental conditions: temperature range, 453.15–493.15 K; injector temperature, 533.15 K; FID temperature, 533.15 K; sample size, 1 μ L; sample is TsAP and TiAP. Other compounds are reference							
Triethylamine	17.28	34.84	34.53	−0.89	31.01	31.14	0.41
<i>n</i> -Pentadecane	54.06	76.77	77.86	1.39	50.08	49.58	−1.00
<i>n</i> -Octadecane	65.43	91.44	91.25	−0.20	55.23	55.29	0.10
<i>n</i> -Nonadecane	69.29	96.40	95.80	−0.62	56.93	57.22	0.50
TsAP	57.18	NA	81.53	–	NA	51.15	–
TiAP	61.48	NA	86.60	–	NA	53.30	–
Mixture 12: experimental conditions: temperature range, 483.15–513.15 K; injector temperature, 533.15 K; FID temperature, 533.15 K; sample size, 1 μ L; sample is TiAP and THP. Other compounds are reference							
Triethylamine	15.04	34.84	34.57	−0.78	31.01	31.17	0.51
<i>n</i> -Pentadecane	51.72	76.77	77.66	1.14	50.08	49.50	−1.17
<i>n</i> -Octadecane	63.41	91.44	91.39	−0.05	55.23	55.34	0.19
<i>n</i> -Nonadecane	67.17	96.40	95.81	−0.61	56.93	57.22	0.50
TiAP	59.26	NA	86.52	–	NA	53.27	–
THP	74.82	NA	104.79	–	NA	61.04	–
Mixture 13: experimental conditions: temperature range, 493.15–523.15 K; injector temperature, 543.15 K; FID temperature, 543.15 K; sample size, 1 μ L; sample is THP and T2MBP. Other compounds are reference							
Triethylamine	15.64	34.84	34.55	−0.84	31.01	31.15	0.44
<i>n</i> -Pentadecane	52.39	76.77	77.78	1.29	50.08	49.55	−1.06
<i>n</i> -Octadecane	63.90	91.44	91.32	−0.13	55.23	55.31	0.14
<i>n</i> -Nonadecane	67.70	96.40	95.79	−0.63	56.93	57.21	0.48
THP	75.45	NA	104.91	–	NA	61.09	–
T2MBP	59.99	NA	86.72	–	NA	53.36	–

Table 2
Summary of enthalpy of vaporization at 298.15 K

Compound	Literature ^b (kJ mol ⁻¹)	GC value ^a (kJ mol ⁻¹)	Percentage of difference between GC and literature (kJ mol ⁻¹)	Predicted ^c from graph (SAS versus GC value) (kJ mol ⁻¹)	Percentage of difference Between GC and SAS (kJ mol ⁻¹)	Molecular descriptor (SAS) (nm ²)
Trihexyl phosphate	NA	104.80 ± 0.08	–	103.03	1.68	77.885
Tri- <i>n</i> -amyl phosphate	NA	91.47 ± 1.16	–	89.75	1.88	66.889
Triisoamyl phosphate	NA	86.56 ± 0.06	–	87.86	–1.50	65.327
Tri-2-methyl butyl phosphate	NA	86.43 ± 0.41	–	82.98	3.99	61.289
Tri-secondary amyl phosphate	NA	81.11 ± 0.59	–	83.00	–2.33	61.308
Tri- <i>n</i> -butyl phosphate	NA	80.57 ± 1.56	–	80.96	–0.48	59.618
Triisobutyl phosphate	NA	73.13 ± 3.09	–	75.07	–2.65	54.746
Tri-secondary butyl phosphate	NA	69.67 ± 0.63	–	73.62	–5.66	53.047
Triethyl phosphate	57.3 ^d	55.73	–2.73	56.89	–2.08	39.701
Trimethyl phosphate	47.3 ^d	47.50	0.42	44.37	6.58	29.346
<i>n</i> -Nonadecane	96.40	95.88 ± 0.17	–0.54	96.19	–0.32	69.882
<i>n</i> -Octadecane	91.44	91.27 ± 0.16	–0.18	91.24	0.03	66.819
<i>n</i> -Heptadecane	86.47	85.88 ± 0.62	–0.68	86.30	–0.48	63.755
<i>n</i> -Hexadecane	81.35	80.94 ± 1.22	–0.50	81.36	–0.51	60.695
<i>n</i> -Pentadecane	76.77	77.08 ± 0.55	0.40	76.41	0.86	57.626
<i>n</i> -Tetradecane	71.73	71.89 ± 1.02	0.22	71.46	0.59	54.561
<i>n</i> -Tridecane	66.68	66.91 ± 0.03	0.34	66.52	0.58	51.500
<i>n</i> -Dodecane	61.52	62.60 ± 0.88	1.75	61.57	1.64	48.436
<i>n</i> -Undecane	56.58	55.73 ± 0.07	–1.50	56.62	–1.59	45.370
<i>n</i> -Decane	51.42	51.71	0.56	51.68	0.05	42.306
<i>n</i> -Octane	41.49	41.33	–0.38	41.79	–1.11	36.176
Triethylamine	34.84	34.64 ± 0.30	–0.57	–	–	–
Butyl acetate	43.86	42.55	–3.07	–	–	–

NA: Values are not available in the literature for reference. $\Delta_1^{\text{g}}H_{\text{vap}}$ here after called as ΔH_{vap} , is vaporization enthalpy.

^a The vaporization enthalpies are average values that have been calculated from the regression equation from each correlation GC experiment. The uncertainties are standard deviation of repeated measurements. Repeated measurements were taken for each compound which is in more than two mixtures (Table 1).

^b From Ref. [25].

^c ΔH_{vap} (pred) predicted from the graph of solvent accessible surface area (SAS) of compounds against ΔH value determined at 298.15 K from this work.

^d In Tables 1 and 2 from Ref. [26].

Table 3
Solubility parameter (δ) at 298.15 K ($\text{J}^{1/2} \text{cm}^{-3/2}$)

Compound	Solubility parameter (δ) ($\text{J}^{1/2} \text{cm}^{-3/2}$)	Compound	Solubility parameter (δ) ($\text{J}^{1/2} \text{cm}^{-3/2}$)
<i>n</i> -Octane	15.46	TMP	19.70
<i>n</i> -Decane	15.87	TEP	17.61
<i>n</i> -Undecane	15.99	TsBP	15.48
<i>n</i> -Dodecane	16.14	TiBP	16.03
<i>n</i> -Tridecane	16.22	T-nBP	16.94
<i>n</i> -Tetradecane	16.29	TsAP	15.52
<i>n</i> -Pentadecane	16.32	T2MBP	16.04
<i>n</i> -Hexadecane	16.36	TiAP	16.08
<i>n</i> -Heptadecane	16.42	T-nAP	16.55
<i>n</i> -Octadecane	16.50	THP	16.50
<i>n</i> -Nonadecane	16.52	TEA	15.20

energy of vaporization. The cohesive energy of a liquid is the energy necessary to break all intermolecular interactions during vaporization of the liquid. The vaporization of liquid and van der Waals forces are correlated and also translates into a correlation between vaporization and solubility behavior. In both cases, the same van der Waals forces must be overcome. The solubility parameter was calculated by using experimental (CGC) value of enthalpy of vaporization and is given in Table 3.

2.6. Correlation with molecular descriptors

A large number of topostructural, topochemical, geometrical and quantum chemical molecular descriptors such as, Information Indices, Zagreb group parameters, Wiener Indices, Balaban J index, Connectivity indices of valence path and cluster type, Solvent accessible surface area (SAS), Connolly molecular surface area, Solvent-excluded volume, Dipole moment, have been correlated with the enthalpy of vaporization. These structural descriptors were calculated using molecular structure represented by Simplified Molecular Input Line Entry System (SMILES) [27] as the only input.

3. Results and discussion

3.1. Retention mechanism

The chromatographic retention time of trialkyl phosphates and hydrocarbons selected in this study mainly depend upon the number of carbon atoms, degree of branching, the presence of heteroatom and the functional group in the molecular skeleton. The retention time of homologous hydrocarbons as well as trialkyl phosphates increase with increase in the carbon chain length for the normal paraffins and phosphates having straight chain alkyl groups, i.e., $\text{TMP} < \text{TEP} < \text{TBP} < \text{TAP} < \text{THP}$. In isomeric phosphates, the retention time increases in the order, $\text{TsBP} < \text{TiBP} < \text{TBP}$ and $\text{TsAP} < \text{T2MBP} < \text{TiAP} < \text{TAP}$. This clearly indicates that retention is affected by both steric and electronic factors. The magnitude of the effect depends on the volatility and number and type of interactions of the solute molecules with the stationary phase. Linear hydrocarbons have higher probability of interaction with the stationary phase

through electronic effects and the strength of the dispersive interaction increases with number of electrons of the molecule. Therefore, the order of elution depends on the molar mass for *n*-homologues. The retention of isomeric compounds can be affected by steric effects, which can decrease the potential influence of the dispersive forces. The substitution of a methyl group away from the alkoxy carbon tends to exhibit behavior like a straight chain trialkyl phosphate.

3.2. Effect of structure on enthalpy of vaporization

The number of carbon atoms and their arrangement in space determine the physical properties of the organic compounds. For completely non-polar organic compounds (hydrocarbons) and less non-polar compounds (phosphate esters), the main intermolecular interactions result from the dispersive forces as well as dispersive and induced dipole forces, respectively. The enthalpy of vaporization is the energy required to remove a molecule from the highly interacting and associated liquid phase into the vapor phase, wherein interactions almost cease to exist. As the carbon chain length in the phosphates increases, its size increases and hence the energy required to transfer a molecule from the liquid to vapor state also increases. This trend is observed in the results of enthalpy of vaporization of homologues of trialkyl phosphates ($\text{TMP} < \text{TEP} < \text{TBP} < \text{TAP} < \text{THP}$) and *n*-hydrocarbon series. In isomers of the tri-*n*-butyl phosphate, the enthalpy of vaporization varies in the order of $\text{TsBP} < \text{TiBP} < \text{TBP}$. In TsBP, the branching occurs immediately adjacent to the phosphoryl carbon resulting in a compact and nearly spherical shape of the phosphate, lessening the strength of intermolecular interactions. Hence, less amount of energy is required for vaporizing TsBP. The branching at the second carbon in triisobutyl phosphate makes it intermediate in behavior with respect to intermolecular attractions and in the resulting enthalpy of vaporization. In the amyl phosphate isomers, branching progressively away from the phosphoryl carbon oxygen also increases the enthalpy of vaporization.

3.3. Correlation of enthalpy of vaporization with molecular descriptors

Connolly [28,29] developed a method to calculate molecular surface area, solvent accessible surface area and solvent-excluded volume to model the topography of protein surfaces. Instead of taking the van der Waal's surface of a molecule, the contact surface obtained by rolling a spherical probe, usually the solvent molecule, over the molecular surface is taken as the molecular surface area. The accessible surface is then the locus of the centre of the solvent probe as it is rolled over the atoms of a molecule. This is called the solvent accessible surface area. The solvent-excluded volume is the volume of the space that the probe is excluded from by collision with the atoms of the molecule. Solvent accessible area, molecular surface area and solvent-excluded volume were calculated using Chem3D Ultra 8 [30], after optimizing the geometries of the molecules using Austin Model 1 (AM1) [31], method. In addition, energies of the highest occupied molecular orbital (E_{HOMO}), the lowest

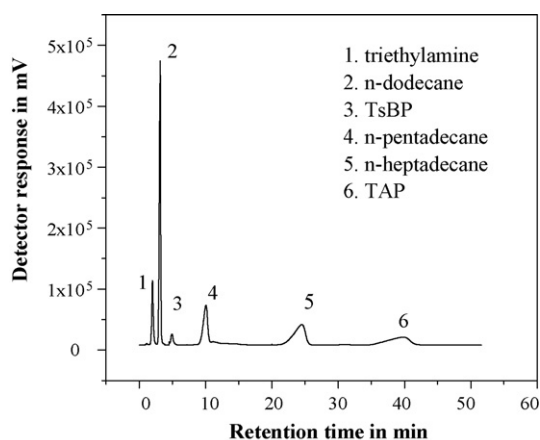


Fig. 1. A typical gas chromatogram obtained for mixture 7 (in Table 1) at 463.15 K.

unoccupied molecular orbital (E_{LUMO}) and heat of formation were calculated for the AM1 optimized geometries.

Statistical calculations were carried out using the statistical package SPSS [32]. In order to avoid collinearity of descriptors and overfitting, in the case of descriptors with intercorrelation >0.95 , only one of the descriptors was retained and the others were omitted. In addition, any descriptors possessing a constant value for all compounds within the data set were dropped. Initial data analysis reduced the descriptors from 28 to 11, the final set of descriptors and their intercorrelation was obtained. Solvent accessible surface area calculated using water as the solvent probe (radius = 0.14 nm) was found to be the most correlated predictor. Addition of any other descriptors did not improve the quality of the model. The single predictor regression Eqs. (2)

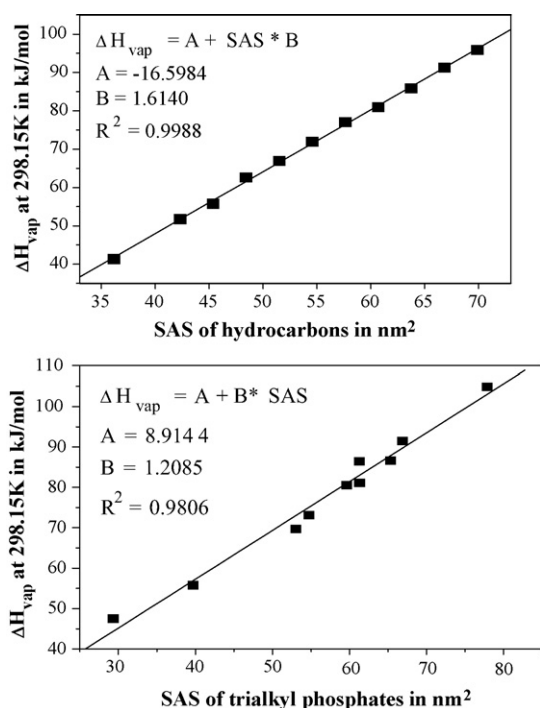


Fig. 2. A plot of molecular descriptor (SAS) versus experimental vaporization enthalpies.

and (3), for trialkyl phosphates and *n*-hydrocarbons, respectively are:

$$\Delta H_{\text{vap}} = 1.2085 \times (\text{SAS}) + 8.9144,$$

$$n = 10; R^2 = 0.9806, \text{SEE} = 2.85; F = 307.6 \quad (2)$$

$$\Delta H_{\text{vap}} = (\text{SAS} \times 1.6140) - 16.5984,$$

$$n = 14; R^2 = 0.9988; F = 9628.2; \text{SEE} = 0.767 \quad (3)$$

The correlation behavior between the enthalpy of vaporization and SAS is depicted in Fig. 2. Enthalpy of vaporization predicted from the correlation plot is given in Table 2.

3.4. Effect of structure on solubility parameter

The solubility parameter is used to give a rough and ready approximation of the solubility behavior of a specific solvent. The values of the solubility parameter are sensitive to the molecular structure of solvents and increases with number of carbon atoms in the hydrocarbon homologues and decreases in the trialkyl phosphate homologues. The isomers with long chains have a higher solubility parameter and the solubility parameter varied with the cohesive forces of isomers with same chain length. Because the molecular structure affects the cohesive forces that hold the molecules in a liquid it has an effect also on the value of solubility parameter.

4. Conclusions

The enthalpy of vaporization of TMP, TEP, TBP, TiBP, TsBP, TAP, TiAP, T2MBP, TsAP and THP were determined for the first time using correlation—gas chromatography and the Hildebrand's solubility parameters of these compounds were derived from the enthalpies of vaporization. The enthalpy of vaporization of normal paraffins used in this study as the reference standards are very close to reported values within normal error. Solvent accessible surface area was found to be the only structural parameter correlating well with the enthalpies of vaporization of the trialkyl phosphates as well as *n*-paraffins.

Acknowledgements

The authors would like to acknowledge with gratitude the help rendered by Dr. R. Natarajan in correlating the enthalpy data with structural parameters. Thanks are also due to Shri A. Suresh and Shri K. Sundararajan for kindly providing the trialkyl phosphates.

References

- [1] W.W. Schulz, J.D. Navratil, *Science and Technology of Tributyl Phosphate*, vol. 1, CRC Press, 1984.
- [2] Z. Kolarik, in: A.J. Freeman, C. Keller (Eds.), *Handbook on the Physics and Chemistry of the Actinides*, Elsevier Science Publishers, 1985, p. 431.
- [3] A.F.M. Barton, *CRC Handbook of Solubility Parameters and other Cohesion Parameters*, second ed., CRC press Inc., 1991 (Chapter 2).

- [4] J.H. Hildebrand, J.M. Prausnitz, R.L. Scott, *Regulated and Related Solutions*, Van Nostrand Reinhold Co., New York, 1970.
- [5] H.P. Diogo, R.C. Santos, P.M. Nunes, M.E.M. Piedade, *Thermochim. Acta* 249 (1995) 113–120.
- [6] St. Perisanu, I. Contineanu, M.D. Banciu, J.F. Liebman, B.S. Farivar, M.A. Mullan, J.S. Chickos, N. Rath, D.M. Hillesheim, *Thermochim. Acta* 400 (2003) 109–120.
- [7] M.A. Kaiser, C.R. Dybrowski, *Physicochemical measurements by gas chromatography*, in: R.L. Grob (Ed.), *Modern Practice of Gas Chromatography*, second ed., Wiley, New York, 1985.
- [8] L.A. Peacock, R. Fuchs, *J. Am. Chem. Soc.* 99 (1977) 5524.
- [9] R. Fuchs, L.A. Peacock, *Can. J. Chem.* 56 (1978) 2493.
- [10] R. Fuchs, L.A. Peacock, *Can. J. Chem.* 57 (1979) 2302.
- [11] R. Fuchs, L.A. Peacock, *Can. J. Chem.* 58 (1980) 2796.
- [12] R. Fuchs, W.K. Stephenson, *Can. J. Chem.* 63 (1985) 349.
- [13] R. Fuchs, E.J. Chambers, W.K. Stephenson, *Can. J. Chem.* 65 (1987) 2624.
- [14] J.S. Chickos, S. Hosseini, D.G. Hesse, *Thermochim. Acta* 249 (1995) 41–62.
- [15] M. Temprado, J.S. Chickos, *Thermochim. Acta* 435 (2005) 49–56.
- [16] J.S. Chikos, J.A. Wilsom, *J. Chem. Eng. Data* 42 (1997) 190–197.
- [17] J.S. Chikos, W. Hanshaw, *J. Chem. Eng. Data* 49 (2004) 77–85.
- [18] M.A.V.R. Silva, M.A.R. Matos, C.A. Rio, V.M.F. Morais, J. Wang, G. Nichols, J.S. Chickos, *J. Phys. Chem. A* 104 (2000) 1774–1778.
- [19] D.R. Stull, *Ind. Eng. Chem.* 39 (1947) 517–540.
- [20] J.S. Chickos Jr., W.E. Acree, *J. Phys. Chem. Ref. Data* 32 (2003) 519–878.
- [21] J.L.M. Abboud, R. Notario, *Pure Appl. Chem.* 71 (1999) 645–718.
- [22] C.R. Noller, G.R. Dutton, *Preparation of trialkyl phosphates and their use as alkylating agents*, *J. Am. Chem. Soc.* 55 (1933) 424.
- [23] C.R. Dutton, C.R. Noller, in: A.H. Blatt (Ed.), *n-Butyl phosphate*, in *Organic Syntheses*, Coll, vol. 2, John Wiley and Sons, New York, 1947, p. 109.
- [24] G. Nichols, J. Orf, S.M. Reiter, J.S. Chickos, G.W. Gokel, *Thermochim. Acta* 346 (2000) 15–28.
- [25] CRC, *Handbook of Chemistry and Physics*, 80th ed., 1999–2000.
- [26] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic solvents. Physical properties and methods of purifications Techniques of Chemistry*, vol. 2, fourth ed., John Wiley & Sons, New York, 1986.
- [27] <http://www.daylight.com/smiles/>, visited January 29, 2007.
- [28] M.L. Connolly, *Measurement of protein surface shape by solid angles*, *J. Mol. Graph.* 4 (1) (1986) 3.
- [29] M.L. Connolly, *Molecular Surface Package ver 3.9.3.*, <http://connolly.best.vwh.net/>, Visited January 29, 2007.
- [30] Chem3D Ultra v.8.0, Cambridge Soft Corporation, Cambridge, MA, USA, 2004.
- [31] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* 107 (1985) 3902–3909.
- [32] *SPSS Base 10.0 Applications Guide*, SPSS, USA, 1999.