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THE DIPOLE MOMENTS OF BROMOBENZENE, METHYL IODIDE, AND IODOBENZENE AS VAPOURS*

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An equation devised empirically by Buckingham and Le Fèvre (1952), to convert apparent dipole moments determined for solutes in benzene into the true values obtainable from measurements on the same solutes as gases, was recently tested by Le Fèvre and Le Fèvre (1954) on 15 compounds dissolved in carbon tetrachloride.

With the three substances of the above title the literature allowed doubt concerning the correct μ_{gas} (obs.) with which to check μ_{gas} (calc.). Debye relationships,

$$P = A + \frac{B}{T}$$

connecting total polarizations and absolute temperatures, were available for the first two vapours only, and the moments deduced therefrom varied, with bromobenzene from $1 \cdot 71$ to $1 \cdot 77$ D and with methyl iodide from $1 \cdot 3$ to $1 \cdot 6$ D. The moment of iodobenzene as a gas had been once recorded (Hurdis and Smyth 1942) but the value quoted, $1 \cdot 70$ D, was deduced by the refractivity method, and was higher than the μ_{gas} (calc.) expected by Le Fèvre and Le Fèvre. (When compiling their Table 3 the last-named authors overlooked the reference to the paper by Hurdis and Smyth, it is omitted also in the M.I.T. Tables of Wesson 1948.) Redeterminations have therefore been made on these materials.

Experimental

Pure dry specimens were redistilled immediately prior to introduction into apparatus of the type described by Le Fèvre (1953, Ch. 2), by which polarizations were measured relatively to carbon dioxide or benzene by methods set out by this author. Results are tabulated (Table 1) under usual headings.

Discussion

The moments now obtained are: CH_3I , 1.64 D; C_6H_5Br , 1.70 D; C_6H_5I , 1.71 D, in each case $\pm 0.03 \text{ D}$. From Table 2 it will be seen that μ_{gas} (calc.) by the equation of Buckingham and Le Fèvre is for these three substances lower than the observed value. The discrepancy is greatest with iodobenzene and least with methyl iodide. The three compounds are instances where $n_1^2 - n_2^2$ is algebraically negative.

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Temp.	Pobs	Peale *	Temp.	Pobs	Pcale *	Temp.	Pobs	Pcale *
(°A)	(c.c.)	(c.c.)	(°A)	(c.c)	(c.c.)	(°A)	(c.c.)	(c.c.)
Bromobe	nzene†		Methyl	iodide†		Iodobenz	 zene‡	
362	$83 \cdot 4$	83.5	291	$75 \cdot 4$	$75 \cdot 0$	432	80.4	80.0
384	$81 \cdot 1$	80.7	292	$74 \cdot 2$	74.8	447	$78 \cdot 2$	78.6
420	$76 \cdot 6$	76.7	313	$70 \cdot 4$	$71 \cdot 0$	458	$77 \cdot 7$	77.7
424	$75 \cdot 7$	76.3	328	$69 \cdot 3$	$68 \cdot 6$	481	$75 \cdot 7$	75.8
441	$74 \cdot 9$	74.7	353	$65 \cdot 0$	$65 \cdot 1$	512	$73 \cdot 2$	$73 \cdot 5$
476	$72 \cdot 2$	71.8	369.5	$63 \cdot 6$	63 · 0	530	$72 \cdot 7$	$72 \cdot 4$
486	$70 \cdot 9$	71.0	389	60.6	60.8	541.5	$71 \cdot 5$	71.7
			411	$58 \cdot 4$	58.5	564	70.5	$70 \cdot 4$
			432	$57 \cdot 0$	56.6			
			457	$53 \cdot 9$	$54 \cdot 5$			1

TABLE 1 TEMPERATURE DEPENDENCE OF POLARIZATIONS

* From the following Debye equations (fitted to $P_{obs.}$ by least squares):

 $\begin{array}{ll} {\rm C}_{6}{\rm H}_{5}{\rm Br}, & P=(34\cdot8\pm1\cdot5)+(17630\pm621)/T, \\ {\rm C}{\rm H}_{3}{\rm I}, & P=(18\cdot6\pm1\cdot1)+(16420\pm399)/T, \\ {\rm C}_{6}{\rm H}_{5}{\rm I}, & P=(38\cdot8\pm1\cdot2)+(17810\pm580)/T, \end{array}$

 $\dagger\,{\rm CO}_{\,\rm 2},\ P\!=\!7\!\cdot\!341$ c.e., as calibrating vapour.

 $\ddagger \mathrm{C_6H_6}, \ P\!=\!27\!\cdot\!0$ c.c., as calibrating vapour.

Compounds	$\mu_{\rm CCl_4}$	µgas Calculated by Formula (1)	µgas Calculated by Le Fèvre and Le Fèvre (1954)	$\mu_{ m gas}$ (obs.)
CH ₃ Cl	1.72	1.84	1.86	1.86
CH ₃ Br	$1 \cdot 70$	$1 \cdot 81$	$1 \cdot 82$	$1 \cdot 82$
СН₃І	$1 \cdot 48$	1.59	1.56	$1 \cdot 64*$
CH ₃ CN	$3 \cdot 38$	3.66	3.73	$3 \cdot 94 - 3 \cdot 98$
$CHCl_3$	$1 \cdot 10$	0.99	0.99	$1 \cdot 01$
(CH ₃) ₂ CO	$2 \cdot 74$	$2 \cdot 85$	$2 \cdot 86$	$2 \cdot 89$
Paraldehyde	$1 \cdot 98$	1.66	$1 \cdot 60$	$1 \cdot 44$
C ₆ H ₅ F	$1 \cdot 38$	$1 \cdot 49$	1.51	1.57
C_6H_5Cl	$1 \cdot 58$	1.74	1.69	1.73
C_6H_5Br	1.51	1.69	1.59	$1 \cdot 70^{*}$
C_6H_5I	$1 \cdot 39$	$1 \cdot 64$	$1 \cdot 44$	1.70*
$C_6H_5NO_2$	$3 \cdot 95$	$4 \cdot 42$	4.18	$4 \cdot 24$
C ₆ H ₅ CN	$4 \cdot 02$	$4 \cdot 46$	$4 \cdot 29$	$4 \cdot 39$
C ₆ H ₅ CH ₃	$0 \cdot 34$	0.37	0.36_{5}	0.37
(CH ₃) ₃ CCl	$2 \cdot 14$	$2 \cdot 13$	$2 \cdot 13$	$2 \cdot 13$

 $\label{eq:table_2} \begin{array}{c} Table \ 2 \\ \mbox{comparison of μgas (calc.) and μgas (obs.)} \end{array}$

* Present work ; for references to other μ_{gas} (obs.) values, see Le Fèvre and Le Fèvre (1954).

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We have explored the possibility of modifying the original empirical expression to avoid the occurrence of negative powers for the term $e - e^{x^2}$. The most satisfactory appears to be formula (1).

$$\frac{\mu^2_{\text{sol.}}}{\mu^2_{\text{gas}}} = 1 + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} [e^{x^2} - (e - e^{x^2})^{2n_2(n_1^2 - n_2^2)^2(1 - e^{x^2})^2}]. \quad \dots \quad (1)$$

Table 2 compares the applicability of the original formula and of formula (1) to the data set out by Le Fèvre and Le Fèvre (1954) in their Table 3.

Formula (1) thus covers the cases of CH_3I , C_6H_5Br , and C_6H_5I adequately enough, although it forecasts slightly less correct moments in some other cases. Considered overall however, column 3 seems a better fit to column 5 than does column 4.

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