larger than that for *n*-hexane whereas $\Delta H^\ddagger$ for toluene and chlorobenzene are close to each other and nearly $1^1/_2$ larger than that of *n*-hexane, indicating that association and dipole-dipole interactions increase the value of $\Delta H^\ddagger$. The negative values of $\Delta S^\ddagger$ for nonassociated liquids viz., *n*-hexane, toluene, and chlorobenzene indicate that the formation of activated complexes introduces increased molecular order while positive values of $\Delta S^\ddagger$ for 1-hexanol show that the formation of activated complexes in this case involves less order probably due to destruction of hydrogen bonds. The values of $\Delta G^\ddagger$ depend on the sign and the magnitude of the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and are positive in each case. The variation of $\Delta G^\ddagger$ at each temperature studied follows the same order as that of $\Delta H^\ddagger$ because the corresponding $\Delta S^\ddagger$ is comparatively smaller in each case.

The values of $\Delta H^\ddagger{}_m$ and $\Delta G^\ddagger{}_m$ are positive for each of the binary systems studied. But $\Delta S^\ddagger{}_m$ values are negative for *n*-hexane–toluene and *n*-hexane–chlorobenzene systems as well as *n*-hexane-rich binaries of the *n*-hexane–1-hexanol system. however, the $\Delta S^\ddagger{}_m$ values for *n*-hexane-poor binaries of the *n*-hexane–1-hexanol system are positive. This indicates that, for *n*-hexane-rich binaries of this system, the chemical effects of H-bond breaking and nonspecific interactions between the real species in the mixture, e.g., 1-hexanol monomers and multimers and also *n*-hexane molecules, lead to less molecular order in the unactivated state than that in the activated state. On the other hand, in the *n*-hexane-poor binaries, *n*-hexane molecules leading to increased molecular order in the unactivated state than that in the activated state. It is interesting to note that $\Delta S^\ddagger{}_m = 0$ for a critical composition $X_1 = 0.42$, obtained from $\Delta S^\ddagger{}_m$ vs. X_1 plots and consequently the *n*-hexane–1-hexanol binary with $X_1 = 0.42$ involves the activated and unactivated states of similar molecular order.

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Glossary

a	adjustable parameter
d	diameter in gaseous state
d	percent deviation
E_s	energy of sublimation
$\Delta G^\ddagger$	free energy of activation of viscous flow
$\Delta H^\ddagger$	enthalpy of activation of viscous flow
h	planck's constant
M	molecular weight
m	mass of a single molecule
N	Avogadro's number
$\Delta S^\ddagger$	entropy of activation of viscous flow
V	molar volume, cm^3 mol^{-1}
V_s	solidlike volume in V, cm^3 mol^{-1}
X	mole fraction
ν	kinematic viscosity, cS
η	absolute viscosity, cP
θ	Einstein characteristic temperatures
κ	transmission coefficient

Subscripts

i	component in a mixture
m	mixture
1, 2	component number in a mixture

Registry No. Hexane, 110-54-3; toluene, 108-88-3; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3.

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Vapor Pressures of *o*- and *m*-Nitrochlorobenzene

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Vapor pressures of *o*- and *m*-nitrochlorobenzene were measured over the pressure range 50–700 mmHg by using a standard Swietoslawski type ebulliometer. The data were fitted by the Antoine equation of the form $\ln P = A - B/(t + C)$. The calculated molal heat of vaporization at the normal boiling point is 12.19 kcal/mol for *o*-nitrochlorobenzene and 12.07 kcal/mol for *m*-nitrochlorobenzene.

Introduction

The nitrochlorobenzenes are important starting materials for the manufacture of azo and sulfur dyes and they also find application in the synthesis of fungicides, preservatives, and pharmaceuticals. While measurements of vapor pressure data were reported for *p*-nitrochlorobenzene (*1*), few data are available on the vapor pressures of ortho and meta isomers. In this paper we present measurements on the vapor pressures of *o*- and *m*-nitrochlorobenzene and their suitable correlations.

Experimental Details

o-Nitrochlorobenzene of laboratory reagent grade supplied by M/s Sisco-Chem Industries, Bombay, India, and *m*-nitrochlorobenzene prepared at the Regional Research Laboratory, Hyderabad, India, were distilled and the middle cuts of the distillates were used in the experimental measurements. The physical constant density, refractive index, and boiling point of the chemicals used are presented in Table I, along with the literature data.

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Table I. Physical Properties of *o*- and *m*-Nitrochlorobenzene

	o-nitrochlorobenzene		*m*-nitrochlorobenzene	
property	exptl	lit. (*2*)	exptl	lit. (*2*)
density, g/cm^3	1.3447 (45 °C)	1.368 (22 °C), 1.305 (80 °C)	1.3414 (50 °C)	1.534 (20 °C), 1.343 (50 °C)
refractive index	1.5520 (45 °C)		1.5545 (50 °C)	
bp, °C	245.4 (753 mmHg; calcd)	245.5 (753 mmHg)	235.7 (760 mmHg; calcd)	235.6 (760 mmHg)

Table II. Vapor Pressures of *o*-Nitrochlorobenzene

	vapor press., mmHg		
temp, °C	measured	calcd	error^a
147.2	48.0	45.7	−4.83
150.3	51.0	51.0	−0.03
155.1	60.0	60.2	0.39
161.2	73.5	74.0	0.70
164.0	83.0	81.2	−2.17
167.9	92.0	92.2	0.19
168.9	98.0	95.2	−2.88
171.2	103.0	102.4	−0.56
172.0	106.5	105.0	−1.36
177.0	124.5	122.8	−1.38
182.4	149.5	144.7	−3.20
187.2	163.0	166.9	2.39
190.4	184.0	183.2	−0.42
196.3	213.5	216.9	1.58
198.8	232.5	232.6	0.05
202.0	253.0	254.1	0.45
208.3	297.0	301.4	1.49
213.2	326.0	343.1	5.25
215.2	363.0	361.4	−0.43
219.4	398.0	402.6	1.15
221.8	428.0	427.8	−0.04
224.8	463.5	461.2	−0.51
227.7	497.5	495.4	−0.42
230.3	529.5	527.9	−0.30
233.0	559.5	563.5	0.71
234.6	586.5	585.8	−0.18
237.0	617.5	619.8	0.37
238.8	648.0	646.6	−0.22
240.3	676.5	669.7	−1.01
243.0	714.0	712.9	−0.16

^{a} = $100[(P_{\text{calcd}} - P_{\text{measured}})/P_{\text{measured}}]$.

Table III. Vapor Pressures of *m*-Nitrochlorobenzene

	vapor press., mmHg		
temp, °C	measured	calcd	error^a
140.5	48.0	46.8	−2.58
144.0	51.0	53.1	4.03
147.6	60.0	60.3	0.46
153.9	73.5	74.9	1.96
156.2	83.0	81.0	−2.41
160.1	92.0	92.2	0.26
161.1	98.0	95.3	−2.73
163.5	103.0	103.1	0.09
164.1	106.5	105.1	−1.30
169.0	124.5	122.9	−1.25
175.2	149.5	149.1	−0.26
178.1	163.0	162.9	−0.07
182.3	184.0	184.7	0.40
187.7	213.5	216.4	1.36
190.6	232.5	235.2	1.17
193.0	253.0	251.8	−0.47
199.1	297.0	298.4	0.48
202.3	326.0	325.7	−0.10
206.4	363.0	363.5	0.15
209.9	398.0	398.7	0.18
212.9	428.0	431.1	0.73
215.5	463.5	460.9	−0.56
218.5	497.5	497.4	−0.02
220.8	529.5	527.0	−0.48
222.8	559.5	553.8	−1.01
225.1	586.5	586.2	−0.06
227.5	617.5	621.5	0.65
229.0	648.0	644.5	−0.54
231.0	676.5	676.2	−0.04
233.4	714.0	716.0	0.28

^{a} = $100[(P_{\text{calcd}} - P_{\text{measured}})/P_{\text{measured}}]$.

Table IV. Antoine Constants for *o*- and *m*-Nitrochlorobenzene

compd	*A*	*B*	*C*	SD, %
o-nitrochlorobenzene	17.787	5462.3	243.9	0.81
m-nitrochlorobenzene	17.957	5469.6	247.1	0.69

The vapor pressure measurements were carried out in two standard Swietoslawski type ebulliometers connected in parallel to a vacuum system. The pressures were measured with a mercury manometer to an accuracy of ±0.5 mmHg. The temperatures were measured, with a copper–constantan thermocouple connected to a digital millivoltmeter. The thermocouple emf was measured to an accuracy of ±0.01 mV (±0.2 °C).

Results and Discussion

The vapor pressure measurements for the two isomers of nitrochlorobenzene are presented in Tables II and III. The data were fitted by the Antoine equation of the form

$$\ln P = A - B/(t + C) \qquad (1)$$

In eq 1 pressure is given in mmHg and temperature in °C. The coefficients *A*, *B*, and *C* were obtained by a least-squares fit of the linear form of the Antoine equation.

Experimental points with relative error greater than two relative standard deviations as defined by eq 2 were not included in the regression analysis:

$$\text{relative standard deviation} = [\phi/(N-3)]^{1/2} \qquad (2)$$

where

$$\phi = \sum[(P_{\text{calcd}} - P_{\text{measured}})/P_{\text{measured}}]^2 \qquad (3)$$

N is the number of points in the regression analysis and the summation is over only those points. The constants *A*, *B*, and *C* for the two nitrochlorobenzenes are listed together with corresponding relative standard deviations of the fit in Table IV.

The calculated molal heats of vaporization at the normal boiling point are 12.19 and 12.07 kcal/mol for o- and *m*-nitrochlorobenzene, respectively. These values compare well with the molal heat of vaporization of 12.20 kcal/mol for *p*-nitrochlorobenzene reported in ref *1*.

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Registry No. *o*-Nitrochlorobenzene, 88-73-3; *m*-nitrochlorobenzene, 121-73-3.

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