On a Relation between Dielectric Constant and Heat of Vaporization of Non-polar Liquids.

By Akiyoshi WADA

(Received May 6, 1952)

The nature of the attractive force between two molecules with no permanent electric moment was first explained by London(1) as a "dispersion force". As is well known, it is due to the polarization of each molecule by the other. Even though each molecule is centro-symmetrical, that is, a non-polar molecule, it always has some instantaneous dipole moment caused by the internal electronic oscillation. Such an instantaneous dipole moment of each molecule polarizes the other and produces an attractive force.

On the other hand, according to Onsager(2), if an electric dipole μ is immersed in a dielectric, whose dielectric constant, ε, is larger than 1, it is stabilized by the amount ΔE:

$$\Delta E=\frac{(\varepsilon-1)}{2\varepsilon+1}\cdot\frac{\mu^2}{a^3}\cdot N, \tag{1}$$

where a is the radius of the molecule, and N is Avogadro's number.

Now if we take ε of Eq. (1) equal to the dielectric constant of the non-polar liquid and μ its instantaneous dipole moment, then the energy of vaporization, E_{evap}, is approximately equal to the mean energy of the ΔE given by Eq. (1);

$$E_{evap}=\frac{(\varepsilon-1)}{2\varepsilon+1}\cdot\frac{\overline{\mu^2}}{a^3}\cdot N. \tag{2}$$

The effective dipole moment of the molecule is estimated as follows: The "dispersion energy" between two molecules separated by distance R is

$$-\frac{3}{4}\cdot\frac{I_0\alpha^2}{R^6}, \tag{3}$$

where α is polarizability and I_0 is the ionization potential of the molecule. While the energy of interaction between polarizability α and the mean dipole moment $\overline{\mu}^2$ is

$$-\frac{2\overline{\mu}^2\alpha}{R^6}. \tag{4}$$

By equating Eqs. (3) and (4), we have

$$\overline{\mu}^2=\frac{3I_0\alpha}{8}. \tag{5}$$

Following Onsager, if the molecule is regarded as a sphere of radius a with a polarizability α, the dielectric constant ε is expressed by the Lorenz-Lorentz formula in the case of non-polar liquid;

$$\alpha=\frac{\varepsilon-1}{\varepsilon+2}\cdot a^3. \tag{6}$$

Using Eqs. (2), (5) and (6), we obtain the final relation between the heat of vaporization H_{evap} and the dielectric constant:

$$H_{evap}=E_{evap}+RT=\frac{(\varepsilon-1)^2}{(2\varepsilon+1)(\varepsilon+2)}\cdot\frac{3NI_0}{8}+RT. \tag{7}$$

This equation provides the temperature dependence of heat of vaporization in terms of the dielectric constant at each temperature.

The ionization potential I_0 can be given by the spectroscopic data, but unfortunately we have no such accurate data extending over the all ranges of frequency, so that it shall now be treated as an empirical parameter.

Table 1

	t°C.	H_{evap}(calc.) kcal./mol.	H_{evap}(obs.) kcal./mol.
Benzene	20	8.08	8.11
	60	7.60	7.61
	100	7.08	7.08
	140	6.59	6.46
	180	6.04	5.80
Carbon bisulphide	0	6.80	6.82
	20	6.67	6.67
	46	6.41	6.41

In Table 1. the heat of vaporization H_{evap}(calc.) of benzene and carbon bisulphide calculated by Eq. (7) is compared with the observed values. The experimental data of ε and H_{evap} are taken from the "International Critical Tables". The parameter I_0 is assumed as 12.4 eV. and 8.0 eV. respectively, and these figures seem reasonable for these molecules compared with observed values 6.0 eV. and 9.6 eV.(3) in the case of benzene. It will be seen that the temperature dependence of the heat of vaporization is well expressed by this relation.

The writer wishes to express his sincere thanks to Professor Yonezo Morino for his kind advice.

Department of Chemistry, Faculty of Science,
Tokyo University, Tokyo

---

(1) F. London, *Z. Physik.* **63**, 245 (1930).

(2) L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).

(3) P. E. Boucher, *Phys. Rev.* **19**, 189 (1922). "Int. Crit. Table," Vol. 6, P. 72.