

STUDIES IN THE DIELECTRIC CONSTANTS OF FATTY ACIDS*

Part III. The Applicability of Jatkar's Equation to Concentrated Solutions of Esters of Fatty Acids

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It is now generally accepted that the Debye-Clausius-Mosotti¹ equation for determining the dipole moment of polar substances is satisfactory, only when applied to vapours at low pressures and to dilute solutions of polar substances in non-polar solvents. The equation is not applicable to pure polar liquids or their concentrated solutions. Jatkar² in 1943 introduced the following equation and claimed that it was applicable to solids, liquids, gases and to concentrated solutions. The equation is

$$\frac{(\epsilon - n^2) M}{d} = \frac{4\pi N \mu^2}{3kT} \left(\frac{j+1}{j} \right),$$

where $j = \infty$ for gases and $\frac{1}{2}$ for solids and liquids.

The experimental errors in the determination of dipole moments, from a study of concentrated solutions and of pure polar liquids, are very much less than those which occur in the case of vapours at low pressures and of dilute solutions. The present author has, therefore, attempted to study the applicability of Jatkar's equation to concentrated solutions of polar liquids. Investigations relating to the dipole moments of ethyl ricinoleate and ethyl ricinelaide in solutions of various concentrations in the following solvents: benzene, petrol, carbon tetrachloride and dioxane are presented in this paper.

EXPERIMENTAL

The experimental technique was the same as described in earlier investigations.^{3, 4}

The benzene, dioxane and carbon tetrachloride employed as solvents, were purified by standard methods as described by Weissberger and Prosskauer.⁵ Aviation petrol was fractionated and the fraction distilling over the range 70–80° C. was collected and further purified by the technique employed for benzene. The purity of the solvents was checked by determining density, boiling point and dielectric constant. The physical constants agreed closely with the standard values.

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To measure densities, a specific gravity bottle fitted with a thermometer was employed.

Refractive indices were determined with an Abbe refractometer, provided with an efficient thermostatic control.

Calculation of Dipole Moment.—The dipole moment was calculated on the basis of Jatkar's² equation†

$$P_0 = \frac{(\epsilon - n^2) \times M}{d} = \frac{4\pi N\mu^2}{kT} = P_2 - P_E$$

P_2 , the molecular polarisation of the solute was calculated by the weight fraction method.

P_E , the electronic polarisation of the solute was calculated by Jatkar's² formula:

$$P_E = (n^2 - 1) \times \frac{M}{d}$$

Values at 25° C. of refractive index and of density of the pure substance were employed. It was assumed that P_E remained constant over the temperature range 25°–40° C.

RESULTS

The results obtained are presented in Tables I to IX.

TABLE I. *Dipole Moment of Ethyl Ricinoleate in Benzene*

$P_E = 407.9$ c.c.

W_2 (Ethyl ricinoleate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Benzene at 25° C.</i>				
0.00000	2.273	0.8740
0.09807	2.430	0.8750	1066.1	1.88
0.1379	2.500	0.8770	1075.1	1.89
0.4076	2.958	0.8870	1075.4	1.89
0.6374	3.492	0.8982	1148.8	1.99
1.0000	4.075	0.9090	1102.8	1.93
<i>Solvent: Benzene at 40° C.</i>				
0.00000	2.243	0.8590
0.09807	2.400	0.8615	1043.5	1.89
0.1379	2.472	0.8642	1077.4	1.94
0.4076	2.882	0.8750	1034.7	1.87
0.6374	3.420	0.8835	1132.5	2.02
1.0000	3.950	0.8990	1069.7	1.93

† The symbols used have the usual meaning.³

TABLE II. Dipole Moment of Ethyl Ricinoleate in Petrol

W_2 (Ethyl ricinoleate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Petrol at 25° C.</i>				
0.0000	1.915	0.7006
0.1001	2.210	0.7206	1215.4	2.08
0.2100	2.320	0.7395	1169.4	2.02
0.3000	2.450	0.7532	1099.4	1.93
0.3811	2.705	0.7760	1187.9	2.05
0.5217	3.030	0.7984	1198.6	2.06
1.0000	4.075	0.9090	1102.8	1.93
} $\mu_{av.} = 2.03$				
<i>Solvent: Petrol at 40° C.</i>				
0.0000	1.885	0.6850
0.1001	2.180	0.7060	1235.9	2.16
0.2100	2.260	0.7260	1109.7	1.99
0.3000	2.436	0.7404	1124.7	2.01
0.3811	2.685	0.7640	1202.6	2.12
0.5217	2.981	0.7876	1259.0	2.20
1.0000	3.950	0.8990	1069.7	1.93
} $\mu_{av.} = 2.09$				

TABLE III. Dipole Moment of Ethyl Ricinoleate in Carbon Tetrachloride

W_2 (Ethyl ricinoleate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Carbon tetrachloride at 25° C.</i>				
0.0000	2.228	1.5850
0.0995	2.555	1.4800	1156.6	2.00
0.1595	2.695	1.4160	1151.6	1.95
0.2833	3.040	1.3080	1155.7	2.00
0.3493	3.252	1.2560	1202.8	2.06
0.5605	3.700	1.1180	1206.5	2.07
1.0000	4.075	0.9090	1102.8	1.93
} $\mu_{av.} = 2.01$				
<i>Solvent: Carbon tetrachloride at 40° C.</i>				
0.0000	2.198	1.5565
0.0995	2.520	1.4600	1140.2	2.03
0.1595	2.665	1.3980	1112.1	1.99
0.2833	2.980	1.2920	1128.7	2.02
0.3493	3.222	1.2380	1207.7	2.12
0.5605	3.617	1.1060	1179.5	2.08
1.0000	3.950	0.8990	1069.7	1.93
} $\mu_{av.} = 2.05$				

TABLE IV. *Dipole Moment of Ethyl Ricinoleate in Dioxane*

W_2 (Ethyl ricinoleate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Dioxane at 25° C.</i>				
0.0000	2.236	1.0277	1123.0	1.96
0.1115	2.475	1.0145	1094.3	1.92
0.2069	2.655	1.0040	1083.1	1.90
0.3432	2.902	0.9854	1170.8	2.02
0.5827	3.486	0.9581	1185.6	2.04
0.7347	3.814	0.9408	1102.8	1.93
1.0000	4.075	0.9090		
$\mu_{av.} = 1.97$				
<i>Solvent: Dioxane at 40° C.</i>				
0.0000	2.206	1.0127	1167.7	2.07
0.1115	2.460	1.0017	1051.9	1.91
0.2069	2.600	0.9925	1040.9	1.90
0.3432	2.830	0.9744	1147.0	2.04
0.5827	3.414	0.9476	1135.5	2.02
0.7347	3.702	0.9405	1069.7	1.93
1.0000	3.950	0.8990		
$\mu_{av.} = 1.99$				

TABLE V. *Dipole Moment of Ethyl Ricinelaiddiate in Benzene* $P_E = 406.1$ c.c.

W_2 (Ethyl ricinelaiddiate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Benzene at 25° C.</i>				
0.0000	2.273	0.8740	1112.6	1.95
0.1512	2.542	0.8800	1131.9	1.97
0.3007	2.820	0.8824	1176.2	2.03
0.4707	3.195	0.8890	1223.5	2.09
0.5841	3.500	0.8936	1248.2	2.12
0.7203	3.845	0.8988	1273.9	2.15
1.0000	4.560	0.9110		
$\mu_{av.} = 2.03$				
<i>Solvent: Benzene at 40° C.</i>				
0.0000	2.243	0.8590	1080.7	1.95
0.1512	2.496	0.8650	1107.4	1.99
0.3007	2.770	0.8704	1169.4	2.07
0.4707	3.150	0.8760	1121.8	2.01
0.5841	3.380	0.8812	1233.9	2.15
0.7203	3.770	0.8848	1228.8	2.15
1.0000	4.400	0.9020		
$\mu_{av.} = 2.03$				

TABLE VI. Dipole Moment of Ethyl Ricinelaideate in Petrol

W_2 (Ethyl ricine- laidiate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Petrol at 25° C.</i>				
0.0000	1.915	0.7006
0.1602	2.190	0.7294	1088.2	1.91
0.3962	2.625	0.7720	1083.0	1.90
0.5298	2.930	0.8000	1106.8	1.94
0.5907	3.150	0.8140	1162.8	2.01
0.7305	3.530	0.8460	1177.5	2.03
1.0000	4.560	0.9110	1273.9	2.15
} $\mu_{av.} = 1.96$				
<i>Solvent: Petrol at 40° C.</i>				
0.0000	1.885	0.6850
0.1602	2.155	0.7144	1082.0	1.95
0.3962	2.595	0.7600	1107.6	1.99
0.5298	2.880	0.7880	1094.4	1.97
0.5907	3.080	0.8020	1139.4	2.03
0.7305	3.460	0.8360	1158.0	2.00
1.0000	4.400	0.9020	1228.8	2.15
} $\mu_{av.} = 1.99$				

TABLE VII. Dipole Moment of Ethyl Ricinelaideate in Carbon Tetrachloride

W_2 (Ethyl ricine- laidiate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Carbon Tetrachloride at 25° C.</i>				
0.0000	2.228	1.5850
0.1012	2.550	1.4849	1119.2	1.95
0.2200	2.800	1.3400	1095.0	1.92
0.4297	3.295	1.2130	1100.3	1.93
0.6384	3.695	1.0885	1121.1	1.96
0.7833	3.925	1.0150	1129.6	1.97
1.0000	4.560	0.9110	1273.9	2.15
} $\mu_{av.} = 1.94$				
<i>Solvent: Carbon Tetrachloride at 40° C.</i>				
0.0000	2.198	1.5565
0.1012	2.505	1.4700	1070.0	1.93
0.2200	2.710	1.3240	1024.0	1.87
0.4297	3.210	1.1950	1070.0	1.93
0.6384	3.585	1.0750	1086.0	1.91
0.7833	3.800	1.0015	1094.1	1.97
1.0000	4.400	0.9020	1228.8	2.15
} $\mu_{av.} = 1.92$				

TABLE VIII. *Dipole Moment of Ethyl Ricinelaideate in Dioxane*

W_2 (Ethyl ricine- laideate)	$\epsilon_{1.2}$	$d_{1.2}$	P_2	$\mu \times 10^{-18}$ (Jatkar)
<i>Solvent: Dioxane at 25° C.</i>				
0.0000	2.236	1.0277	..	2.04
0.1003	2.460	1.0105	1178.9	1.94
0.2363	2.720	0.9979	1110.7	1.97
0.3600	2.980	0.9817	1129.2	2.08
0.6246	3.640	0.9529	1210.4	2.09
0.7070	3.820	0.9439	1215.0	2.15
1.0000	4.560	0.9110	1273.9	..
$\mu_{av.} = 2.02$				
<i>Solvent: Dioxane at 40° C.</i>				
0.0000	2.206	1.0127	..	2.05
0.1003	2.420	0.9960	1151.1	1.96
0.2363	2.674	0.9856	1088.5	1.99
0.3600	2.920	0.9679	1106.1	2.07
0.6246	3.525	0.9409	1167.4	2.07
0.7070	3.680	0.9322	1164.8	2.15
1.0000	4.400	0.9020	1228.8	..
$\mu_{av.} = 2.04$				

TABLE IX. *Dipole Moments of Ethyl Ricinoleate and Ethyl Ricinelaideate in Various Solvents*

$t^\circ C.$	Solvent	Ethyl Ricinoleate $\mu_{av.}$	Ethyl Ricinelaideate $\mu_{av.}$
25	(Pure Liquid)	..	2.15
40	(Pure Liquid)	..	2.15
25	Benzene	1.93	2.03
40	Benzene	1.91	2.03
25	Petrol	1.93	1.96
40	Petrol	2.03	1.99
25	Carbon tetrachloride	2.09	1.94
40	Carbon tetrachloride	2.01	1.92
25	Dioxane	2.05	2.02
40	Dioxane	1.97	2.04
		1.99	

DISCUSSION

Tables I to VIII give the dipole moments of the two esters in different solvents. In Table IX, the values recorded for ($\mu_{av.}$) are averages of those obtained for various concentrations in the same solvent. It will be noticed

that the moments are unaffected by temperature. With different concentrations, maximum deviation from the average value of the dipole moment is not more than 6 per cent. This shows that Jatkar's equation gives consistent values of dipole moments when applied to pure liquids and their concentrated solutions.

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