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Relationes

Vaporization Energy Change and Vibrational Frequency Shift in Substituted Mono-Halo-Benzenes

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Direct linear relation exists between the reduced vaporization energy change ($\Delta H_v/RT_B$) of benzene and its homologues, C_6H_5X ($X = F, Cl, Br, I$) and the X-sensitive dimensionless frequency ($hc\nu/kT_B$) at their respective normal boiling point (T_B) temperatures.

Recent communications [1] have indicated the existence of correlation between normal boiling points and melting points and the internal molecular vibrations in several homologous *n*-paraffins, cycloparaffins and *n*-alcohols. Lielmezs [2, 3] has shown that a semilogarithmic relation exists between the normal boiling point change and vibrational frequency shift in the methyl and ethyl halide series.

In this note direct linear relationships (Fig. 1) are found between the reduced vaporization energy change, $\Delta H_v/RT_B$, (ΔH_v is the normal vaporization energy change formed between the vaporization energy values of benzene and its substituted homologues C_6H_5X, where $X = F, Cl, Br, I$; R is the universal gas constant and T_B the normal boiling point values for the given compound) and the dimensionless frequency, $hc\nu/kT_B$ (ν's are the X-sensitive fundamental frequencies ν'_{20}, ν'_{14}, ν'_{19}, and ν'_2 of mono substituted halo-benzenes; h is the Planck's constant, c the speed of light and k is the Boltzmann's constant). The data are presented in the table. As shown in Fig. 1, the heat of vaporization change, ΔH_v, is solely a linear

Table. *Summary of data*

Compound	T_B(°K)	Ref.	S^0/R at 298.15 °K (Ideal Gas)	Ref.	H_v at normal B.P. (cal/mole)	Ref.	$\frac{\Delta H_v}{RT_B}$	$\frac{hc\nu'_{20}}{kT_B}$	$\frac{hc\nu'_{19}}{kT_B}$	$\frac{hc\nu'_{14}}{kT_B}$	$\frac{hc\nu'_2}{kT_B}$	Ref.
Benzene	353.26	7	32.43	12	7352	11	–	–	–	–	–	
Fluoro-Benzene	357.89	8	36.39	13	7457	8	0.15	0.969	2.01	1.63	3.24	13
Chloro-Benzene	405.16	9	37.70	13	8733	10	1.72	0.696	1.66	1.05	2.49	13
Bromo-Benzene	429.06	10	39.13	13	9038	10	1.98	0.607	1,54	0.852	2.25	13
Iodo-Benzene	461.49	11	40.18	13	9439	8	2.39	0.518	1.40	0.700	2.04	13

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function of this dimensionless frequency defined as a ratio between the energy quanta ($h\nu$) and the thermal energy (kT_B) of the excited molecule at the normal boiling point of the liquid. Figs. 2 and 3 further strengthen this assertation. Fig. 2 shows that the dimensionless entropy (S^0/R) of the mono-halo-benzenes in the ideal gas state at 1 atm. pressure and at 298.15° K. correlates with the X-sensitive frequencies of these compounds. These correlations while yielding smooth curves, are nearly linear (ν'_{19}) implying that the X-sensitive frequencies may interact [2], although not appreciably with other characteristic modes of the molecule. Fig. 3 presents a relation between the logarithm of the normal boiling point against the

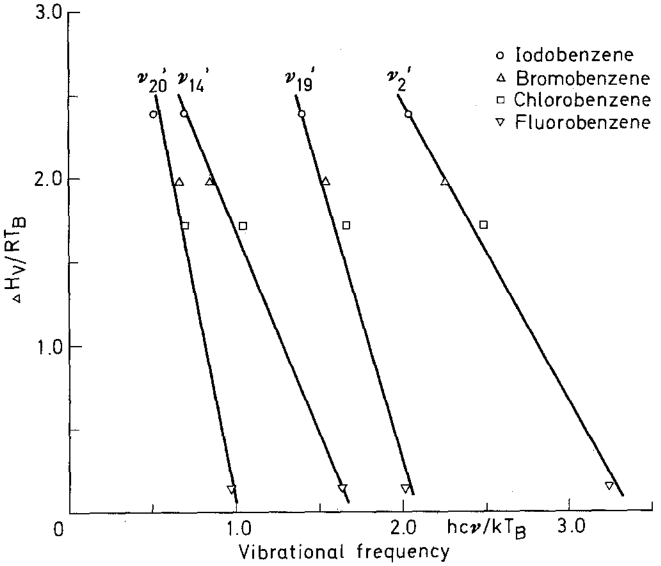

Fig. 1. Relation between the reduced vaporization energy change, $\Delta H_v/RT_B$, and the dimensionless frequency, $hc\nu/kT_B$

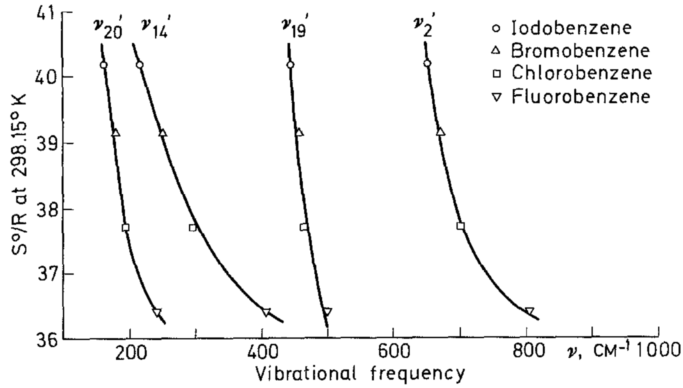

Fig. 2. Relation between the ideal gas state dimensionless entropy, S^0/R, and the X-sensitive vibrational frequency ν

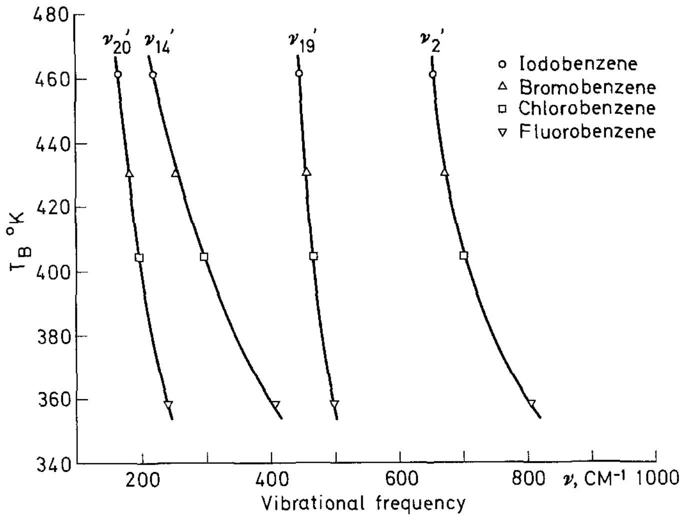

Fig. 3. Semilogarithmic relation between the normal boiling point values and the X-sensitive vibrational frequencies ν

vibrational frequency shift in the mono-halo-benzenes. This correlation is consistent with that for methyl and ethyl halides [3], and again yields smooth nearly linear (especially ν'_{19} frequency) curves.

Comparing Figs. 2 and 3 with Fig. 1, it can be observed that by introduction of the dimensionless frequency, $hc\nu/kT_B$, the possible interaction between the characteristic modes [2, 3] associated with the nature of halogen-benzene ring bond itself and the additional steric and electrostatic effects of the substituent atom, has disappeared; i.e. the relation between the reduced vaporization energy and the dimensionless frequency is found to be linear. It appears that the X-sensitive excited vibrational frequencies may influence the evaporation process even if there presently is an agreement [4] that since the vibrational frequencies are approximately the same in the two phases [5] for the same compound, the evaporation process is essentially controlled by the molecular rotational partition function. Whether it is indeed so and what in effect is the actual evaporation mechanism in terms of these excited frequencies and the quantum theory of intermolecular forces of the liquid, [1, 6], is a subject matter worthy of further study.

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