



Prediction of enthalpy and standard Gibbs energy of vaporization of haloaromatics from atomic properties



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HIGHLIGHTS

- A new method for estimation volatility properties of haloaromatics is presented.
- Contribution of atomic properties of the halogens to volatility is discussed.
- Estimated and experimental enthalpies of vaporization are compared.
- Estimated and experimental vapor pressures are compared.

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ABSTRACT

Halogenated benzenes form a class of pollutants with a huge number of members – 1504 distinct benzene compounds, where one or more hydrogen atoms are replaced by halogens, may exist theoretically. This study presents a user friendly method for accurate prediction of vapor pressures and enthalpies of vaporization, at 298.15 K, of any mono or poly halobenzene compound. The derived equations for the prediction of those vaporization properties depend just on the number of each constituent halogen atom. This is a consequence of the absence of intramolecular interactions between the halogen atoms, revealed after examining vaporization results of ca. 40 halogenated benzenes. In order to rationalize the estimation equations, the contribution of the halogen atoms for the referred to above properties of vaporization was decomposed into two atomic properties – the volume and electron affinity. Extension of the applicability of the estimation method to substituted benzenes containing other substituent groups beyond halogen atoms as well as to some polycyclic aromatic species was tested with success.

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1. Introduction

Halogenated organic compounds are ubiquitous contaminants in the environment, their physico-chemical properties being strongly influenced by the halogen substituents. Halobenzenes (where halo stands for fluorine, chlorine, bromine and iodine atoms) form a class of aromatic compounds with a huge number of members – 1504 distinct halobenzenes may exist theoretically as shown in [Table S1 in supplementary information](#). Haloaromatic compounds are well known pollutants that have several industrial uses some of them produced in very large amounts. Smaller halogenated benzenes are absorbed by mammals through the skin while the ones with larger number of halogen atoms tend to be poorly absorbed, though when absorbed they will

accumulate in fatty tissue. Chronic effects due to exposure include porphyria, necrosis of liver, lung, and kidneys, and blood anomalies (USEPA, 1977).

For the prediction of the fate and transport of these pollutants in the environment, accurate data of vapor pressures and enthalpies of vaporization are needed to derive their volatility and other transport properties – the distribution of a chemical between air, water and soil depends on key properties including vapor pressure, solubility in water, and partition and distribution coefficients (Delle Site, 1997). In this work we present a simple method for estimating vapor pressures and enthalpies of vaporization for mono to hexa halogenated substituted benzenes that can be useful when experimental values are lacking or to screen the reliability of the ones reported in the literature.

In previous works correlations derived for *p*-halogenated benzoic acids and methyl benzoates (Almeida and Monte, 2013a), and for *p*-halogenated phenols (Almeida and Monte, 2013b) show

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a regular dependence of vapor pressures and enthalpies of sublimation or vaporization on the volume of the halogen substituent. In order to investigate if this influence is additive in terms of the constituent halogen atoms we collected experimental results of vapor pressure and enthalpies of vaporization of a series of halobenzenes. We concluded that the effect of volume on these properties is not additive per se but an appropriate combination of volume and electron affinity of the halogen atoms multiplied by their number could yield a very simple method to estimate the vapor pressures and enthalpies of vaporization, at 298.15 K, of halobenzene compounds independent of the number and relative position of the halogen substituents. The influence of other

atomic properties, such as ionization potential and Hammett inductive constant (σ_I), were also considered but turned out to be less effective than electron affinity. Application of the method to substituted halobenzenes and to halogenated polycyclic aromatic compounds is also discussed.

2. The estimation method

The data base used in this study is presented in Table 1 that includes results of enthalpy and standard Gibbs energy of vaporization, at the temperature 298.15 K, of 42 halobenzenes

Table 1
Experimental and estimated standard ($p^\circ = 0.1$ MPa) properties of vaporization, at 298.15 K, of halobenzenes.

Compound	$\Delta_f^\circ G_m^\circ$ (kJ mol ⁻¹)		p° (kPa)		$\Delta_f^\circ H_m^\circ$ (kJ mol ⁻¹)		Reference ^e
	(exp.) ^b	(est.) ^c	(exp.)	(est.)	(exp.) ^b	(est.) ^d	
Benzene	5.1 ^f		$1.3 \cdot 10$		34.0 ^g		
Fluorobenzene	5.7	5.2	$1.0 \cdot 10$	$1.2 \cdot 10$	34.5	34.4	Verevkin et al. (2014a)
Chlorobenzene	10.3	10.0	1.6	1.8	41.2	41.0	Verevkin et al. (2014a)
Bromobenzene	12.9	12.6	$5.5 \cdot 10^{-1}$	$6.2 \cdot 10^{-1}$	44.3	44.5	Verevkin et al. (2015a)
Iodobenzene	16.3	16.3	$1.4 \cdot 10^{-1}$	$1.4 \cdot 10^{-1}$	48.5	49.5	Verevkin et al. (2015a)
1,2-Difluorobenzene	6.6	5.3	7.0	$1.2 \cdot 10$	36.2	34.9	Scott et al. (1963)
1,3-Difluorobenzene	5.5	5.3	$1.1 \cdot 10$	$1.2 \cdot 10$	34.9	34.9	Osborn and Scott (1980) ^h
1,4-Difluorobenzene	6.1	5.3	8.5	$1.2 \cdot 10$	36.0	34.9	Osborn and Scott (1980) ^h
1,2-Dichlorobenzene	15.5	14.9	$1.9 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	48.0	48.0	Rohac et al. (1999)
1,3-Dichlorobenzene	14.7	14.9	$2.7 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	47.3	48.0	Dreisbach and Shrader (1949) ^h
1,4-Dichlorobenzene ⁱ	14.8	14.9	$2.6 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	48.3	48.0	Rohac et al. (1998)
1,2-Dibromobenzene	20.9	20.1	$2.2 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	54.3	55.0	Solomonov et al. (2015)
1,3-Dibromobenzene	20.1	20.1	$3.0 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	54.9	55.0	Solomonov et al. (2015)
1,4-Dibromobenzene ⁱ	20.0	20.1	$3.1 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	54.6	55.0	Oonk et al. (2000)
1,2-Diiodobenzene	27.7	27.5	$1.4 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	65.6	65.0	Verevkin et al. (2014b)
1,3-Diiodobenzene ⁱ	27.8	27.5	$1.3 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	66.1	65.0	Verevkin et al. (2014b)
1,4-Diiodobenzene ⁱ	27.7	27.5	$1.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	66.8	65.0	Verevkin et al. (2014b)
2-Chlorofluorobenzene	10.8	10.1	1.3	1.7	44.0	41.4	Verevkin et al. (2015b)
3-Chlorofluorobenzene	9.9	10.1	1.8	1.7	43.0	41.4	Verevkin et al. (2015b)
4-Chlorofluorobenzene	9.5	10.1	2.2	1.7	42.8	41.4	Verevkin et al. (2015b)
2-Bromofluorobenzene	13.3	12.7	$4.7 \cdot 10^{-1}$	$6.0 \cdot 10^{-1}$	47.0	44.9	Verevkin et al. (2015b)
3-Bromofluorobenzene	12.2	12.7	$7.3 \cdot 10^{-1}$	$6.0 \cdot 10^{-1}$	44.3	44.9	Verevkin et al. (2015b)
4-Bromofluorobenzene	12.7	12.7	$6.0 \cdot 10^{-1}$	$6.0 \cdot 10^{-1}$	44.0	44.9	Verevkin et al. (2015b)
2-Iodofluorobenzene	16.6	16.4	$1.2 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$	51.5	49.9	Verevkin et al. (2015b)
3-Iodofluorobenzene	16.0	16.4	$1.6 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$	48.6	49.9	Verevkin et al. (2015b)
4-Iodofluorobenzene	15.9	16.4	$1.6 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$	49.6	49.9	Verevkin et al. (2015b)
2-Chlorobromobenzene	18.0	17.5	$7.0 \cdot 10^{-2}$	$8.6 \cdot 10^{-2}$	52.0	51.5	Verevkin et al. (2014b)
3-Chlorobromobenzene	17.5	17.5	$8.6 \cdot 10^{-2}$	$8.6 \cdot 10^{-2}$	51.3	51.5	Verevkin et al. (2014b)
4-Chlorobromobenzene ⁱ	17.4	17.5	$8.9 \cdot 10^{-2}$	$8.6 \cdot 10^{-2}$	52.3	51.5	Verevkin et al. (2014b)
2-Chloriodobenzene	21.6	21.2	$1.6 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	57.3	56.5	Verevkin et al. (2014b)
2-Bromiodobenzene	24.1	23.8	$6.0 \cdot 10^{-3}$	$6.8 \cdot 10^{-3}$	59.6	60.0	Verevkin et al. (2014b)
3-Bromiodobenzene	23.8	23.8	$6.8 \cdot 10^{-3}$	$6.8 \cdot 10^{-3}$	60.8	60.0	Verevkin et al. (2014b)
4-Bromiodobenzene ⁱ	23.6	23.8	$7.3 \cdot 10^{-3}$	$6.8 \cdot 10^{-3}$	59.8	60.0	Verevkin et al. (2014b)
1,3,5-Trifluorobenzene	4.9	5.4	$1.4 \cdot 10$	$1.2 \cdot 10$	34.5	35.3	Findlay (1969)
1,2,3-Trichlorobenzene ⁱ	20.3	19.8	$2.8 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$	55.2	55.0	Rohac et al. (1999)
1,3,5-Trichlorobenzene ⁱ	19.1	19.8	$4.5 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$	54.9	55.0	Rohac et al. (1999)
1,2,4-Trichlorobenzene	19.6	19.8	$3.7 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$	54.6	55.0	Rohac et al. (1999)
1,2,3,4-Tetrafluorobenzene	6.7	5.5	6.7	$1.1 \cdot 10$	36.8	35.7	Findlay (1969)
1,2,3,5-Tetrafluorobenzene	5.7	5.5	$1.0 \cdot 10$	$1.1 \cdot 10$	36.0	35.7	Findlay (1969)
Pentafluorobenzene	6.0	5.6	8.9	$1.1 \cdot 10$	36.8	36.2	Ambrose (1968) ^h
Pentachlorobenzene ⁱ	29.1	29.6	$8.0 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$	68.6	69.0	Rohac et al. (1999)
Chloropentafluorobenzene	9.3	10.5	2.3	1.5	41.5	43.2	Ambrose (1968) ^h
Hexafluorobenzene	5.4	5.6	$1.1 \cdot 10$	$1.0 \cdot 10$	36.1	36.6	Ambrose et al. (1990)

^a Vapor pressures calculated from experimental and estimated values of $\Delta_f^\circ G_m^\circ$ through Eq. (1).

^b Results published by the authors or derived in the present study from original source data (values in italics were not considered to derive the estimation equation).

^c Values estimated through Eq. (4); the standard uncertainty of each estimated value can be calculated from the number of each constituent halogen atom as $u(\Delta_f^\circ G_m^\circ)$

$$\text{kJ mol}^{-1} = \sqrt{0.2^2 + (0.06 \cdot n_F)^2 + (0.1 \cdot n_{Cl})^2 + (0.1 \cdot n_{Br})^2 + (0.1 \cdot n_I)^2}$$

^d Values estimated through Eq. (5); the standard uncertainty of each estimated value can be calculated from the number of each constituent halogen atom as $u(\Delta_f^\circ H_m^\circ)$

$$\text{kJ mol}^{-1} = \sqrt{0.4^2 + (0.13 \cdot n_F)^2 + (0.2 \cdot n_{Cl})^2 + (0.2 \cdot n_{Br})^2 + (0.3 \cdot n_I)^2}$$

^e References of original source of vapor pressure data.

^f Mean value assigned from two ebulliometry results (Deshpande and Pandya, 1967; Ambrose et al., 1990).

^g Mean value assigned from two calorimetric results (Dong et al., 1988; Svoboda et al., 1973) and from two ebulliometry results (Deshpande and Pandya, 1967; Ambrose et al., 1990).

^h Also reported by Dykyj et al. (1999).

ⁱ Supercooled liquid at the temperature 298.15 K.

^j Supercooled liquid at the temperature 298.15 K; the experimental values of $\Delta_f^\circ G_m^\circ$ and vapor pressure were estimated from the sublimation ones and $\Delta_f^\circ C_{p,m}^\circ$ value reported in the original source and from the results of the enthalpy and temperature of fusion (van Miltenburg et al., 2001).

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