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Note

HEAT OF VAPORIZATION OF *o*-, *m*- AND *p*-NITROANILINE

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Continuing our research program on the determination of thermodynamic properties associated with the vaporization processes of organic compounds [1,2], *o*-, *m*- and *p*-nitroanilines (hereafter referred to as *o*-, *m*- and *p*-NA, respectively) were studied.

At present, except for the old data reported by Ohe [3] and those selected by Malaspina et al. [4], apparently no other vapor pressure and heat of vaporization data of these compounds are available. A new set of tensimetric values was therefore measured with a torsion effusion apparatus in order to derive the corresponding heats of vaporization.

The method and assembly were as described previously [5]. Commercial samples of *o*-, *m*- and *p*-NA, supplied by Koch Light (99.99%), were used in this work. Two graphite cells with different diameter effusion holes were

TABLE 1

Summary of the results obtained for each experimental run

Run	State	Cell	T (K)	No. of points	$\log P$ (kPa) $= A - B/T$	
					A [a]	B [a]
o-*Nitroaniline*						
4.06	solid	A	313–342	14	12.04 ± 0.26	4759 ± 85
	liquid	A	346–381	15	8.46 ± 0.10	3531 ± 37
4.11	solid	B	318–341	7	12.02 ± 0.84	4747 ± 27
	liquid	B	350–370	9	9.82 ± 0.51	4012 ± 18
m-*Nitroaniline*						
4.07	solid	A	339–376	19	13.76 ± 0.19	5680 ± 69
4.01	solid	A	343–383	19	13.65 ± 0.20	5673 ± 74
4.09	solid	B	337–385	11	13.70 ± 0.18	5653 ± 66
p-*Nitroaniline*						
4.05	solid	A	366–416	29	13.10 ± 0.13	5850 ± 51
4.03	solid	B	368–411	9	11.56 ± 0.12	5223 ± 49
4.12	solid	B	359–393	8	11.09 ± 0.19	5095 ± 71

[a] The errors quoted are standard deviations.

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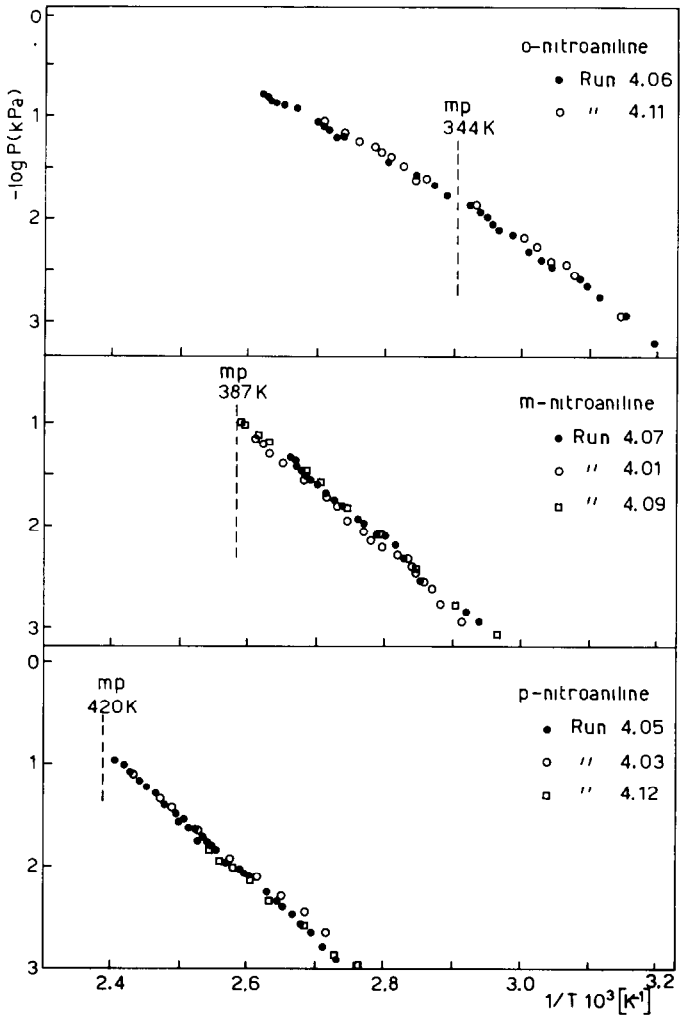

Fig. 1. Vapor pressures of *o*-, *m*- and *p*-NA measured by the torsion effusion method.

employed. Before and after the study of these compounds the vapor pressures [6] of pure standards (naphthalene, sulfur and zinc) were determined in order to test the reliability of the data obtained.

The vapor pressure values of *o*-, *m*- and *p*-NA are plotted in Fig. 1 as log P vs. $1/T$ and the corresponding $P-T$ equations obtained by a linear least-squares treatment of the data for each run are reported in Table 1. From the results obtained the following equations were selected weighing the corresponding constants proportionally to the number of the experimental points

o-nitroaniline (s): $\log P\ (\text{kPa}) = 12.0 \pm 0.9 - (4750 \pm 130)/T$

TABLE 2

Thermodynamic parameters of *o*-, *m*- and *p*-NA

Compound	ΔS_T^0 (J mol^{-1} K^{-1})	ΔH_T^0 (kJ mol^{-1})		
		Present data	Literature data [3]	[4]
o-NA(s)	191 ± 17	90 ± 3	82	–
o-NA(l)	132 ± 10	71 ± 2	66	–
m-NA(s)	224 ± 8	108 ± 3	89	96.6 ± 1.4
p-NA(s)	199 ± 7	107 ± 3	94	100.4 ± 1.4

o-nitroaniline (l): $\log P$ (kPa) = $8.9 \pm 0.5 - (3710 \pm 60)/T$
m-nitroaniline (s): $\log P$ (kPa) = $13.7 \pm 0.4 - (5670 \pm 140)/T$
p-nitroaniline (s): $\log P$ (kPa) = $12.4 \pm 0.3 - (5595 \pm 110)/T$

where the associated errors were estimated taking into account the calibration factors and the uncertainties in the temperature determinations.

From the slopes and intercepts of these equations the second-law enthalpy and entropy changes associated with the vaporization processes of the compounds studied were derived and the values obtained are summarized in Table 2.

Opportunely combining the results found for *o*-NA, the heat of fusion of this compound ($\Delta H_{fus} = 19 \pm 5$ kJ mol^{-1}) was derived. The value agrees with that reported in the literature (16 kJ mol^{-1}) [7]. Our enthalpies seem to be higher, especially for *m*-NA, than the corresponding values obtained by the vaporization enthalpies reported by Ohe [3] over the liquid phase combined with heats of fusion reported in the literature [7] and the data selected by Malaspina et al. [4].

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