# 25. *Molecular Polarisability. The Molar Kerr Constants at Infinite Dilution in Benzene of Seven Normal Alcohols.*

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The molar Kerr constants of the normal alcohols from methyl to hexyl, and of n-decyl alcohol, have been measured in benzene. The much larger values of $_{\mathrm{m}}K$ reported byTsvetkov and Marinen in 1948 can be understood if these authors used concentration ranges which started roughly where those of the present work terminate.

THE preceding paper [1] mentioned that the molar Kerr constants reported by Tsvetkov and Marinen [2] for a number of alcohols dissolved in benzene were notably larger than those determined by us in carbon tetrachloride. While it seemed probable that the causes of these differences lay in concentration-dependent associations of the solute molecules, the absence of detailed observational data from ref. 2 rendered impossible any confirmation of this. Accordingly, Kerr effects and refractivities have been examined in benzene for the first six normal alcohols and decyl alcohol; of these, propyl, butyl, and pentyl are among those previously studied by the Russians.[2]

Results are listed under our usual headings in Tables 1—3; density and dielectric-constant factors, required for the final computation of $_{\infty}(_{\mathrm{m}}K_2)$, are taken from ref. 3.

[1] Le Fèvre, Le Fèvre, Rao, and Williams, preceding paper.

[2] Tsvetkov and Marinen, *Doklady Akad. Nauk, S.S.S.R.*, 1948, **62**, 67.

[3] Le Fèvre and Williams, *J.*, 1960, 108.

TABLE 1. *Incremental Kerr effects and refractive indexes for solutions of n-alcohols in benzene at 25°.*

| $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ | $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ | $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ | $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Methyl* | | | *Ethyl* | | | *Propyl* | | | *Butyl* | |
| 700 | −0·003 | −16 | 680 | −0·003 | −10 | 860 | *ca.* 0 | −15 | 2006 | −0·003 | −22 |
| 825 | −0·007 | −15 | 837 | −0·003 | −12 | 1675 | *ca.* 0 | −26 | 2688 | −0·004 | −31 |
| 1418 | −0·007 | −25 | 1220 | −0·003 | −20 | 2144 | *ca.* 0 | −31 | 3074 | −0·005 | −40 |
| 1502 | −0·007 | −26 | 1703 | −0·007 | −28 | 2698 | *ca.* 0 | −37 | 4558 | −0·010 | −55 |
| 2063 | *ca.* 0 | −36 | 1754 | −0·005 | −29 | 3334 | −0·003 | −44 | 4745 | −0·016 | −58 |
| 2692 | +0·007 | −49 | 2101 | −0·003 | −30 | 3344 | −0·007 | −48 | 5170 | −0·015 | −60 |
| 2883 | +0·011 | −49 | 3102 | *ca.* 0 | −47 | 4162 | −0·011 | −52 | 5503 | −0·020 | −65 |
| 3639 | +0·026 | −61 | 4020 | *ca.* 0 | −60 | 4607 | −0·013 | −63 | 7237 | −0·036 | −86 |
| 3746 | +0·032 | −70 | 5326 | *ca.* 0 | −82 | 4614 | −0·012 | −62 | 8503 | −0·051 | −100 |
| 5743 | — | −104 | 6340 | *ca.* 0 | −99 | 5927 | −0·020 | −80 | 12,168 | −0·101 | −142 |
| | | | | | | 6020 | −0·023 | −81 | | | |
| | | | | | | 7253 | −0·038 | −99 | | | |
| | | | | | | 7332 | −0·031 | −99 | | | |
| | | | | | | 7338 | −0·036 | −99 | | | |

| $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ | $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ | $10^5w_2$ | $10^7\Delta B$ | $10^4\Delta n$ |
|---|---|---|---|---|---|---|---|---|
| | *Pentyl* | | | *Hexyl* | | | *Decyl* | |
| 2613 | −0·003 | −27 | 771 | *ca.* 0 | −9 | 2265 | *ca.* 0 | −20 |
| 3502 | −0·004 | −38 | 1224 | *ca.* 0 | −11 | 2990 | −0·005 | −29 |
| 4543 | −0·011 | −50 | 1293 | *ca.* 0 | −12 | 4200 | −0·010 | −40 |
| 4664 | −0·010 | −49 | 2356 | −0·004 | −25 | 4812 | −0·016 | −40 |
| 5352 | −0·016 | −56 | 2569 | −0·004 | −28 | 5715 | −0·020 | −50 |
| 7659 | −0·040 | −80 | 3404 | −0·008 | −32 | 6087 | −0·023 | −52 |
| 8920 | −0·055 | −97 | 3949 | −0·010 | −40 | 7548 | −0·028 | −64 |
| 10,963 | −0·089 | −113 | 4224 | −0·010 | −41 | 7761 | −0·031 | −67 |
| | | | 4474 | −0·012 | −43 | 8118 | −0·032 | −70 |
| | | | 4834 | −0·015 | −49 | | | |
| | | | 5815 | −0·023 | −58 | | | |
| | | | 7278 | −0·037 | −70 | | | |

TABLE 2. *Coefficients* a *and* b *in equations* $10^7\Delta B = aw_2 + bw_2^2$, *also values of the quotients* $\sum\Delta n/\sum w_2$ *for the n-alcohols in benzene at 25°.*

| Solute alcohol | $10^5w_2$ range | *a* | *b* | $\Sigma\Delta n/\Sigma w_2$ |
|---|---|---|---|---|
| Methyl | 0—825 | ? (see text) | — | −0·179 |
| Ethyl | 0—1754 | −0·289 * | — | −0·154 |
| Propyl | 0—4162<br>0—7338 | $+0·261_5$<br>$+0·131_7$ | −12·3 †<br>$-8·3_7$ | −0·091 |
| Butyl | 0—5503<br>0—12,168 | $+0·039_2$<br>$+0·041_9$ | $-6·9_0$ †<br>$-7·2_3$ | −0·079 |
| Pentyl | 0—5352<br>0—10,963 | $+0·131_3$<br>$+0·181_7$ | $-7·8_8$ †<br>$-9·0_4$ | −0·112 |
| Hexyl | 0—7278 | $+0·060_0$ | $-7·7_6$ | −0·099 |
| Decyl | 0—8118 | $-0·096_1$ | $-3·8_9$ | −0·087 |

* Calc. as $\sum\Delta B/\sum w_2$ for solutions having $w_2$ between 0 and 0·021.

† The upper line in each of these sets relates to $w_2$ ranges over which association effects were not shown by dielectric polarisation measurements (ref. 3).

TABLE 3. *Calculations of molar Kerr constants of the normal alcohols at infinite dilution in benzene at 25°.*

| Solute alcohol | $10^5w_2$ range | $\alpha\varepsilon_1$ | $-\beta$ | $-\gamma$ | $\delta$ | $_\infty(_mK_2) \times 10^{12}$ |
|---|---|---|---|---|---|---|
| Methyl | 0—825 | 9·91 | $0·123_8$ | 0·119 | ? | ? |
| Ethyl | 0—1754 | 6·71 | $0·134_6$ | 0·102 | $-0·70_5$ | −9·0 |
| Propyl | 0—4162<br>0—7338 | 5·03 | $0·122_3$ | 0·091 | +0·64<br>+0·32 | −2·2<br>−3·7 |
| Butyl | 0—5503<br>0—12,168 | 4·06 | $0·111_0$ | 0·079 | $+0·09_6$<br>+0·10 | −3·4<br>−3·4 |
| Pentyl | 0—5352<br>0—10,963 | 3·06 | $0·093_5$ | 0·074 | +0·32<br>+0·44 | +0·4<br>$+1·2_5$ |
| Hexyl | 0—7278 | 2·68 | $0·090_4$ | 0·066 | +0·15 | −0·4 |
| Decyl | 0—8118 | 2·03 | $0·056_7$ | 0·065 | −0·23 | −0·6 |

## DISCUSSION

The molar Kerr constants in Table 3 resemble in magnitude those found when carbon tetrachloride is used as solvent. The detailed differences between the two sets are not those expected, from previous work,[4,5] to follow a change of medium. We attribute them mainly to experimental errors arising from two unavoidable sources. First, because benzene is much more anisotropic than carbon tetrachloride, both segments of the compensator field are more brightly illuminated with the former liquid than with the latter, so that precise matching is more difficult: values of $\Delta B$ which may confidently be recorded with carbon tetrachloride may escape detection with benzene; secondly, it is unfortunate that over the concentration ranges where alcohols are likely to exist largely as monomers, the $\Delta B$'s caused by the solutes are small and somewhat uncertain, consequently the relationships (Table 2) connecting $\Delta B$ with $w_2$ may easily be misleading.

Where methyl alcohol is concerned, the dielectric polarisation $-w_2$ data [3] indicate that relevant Kerr effect observations should be taken only on solutions having values of $w_2$ less than *ca.* 0·8% in benzene: since to do so is impracticable, entries for $\delta$ and $_\infty({}_\mathrm{m}K_2)$ are omitted from Table 3; the production of an $_\infty({}_\mathrm{m}K_2)$ of *ca.* $2 \times 10^{-12}$ requires an "*a*" term (Table 2) of +1·05, verification of which must await improvements in techniques for handling very high dilutions. In the case of ethyl alcohol, $\delta$ (Table 3) has been estimated from the mean $\sum\Delta B/\sum w_2$ (Table 2); $\delta$ is thus probably too negative, so that an $_\infty({}_\mathrm{m}K_2)$ of *ca.* $-4 \times 10^{-12}$ (as in carbon tetrachloride) is clearly not impossible.

Attention is drawn to the fact (Table 1) that, with all the alcohols except the first two, $\Delta B$ increases in negativity as $w_2$ becomes greater; for methyl alcohol $\Delta B$ is positive above concentrations of *ca.* 2%; for ethyl alcohol the trend with stronger solutions is not clear. The literature [6] contains Kerr constants of six pure alcohols, expressed relatively to $B_{\mathrm{CS}_2}$. These, transformed into absolute values (the Kerr constant of carbon disulphide [6] for Na light at 20° being $3{\cdot}226 \times 10^{-7}$), and incorporated with appropriate densities, dielectric constants, and refractive indexes, yield the specific Kerr constants shown in Table 4; only for ethyl alcohol is ${}_\mathrm{s}K_2$ positive. Presumably therefore the $\Delta B$'s (Table 1) for solutions of ethanol with $w_2$ above 7% would, if explored, display a small increase of positivity; for the alcohols from propyl to octyl, negativity is to be expected.

TABLE 4. *Specific Kerr constants of liquid alcohols.**

| Alcohol | $t$ | $B \times 10^7$ | $\varepsilon_t$ | $d_4^t$ | $n_4^t$ | ${}_\mathrm{s}K_\mathrm{liq} \times 10^{12}$ |
|---|---|---|---|---|---|---|
| Ethyl ................. | 17° | 0·779 | 25·5 | 0·7910 | 1·3614 | +0·004 |
| Propyl ................. | 20 | −2·516 | 20·8 | 0·8043 | 1·3856 | −0·019 |
| Butyl ................. | ,, | −3·645 | 17·8 | 0·8104 | 1·3993 | −0·036 |
| Pentyl ................. | ,, | −3·161 | 14·3 | 0·8136 | 1·4100 | −0·046 |
| Heptyl ............. | ,, | −7·517 | 12·2 | 0·8219 | 1·4235 | −0·141 |
| Octyl ................. | ,, | −7·613 | 10·34 | 0·8273 | 1·4293 | −0·187 |

* Sources of data: $B$'s, ref. 6; $\varepsilon$'s, "Table of Dielectric Constants of Pure Liquids," Nat. Bur. Stand. Circular 514, issued 10/8/51; U.S. Government Printing Office, Washington, D.C.; $d$'s and $n$'s, Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950, and Vogel, *J.*, 1948, 1815; 1952, 514.

A plausible explanation of the values of ${}_\mathrm{m}K$ found by Tsvetkov and Marinen [2] is therefore that they were drawn from solutions lying in concentration ranges higher than those used by us. Table 1 can provide indications which support this suggestion: if from our data for propyl, butyl, and pentyl alcohols we had used only information relating to solutions containing above about 6% of solute, then by calculating $\delta$ as $\sum\Delta B/B_1\sum w_2$ and with other factors as in Table 3, the following results would have emerged:

| Alcohol | $\delta$ | $({}_\mathrm{m}K_\mathrm{apparent}) \times 10^{12}$ | ${}_\mathrm{m}K \times 10^{12}$ (T. and M.) |
|---|---|---|---|
| Propyl ........................... | −1·12 | −10 | −9·3 |
| Butyl ........................... | −1·64 | −13 | −16·0 |
| Pentyl ........................... | −1·63 | −13 | −17·0 |

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[4] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; Armstrong, Aroney, Le Fèvre, Le Fèvre, and Smith, *J.*, 1958, 1474; Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, 5, 261.

[5] Buckingham, *Trans. Faraday Soc.*, 1956, 52, 611.

[6] I.C.T., Vol. VII, pp. 110—112 (1st Edn., 1930).

Our highest concentrations were 10—12%; had we proceeded above this limit it seems possible that an even better reconciliation could be effected between our observational data and those of the Russians.

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