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# Effect of Solvent on Dipole Moment of Aliphatic Mercaptans

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Evidence of donor-acceptor complexes as a result of interaction between thiols and carbon tetrachloride has been obtained from the studies of dipole moment at 30 °C. Our polarisation data in other solvents except benzene are new. The results obtained have been discussed in terms of the influence of solvent on dipole moments in the light of general theory of Higasi.[1-3]

A survey of the literature reveals that only a few workers[4-6] have determined the dielectric-polarisation of alkanethiols, either to examine the equations derived from current theories of dielectric polarisation or to study the effect of sulfur replacing oxygen in an alcoholic group. The dipole moment value available[4,5] for these compounds are widely divergent. The present work has therefore been undertaken to re-examine the value of dipole moment as well as to assist in understanding the application of general theory of Higasi in case of aliphatic mercaptans.

## Experimental

The method and technique have been described earlier.[7]

*Purification.* All the alkanethiols were purified[8] before use by distilling over anhydrous sodium sulfate in a quick fit apparatus where there was no possibility for the liquid to be in contact with atmospheric moisture or carbon dioxide. Table 1 contains the physical quantities experimentally measured for the liquids studied in the present paper.

The non polar solvents, benzene and carbon tetrachloride of grade E. Merck (G.R.) and dioxane of grade B.D.H. (A.R.) were used as such as the measured dielectric constants of these solvents agreed within ±0.001 unit with the literature values.[6]

Table 1. Experimental physical constants

| Name of substance | Density | Refractive index | Boiling point |
|---|---|---|---|
| Propyl mercaptan | 0.82995 | 1.4330 | 66.1 °C |
| Butyl mercaptan | 0.83134 | 1.4375 | 96.2 °C |
| Isobutyl mercaptan | 0.82334 | 1.4340 | 40.0 °C |
| *t*-Butyl mercaptan | 0.78888 | 1.4175 | 61.0 °C |

Cyclohexane (B.D.H. Laboratory reagent) was distilled twice and the fraction boiling at 78 °C was used.

The solution moment values have been evaluated from the usual expression

$$\mu_S = 0.01281\times10^{-18}(P_{2\infty}-P_e)^{1/2}T^{1/2} \qquad (1)$$

The solute-polarisation at infinite dilution *i.e.* $P_{2\infty}$ has been calculated by the method of Halverstadt and Kumler.[9] The values of the constants $\alpha$, $\beta$, $\varepsilon_1$ and $V_1$ in Halverstadt and Kumler equation have been evaluated by the method of least squares and are given in Table 2. The electronic polarisation ($P_e$) is the same as molecular refraction for sodium D line and has been taken from literature.[10] Atomic polarisation ($P_a$) has not been taken into consideration according to the suggestion of Debye,[11] *viz.* the electronic polarisation calculated from sodium D line partly compensates the neglect of atomic polarisation.

Table 2. Evaluated constants in halverstadt and Kumler pquation

| Name of solvent | $\alpha$ | $\beta$ | $\varepsilon_1$ | $V_1$ (ml) | $P_{2\infty}$ (ml) | $\mu$ (in Debye) |
|---|---|---|---|---|---|---|
| | | (Propyl mercaptan) | | | | |
| Benzene | 3.002 | +0.0701 | 2.2533 | 1.1517 | 72.24 | 1.55 |
| Carbon tetrachloride | 2.8613 | +0.2901 | 2.2041 | 0.6352 | 74.10 | 1.58 |
| Dioxane | 3.0222 | +0.1988 | 2.2102 | 0.9788 | 70.57 | 1.52 |
| Cyclohexane | 2.0795 | −0.1613 | 2.0023 | 1.3037 | 69.00 | 1.43 |
| | | (Butyl mercaptan) | | | | |
| Benzene | 3.0882 | +0.0759 | 2.2448 | 1.1518 | 78.46 | 1.57 |
| Carbon tetrachloride | 2.8105 | +0.3521 | 2.2086 | 0.6346 | 94.39 | 1.58 |
| Dioxane | 3.1333 | +0.2440 | 2.2006 | 0.9790 | 77.33 | 1.56 |
| Cyclohexane | 2.1963 | −0.0830 | 1.9961 | 1.3021 | 68.16 | 1.50 |
| | | (Isobutyl mercaptan) | | | | |
| Benzene | 2.7938 | +0.0712 | 2.2635 | 1.1551 | 74.14 | 1.50 |
| Carbon tetrachloride | 2.6814 | +0.3547 | 2.2112 | 0.6353 | 76.50 | 1.54 |
| Dioxane | 3.0023 | +0.2494 | 2.2010 | 0.9788 | 75.53 | 1.53 |
| Cyclohexane | 2.5910 | +0.6623 | 1.9860 | 1.3026 | 68.88 | 1.41 |
| | | (*t*-Butyl mercaptan) | | | | |
| Benzene | 3.1010 | +0.1276 | 2.2534 | 1.1520 | 79.82 | 1.59 |
| Carbon tetrachloride | 3.0530 | +0.3858 | 2.2082 | 0.6351 | 84.02 | 1.65 |
| Dioxane | 3.3553 | +0.2760 | 2.2020 | 0.9796 | 81.41 | 1.61 |
| Cyclohexane | 1.6942 | +0.0598 | 2.0174 | 1.2948 | 65.09 | 1.34 |

Table 3. Excess polarisation values (ml)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | (Propyl mercaptan+carbon tetrachloride) | | | | | | |
| $f_1f_2$ | 0.0192 | 0.0374 | 0.0464 | 0.0541 | 0.0616 | 0.0695 | 0.0767 |
| $P^E$ | +0.329 | +0.615 | +0.717 | +0.866 | +1.034 | +1.134 | +1.260 |
| | (Butyl mercaptan+carbon tetrachloride) | | | | | | |
| $f_1f_2$ | 0.020 | 0.0388 | 0.0474 | 0.0556 | 0.0631 | 0.0710 | 0.0783 |
| $P^E$ | +0.366 | +0.574 | +0.744 | +0.970 | +0.992 | +1.102 | +1.125 |
| | (Isobutyl mercaptan+carbon tetrachloride) | | | | | | |
| $f_1f_2$ | 0.0201 | 0.0397 | 0.0478 | 0.0577 | 0.0658 | 0.0728 | 0.0931 |
| $P^E$ | +0.246 | +0.400 | +0.537 | +0.687 | +0.810 | +0.822 | +1.183 |

Table 4. Apparent dipole moment values of thiols in Debye units ($\mu_s$)

| Solute | Benzene $\varepsilon_1=2.2645$ | | | Carbon tetrachloride $\varepsilon_1=2.2176$ | Dioxane $\varepsilon_1=2.2015$ | Cyclohexane $\varepsilon_1=2.0070$ |
|---|---|---|---|---|---|---|
| | by Hunter and Partington | by Mathias and E. D. Carvalhofilho | by present authors | by present authors | | |
| Propyl mercaptan | 1.33 | 1.51 | 1.55 | 1.58 | 1.52 | 1.43 |
| Butyl mercaptan | 1.32 | 1.53 | 1.57 | 1.58 | 1.56 | 1.50 |
| Isobutyl mercaptan | — | 1.53 | 1.50 | 1.54 | 1.53 | 1.41 |
| *t*-Butyl mercaptan | — | 1.59 | 1.59 | 1.65 | 1.61 | 1.34 |

## Results and Discussion

The solvent effect in mercaptan can be understood with reference to the structure of $H_2S$. Hydrogen sulfide is an asymmetrical top molecule and has two-fold axis of symmetry. The molecule may be considered to consist of two ellipsoids with a common axis '$c$' and with a dipole in its axis of symmetry at a distance $a_1$ from one end of the diameter and $a_2$ from the other end (diameter along axis of symmetry $2a=a_1+a_2$). The value of $a_1$, $a_2$, and $c$ have been calculated from the spectroscopic[12)] data for the H–S bondlength (1.328 Å) and ∠HSH (92°2′). Thus

$$c=0.9568\,\text{Å},\quad a_1=0.0544\,\text{Å},\quad a_2=0.8663\,\text{Å}$$

According to the theory of Higasi[1-3)] if $a<c$, $a_1<c$ and $a_2<c$, the induced moment is evaluated by the expression

$$\mu_1=2\pi n\alpha\mu(B_1+B_2) \tag{2}$$

where the value of $B_1$ and $B_2$ may be obtained from the expression

$$B=\frac{k'^2}{k'^2-1}\left|1-\frac{1}{(k'^2-1)^{1/2}}\sin^{-1}\frac{(k'^2-1)^{1/2}}{k'}\right|-\frac{1}{3} \tag{3}$$

(where $k'=c/a>1$) by substituting $k'=c/a_1$ and $k'=c/a_2$ respectively. From the calculated values of $B_1=+0.5833$ and $B_2=0.0286$, it is observed that $B_1$ and $B_2$ are both positive and therefore as suggested by Higasi, the solvent effect would be positive *i.e.* $\mu_s>\mu_v$. Literature value[13)] 0.97 D for $\mu_s$ of $H_2S$ in benzene, appears to be much convincing and is greater than 0.93 D,[14)] a value in the vapour state. The observed ratio for $\mu_s/\mu_v$ is therefore 1.04. The value calculated for $\mu_s/\mu_v$ on the basis of Higasi's treatment comes to be 1.09. This shows that theory of Higasi is correctly applicable[7)] in case of $H_2S$ molecule. If one of the hydrogen atom of $H_2S$ is replaced by an alkyl group, this will lead to an increase in the value of '$c$' and $c$ would be further greater than $a_1$ and $a_2$. Therefore it is expected that $k'$ would be greater than one and $\mu_s$ would be greater than $\mu_v$ in case of mercaptans studied here. Unfortunately the data in vapor state are not available in case of alkanethiols. However, in case of positive solvent effect, according to the suggestion of Higasi, the solution moment should be greater in the solvent having higher dielectric constant and as such $\mu_s$ (benzene) should be greater than $\mu_s$ in the other three solvents.

The unexpected higher values for last two mercaptans (Table 4) in dioxan than the values in benzene may be regarded due to hydrogen bonding between hydrogen atoms of the solute and the donor oxygen atoms of the solvent molecules, an effect which would give rise both to the lengthening of the S–H bond and polarisation of solvent molecules. The high values are therefore best considered as due to an "interaction polarisation." This is further supported by the observation of Taylor[15)] reporting that smaller is the ionisation constant of the acid, the stronger is the hydrogen bond. The ionisation constant values,[16)] $2.26\times10^{-11}$, $2.21\times10^{-11}$ and $0.89\times10^{-11}$ for propyl mercaptan, butyl mercaptan and *t*-butyl mercaptan respectively suggest therefore that the possibility of hydrogen bonding in the last case is more and as such a high value is expected. The decreasing order of ionisation constant leads to anticipate that isobutyl mercaptan (the ionisation constant of which is not available) has a greater tendency of hydrogen bonding in dioxane than the first two thiols. Consequently the solution moment value of isobutyl mercaptan happens to be greater than that in benzene but the value is certainly less than that of butyl mercaptan in dioxane, as expected.

The moment values in carbon tetrachloride has been examined in the light of Earp and Glasstone[17)] theory. Accordingly it has been shown in Fig. 1 (data shown in Table 3) that for these systems the excess polarisation $P^E$ is a linear function of $f_1f_2$ and passes through the origin, confirming that the contact pairs are exclusively

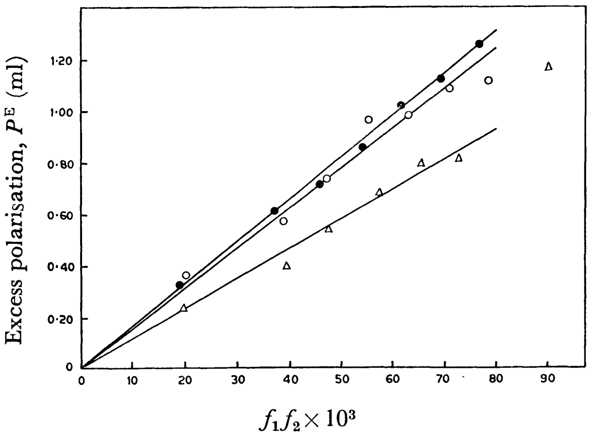

Fig. 1. $P^E$ *vs.* $f_1f_2$.
Solvent: carbon tetrachloride.
●: Propyl mercaptan, ○: butyl mercaptan, △: isobutyl mercaptan.

formed. The unexpected higher values for all the four thiols in carbon tetrachloride than those in benzene may therefore be due to the formation of donor-acceptor type complexes. Praunitz and coworkers[18] have also adduced evidence that carbon tetrachloride behaves as an electron acceptor. Besides, the support for complex formation between benzene and carbon tetrachloride (acceptor) is recently[19] reported. Literature[20] also reports the behavior of mercaptans as donor.

The dipole moment value determined by Hunter and Partington[4] in Table 4 appears to be low. This observation is further supported by the data of Walls and Smith[21] and Mathias[5] who have found higher values. It is expected that with larger atoms or groups in place of hydrogen in $H_2S$, the bond angles would be larger and as such the dipole moment value for butyl mercaptan should be higher than that of propyl mercaptan. This contention is also supported by Mathias,[5] who observed that the dipole moment calculated by Debye's equation increases with the extention of the carbon chain in the normal thiols. It is pertinent to mention that out moment values fairly agree with those obtained by Mathias.[5] Our data in Table 4 amply demonstrate the above facts.

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