SHORT COMMUNICATIONS

SOLVENT SHIFT OF C=O STRETCHING FREQUENCY AND POLARIZABILITY*

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It has recently been shown (Armstrong *et al.* 1958) (*a*) that the effect of change of state on apparent molecular polarizability can be predicted by equations of the type

$$b_i^s/b_i^v = 1-(n_1^2-1)(0\cdot333-k_i)/(n_1^2+2), \tag{1}$$

where b_i^s and b_i^v denote the polarizabilities, along the direction i, of a molecule respectively as a solute and as a vapour, k_i is an anisotropy factor for the molecule, and n_1 is the refractive index of the solvent; all b's are herein quoted in 10^{-23} c.c. units; and (*b*) that stretching frequencies of bonds can be empirically connected (Le Fèvre 1959) with longitudinal polarizabilities by relations such as

$$\nu_{XY} = (9273/r_{XY}^2)/(b_L^{XY}/\overline{M})^{\frac{1}{2}}-254, \tag{2}$$

where r_{XY} is the inter-centre distance in Å units for the bond XY, $\overline{M}$ is the reduced mass, and b_L^{XY} is the longitudinal polarizability of XY; ν_{XY} is in cm^{-1}. In combination, (1) and (2) should allow solvent shifts of stretching frequencies to be calculated *a priori*; this possibility has now been examined with the data for $\nu_{C=O}$ in acetone listed by Bellamy and Williams (1959).

In Armstrong *et al.*'s (1958) paper the factors k_i were approximations estimated from scale drawings; however since the principal polarizabilities of acetone are known (Le Fèvre and Rao 1947) to be $b_1=0\cdot701$, $b_2=0\cdot684$, and $b_3=0\cdot482$ in carbon tetrachloride, k_1 is here obtained as $0\cdot279$ from the ratios b_3/b_1 and b_2/b_1 in conjunction with the graphs published by Osborn (1945). For acetone in carbon tetrachloride therefore $b_1^s/b_1^v=0\cdot9853$; if the changes with medium of b_1 for acetone are assumed to be changes of $b_L^{C=O}$, then (since $b_L^{C=O}$ deduced from measurements by Le Fèvre, Le Fèvre, and Rao (1959) on solutions in carbon tetrachloride is $0\cdot230_5$), $(b_L^{C=O})^v$ appears as $0\cdot234$. Insertion of this value in equation (2) gives $(\nu_{C=O})^v$ as $1737\cdot5$ cm^{-1} if $r_{C=O}$ is $1\cdot22_9$ Å, whilst the ν of 1719 cm^{-1} recorded for acetone in carbon tetrachloride requires an $r_{C=O}$ of $1\cdot23_{15}$ Å; both these are within the limits $1\cdot22\pm0\cdot03$ (quoted in Chem. Soc. Spec. Publ., No. 11, 1958, *M* 150); the larger $r_{C=O}$ has been used in calculating $Q=(1/r_{C=O}^2)(b_L^{C=O}/\overline{M})^{\frac{1}{2}}$ from the apparent longitudinal polarizabilities of the C=O group in the solutions, these in turn being obtained via (1) as $0\cdot234b_i^s/b_i^v$.

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Results are in Table 1 (4th column). In an attempt to improve the ν's forecast for the more polar solvents, equation (1) has been modified to equations (1*a*) or (1*b*) respectively by substituting $(n^2-1)/(n^2+2)$ by $(\varepsilon-1)/(\varepsilon+2)$ or by $(\varepsilon-1)/(2\varepsilon+1)$; columns 5 and 6 show the effects of such changes. (Refractive indexes and dielectric constants are from Timmermans 1950, or Maryott and Smith 1951.)

TABLE 1

CALCULATED AND OBSERVED CARBONYL STRETCHING FREQUENCIES FOR ACETONE IN 28 SOLVENTS

Solvent	n_D^{25}	ε^{25}	$\nu_{C:O}$ via (1)	$\nu_{C:O}$ via (1*a*)	$\nu_{C:O}$ via (1*b*)	$(\nu_{C=O})^s_{obs.}$
n-C_6H_{14} ..	1·3722	1·882	1720	1721	1723	1723·5
Cyclo-C_6H_{12}	1·4236	2·015	1720	1720	1722	1723
Et_2O ..	1·3527	4·235	1721	1710	1717·5	1721
$(n\text{-}C_4H_9)_2O$	1·3935	3·06	1720	1715	1719	1721
Et_3N ..	1·3983	2·42	1720	1718	1720	1720
C_2Cl_4 ..	1·5002	2·30	1718	1918·5	1721	1720
CCl_4 ..	1·4575	2·227	1719	1719	1721	1719
C_6H_5Me ..	$1·4940_5$	2·379	1718	1718	1721	1719
1,2,4-$C_6H_3Me_3$	1·5025	2·42 (17°)	1718	1718	1720	1719
CS_2	1·6243	2·6246	1716	1716·5	1720	1717·5
C_6H_6 ..	1·4973	2·2725	1718	1718	1721	1717
Dioxan ..	1·4202	2·209	1719	1719	1721	1715·5
MeI ..	1·5285	6·86	1718	1705	1715	1715
MeCN ..	$1·3415_5$	36·7	1721	1696	1712	1715
Me_2CO ..	1·3566	20·70	1721	1698	1712	1714·5
$C_2H_4Cl_2$ ..	1·4425	10·36	1719	1702	1714	1714
C_5H_5N ..	1·5074	12·01	1718	1701	1710	1713
$C_2H_4Br_2$ ..	1·5358	4·78	1718	1709	1715	1713
CH_2Cl_2 ..	1·4216	8·90	1720	1703	1714	1713
$MeNO_2$ ..	1·3794	36·67	1720	1696	1712	1712
$CHCl_3$ ..	1·4430	4·724	1719	1709	1716	1712
CH_2Br_2 ..	1·5370	7·23	1718	1704	1715	1711
$C_2H_2Cl_4$ ..	1·4917	8·20 (20°)	1718	1704	1714	1709
$CHBr_3$ ..	1·5949	4·337	1716	1710	1717	1708
CH_2I_2 ..	1·7379	5·32	1713	1708	1716	1707
Pyrrole ..	1·503	7·48 (18°)	1718	1705	1715	1706
$C_6H_5NH_2$ ..	1·584	6·77	1717	1704	1714	1703
MeOH ..	1·3267	32·63	1721	1696	1712	{1721 sh, 1708

To cover adequately the observed 28 frequencies, the equations need to yield predictions ranging from 1723·5 to 1703 cm^{-1}, or—if the three solvents (pyrrole, aniline, and methanol) be excepted, in which H-bonding with C=O may occur—from 1723·5 to 1707 cm^{-1}. Equation (1) is seen to provide a range over the remaining 25 cases which is insufficient, and (1a) one which is excessive. Equation (1*b*) fits the experimental data best, the algebraic sums of $\nu_{calc.}-\nu_{obs.}$ being +73·5 for (1), −146 for (1*a*), and +42 cm^{-2} for (1*b*). With (1*b*), agreement is worst with $CHBr_3$ and CH_2I_2 ; incipient compound formation between acetone and chloroform or bromoform, as suspected by Glasstone (1937) during dielectric polarization measurements, are possibly responsible for the low $\nu_{obs.}$. However, it is a consequence of the present treatment that ν_{CO} should shift with concentration, as ε_{12} varies, and $(\nu_{CO})^s$ properly requires an extrapolation to infinite dilution. Between different observers (Hartwell, Richards, and Thompson 1948; Bayliss, Cole, and Little 1955; Bellamy and Williams 1959), differences of 4–6 cm^{-1} are sometimes found. Equation (1b) will be tested on other solute ketones when their principal polarizabilities become available.

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