Thermochimica Acta 495 (2009) 1–4

Contents lists available at ScienceDirect

Thermochimica Acta

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

Enthalpies of vaporization of N,N-dialkyl monamides at 298.15 K

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ARTICLE INFO

Article history:
Received 27 March 2009
Received in revised form 8 May 2009
Accepted 12 May 2009
Available online 20 May 2009

Keywords:
Enthalpy of vaporization
Correlation gas chromatography
N,N-dialkyl monamides
Molecular descriptors
QSPR

ABSTRACT

Enthalpies of vaporization of several N,N-dialkyl monamides have been measured by correlation gas chromatography. The enthalpy values of the compounds are derived by an extrapolative method using the known enthalpy of vaporization values of basic amides at 298.15 K, used as standards. First order molecular connectivity valence indices of these amides (${}^{1}\chi_{\nu}$) as described by Kier and Hall have been evaluated and are found to have an excellent correlation with measured enthalpies of vaporization in addition to several other indices, such as, solvent accessible surface area (SAS), molecular surface area (MSA) and solvent excluded volume (SEV). The quantitative structure–property relationship (QSPR) approach is used to predict the enthalpies of vaporization from molecular connectivity valence index.

1. Introduction

N,N-dialkyl monamides are being developed as the extractants for applications in Plutonium Uranium Reduction Extraction (PUREX) and Thorium Uranium Extraction (THOREX) processes which selectively recover U, Pu and U, Th selectively from fission products from the spent nuclear fuel solutions [1–5]. These amides have a distinct merit over the currently employed trialkyl phosphates due to reasons such as, the formation of innocuous radiolytic, thermal and hydrolytic degradation products, complete incinerability and the possibility of stripping the extracted uranium and plutonium just with variation of acid concentration.

Enthalpies of vaporization are indispensable for the design of chemical processes and for the design and operation of vapor–liquid equilibrium based processes such as distillation, evaporation, etc., where the enthalpy of vaporization must be known for at least one temperature. It is also an important parameter in the prediction of partitioning properties; viz., the temperature dependence of solubility parameters that are used in many applications such as the selection of solvents for paints, polymers, etc.

Correlation gas chromatography (CGC) is an attractive technique in which the retention time of a particular compound is measured using gas chromatography for determining the enthalpies of transfer from solution to gas phase on the stationary phase, $\Delta_{\mathrm{soln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$. It is a well established technique for measuring the enthalpies of vaporization for homologous [6–9] and analogous [10] organic compounds. A linear correlation exists between the enthalpies of transfer from solution to gas phase on the stationary phase and the vaporization enthalpies $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ at reference temperature, usually 298.15 K. An empirical relationship exists between these two parameters for simple homologues and analogous compounds. An interpolative [6–11] and extrapolative [12] method can be used to derive the enthalpies of vaporization of target compounds using the linear correlation exhibited between $\Delta_{\mathrm{soln}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$. The correlation gas chromatographic technique has several merits over other techniques that are employed for the determination of the enthalpy of vaporization, because it is fast, easy to perform and requires only a few microliters of sample. The technique also tolerates impurities and can measure the enthalpy of vaporization of more than one sample in a single an experimental run. The limitation of this technique is that accuracy of the results relies heavily on the selection of appropriate standards with known enthalpy of vaporization at the reference temperature.

Kier and Hall's molecular connectivity index describes the structural features of organic compounds such as size, branching, unsaturation, hetero-atom content and the cyclic nature of the molecule. Each of substructure fragments encoded are incorporated into numerical indices [13]. This index used in several quantitative structure–property relationships has been used in the present study for correlating the enthalpies of vaporization with the index.

2. Experimental

2.1. Materials

N,N-dimethyl formamide (extrapure), N,N-dimethyl acetamide (extrapure) and N,N-diethyl acetamide (Alfa aesar) which are used

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doi:10.1016/j.tca.2009.05.007

as standards were of commercial origin and were used as procured. Other N,N-dialkyl amides were synthesized according to the described method [14], purified and the purity of the yield determined [15] and characterized by Fourier transform infrared spectroscopy (FTIR), Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) and elemental analysis of carbon, hydrogen and nitrogen (CHN analysis).

2.2. Equipment

Retention times of N,N-dialkyl monamides were measured using Shimadzu GC-9A gas chromatograph equipped with splitless injector and flame ionization detector (FID). The injector and FID temperatures were set at 518.15 and 523.15 K, for vaporization and detection of analytes, respectively. Argon was used as mobile phase with a flow rate of 55 mL/min. The separation was carried out using a 4 m × 3.2 mm, 10% Apiezon® L packed column. Hydrogen (50 mL/min) and air (500 mL/min) were fed into FID to burn the eluted compounds. Data acquisition and report creation of the chromatograms were performed by ASHCO® software.

2.3. Retention time measurements

The retention times (t_R) of N,N-dibutyl octanamide (DBOA), N,N-di(2-ethyl)hexyl isobutyramide (D2EHIBA), N,N-dihexyl hexanamide (DHHA), N,N-dihexyl octanamide (DHOA) and N,N-dioctyl hexanamide (DOHA) along with standards N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc) and N,N-diethyl acetamide (DEAc) were measured over a 50 K range at 10 K intervals of column temperature. A different set of target compounds mixed with standards were injected into the gas chromatograph under isothermal conditions to ensure the reproducibility of the computed values. The sample size for all measurements was 2 μL. Methanol was used as an unretained compound and its retention time (t_M) was obtained at all experimental temperatures which increased with an increase in temperature. Adjusted retention times (t_R') of each compound was obtained by subtracting t_M from

Table 1
Enthalpies of transfer from solution to gas ($\Delta_{sol}{}^{g}H_m(T_m)$) and vaporization enthalpies ($\Delta_l{}^{g}H_{vap}$).

Compounds and column temperature range	Slope	Intercept	Correlation coefficient (R^2) of $\ln(t_0/t_R')$ versus $1/T$ (K)	$\Delta_{sol}{}^{g}H_m(T_m)$ (kJ mol^{-1})	$\Delta_l{}^{g}H_{vap}$(298.15 K) (kJ mol^{-1})	
					Evaluated	Literature [16]
Mixture: 1 (473.15–513.15 K)						
N,N-dimethyl formamide (DMF)	−2655.75	6.8091	0.9832	22.07	47.45	46.89
N,N-dimethyl acetamide (DMAc)	−3025.75	7.2688	0.9888	25.15	49.44	50.24
N,N-diethyl acetamide (DEAc)	−3939.50	8.7057	0.9906	32.75	54.33	54.1
N,N-dibutyl octanamide (DBOA)	−7831.25	13.3842	0.9970	65.10	75.14	–
N,N-dioctyl hexanamide (DOHA)	−10377.75	16.3301	0.9980	86.28	88.79	–
$\Delta_l{}^{g}H_{vap}(298.15\,K) = 33.2587 + 0.6434 \times \Delta_{sol}{}^{g}H_m$	$R^2 = 0.9609$					
Mixture: 2 (473.15–513.15 K)						
N,N-dimethyl formamide (DMF)	−1910.00	5.3882	0.9942	15.87	46.31	46.89
N,N-dimethyl acetamide (DMAc)	−2884.00	7.0585	0.9986	23.97	51.04	50.24
N,N-diethyl acetamide (DEAc)	−3351.25	7.5142	0.9970	27.56	53.14	54.1
N,N-dihexyl hexanamide (DHHA)	−8713.00	14.4595	0.9968	72.43	79.37	–
N,N-dihexyl octanamide (DHOA)	−9422.75	15.2156	0.9984	78.34	82.82	–
$\Delta_l{}^{g}H_{vap}(298.15\,K) = 37.0416 + 0.5844 \times \Delta_{sol}{}^{g}H_m$	$R^2 = 0.9410$					
Mixture: 3 (473.15–513.15 K)						
N,N-dimethyl formamide (DMF)	−2392.00	6.3095	0.9407	19.88	46.80	46.89
N,N-dimethyl acetamide (DMAc)	−3031.25	7.3211	0.9551	25.20	50.40	50.24
N,N-diethyl acetamide (DEAc)	−3673.00	8.1438	0.9860	30.53	54.01	54.1
N,N-di(2-ethyl hexyl isobutyramide) (D2EHIBA)	−8241.25	13.9736	0.9972	68.51	79.72	–
N,N-dihexyl hexanamide (DHHA)	−8692.75	14.4433	0.9976	72.27	82.27	–
$\Delta_l{}^{g}H_{vap}(298.15\,K) = 33.3470 + 0.6770 \times \Delta_{sol}{}^{g}H_m$	$R^2 = 0.9982$					
Mixture: 4 (473.15–513.15 K)						
N,N-dimethyl formamide (DMF)	−2979.18	7.5916	0.9712	24.76	46.56	46.89
N,N-dimethyl acetamide (DMAc)	−3763.03	8.8721	0.9968	31.28	51.32	50.24
N,N-diethyl acetamide (DEAc)	−4095.79	9.0312	0.9968	34.05	53.34	54.1
N,N-dibutyl octanamide (DBOA)	−7701.01	13.0745	0.9992	64.02	75.19	–
N,N-dihexyl hexanamide (DHHA)	−8441.54	13.9291	0.9994	70.18	79.66	–
$\Delta_l{}^{g}H_{vap}(298.15\,K) = 28.5147 + 0.7291 \times \Delta_{sol}{}^{g}H_m$	$R^2 = 0.9289$					
Mixture: 5 (463.15–503.15 K)						
N,N-dimethyl formamide (DMF)	−3104.00	7.8768	0.9719	25.80	46.60	46.89
N,N-dimethyl acetamide (DMAc)	−3903.00	9.1949	0.9818	32.44	51.02	50.24
N,N-diethyl acetamide (DEAc)	−4368.00	9.6213	0.9858	36.31	53.60	54.1
N,N-dibutyl octanamide (DBOA)	−8484.50	14.7047	0.9964	70.54	76.41	–
N,N-di(2-ethyl hexyl isobutyramide) (D2EHIBA)	−8851.75	15.2391	0.9964	73.59	78.44	–
$\Delta_l{}^{g}H_{vap}(298.15\,K) = 29.4098 + 0.6663 \times \Delta_{sol}{}^{g}H_m$	$R^2 = 0.9637$					
Mixture: 6 (473.15–513.15 K)						
N,N-dimethyl formamide (DMF)	−1988.50	5.5758	0.9368	16.53	46.16	46.89
N,N-dimethyl acetamide (DMAc)	−2901.00	7.1134	0.9623	24.11	50.77	50.24
N,N-diethyl acetamide (DEAc)	−3496.50	7.8146	0.9900	29.06	53.78	54.1
N,N-dihexyl octanamide (DHOA)	−9268.50	14.9076	0.9988	77.05	82.96	–
N,N-dioctyl hexanamide (DOHA)	−10141.00	15.9048	0.9990	84.31	87.38	–
$\Delta_l{}^{g}H_{vap}(298.15\,K) = 36.1189 + 0.6080 \times \Delta_{sol}{}^{g}H_m$	$R^2 = 0.9830$					

Table 2
Different substituents in R′, R″ and R‴ of N,N-dialkyl monamides.

Compounds	Molecular weight	R′	R″	R‴
DMF	73	H	CH_3	CH_3
DMAc	87	CH_3	CH_3	CH_3
DEAc	115	CH_3	CH_2CH_3	CH_2CH_3
DBOA	255	$(CH_2)_6CH_3$	$(CH_2)_3CH_3$	$(CH_2)_3CH_3$
DHHA	283	$(CH_2)_4CH_3$	$(CH_2)_5CH_3$	$(CH_2)_5CH_3$
DHOA	307	$(CH_2)_6CH_3$	$(CH_2)_5CH_3$	$(CH_2)_5CH_3$
D2EHIBA	311	$CH(CH_3)_2$	$CH_2CH(CH_2CH_3)(CH_2)_3CH_3$	$CH_2CH(CH_2CH_3)(CH_2)_3CH_3$
DOHA	339	$(CH_2)_4CH_3$	$(CH_2)_7CH_3$	$(CH_2)_7CH_3$

t_R (i.e., the amount of time the analyte remains on the stationary phase).

2.4. Evaluation of enthalpies of vaporization

Enthalpies of transfer from solution to gas on stationary phase were evaluated from the temperature dependent retention times of the analytes. A plot of $\ln(t_0/t_R')$ versus $1/T$ (K), where $t_0 = 1$ min and the adjusted retention time (t_R'), ($t_R' = t_R - t_M$), is proportional to the reciprocal of the vapor pressure of the compounds on the stationary phase at the experimental temperature (T) was constructed. The slope of the linear fit is enthalpy of transfer from solution to gas phase on the stationary phase divided by universal gas constant (R), $-\Delta_{soln}{}^{g}H_m(T_m)/R$. Another plot $\Delta_{soln}{}^{g}H_m(T_m)$ versus $\Delta_l{}^{g}H_m(298.15\,K)$ was constructed to derive the vaporization enthalpy of standards at reference temperature. The resulting linear fit equation was used to evaluate the vaporization enthalpies of the target compounds. A summary of evaluated enthalpies of vaporization ($\Delta_l{}^{g}H_m$) at 298.15 K, enthalpies of transfer from solution to gas ($\Delta_{soln}{}^{g}H_m$) and the literature value [16] are given in Table 1.

2.5. Molecular descriptors

Topological descriptors are easy to derive with present computing facilities and are used for predicting several physical properties of the compounds, their gas chromatographic retention behaviour, pharmo-chemical activities, toxicity, etc. Topological descriptors, such as, solvent accessible surface area (SAS), molecular surface area (MSA), solvent excluded volume (SEV), Kier and Hall's valence connectivity index of order "n" (${}^n\chi_\nu$), Wiener's index (W), etc. are derived for dialkyl monamides by using facilities [17–20] and attempts were made to correlate these descriptors with the enthalpies of vaporization.

3. Results and discussions

3.1. Enthalpies of vaporization

Enthalpies of vaporization of dialkyl monamides increase with molecular weight, except for D2EHIBA and this deviation in this amide is due to a lower packing order caused by steric hindrance resulting from the repulsion between ethyl substituents. The molecular weight and description of the alkyl moieties R′, R″ and R‴ of dialkyl amides are given in Table 2. The structure of the alkyl moieties influence the electronic environment and consequently affect the intermolecular interactions. The increment in enthalpy of vaporization from DMF, DMAc to DEAc is about 3 kJ mol^{-1} due to successive inclusion of –CH_2– groups in their molecular skeleton. The enthalpy of vaporization of DOHA is the highest among the compounds studied. Among DHHA and DHOA which have same substituents on nitrogen and dissimilar carbonyl substituents, DHHA with a smaller spatial requirement exhibits a lower enthalpy of vaporization.

3.2. Quantitative structure–property relationship

Attempts to correlate the enthalpies of vaporization with topological indices resulted in very good correlations for the solvent accessible surface area (SAS), molecular surface area (MSA), solvent excluded volume (SEV) and Kier and Hall's valence connectivity Index of I order (${}^1\chi_\nu$). The equations of fit and the information on correlation coefficient (R^2), standard deviation (SD) of the fit and number of compounds (N) used for correlations are provided below for all the descriptors.

$$\Delta H_{vap} = (\mathrm{SAS} \times 13.1061) - 397.4465$$
$$R^2 = 0.998, \quad \mathrm{SD} = 11.4406, \quad N = 8 \tag{1}$$

$$\Delta H_{vap} = (\mathrm{MSA} \times 8.3035) - 299.6715$$
$$R^2 = 0.998, \quad \mathrm{SD} = 6.7813, \quad N = 8 \tag{2}$$

$$\Delta H_{vap} = (\mathrm{SEV} \times 8.4891) - 335.6203$$
$$R^2 = 0.988, \quad \mathrm{SD} = 16.2192, \quad N = 8 \tag{3}$$

$$\Delta H_{vap} = ({}^1\chi_\nu \times 42.0589) + 4.0796$$
$$R^2 = 0.988, \quad \mathrm{SD} = 16.2192, \quad N = 8 \tag{4}$$

Fig. 1 depicts a typical correlation obtained between enthalpy of vaporization and (${}^1\chi_\nu$). Variation in enthalpies of vaporization

Table 3
Summary of enthalpies of vaporization of N,N-dialkyl monamides at 298.15 K.

Compounds	$\Delta_l{}^{g}H_{vap}$ at 298.15 K (kJ mol^{-1}) evaluated[a]	Predicted from the plot of evaluated $\Delta_l{}^{g}H_{vap}$ versus ${}^1\chi_\nu$	Kier and Hall index, ${}^1\chi_\nu$
DMF	46.65 ± 0.45	47.73	1.39
DMAc	50.66 ± 0.67	49.48	1.82
DEAc	53.70 ± 0.44	54.17	2.97
DBOA	75.58 ± 0.72	74.86	8.04
D2EHIBA	79.08 ± 0.90	81.95	9.78
DHHA	80.44 ± 1.60	78.94	9.04
DHOA	82.89 ± 0.09	83.02	10.04
DOHA	88.08 ± 0.99	87.10	11.04

[a] The enthalpies of vaporization are average values that have been evaluated from the correlation equation from each correlation GC experiment. The uncertainties represent the standard deviation.

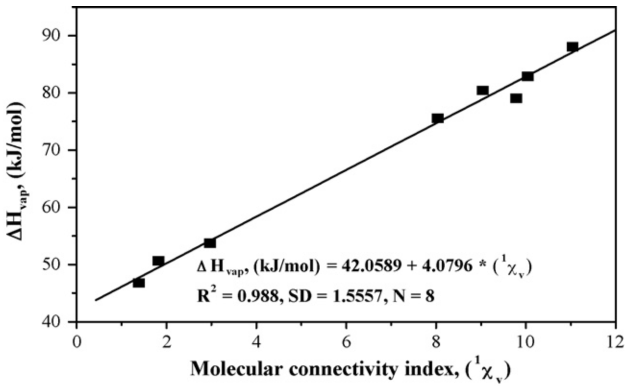

Fig. 1. Plot of molecular connectivity index versus experimental vaporization enthalpies.

would be expected to be molecular shape dependent and this in turn influences packing ability would be reasonably well accounted for correlation coefficients of SAS, MSA and SEV descriptors. The first order Kier and Hall valence index, $^1\chi_v$, increases with increasing enthalpies of vaporization as expected because of the increase in strength of intermolecular interactions with molecular size. The evaluated and predicted values are compared with the available literature data. The summary of enthalpies of vaporization obtained by CGC and predicted from the plot is given in Table 3.

4. Conclusions

The enthalpies of vaporization of N,N-dialkyl monamides were determined for the first time by correlation gas chromatography and the determined values for the standards agree well with the literature values. The enthalpies of vaporization have been found to exhibit excellent linear correlation with Kier and Hall's connectivity index of I order and other descriptors such as solvent accessible surface area (SAS), solvent excluded volume (SEV) and molecular surface area (MSA). The correlations corroborate the internal consistency of the data and help to establish the enthalpies for unknown analogous dialkyl monamides.

Acknowledgments

The authors are grateful to Dr. V. Vidhyalakshmi and Dr. N. Sivaraman for providing synthesized dialkyl amides and methanol, respectively and to Dr. R. Natarajan for correlating enthalpies of vaporization with molecular descriptors.

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