

Dumas' determinations inaccurate and calorific values subject to error. It would proclaim a new property of nitrogen, which has been proved not to be possible by thousands of able chemists, namely, the ability to support combustion. Therefore I wish to point out the fallacies of Lidov's writings.

Summary

1. The author has shown that $(\text{CNO})_x$ cannot be obtained by any of the methods described by Lidov.

2. He has proved that salts, such as Na_2CNO_2 , $\text{Fe}(\text{NCO})_3$ or BaCNO_2 , cannot be prepared as described.

3. He has shown that Lidov's peculiar observations are due to inaccurate work. This is particularly true of the density determinations.

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ELECTRIC MOMENT AND MOLECULAR STRUCTURE. IV. THE GLYCOLS

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In the first paper¹ of this series the effect upon the resultant electric moment of the molecule produced by separating the component moments by a carbon chain of varying length was investigated, the complex $-\text{CO}-\text{OC}_2\text{H}_5$ group being placed at each end of the chain. In the present investigation the simpler $-\text{OH}$ group has been attached to the carbon chain. The low solubility of the glycols in the non-polar liquids, benzene and heptane, usually used as solvents in the determination of electric moments, has made it desirable to use 1,4-dioxane, which has been employed by Williams for a similar purpose.² Williams found values for the moments of chlorobenzene, chlorocyclohexane, diethyl *o*-phthalate, and water measured in dioxane in good agreement with the values obtained in other ways. It was feared, however, that the glycols might form addition products with the dioxane which would lead to incorrect values for the moments. In order to test the possibility of such errors, *n*-butyl alcohol, which had been thoroughly investigated in the vapor state³ and in solution in other solvents,⁴ was measured in dioxane. The monohydric alcohol would be expected to resemble to some extent, at least, the glycols in the possible formation of addition products and, therefore, in the error in the moment arising from such formation. The resemblance should be close in the case of the long-chain glycols.

¹ Smyth and Walls, *THIS JOURNAL*, **53**, 527 (1931).

² Williams, *ibid.*, **52**, 1838 (1930).

³ Miles, *Phys. Rev.*, **34**, 964 (1929).

⁴ Smyth and Stoops, *THIS JOURNAL*, **51**, 3312 (1929).

Preparation of Materials

The refractive indices and densities of the pure liquids, which give evidence of the purity of the materials, are listed in Table I. Other criteria of purity are given under each substance below.

1,4-Dioxane.—1,4-Dioxane from the Eastman Kodak Company, m. p. 9.5–10.5°, was dried over sodium and fractionally distilled; b. p. 100.5–100.7°.

***n*-Butyl Alcohol.**—*n*-Butyl alcohol from the Commercial Solvents Corporation was refluxed over freshly ignited calcium oxide and fractionally distilled three times; b. p. 117.2–117.4°.

Ethylene Glycol.—Material from the Carbide and Carbon Chemicals Corporation was fractionally distilled under reduced pressure and the middle fraction collected. This fraction was dried over anhydrous sodium sulfate, decanted and twice fractionally distilled; b. p. 197.2–197.3°.

Propylene Glycol.—Material from the Eastman Kodak Company, b. p. 85–86° (10 mm.), was fractionally distilled under reduced pressure, dried over anhydrous sodium sulfate, decanted and twice redistilled; b. p. 104° (32 mm.).

Trimethylene Glycol.—Material from the Eastman Kodak Company, b. p. 123–125° (30 mm.), was twice fractionally distilled under reduced pressure. The middle fraction was dried over anhydrous sodium sulfate, decanted and twice fractionally redistilled under reduced pressure; b. p. 127° (33 mm.).

Hexamethylene Glycol.—Material kindly loaned to us by Dr. Wallace H. Carothers of E. I. du Pont de Nemours & Company, b. p. 145–147° (13 mm.), was twice fractionally crystallized and allowed to stand in an evacuated desiccator; m. p. 42.8°.

Decamethylene Glycol.—Material loaned by Dr. Carothers was crystallized from hot, dried benzene, washed twice with cold benzene and carefully dried in an evacuated desiccator; m. p. 72.2°.

Experimental Results

The densities and dielectric constants of these solutions were measured with the apparatus and methods previously employed,¹ a wave length of 1000 meters being used in the dielectric constant determinations. The refractive indices for the D sodium line and the densities of the pure liquids determined for use in the calculation of the molar refractions MR_D and as criteria of purity are listed in Table I. Similar measurements on the solutions of the solids made possible the calculation of MR_D , the values of which are listed in Table II. In Table I the first column gives the mole fraction c_2 of the butyl alcohol or the glycol in the dioxane solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ and the densities d of the solutions and the polarizations P_2 of the polar substance. P_2 is calculated by means of the usual equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_1} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2 , M_1 and M_2 , and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The extrapolation of the P_2 - c_2 curve to infinite dilution, that is, $c_2 = 0$, gives the value of P_∞ at the

absolute temperature T , from which the electric moment μ is calculated by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

The absolute values of the moments are probably a little high because of the neglect of the atomic polarization P_A .

TABLE I
REFRACTIVE INDICES AND DENSITIES OF THE PURE LIQUIDS

	n_D^{20}	n_D^{25}	d_4^{25}	d_4^{30}
1,4-Dioxane.....	1.42290	1.42032	1.0311	1.0027
<i>n</i> -Butyl alcohol.....	1.39922	1.39727	0.8060 ⁵	0.7867 ⁵
Ethylene glycol.....	1.43180	1.43055	1.1099	1.0923
Propylene glycol.....	1.43291	1.43143	1.0328	1.0138
Trimethylene glycol.....	1.43965	1.43832	1.0503	1.0344

TABLE II
DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

ϵ_2	25° ϵ	50°	25° d	50°	25° P_2	50°
<i>n</i> -Butyl Alcohol						
0.00000	2.306	2.251	1.0311	1.0027	(25.91	25.85 = P_1 of 1,4-dioxane)
.01927	2.391	2.321	1.0263	0.9981	88.2	80.3
.02893	2.430	2.355	1.0238	.9957	86.1	79.5
.03023	2.439	2.362	1.0236	.9955	87.2	80.5
.06606	2.606	2.507	1.0145	.9866	87.2	81.7
.07914	2.675	2.563	1.0112	.9834	88.0	82.1
.11647	2.876	2.729	1.0018	.9744	88.5	82.4
Ethylene Glycol						
0.02181	2.480	2.405	1.0325	1.0042	121.7	115.3
.04475	2.676	2.580	1.0339	1.0059	120.2	114.4
.05309	2.745	2.638	1.0345	1.0065	118.4	112.1
.08938	3.105	2.956	1.0366	1.0090	117.7	112.0
.10838	3.317	3.143	1.0377	1.0102	117.3	111.8
.13227	3.598	3.383	1.0394	1.0122	115.7	110.3
Propylene Glycol						
0.02311	2.484	2.410	1.0313	1.0029	123.7	118.5
.03782	2.606	2.519	1.0312	1.0030	124.0	118.7
.06184	2.815	2.701	1.0311	1.0031	123.1	117.2
.07692	2.964	2.834	1.0311	1.0032	123.8	118.3
Trimethylene Glycol						
0.01068	2.408	2.340	1.0316	1.0033	149.5	139.1
.02455	2.542	2.458	1.0320	1.0037	146.5	137.8
.04267	2.725	2.619	1.0324	1.0043	144.3	136.2
.06356	2.955	2.821	1.0328	1.0051	143.0	135.3
.08037	3.155	2.992	1.0332	1.0057	142.0	134.2
.10385	3.453	3.250	1.0337	1.0064	140.2	132.9

⁵ Value taken from measurements of Smyth and Stoops, Ref. 4 on the same material.

TABLE II (Concluded)

c	25°	20°	25° ^d	50°	25° ^{P₂}	50°
Hexamethylene Glycol						
0.00980	2.397	2.330	1.0306	1.0024	161.6	150.9
.02563	2.546	2.460	1.0292	1.0012	160.1	150.3
.04354	2.725	2.615	1.0278	1.0002	160.0	150.4
.06313	2.938	2.795	1.0262	0.9990	160.5	150.
Decamethylene Glycol						
0.00645	2.366	2.304	1.0297	1.0014	184.0	174.7
.01183	2.414	2.348	1.0282	1.0002	182.3	174.6
.02290	2.517	2.434	1.0254	0.9977	182.2	171.8
.02744	2.562	2.470	1.0241	0.9967	183.3	171.3

TABLE III

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

	MR_D	25° ^{P_∞}	50° ^{MR_D}	25° ^{μ × 10⁻¹⁸}	50°
OC ₄ H ₈ O	21.63	4.28	4.22	(0.45)	(0.47)
<i>n</i> -C ₄ H ₉ OH	22.15	68.3	59.1	1.81	1.75
HO(CH ₂) ₂ OH	14.47	108.3	101.9	2.28	2.30
CH ₃ CH(OH)CH ₂ OH	19.08	105.0	100.0	2.25	2.28
HO(CH ₂) ₃ OH	19.02	130.0	121.0	2.50	2.51
HO(CH ₂) ₆ OH	32.7	128.1	118.1	2.48	2.48
HO(CH ₂) ₁₀ OH	51.3	132.6	123.6	2.52	2.54

Discussion of Results

The values given for 1,4-dioxane under $P_{\infty} - MR_D$ are the differences between the polarizations of the pure liquid and the refraction. As the unknown atomic polarization P_A is disregarded in the calculation of the moment, the result merely shows that the value of the moment is not far from zero. Williams⁶ reports a decrease in the polarization of dioxane with decreasing concentration in dilute benzene solution, which seems curious in view of the small or zero moment of the molecule. However, his value of P_{∞} , 26, is in excellent agreement with the values in Table II for P_1 , which might be expected to be practically identical with P_{∞} in this case. Williams calculates a value, $\mu = 0.4 \times 10^{-18}$, but concludes that the moment "can differ but slightly, if at all, from zero." The apparent symmetry of the molecule would lead one to expect a small or zero moment.

The values of P_2 for *n*-butyl alcohol in Table II show a minimum, as do those for the alcohol in benzene solution⁴ in the same region of temperature and concentration. The values at 25° are 3 or 4 units higher than those at the same concentrations in benzene solution, probably because of a slightly high value used for P_1 in the latter, while the polarizations in the two solvents at 50° differ from one another by less than one unit. In both solvents the minimum in the P_2 - c_2 curve at such low concentrations makes

⁶ Williams, THIS JOURNAL, 52, 1831 (1930).

difficult an accurate extrapolation to obtain P_{∞} . The value of the moment found in dioxane solution at 25° is a little high, but that at 50° is in excellent agreement with the mean value, 1.74×10^{-18} , obtained from the benzene solutions. As benzene is the most generally used solvent and as this value of the moment is in fair agreement with the value, 1.65×10^{-18} , found by Miles³ for the vapor, dioxane appears to be an adequate solvent for the alcohol. As the glycols should resemble the monohydric alcohols in their action upon the solvent, it may be concluded that dioxane solutions of the glycols should give satisfactory values of the moments. The previously mentioned work of Williams gives further justification for the conclusion.

The moment found for ethylene glycol is much higher than the value 1.5×10^{-18} obtained by Williams⁷ from measurements in benzene solution. However, the very low solubility of the glycol in benzene renders it difficult to obtain an accurate value in this solvent. It had been hoped that some of the higher glycols would prove sufficiently soluble in benzene to render measurements possible for comparison with those in dioxane, but the insolubility was such that no accurate determination could be made.

The moment of a monohydric alcohol is, in the main, the resultant of the moments of two doublets, one in the line of the C-O bond and the other in that of the H-O bond.⁸ By empirical methods, Eucken and Meyer⁹ have calculated the moment of the former doublet as 0.7×10^{-18} and that of the latter as 1.6×10^{-18} . The method is necessarily somewhat arbitrary, the moments of ethyl ether and of water being used for the calculation and the two oxygen valences being assumed to act at an angle of 110° to one another. When these assumptions, together with the assignment of a moment, 0.4×10^{-18} , to the H-C bond, are used to calculate the moment of a monohydric alcohol, the value obtained, 1.61×10^{-18} , agrees satisfactorily with those observed, which, for the most part, lie between 1.65×10^{-18} and 1.70×10^{-18} . Calculation further shows that the resultant of the C-O and H-O moments, 1.52×10^{-18} , should make an angle of 84° with the direction of the C-O bond. This angle has been suggested as the reason for the absence of induced moments along the carbon chains of the alcohols as shown by the absence of increase in the moment of the alcohols with increase in the number of carbons.

The resolution of the two C-O and the two H-O moments in ethylene glycol is a complicated matter because the angle between the two resultants, 1.52×10^{-18} , of the C-O and H-O moments is variable as the result of the rotation about the C-O and C-C bonds. Moreover, there is a small mutual inductive effect of the moments in the two halves of the molecule upon one another. In view of these complexities which cannot be treated

⁷ Williams, *Z. physik. Chem.*, [A] **138**, 75 (1928).

⁸ Cf. Smyth, *THIS JOURNAL*, **46**, 2151 (1924).

⁹ Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

accurately, it seems best to attempt to obtain merely a rough idea of the magnitude of the resultant moment. It has been shown that the resultant of the C-O and H-O moments acts nearly at a right angle to the direction of the C-O bond, which makes an angle to that of the C-C bond. If the total resultant moment in each half of the molecule is taken equal to that of a monohydric alcohol, 1.7×10^{-18} , and assumed to act at right angles to the C-C bond and if all positions of one moment relative to the other around the C-C bond are assumed to be equally probable, the average moment found for the molecule should be $1.41 \times 1.7 \times 10^{-18} \times \sin 90^\circ = 2.4 \times 10^{-18}$,¹⁰

When the doublets are close together, as in ethylene and propylene glycol, their considerable mutual potential energies tend toward a minimum by bringing the doublets as far as possible into opposition to one another and so reducing the resultant moment. As would be expected, the replacement of a hydrogen in ethylene glycol by a methyl group to form propylene glycol has a negligible effect upon the moment as it does not alter the positions of the hydroxyl groups relative to one another. This should not be the case, however, if the replacement of the hydrogen by methyl produced any considerable change in the energies of the other bonds. Similarly, practically identical values were found by Gross¹¹ for the moments of ethylene chloride, 1.86×10^{-18} , and propylene chloride, 1.85×10^{-18} . When the doublets are more widely separated as in trimethylene glycol, their mutual potential energies are less and, indeed, appear to be so small as to have a negligible effect upon the positions of the doublets relative to one another. This is evident in the higher moment found for trimethylene glycol and in the fact that the further separation of the hydroxyl groups in hexamethylene and decamethylene glycol has no apparent effect upon the moment. The rough value 2.4×10^{-18} calculated for the moment of ethylene glycol is evidently of the right order of magnitude for it lies between those of the glycols in which the hydroxyls are on adjacent carbons and those in which the hydroxyls are more widely separated.

It is of interest now to consider qualitatively the effect of the valence angles of the carbons and the possible bending of the carbon chains. Of the dihydroxybenzenes, only the ortho compound, catechol, has been measured,¹² the moment found being 2.16×10^{-18} , a value higher than that for phenol, 1.70×10^{-18} ,¹³ by an amount slightly less than the difference between ethylene glycol and the monohydric alcohols. The angle between the two C-O valences in catechol is fixed at 60° , while in ethylene glycol it may vary from 40 to 180° . The moments of the ethers of the

¹⁰ Cf. the calculations on the dicarboxylic acid esters (Smyth and Walls, Ref. 1).

¹¹ Gross, *Z. physik. Chem.*, [B] 6, 215 (1929).

¹² Weissberger and Sängewald, *Physik. Z.*, 30, 792 (1929).

¹³ Williams, *ibid.*, 29, 174 (1928); Smyth and Morgan, *THIS JOURNAL*, 49, 1030 (1927).

dihydroxybenzenes are smaller because the C-O moment is smaller than the H-O but the valence angles involved and the dependence of the moments upon these angles should be much the same. *o*-, *m*- and *p*-dimethoxybenzene have the moments 1.31, 1.58 and 1.81×10^{-18} , respectively, while *o*-, *m*- and *p*-diethoxybenzene have the values 1.37, 1.70 and 1.76×10^{-18} .¹² The moments of the ortho compounds may be somewhat lowered by the mutual inductive action of the moments and by the tendency of their mutual potential energies to reach a minimum by bringing the doublets as far as possible into opposition to one another. Lowering due to these causes should be slight, if not negligible, in the meta compounds where the separation of the doublets is greater, and certainly negligible in the para compounds. Although this lowering of the moment reduces the significance of the differences between the ortho, the meta and the para compounds, it would appear that the moment increases as the angle between the lines joining the oxygens to the ring carbons increases from approximately 60 to 120, to 180°.

The fact has been cited in the first paper of this series¹ that dimethyl *o*-phthalate has a moment 2.5×10^{-18} , while that of dimethyl terephthalate is 2.2×10^{-18} , that is, when the two -COOCH₃ groups are attached to the ring in such a way that the group bonds make an angle of about 60° with one another, the moment is a little higher than when the group bonds point in opposite directions. This behavior was contrasted with that of the substituted benzenes in which the substituent could be regarded as giving rise to a single moment in the plane of the ring. In such cases the behavior is very different, as illustrated by the moments of the dichlorobenzenes, the ortho compound having a moment, 2.25×10^{-18} , the meta, 1.48×10^{-18} and the para, 0.¹⁴ The behavior of the di-ethers is in even more marked contrast to that of the dichlorobenzenes for the change of moment with change in the angle between the group bonds is different not only in magnitude but also in direction.

Evidently, rotation around the C-O bonds makes possible so many different orientations of the hydroxyl moments relative to one another in a dihydroxy compound that the angle between the C-O bonds does not have a large effect upon the moment. When to this is added the effect of the rotation about the C-C bonds in the glycols, it appears that lengthening of the carbon chain between the two hydroxyls should have little effect upon the resultant moment once the hydroxyls are so far removed from one another that the mutual potential energies of their doublets are small. The marked increase in moment observed when the number of carbons between the hydroxyl groups is increased from two to three may result in part from change in the angles between the C-O bonds because of the valence angles of the added carbon, but is probably due mainly to the

¹⁴ Smyth, Morgan and Boyce, *THIS JOURNAL*, 50, 1536 (1928).

greater distance between the doublets, which permits freedom of rotation and orientation relative to one another and renders negligible the lowering of the moments by mutual inductive action. Further lengthening of the chain should have little effect unless it should give rise to bending to form a ring-like structure. Unfortunately, the tetra- and pentamethylene glycols, which should be most apt to form a ring structure, have not been secured for measurement. In spite of the smallness of the effect of the angle between the C-O bonds upon the moment, it would seem that any very pronounced bending of the carbon chain might cause noticeable differences between the moments of molecules possessing chains of different lengths. Certainly, if any one molecule were so bent as to bring its hydroxyl groups into contact with each other, its moment would be materially different from those in which such proximity between the hydroxyl groups did not occur.

The difference between the value found for hexamethylene glycol and that for decamethylene glycol, though slightly greater than the probable experimental error, is too small to be significant. The differences between all the values found at 25° and those at 50° are no greater than the experimental error, although measurement over a wide temperature range should show an increase in the moments of ethylene and propylene glycol if they are low because of the mutual potential energies of their doublets. If there were any pronounced ring formation in the longer molecules, they might be expected to be affected by change of temperature and show a change of moment such as was found for diethyl succinate.¹ It may be concluded that the moments of the glycols give no indication of ring formation in the molecule or of very pronounced bending of the carbon chain, although they do not preclude the possibility of some bending of the chain.

Summary

The dielectric constants and densities of *n*-butyl alcohol and of five glycols have been measured in solution in 1,4-dioxane at 25° and at 50° and the refractive indices of the substances in the pure liquid state or in solution have been determined.

The data have been used to calculate the electric moments of the molecules and the agreement of the value for *n*-butyl alcohol with that obtained by other methods is regarded as evidence of the correctness of the results for the glycols.

Because of rotation around the bonds the relative positions of the two hydroxyl groups in the molecule do not have large effects upon the moment, but the absence of any significant difference in moment between trimethylene, hexamethylene and decamethylene glycol is regarded as indicating that there is no very pronounced bending of the carbon chain.