

117. *The Apparent Dipole Moment of Paraldehyde in Various Solvents.*

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THESE measurements were started because paraldehyde was reported to have a large negative Kerr constant (*viz.*,  $-713$ ; cf. Wolf, *Leipzige Vorträge*, 1929, 129). Owing, however, to the fact that even carefully purified paraldehyde, which had been several times frozen, etc., always gave positive aldehyde tests with dinitrophenylhydrazine, observations on this substance were excluded from the preceding paper. If the position of the equilibrium  $(C_2H_4O)_3 \rightleftharpoons 3CH_3\cdot CHO$  is altered by solvents,\* the interpretation of our results would be significantly affected, because, whereas the moment of paraldehyde is evidently of the order 2 D units, that of acetaldehyde is 2.7 or even higher.

Our numerical results are tabulated as in the previous paper.

*Polarisations and apparent moments of paraldehyde in various solvents.*

Solvent.	Total poln., c.c.	Orientn. poln., c.c.	Apparent $\mu$ .
(Paraldehyde) .....	106.6	73.5	1.89
Carbon tetrachloride .....	126.1 (125) *	93 (92)	2.12 (2.11)
Benzene .....	117.8 (122)	85 (89)	2.03 (2.08)
Chloroform .....	138.2 (139)	105 (106)	2.26 (2.27)
Dimethylaniline .....	91.4 (92)	58.5 (59)	1.68 (1.69)
Chlorobenzene .....	98.1 (98)	65	1.77
Ethyl benzoate .....	97.2 (97)	64	1.76
<i>o</i> -Dichlorobenzene .....	100.4 (98)	67 (65)	1.80 (1.77)
Benzonitrile .....	111.3 (111)	78	1.94
Nitrobenzene .....	112.8 (113)	80	1.97

\* The significance of data in parentheses is explained in the preceding paper (p. 494).

*Solvent constants used* (supplementary to those recorded in the previous paper, except those for chlorobenzene).

Solvent.	A.	B.	C.	Solvent.	A.	B.	C.
CCl <sub>4</sub> .....	0.1832	97.20	16.32	Ph·CO <sub>2</sub> Et .....	0.5876	143.61	7.144
NPhMe <sub>2</sub> .....	0.5904	127.10	8.128	<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> .....	0.5102	113.42	4.337
PhCl .....	0.5503	102.17	5.290	Ph·CN .....	0.8886	102.87	0.4171

*Dielectric-constant and density coefficients for solutions of paraldehyde in the following solvents.*

Solvent.	<i>a</i> .	$\beta$ .	Solvent.	<i>a</i> .	$\beta$ .
CCl <sub>4</sub> .....	5.36	-0.814	C <sub>6</sub> H <sub>5</sub> Cl .....	3.49	-0.124
C <sub>6</sub> H <sub>6</sub> .....	5.29	0.157	Ph·CO <sub>2</sub> Et .....	2.25	-0.0420
CHCl <sub>3</sub> .....	12.30	-0.714	<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> .....	2.62	-0.335
NPhMe <sub>2</sub> .....	2.05	0.0426	Ph·CN .....	-13.9	0.00160
Ph·NO <sub>2</sub> .....	-26.00	-0.222			

*Paraldehyde*.—This was a commercially pure specimen; after redistillation and freezing, it had b. p. 124°/760 mm., m. p. 10—12°,  $d_4^{25}$  0.98960, and  $\epsilon_{25}$  12.934 (Walden, *Z. physikal. Chem.*, 1903, 46, 176, gives  $\epsilon_{20}$  for a wave-length of 72 cm. as *ca.* 11.8). From these data the total polarisation is 106.6 c.c.

The data for solutions in various solvents at 25° follow.

<i>In carbon tetrachloride.</i>					
$f_1 \cdot 10^6$ .....	0	22385	56869	83079	123846
$\epsilon$ .....	2.2270	2.3457	2.5331	2.6733	2.8920
$d$ .....	1.58440	1.56628	1.53745	1.51644	1.48515
$P_1$ .....	—	123.60	122.94	121.09	118.49
<i>In benzene.</i>					
$f_1 \cdot 10^6$ .....	0	27225	39252	45045	61544
$\epsilon$ .....	2.2725	2.4159	2.4802	2.5079	2.6027
$d$ .....	0.87370	0.87796	0.87988	0.88074	0.88334
$P_1$ .....	—	115.98	115.62	114.47	110.09

\* A calculation on the basis of Pauling's figures shows that the energy changes involved in the passage from the right to the left side of this equation are of the same order as those for the keto  $\rightleftharpoons$  enol change, which, as K. H. Meyer has demonstrated, is sensitive to the solvent employed.

										<i>In chloroform.</i>									
$f_1 \cdot 10^6$	.....										0	27472	49000	80923	142580				
$\epsilon$	.....										4.7240	5.0617	5.3293	5.7204	6.4533				
$d$	.....										1.46814	1.44803	1.43258	1.41078	1.36987				
$P_1$	.....										—	136.92	135.80	133.42	129.42				
										<i>In dimethylaniline.</i>					<i>In chlorobenzene.</i>				
$f_1 \cdot 10^6$	...	0	41355	49434	82316						0	37117	48490	76503	89248				
$\epsilon$	.....	4.8495	4.9386	4.9489	5.0133	5.6120					5.7415	5.7836	5.8778	5.9219	5.9219				
$d$	.....	0.95198	0.95381	0.95403	0.95544	1.10110					1.09655	1.09507	1.09157	1.08999	1.08999				
$P_1$	.....	—	91.92	90.96	90.62	—					97.94	98.29	97.94	97.92	97.92				
										<i>In ethyl benzoate.</i>					<i>In o-dichlorobenzene.</i>				
$f_1 \cdot 10^6$	.....										0	70508	135423						
$\epsilon$	.....										5.7658	5.9256	6.0680	6.857	6.997				
$d$	.....										1.04446	1.04153	1.03872	1.29608	1.27846				
$P_1$	.....										—	96.82	96.28	—	98.37				
										<i>In benzonitrile.</i>					<i>In nitrobenzene.</i>				
$f_1 \cdot 10^6$	...	0	43816	110430	140900						0	32364	38657	107852	107852				
$\epsilon$	.....	25.200	24.630	23.625	23.172	34.890					34.082	33.862	32.037	32.037	32.037				
$d$	.....	1.00127	1.00193	1.00308	1.00361	1.19861					1.19150	1.19000	1.17460	1.17460	1.17460				
$P_1$	.....	—	110.29	109.26	108.99	—					112.78	112.61	112.51	112.51	112.51				

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