[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Nitromethane: The Heat Capacity of the Gas, the Vapor Density, and the Barrier to Internal Rotation

BY KENNETH S. PITZER AND WILLIAM D. GWINN

The molecular structure of nitromethane is now rather completely known except for the potential barrier to internal rotation about the C–N bond. The electron diffraction investigation of Brockway, Beach and Pauling[1] gave the bond distances and angles, while the spectroscopic studies of Wells and Wilson[2] yielded all of the ordinary vibration frequencies. In this research the heat capacity of gaseous nitromethane was measured over the range 340–450°K. and at pressures from 0.11 to 1.0 atm. In order to check further on gas imperfection, the vapor density of nitromethane was measured over the range 380 to 425°K. From these data the heat capacity of the ideal gas was obtained and from it, the potential barrier to internal rotation.

Experimental Methods.—The nitromethane was purified by drying and fractionating in a 25 plate column at 16 cm. pressure. The heat capacity was measured in the flow calorimeter recently described by one of us.[3] Since the data of Eucken and Meyers[4] indicated that the gas imperfection of nitromethane was abnormal, it seemed desirable to measure the heat capacity at reduced pressures. The heat capacity of the ideal gas was then obtained by extrapolating linearly to zero pressure.

The calorimeter was adapted for measurements at reduced pressures by connecting the condensers to a pressure regulating device. This consisted of an 18-liter bottle as a reservoir which was connected to a vacuum pump through a solenoid valve. This valve was in turn operated by an electrical contact in a mercury manometer. The system was sufficiently free from leaks so that no appreciable change in pressure occurred during a run of about thirty minutes even if the regulator was disconnected.

The vapor densities were measured by the Dumas method, immersing the bulb in an oil thermostat.

Gas Heat Capacity.—The results of the gas heat capacity measurements are presented in Table I. The direct experimental data at various rates of flow are shown in Fig. 1 for all the measurements at 0.24 atm. It may be observed that the extrapolations to infinite rate of flow are quite definite, and that the data from the two thermometers after the heater lead to concordant re-

TABLE I

THE HEAT CAPACITY OF NITROMETHANE

Units: C_p in cal. per mole per degree, P in atm.

t, °C.		68	100	133	175
T, °K.		341	373	406	448
C_p	$P = 1.00$ exp.			18.12	18.8
	$P = 0.24$ exp.		16.70	17.17	18.33
	$P = 0.11$ exp.	15.86	16.38		
	$P = 0$	(15.25)	16.11	16.87	18.18
$C_{\text{t.}+\text{r.}+\text{vib.}}$		13.93	14.94	15.89	17.08
$C_{\text{I.R. exp.}}$		(1.32)	1.17	0.98	1.10
$C_{\text{I.R.}}$ calcd.	$V = 0$	0.99	0.99	0.99	0.99
	800	1.20	1.17	1.14	1.11
	1100	1.34	1.29	1.25	1.21
	4000	1.65	1.72	1.81	1.88
	8000	1.10	1.23	1.35	1.51
	10000	0.88	1.00	1.13	1.30
dC_p/dp exp.		...	2.5	1.25	0.6
dC_p/dp calcd.	(eq. 1)	4.1	2.2	1.24	0.69
	(eq. 2)	5.5	2.5	1.24	0.56

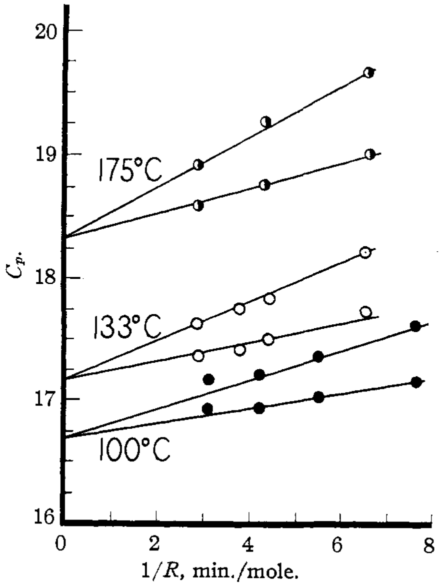

Fig. 1.—The apparent heat capacity of nitromethane at various rates of flow. All data are for 0.24 atm. The upper set of points for each temperature was obtained with a thermometer farther along the path of the gas than the thermometer giving the lower set of points.

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[1] L. O. Brockway, J. Y. Beach and L. Pauling, THIS JOURNAL, 57, 2693 (1935).

[2] A. J. Wells and E. B. Wilson, Jr., *J. Chem. Phys.*, 9, 314 (1941).

[3] K. S. Pitzer, THIS JOURNAL, 63, 2413 (1941).

[4] A. Eucken and L. Meyers, *Z. physik. Chem.*, B5, 452 (1929).

sults. The experimental results at 0.11 atm. were similar, while those at 1.0 atm. were somewhat less concordant than those shown in Fig. 1. The estimated uncertainty in the heat capacity values given in Table I is 0.2 cal. per degree.

The values for zero pressure were obtained by linear extrapolation of the experimental data at the three higher temperatures. The values of the slopes ($\mathrm{d}C_p/\mathrm{d}p$) are also given in Table I. These ($\mathrm{d}C_p/\mathrm{d}p$) values were extrapolated in a manner described below to give this quantity at 341°K. and thereby to correct the heat capacity at that temperature to zero pressure. This last extrapolation is necessarily somewhat uncertain; consequently one cannot rely with certainty on the value at 341°K.

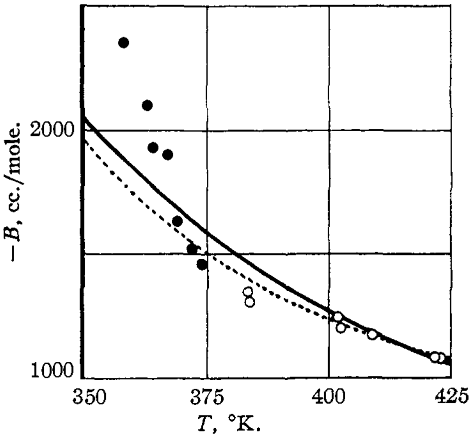

Fig. 2.—The second virial coefficient of nitromethane: solid circles, Eucken and Meyers[4]; open circles, this research; solid curve, equation 1; dotted curve, equation 2.

Gas Imperfection.—There are two kinds of information concerning the imperfection of gaseous nitromethane: first, the P, V, T work itself, and second, the values of $\mathrm{d}C_p/\mathrm{d}p$. Figure 2 shows the second virial coefficient, B, as derived from the vapor density measurements by the equation, $V = RT/P + B$. It is at once apparent that an ordinary equation of state cannot be fitted accurately to all the data of this research and that of Eucken and Meyers.[4] Furthermore, equations fitted to one series of data or the other fail to give values of ($\mathrm{d}C_p/\mathrm{d}p = -T\,\mathrm{d}^2B/\mathrm{d}T^2$) in agreement with our experimental ones. It is possible, however, to fit within reasonable limits the $\mathrm{d}C_p/\mathrm{d}p$ values and all the vapor density data above 368°K. from both researches. Since errors from adsorption are most likely to be serious at low temperatures, this appears to be the best solution of the problem. Figure 2 shows two curves calculated from equations 1 and 2, respectively, while the $\mathrm{d}C_p/\mathrm{d}p$ values are listed in Table I. In both equations the high temperature limiting value, $B = 100$ cc., was estimated from the volume of liquid nitromethane. Its exact value is of no consequence in the region of interest.

$$B = 100 - (1.95 \times 10^5/T)\ \mathrm{exp.}\ (1.65 \times 10^5/T^2)\ \mathrm{cc./mole} \quad (1)$$

$$B = 100 - (4.19 \times 10^5/T) - (1.91 \times 10^{23}/T^8)\ \mathrm{cc./mole} \quad (2)$$

The form of equation 1 has the justification that it was used by Keyes, Smith and Gerry[5] for steam and later by Keyes[6] for ammonia. Both of these gases, like nitromethane, have highly polar molecules. On the other hand, equation 2 appears to be a better empirical representation of the nitromethane data. Equation 2 was used to correct the heat capacity at 341°K. to zero pressure.

Heat of Vaporization.—In connection with the heat capacity measurements the value 8225 ± 25 cal. per mole was obtained for the heat of vaporization at the boiling point. This may be compared with the results of Mathews,[7] 8235, and of Philips and Waterton,[8] 8260.

Internal Rotation.—The heat capacity contributions from translation, rotation, and ordinary vibration were calculated by the usual methods and the total is listed in Table I for each of the four temperatures of the experiments. The vibration frequencies of Wells and Wilson[2] were used. The difference between the experimental heat capacity and this total is taken as the heat capacity due to internal rotation, since all other degrees of freedom are accounted for. This difference ($C_{\mathrm{I.R.}}$ in Table I) may then be compared with values calculated for barriers of various magnitudes. The tables previously published by one of us[9] were used for the calculations.

From the values of Table I it appears that 800 cal. per mole is the most probable value for the height of the barrier. However, any value in the range 0 to 1100 cal. per mole is acceptable. A possibility also exists that the barrier is between 8000 and 10,000 cal. per mole. In this region the calculated heat capacity rises sharply with increasing temperature, while the experimental

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(5) F. G. Keyes, L. B. Smith and H. T. Gerry, *Proc. Nat. Acad. Arts. Sci.*, **70**, 319 (1926).

(6) F. G. Keyes, THIS JOURNAL, **60**, 1761 (1938).

(7) J. H. Mathews, *ibid.*, **48**, 562 (1926).

(8) J. C. Philips and S. C. Waterton, *J. Chem. Soc.*, 2783 (1930).

(9) K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

values show a trend downward. Nevertheless, the range of our experiments is hardly sufficient to exclude barriers in this range. Barriers between 1100 and 8000 cal. and those above 10,000 cal. give, respectively, too large and too small heat capacities. It is, of course, also conceivable that an error is present in the vibrational assignment or that a very peculiar accumulation of errors has arisen in the treatment of our experimental data. If an experimental entropy value, possibly from low temperature heat capacity measurements, agrees with the 800 cal. barrier, these other possibilities will be definitely excluded.

Before discussing possible sources of a barrier to internal rotation in nitromethane, it seems best to reconsider briefly the ethane case in the light of all evidence now available. It now seems certain, not only that a barrier of about 2800 cal. per mole exists, but that the position of minimum energy is the staggered or *trans* configuration (symmetry D_{3d}). The evidence leading to the latter conclusion includes structures determined by electron diffraction or X-ray methods for *sym* $C_2H_4Cl_2$[10] and $C_2H_4Br_2$,[11] for 2,3-dibromobutane,[12] and for solid long chain paraffins.[13] All these molecules show the staggered configuration and most of them are known to have barriers to internal rotation of the same order of magnitude as ethane. Cyclopentane provides very important evidence. Consideration of the ordinary strain of C–C–C bond angles would predict that all five carbon atoms lie in a plane, whereas Aston, Schumann, Fink, and Doty[14] have found that the ring is actually puckered. The planar structure would place all C–C bonds in the opposed position with respect to internal rotation so that the puckering represents a tendency to escape from this position even at the expense of additional strain energy. The heats of combustion per CH_2 group of cyclopentane and cyclohexane confirm these conclusions, the former being greater by over 1000 cal. per mole.[15] Cyclohexane naturally assumes a puckered and staggered structure.

Although no really quantitative theory has yet been developed with respect to the potential barrier in ethane, it seems almost certain that the barrier arises from the repulsion of the electrons involved in the C–H bonds in the different methyl groups. This is just the same sort of repulsion as that which keeps different molecules from approaching one another too closely. An equivalent statement would be that the barrier arises from the repulsion of hydrogen atoms and from the distortion of the carbon atoms from axial symmetry induced by the hydrogen atoms.

Returning to nitromethane, this same sort of barrier might be present there. However, since there are now six equivalent positions per revolution of the methyl group, the height of the potential peaks above the valleys might be expected to be much less. Indeed, if the interaction of each oxygen atom with the methyl group should lead to a cosine potential curve, then the interactions of the two oxygens would exactly cancel.

The other probable source of barrier in nitromethane might be expected to be electrostatic interactions of the negative oxygens with positive hydrogens. However, assuming charges of $-0.5e$ and $+0.06e$, respectively, the height of the barrier calculated is only about 10 cal. per mole. Thus one merely concludes that the 800 cal. probable value and the 0 to 1100 cal. range is entirely reasonable from a theoretical point of view.

Entropy.—Making use of the 800 cal. value for the potential barrier determined above, together with the other molecular structure data mentioned,[1,2] a value can be calculated for the entropy of nitromethane. This is shown in Table II. The uncertainty shown in Table II allows for the 0 to 1100 cal. range in the potential barrier but makes no allowance for the other possibilities mentioned above.

TABLE II

ENTROPY OF NITROMETHANE AT 298.1°K. HYPOTHETICAL PERFECT GAS AT 1 ATM. PRESSURE

Translation and over-all rotation	61.75
Vibration	1.88
Free internal rotation	2.15
Correction for 800 cal. barrier	−0.14
$S^0_{298.1}$ =	65.64 ± 0.15 cal./deg. mole

Summary

The heat capacity of gaseous nitromethane was measured in the range 340–450°K. at pressures from 0.11 to 1.0 atm. The vapor density was also measured from 380 to 425°K., and the heat of vaporization at the boiling point. These data

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[10] J. Y. Beach and K. J. Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

[11] J. Y. Beach and A. Turkevich, THIS JOURNAL, **61**, 303 (1939).

[12] D. P. Stevenson and V. Schomaker, *ibid.*, **61**, 3173 (1939).

[13] C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

[14] J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, THIS JOURNAL, **63**, 2029 (1941).

[15] Personal communication from H. M. Huffman.

were combined with others from the literature to give the second virial coefficient, the heat capacity of the perfect gas, the barrier to internal rotation, and the entropy.

The general picture of the nature and cause of barriers to internal rotation is discussed briefly and applied to nitromethane.

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[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES]

Macromolecular Properties of Linear Polyesters. The Viscous Flow and Kinetic Interaction in Solution of ω-OH-Undecanoic Self-polyesters

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In a previous paper,[1] fourteen members of a polymer-homologous series of the self-polyesters of ω-OH-undecanoic acid have been characterized by several independent methods of molecular weight determination. Because of their linearity, accurately known molecular structure and known average size distribution, these compounds are excellent subjects for investigation of the viscosity of high polymeric solutions.[2–10] The present work is intended as a critical study over a range of concentration of the viscosity behavior of these well characterized polymers. The results obtained, which agree with published data on analogous compounds,[7,10] supplement and extend previous work. Thus, several properties of linear polymer solutions not heretofore emphasized, which are significant in the application of viscosity measurements to the determination of molecular weight, are treated.

Experimental Methods

The same compounds and techniques described previously[1] were employed. Each concentration was prepared separately by weighing, to avoid dilution errors. The tabulated concentrations are in grams per 100 cc. of solution. Where significant, the densities of the solutions were accounted for in the kinematic relative viscosity. Duplicate measurements were made repeatedly and particular care was taken to obtain precise values at low concentrations. As before,[1] measurements were at 25.00 ± 0.02° in reagent grade chloroform of uniform purity. The polymers were stable during all measurements. All samples contained their "natural" distribution of molecular weights, as encountered in practice. The deviations from linearity at the lowest concentrations in Fig. 1 are within the experimental error, which rises rapidly on dilution because of both low η_r and low c.

Results and Discussion

Table I includes representative values for the concentration dependence of the relative viscosities in chloroform of more than a hundredfold variation in chain length, from the monomer, ω-OH undecanoic acid, upward. The solution viscosity of linear polymers extrapolated to $c = 0$ is related to the average molecular weight by[7–10]

$$\ln \eta_r/c = K_w M_w + B \qquad (1)$$

The data appear in Fig. 1. The function $\ln \eta_r/c$, however, is evidently not concentration independent, even for polyundecanoate U1, of weight average molecular weight[1] $M_w = 5000$. This agrees with the observations of Lovell and Hibbert[11] on three monodisperse polyoxyethylene glycols, and with the majority of other literature data when examined by a similar plot. The slopes in Fig. 1 connote a polymer–polymer or polymer–solvent interaction increasing with chain length unaccounted for in any of the present configurational or hydrodynamic[12–16] solution viscosity theories. Also, from Fig. 1

$$\frac{d(\ln \eta_r)/c}{dc} = M_w + d \qquad (2)$$

which represents the simple relation of the concentration dependence of $\ln \eta_r/c$ to chain length.

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[1] Baker, Fuller and Heiss, THIS JOURNAL, **63**, 2142 (1941).

[2] Arrhenius, *Z. physik. Chem.*, **1**, 287 (1887).

[3] Berl, *Z. ges. Schiess- u. Sprengstoffe*, **4**, 81 (1909).

[4] Schidrowitz and Goldsborough, *J. Soc. Chem. Ind.*, **28**, 3 (1909).

[5] F. Baker, *J. Chem. Soc.*, **103**, 1653 (1913).

[6] Staudinger, *Ber.*, **65**, 267 (1932); "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

[7] Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

[8] Meyer and van der Wijk, *Helv. Chim. Acta*, **18**, 1067 (1935).

[9] Fordyce and Hibbert, THIS JOURNAL, **61**, 1912 (1939).

[10] Flory and Stickney, *ibid.*, **62**, 3032 (1940).

[11] Lovell and Hibbert, *ibid.*, **62**, 2140 (1940).

[12] Kuhn, *Z. physik. Chem.*, **A161**, 1, 247 (1932).

[13] Kuhn, *Kolloid. Z.*, **68**, 2 (1934); **76**, 258 (1936); **87**, 3 (1939).

[14] Haller, *ibid.*, **56**, 257 (1931); **61**, 26 (1932).

[15] See also E. Guth and H. Mark, *Monatsh.*, **65**, 93 (1934).

[16] Huggins, *J. Appl. Physics*, **10**, 700 (1939).