

lar association of dodecylammonium butyrate to some extent in benzene is evidenced by the data presented.

Further evidence of molecular association is indicated by the rather irregular displacement of the solubility curves of dodecylamine salts toward the ethanol and benzene axes. Similar behavior of the higher fatty acids in benzene has been attributed¹² to molecular association in solution.

Summary

1. The solubilities of dodecylammonium formate, acetate, *n*-propionate, *n*-butyrate, chloride, bromide, iodide, dodecylcarbamate, primary and secondary phosphates and acid and normal sulfates, N-methyldodecylammonium chloride and N-dimethyldodecylammonium chloride and acetate in water, ethanol and benzene have been determined.

2. The phase changes of the water systems of dodecylammonium formate, acetate, propionate and N-dimethyldodecylammonium acetate have been investigated, and the hydrates formed by these salts are reported.

(12) Powney and Addison, *Trans. Faraday Soc.*, **34**, 625 (1938).

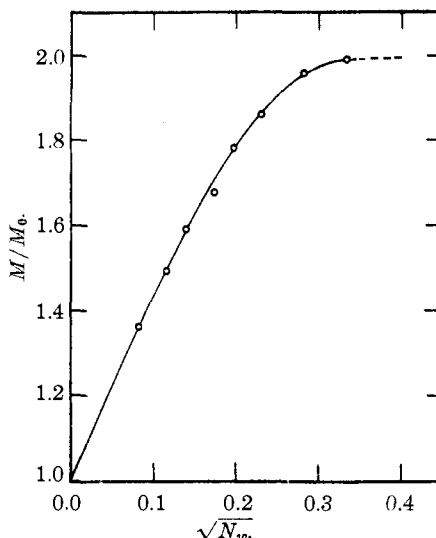


Fig. 9.—Molecular weight of dodecylammonium butyrate in benzene solutions.

3. The colloidal nature of aqueous solutions of these salts has been demonstrated by a study of their osmotic coefficients.

4. Molecular association of dodecylammonium butyrate in benzene has been discussed.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment, Induction and Resonance in Nitroethane and Some Chloronitroparaffins

BY EVERETT C. HURDIS AND CHARLES P. SMYTH

Recent investigations¹ have shown an increase of moment of 0.21–0.23 from nitromethane to α - and β -nitropropane and 2-methyl-2-nitropropane, presumably because of the effect of induction upon the α - and β -carbons, since branching of the carbon chain did not increase the moment appreciably above that of the straight-chain nitropropane. One would, therefore, expect the moment of nitroethane to be close to those of the nitropropanes and nitrobutanes. This appeared to be true in the earlier measurements of Groves and Sugden,² who found 3.58, 3.57 and 3.55 for nitroethane, α -nitropropane and α -nitrobutane, values barely distinguishable from their value 3.54 for nitromethane. As this discrepancy between the two sets of investigations left a slight possibility of further increase of moment and, hence, of inductive effect, from nitroethane

to the propanes, it seemed desirable to make a careful redetermination of the moment of nitroethane. This has been done, together with measurements upon three chloronitroparaffins, from which conclusions as to induction effects may be drawn. At the same time, measurements upon certain previously measured substances have been carried out as a check upon the absolute accuracy of the determinations.

Preparation and Purification of Materials

Carbon Dioxide.—The gas was taken from a cylinder of commercial material, passed through a tube containing eight-mesh calcium chloride and used without further purification.

Benzene.—The material used had been purified by Dr. P. F. Oesper for use in solution measurements and had been dried over sodium wire.

***n*-Octane.**—This hydrocarbon was supplied as a part of the American Petroleum Institute Pure Hydrocarbon Program. It was prepared and/or purified at the Pure Hydro-

(1) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

(2) Groves and Sugden, *J. Chem. Soc.*, 158 (1937).

carbon Laboratory, Department of Chemistry, operating as project No. 31 of the Ohio State University Research Foundation. A full description of this product will be published at a later date.

Water.—Ordinary distilled water was used for this measurement.

Nitroethane, Sample I.—Material kindly furnished by the Commercial Solvents Corporation was dried over calcium chloride and fractionally distilled under low pressure. The fraction used for measurements had a boiling point of 65.6° (153 mm.), n_{D}^{20} 1.3917.

Nitroethane, Sample II.—Material prepared by the reaction of silver nitrite with ethyl bromide³ was fractionally distilled under low pressure. The fraction used for measurements had a boiling point of 81.5–82.0° (263 mm.), n_{D}^{20} 1.3912.

Monochloronitromethane.—Material kindly furnished by Professor R. H. Ewell of Purdue University was fractionally distilled under vacuum in an all glass trap system connected to the gas apparatus.

1-Chloro-1-nitroethane.—Material kindly furnished by Professor Ewell was fractionally distilled under low pressure in an all glass system. The fraction used for measurements had a boiling point of 55° (60 mm.), n_{D}^{20} 1.4224.

1-Chloro-1-nitropropane.—Material kindly furnished by Professor Ewell was fractionally distilled under low pressure in an all glass system. The fraction used for measurements had a boiling point of 67° (56 mm.), n_{D}^{20} 1.4251.

Experimental Method

The dielectric constants of the vapors were measured with the apparatus and much the same technique as that previously described.⁴ A polarization value, P , was usually obtained at an absolute temperature, T , by plotting the results over a wide range of pressure and thus eliminating the error caused by possible deviations from the ideal gas law. This method, which we have generally employed, will be referred to as the "extrapolation method." However, in some cases, such as those of substances undergoing slight thermal decomposition with the passage of time, better results could be obtained by making one measurement at 10–30 millimeters pressure and another at a pressure, generally about 200 millimeters, for which experience showed the gas law deviation to be within the experimental error. These pressures were about twice those for which Brockway and Coop⁵ calculated a possible error of 0.002×10^{-18} in dipole moment due to gas law deviation. In general, successive measurements by the "two-point method" showed considerable variation, but, if the results of four to six such measurements were averaged at each temperature studied, the averages showed excellent agreement over a wide temperature range.

The oil-bath in which the dielectric constant cell was immersed was altered so that it could be kept constant to within 0.02° at any temperature from room temperature to 250°. A very sensitive mercury-bulb temperature regulator was made by bending ten feet of 1-cm. "Pyrex" tubing into a coil. The fixed contact was a tungsten rod sealed into the glass and the movable contact was steel

piano wire, which was much more resistant than platinum to the mercury at the higher temperatures.

The calibration of the apparatus was carried out by an absolute method, for the use of which it was not necessary to rely on the purity of any compound. A system of parallel compensating and measuring condensers was so constructed that a small precision measuring condenser with a scale 2500 divisions and a variable capacity of only 7 $\mu\mu f$ could be balanced against a large precision condenser, 1000 units on the small condenser having to be successively added 128.09 times to cover 400 units on the large condenser. The large condenser was thus calibrated by comparison with the small condenser, which, in turn, was calibrated in the manner previously described⁴ by successive insertions of a small unit of about 0.05 $\mu\mu f$ capacity equal to about 25 scale divisions on the small condenser. The capacity of the gas cell was measured on the large condenser and its lead capacity determined from that of a set of dummy leads. Subtraction of this fixed capacity from the total capacity of the cell gave the geometrical capacity used in calculating the dielectric constant. The total cell capacity of about 200 $\mu\mu f$ was measured frequently on the large condenser and converted into units of the small condenser by multiplying by the conversion factor 320.2. It was remeasured whenever the temperature of the oil-bath was changed more than about 10°. The cell showed a temperature coefficient of capacity of about 0.0015% per degree, superimposed on a slow continuous downward drift of capacity. As the cell had been taken apart, cleaned, and reassembled before the measurements were begun, this downward drift in capacity may have been due to the opportunity afforded by thermal expansion and contraction for the relief of strains. During twelve months of operation, the capacity of the cell decreased by 5%, showing the importance of frequent checking. Care was taken to carry out both calibration and measurements at a constant frequency of 780 ± 3 kilocycles. Under these conditions, the effects introduced by lead and condenser inductances were constant and cancelled out in the measurements.

The platinum resistance thermometer in the cell was calibrated by comparison with a Bureau of Standards calibrated platinum resistance thermometer. As the platinum wire was exposed to the vapor in the cell, it was occasionally necessary to bake out the cell at 250° for a few days to avoid adsorption effects which lowered the apparent temperature reading. Temperatures as measured are believed accurate to within 0.2°.

Three compounds were measured as calibration checks: carbon dioxide, benzene and water. Carbon dioxide was measured by the two-point method, the pressures used being about 35 and 950 millimeters. The effect of frequency drift was corrected for by repeating each measurement in the reverse direction and averaging the two figures obtained. The observed pressures were corrected by the use of van der Waals constants. The average of six successive measurements on carbon dioxide was $(\epsilon_{760} - 1) \times 10^6 = 988 \pm 2$, reduced to 0°, in excellent agreement with the values of McAlpine and Smyth,⁶ 989, and Stuart,⁷ 987.

Benzene was measured at 140° by the extrapolation

(3) Kissel, *Ber.*, **15**, 1574 (1882); Gotting, *Ann.*, **243**, 115 (1888).

(4) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941).

(5) Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1434 (1938).

(6) McAlpine and Smyth, *This Journal*, **55**, 453 (1933).

(7) Stuart, *Z. Physik*, **47**, 457 (1928).

method. The average of four measurements gave a polarization of 27.1 cc., in agreement with the previously determined⁸ value of 27.0 cc.

The polarization of a sample of pure *n*-octane, kindly given us by Dr. C. E. Boord, was also measured. This served in a sense as a calibration check, as the expected small increase in polarization over the liquid value was observed. The average of four measurements at 160° gave a polarization of 40.1 cc. The polarization of the same material in the liquid phase was 39.7 cc., as measured by Dr. P. F. Oesper in this Laboratory.

The dipole moment of water vapor was measured, using the two-point method, over the temperature range 111 to 250°, the average moment value obtained being 1.844 Debye units. This figure is in good agreement with those reported by Sanger, Steiger and Gachter,⁸ 1.852 ± 0.008, and by Groves and Sugden,⁹ 1.850 ± 0.01, values which have been recalculated with the currently accepted factor, 0.01281, in the Debye equation.

Experimental Results

The results of individual runs are given in Table I for the dielectric constant ϵ minus 1 for

TABLE I
POLARIZATIONS AND DIPOLE MOMENTS

Carbon dioxide (measured at 299°K., reduced to 0° and 760 mm.)		Benzene <i>P</i> (413.1°K.)	<i>n</i> -Octane <i>P</i> (433.1°K.)
($\epsilon - 1$) × 10 ⁸	<i>P</i>		
985	7.36	27.6	40.7
984	7.35	26.9	40.1
995	7.43	27.0	40.2
990	7.40	27.0	39.6
984	7.35	Av. 27.1	40.2
992	7.41		
Av. 988	7.38		

<i>T</i> , °K.	Water <i>P</i>	μ (× 10 ¹⁸)		1-Chloro-1-nitropropane <i>P</i>	<i>P</i> _{av.}	μ (× 10 ¹⁸)
384.3	57.5	1.84	416.3	205	206.6	3.51
	57.3	1.84		208		
420.1	53.6	1.85		212		
	53.6	1.85		207		
	53.4	1.85	436.2	198.8	200.7	3.53
444.7	50.1	1.84		202.8		
484.1	46.9	1.85		199.0		
	46.7	1.85		202.6		
522.0	43.4	1.84		199.2		
	42.4	1.82	451.9	189.9	193.4	3.52
	43.4	1.84		191.0		
				193.9		
				198.0		
415.6	217.3	3.70		194.0		
442.0	205.3	3.70	472.9	190	187.5	3.54
	206.8	3.71		186		
	206.4	3.71		185.4		
484.3	186.4	3.68		188.0		
	188.6	3.70	493.1	180.7	178.9	3.51
	188.1	3.69		178.1		
	188.9	3.70		175.0		
				179.5		
				181.0		

(8) Sanger, Steiger and Gachter, *Helv. Phys. Acta*, **5**, 200 (1932).

(9) Groves and Sugden, *J. Chem. Soc.*, 971 (1935).

Nitroethane (Sample II)		
397.5	225.9	3.69
413.6	218.4	3.70
418.1	215.0	3.69
421.1	214.7	3.70

Monochloronitromethane		
411.5	144.2	2.93
424.4	138.1	2.89
434.8	138.4	2.94
447.6	131.1	2.89
459.4	131.5	2.93
466.7	128.2	2.91
484.0	122.7	2.89

<i>T</i> , °K.	<i>P</i>	<i>P</i> _{av.}	μ (× 10 ¹⁸)
414.5	182.4	184.5	3.33
	186.2		
	185.1		
	184.0		
	185.0		
432.3	176.9	177.6	3.32
	178.1		
	177.1		
	178.2		
442.7	175.3	175.0	3.34
	174.5		
	178.0		
	172.8		
	176.6		
	173.1		
467.5	169.3	166.5	3.33
	166.7		
	166.1		
	163.9		

1-Chloro-1-nitropropane			
416.3	205	206.6	3.51
	208		
	212		
	207		
436.2	198.8	200.7	3.53
	202.8		
	199.0		
	202.6		
	199.2		
451.9	189.9	193.4	3.52
	191.0		
	193.9		
	198.0		
	194.0		
472.9	190	187.5	3.54
	186		
	185.4		
	188.0		
493.1	180.7	178.9	3.51
	178.1		
	175.0		
	179.5		
	181.0		

carbon dioxide, for the polarization P for all the substances, and for the dipole moment μ for the polar substances except the last two. For these two, a tendency toward decomposition and the consequent use of the two-point method of measurement increased the error in individual P values and made desirable an increased number of runs and the use of an average of the results, $P_{av.}$, to calculate the moment. The molar refraction for the sodium D line, MR_D , is listed in Table II for each nitro compound, together with the average of the moment values for the substance in Table I.

TABLE II
MOLAR REFRACTIONS AND MOMENT VALUES

	MR_D	μ ($\times 10^{18}$)
Nitroethane	17.0 ^a	3.70
Monochloronitromethane	17.4 ^b	2.91
1-Chloro-1-nitroethane	21.9 ^b	3.33
1-Chloro-1-nitropropane	26.3 ^b	3.52

^a Landolt-Börnstein (fifth edition). ^b Calculated from refractions in Landolt-Börnstein (fifth edition).

Discussion of Results

The results obtained for the substances measured as a test of the accuracy of the apparatus agree so well with previously published data as to indicate an absolute accuracy almost as great as the relative accuracy, about 0.01×10^{-18} in moment. The slight elevation of the polarization value found for *n*-octane vapor over that of the liquid at 25° parallels that previously observed for benzene⁶ and noted again in the present measurements and similar behavior on the part of other non-polar substances previously discussed.¹⁰ It is to be noted that Sample I of nitroethane, a material prepared commercially by vapor phase nitration of hydrocarbons, gives a moment value identical with that for Sample II, prepared by the reaction of silver nitrite with ethyl bromide, which, taken in conjunction with the accuracy established for the apparatus, seems to establish definitely the correctness of the value. The average moment, 3.70×10^{-18} , may be compared with the value of Smyth and McAlpine¹¹ for nitromethane, 3.50 (recalculated on the basis of MR_D) and with the value of Wiswall and Smyth¹ for 1-nitropropane, 3.72×10^{-18} . From these results it appears that the inductive effect of the nitro group is barely, if at all, detectable by dipole moments beyond the first two carbons in the chain.

(10) Smyth and McAlpine, *J. Chem. Phys.*, **2**, 571 (1934).

(11) Smyth and McAlpine, *THIS JOURNAL*, **56**, 1697 (1934).

This conclusion is consistent with the indications of the previous measurements and the accuracy of the previously reported¹ 0.2 rise in moment caused by lengthening of the carbon chain is confirmed.

Monochloronitromethane was measured by the extrapolation method over a range of 73°. As there was some evidence of decomposition, however, it was thought best to use the two-point method for 1-chloro-1-nitroethane and 1-chloro-1-nitropropane. In this way low pressures (200 mm.) could be used, and the vapor remained in the cell at this pressure for no longer than fifteen minutes for each determination of dielectric constant. The possibility of appreciable decomposition was further minimized by limiting the temperatures used to 220° or lower.

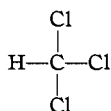
Calculation of the moment of monochloronitromethane by vector addition of the moments of methyl chloride (1.87×10^{-18}) and nitromethane (3.50×10^{-18}), assuming tetrahedral carbon, gives a resultant moment of 3.40×10^{-18} . The observed moment, 2.91, may, for the time being, be taken to indicate that the lowering due to mutual induction between the chloro and nitro groups is 0.49. This is comparable in magnitude to the lowering observed in methylene chloride, where the moment calculated is 2.16 and the observed is 1.58,¹² so that the apparent inductive lowering is 0.58. Since the inductive lowering observed for the dichloro compound is slightly larger than that for the chloronitro compound, while the moment of nitromethane is nearly twice that of methyl chloride, it appears that the nitro group is considerably less susceptible to inductive lowering of its moment than the chlorine atom. This conclusion is consistent with the previous interpretation¹³ of the moment of nitroform in carbon tetrachloride solution, which is only 0.49 lower than the solution moment of nitromethane. This lowering may be compared with that for chloroform, which has a moment 0.85 lower than that of methyl chloride.

The moment of 1-chloro-1-nitroethane, calculated by vector addition of the moments of ethyl chloride and nitroethane is 3.60×10^{-18} . The observed moment, 3.33, indicates that the apparent inductive lowering is 0.27 as compared with 0.49 for monochloronitromethane. The moment rise expected between monochloronitromethane and 1-chloro-1-nitroethane is 3.60 —

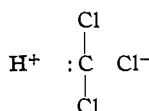
(12) Maryott, Hobbs and Gross, *ibid.*, **63**, 659 (1941).

(13) Lewis and Smyth, *ibid.*, **61**, 3067 (1939).

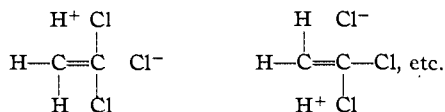
3.40 = 0.20, while the observed rise is 0.42. For the moment of 1-chloro-1-nitropropane we have: moment calculated—3.62, moment observed—3.52, apparent inductive lowering—0.10; expected rise from 1-chloro-1-nitroethane—0.02, observed rise from 1-chloro-1-nitroethane—0.19. Analogous rises are found in the values for 1,1-dichloroethane and 2,2-dichloropropane¹² and the solution value for 1,1-dichloropropane,¹⁴ the increases again being larger than estimated. A large elevation of an apparent inductive rise was found in the difference between chloroform and methyl chloroform, which was found to be 0.77 higher.^{1,12} Maryott, Hobbs and Gross¹² attribute this elevation in methyl chloroform, and, analogously, in ethylidene chloride and 2,2-dichloropropane, to "first, the transfer of charge that takes place from the methyl carbon to the other carbon atom, and second, the transfer of some of this new charge from the chloroform carbon to the chlorine atoms." A more specific mechanism may be proposed to account for the effect by assigning ionic character to the hydrogen-carbon bonds and considering the possible resonating structures. The normal covalent structure of chloroform would be



but three ionic structures of the type



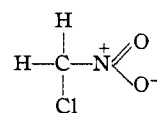
could make small contributions. Contributions from these three structures would increase the positive character of the hydrogen and probably account for its apparent ability to take part in hydrogen bonding and for its slightly tighter binding to the carbon as evidenced by Raman spectra. In methyl chloroform, instead of three such polar structures, nine can be written



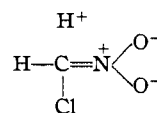
The result of small contributions from these nine structures would be an increase of moment considerably in excess of what would be expected merely from the forces exerted on the methyl group electrons by the three C-Cl dipoles. Anal-

ogous structures would contribute to the moment of ethyl chloride, but the presence of only one, instead of three, chlorines would involve a smaller accumulation of negative charge and a correspondingly smaller influence in increasing the moment. Similar considerations account for the smaller moment elevations of 1,1-dichloroethane and 2,2-dichloropropane.

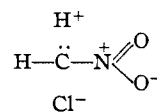
In the discussion of the chloronitroparaffins the difference between observed and calculated values, which has been referred to as the apparent inductive lowering of the moment, contains a rather large negative contribution from resonance effects similar to those just considered. The lowering of moment by mutual induction between the chlorine and the nitro group should be approximately the same in each of these three chloronitroparaffins, and the inductive effect of each of the two dipoles upon the carbon chain was taken care of approximately in calculating the moment of the chloronitro compound by using the moments of methyl chloride and nitromethane in calculating that of the disubstituted methane, of ethyl chloride and nitroethane for the disubstituted ethane, and of propyl chloride and 1-nitropropane for the disubstituted propane. The moment observed for the methane was, as previously stated, 0.49 lower than the calculated, that for the ethane, 0.27 lower than the calculated, and that for the propane 0.10 lower than the calculated. In other words, the moment of the chloronitroethane is 0.22 higher, and that of the propane 0.39 higher than would be expected on the basis of the moment of chloronitromethane and those of the monosubstituted compounds. In addition to a normal structure for chloronitromethane such as



one may write two polar structures such as



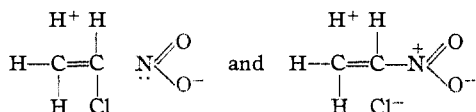
and two such as



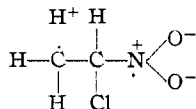
which would, by their contributions, raise the moment as in the case of analogous structures for

(14) Gross, *Physik. Z.*, **32**, 587 (1930).

chloroform. In chloronitroethane, a further increase in moment should result from contributions from structures such as



and



in addition to those from structures like those just written for the methane. For the substituted propane, analogous structures can be written, the number of possible polar structures being increased by the presence of the additional methylene group. The smallness of the increase in moment from the monosubstituted ethane to the monosubstituted propane shows that the contributions from these additional polar structures are extremely small in the monosubstituted compounds, where the concentration of negative charge on a single group would lessen the stabilities of the polar structures. In the disubstituted compounds, the distribution of negative charge between the chlorine and the nitro group would tend to stabilize the polar forms and thus increase the molecular moment. That this stabilizing effect extends, at least to a small extent, to the structures with maximum charge separation in 1-chloro-1-nitropropane is indicated by its considerable increase in moment over 1-chloro-1-nitroethane. It is to be noted that the resonance which has been proposed for these molecules gives rise to hyperconjugation.

It may be pointed out that the previously examined¹¹ moment of chloropicrin, 1.88, which must lie in the axis of symmetry of the Cl_3CNO_2 molecule, the C-N line, is very close to the difference between the moment of $(\text{CH}_3)_2\text{CNO}_2$ and that of Cl_3CCH_3 , $3.71 - 1.77 = 1.94$, as it should be, while if the moment of nitromethane, 3.50, is used in the calculation, the result is 0.15 lower than the observed instead of 0.06 higher. In view of the several effects involved, neither calculated value can be regarded as far from the observed.

Summary

The dielectric constants of the vapors of nitroethane, chloronitromethane, 1-chloro-1-nitroethane and 1-chloro-1-nitropropane have been measured and used to calculate the dipole moments of the molecules. As a check on the absolute accuracy of the determination, measurements have been made upon carbon dioxide, benzene, *n*-octane and water vapor, the results obtained being in excellent agreement with those already in the literature.

The moment of nitroethane is 0.20 higher than that of nitromethane and very close to those of α - and β -nitropropane and 2-methyl-2-nitropropane, confirming the indications of their values that the inductive effect is inappreciable beyond the first two carbon atoms of the molecular chain.

The considerable increases in moment from chloronitromethane to the ethane and from the ethane to the propane are attributed to increased stabilization of resonating polar forms by the distribution of the negative charge over two groups in the disubstituted compounds instead of its localization on one group as in the monosubstituted compounds.

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