

The Constancy of Two Dipole Moments in the Vapor State and Their Apparent Variation in Solution

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the two which are much greater than the error in determining the absolute rate. It is therefore advisable perhaps, first of all to compare the velocity constants at some definite temperature. At 189.9°C we have

<i>Methyl</i>	$K = 0.97 \times 10^{-4} \text{ sec.}^{-1}$,
<i>Ethyl</i>	$K = 1.89 \times 10^{-4} \text{ sec.}^{-1}$,
<i>Propyl</i>	$K = 3.95 \times 10^{-4} \text{ sec.}^{-1}$.

Whence we have

$$K_{Me} : K_{Et} : K_{Pr} = 1 : 1.95 : 4.07.$$

In other words the rate is almost exactly doubled on going from one member to the next. This is also equivalent to stating that, if we assume that the variations in E are due to experimental error, then A is approximately doubled as we go from one member of the series to the next. It seems, however, very unlikely that E should remain constant while A varies in this way, since the variation in the collision number will be comparatively small. In any case, however, there is no doubt that E changes only very slightly as we go up the series.

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The Constancy of Two Dipole Moments in the Vapor State and Their Apparent Variation in Solution

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The validity of the solution method for the determination of dipole moment is considered with particular reference to the possible variation of moment with temperature. The moments of heptyl bromide and butyl chloride in the vapor state are found to be 2.07 ± 0.05 and 2.04 ± 0.01 , respectively, which show the absence of appreciable increase in moment in the normal alkyl chlorides and

bromides with increase in the length of the carbon chain beyond ethyl. Consideration of these values together with data for the alkyl halides in solution leads to the following estimated moment values for the vapor state: *n*-propyl bromide and *n*-butyl bromide, 2.04 ± 0.03 ; *n*-propyl iodide and *n*-butyl iodide, 1.93 ± 0.04 .

THESE measurements in the vapor state were made for the sake of careful comparison with previous measurements in solution upon two substances which apparently showed abnormally and improbably high values of the atomic polarization. The comparison takes on added interest now because of recent work on the effect of solvent upon the apparent value of a dipole moment determined in solution.

Because of the rise of the apparent value of the dipole moment determined in solution with rising temperature, Jenkins¹ has stated that measurements in solution cannot be used for studying the variation of the real moment with temperature. Obviously, a small variation of the apparent moment in solution with rising temperature is not to be taken as evidence of variation in the real moment of the molecule, nor has it been generally so regarded. Many apparent

small rises in moment from 25° to 50° in solution² have not been treated as significant. An abnormally large rise, however, in the case of diethyl succinate led to further investigation³ which established the reality of the effect along with the rise of moment with temperature in ethylene chloride and chlorobromide. At the same time, an apparent smaller rise for ethyl acetate was disregarded.

Obviously, as the real variation of moment with temperature depends upon the potential energy between the movable parts containing the dipoles, the presence of a solvent around the molecule may be expected to affect the effective value of the moment as well as its variation. Thus, the moments found for ethylene chloride,

² C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **53**, 527, 2115 (1931); *ibid.* **54**, 1854, 3230 (1932).

³ C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **53**, 4242 (1931).

¹ H. O. Jenkins, *Trans. Faraday Soc.* **30**, 739 (1934).

chlorobromide and bromide^{3, 4} in heptane solution are somewhat higher than those found for the vapors of these substances at the same temperatures⁵ and show a 50 percent greater increase with temperature. The moments in benzene solution are much higher and almost independent of temperature, presumably, because of some specific effect of the solvent.⁶ Ethylene chloride in solution in carbon disulfide, carbon tetrachloride and chloroform has moment values very slightly lower than in heptane⁶ and with temperature coefficients like that of the vapor. Because of the tendency toward variation with temperature of apparent moment values in solution, small differences in these temperature coefficients cannot be regarded as significant. Since no relation has been found between the apparent moment of ethylene chloride in solution^{6, 7} and the dielectric constant of the solvent, the moment being higher in solution than in the vapor state instead of lower as usually found, it is impossible to apply to these molecules with movable dipoles any of the empirical relations which have been developed between apparent moment and dielectric constant of the solvent. In the case of such molecules, it is obvious that the variation of polarization with temperature cannot be used to calculate the atomic polarization. Such values calculated by Smyth and Kamerling⁴ for four polymethylene bromides containing two movable dipoles were enclosed in parentheses and taken as evidence of variation of the moment with temperature which made the calculated atomic polarization impossibly high. These values should not, therefore, be cited as evidence of the incorrectness of the temperature-solution method of obtaining moments.¹

PURIFICATION OF MATERIALS

n-Heptyl bromide

Material from the Eastman Kodak Company was purified as in earlier work;⁸ n_D^{20} 1.45058.

⁴ C. P. Smyth and S. E. Kamerling, J. Am. Chem. Soc. **53**, 2988 (1931).

⁵ C. T. Zahn, Phys. Rev. **38**, 521 (1931); *ibid.* **40**, 291 (1932).

⁶ A. E. Stearn and C. P. Smyth, J. Am. Chem. Soc. **56**, 1667 (1934).

⁷ H. Müller, Physik. Zeits. **34**, 689 (1933).

⁸ C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. **52**, 2227 (1930).

Two samples were used in the dielectric constant measurements, identical results being obtained.

n-Butyl chloride

Material from the Eastman Kodak Company was refluxed gently with concentrated sulfuric acid, washed several times with water, dried over two portions of calcium chloride and distilled; b.p. 78.4–78.6°; n_D^{20} 1.40230. Repeated treatment did not change the refractive index.

EXPERIMENTAL RESULTS

The dielectric constants ϵ were determined with the apparatus previously described,⁹ heptyl bromide being measured in a copper cell and butyl chloride in a gold-palladium cell. The polarization P was calculated by means of the equation $P = [(\epsilon - 1)/(\epsilon + 2)]V$, in which V is the molar volume. For heptyl bromide, the polarization at each temperature was taken as the average of from three to eight measurements at pressures between 35 and 162 mm, the error caused by deviation from the ideal gas laws at these pressures being small. For butyl chloride, five to eight determinations at each temperature were made over a range of pressure extending to higher values and extrapolated to zero pressure to obtain a value P_0 which should be free from error due to gas law deviations. For heptyl bromide the temperature range of the measurements was so limited by the tendency toward thermal decomposition at higher temperatures that the dipole moment μ was calculated at each temperature by means of the equation $\mu = 0.01273[(P - MR_D)T]^{\frac{1}{2}}$, in which MR_D is the molar refraction for the D sodium line. The more accurate equation $P = a + b/T$ was applied to the butyl chloride results and the moment was calculated as $\mu = 0.01273 \times 10^{-18} b^{\frac{1}{2}}$, while the atomic polarization was obtained as $P_A = a - P_E$, the difference between a , the total induced polarization, and P_E , the molar refraction extrapolated to infinite wavelength.

DISCUSSION OF RESULTS

The two values previously found for the moment of heptyl bromide, 1.83 in heptane

⁹ K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. **55**, 453 (1933).

solution⁸ and 1.85 in benzene solution,¹⁰ were in excellent agreement, but the value obtained in heptane solution was calculated from the variation of the polarization with temperature. This method gave the high value 15.5 for the atomic polarization, values of this magnitude having since been shown to be incorrect,¹¹ and a correspondingly low value for the moment. When the moment is calculated from the value obtained by Smyth and Rogers for the polarization at each temperature by means of the equation $\mu = 0.01273[(P_{\infty} - MR_D)T]^{1/2}$, the values rise from 1.97 at 223°K to 2.02 at 303°K. One may apply to these data the empirical equation of Müller,⁷ $P_{M\text{gas}} = P_{M\text{sol}}/[1 - 0.075(\epsilon - 1)^2]$, where $P_M = P_{\infty} - MR_D$ and ϵ is the dielectric constant of the solvent. The moment values obtained from these values of P_M calculated for the gaseous condition increase from 2.05 at 223°K to 2.09 at 303°K. If 3.5 is added to the value 42.3 used for MR_D in order to account for the atomic polarization, the moment calculated for the gas from the liquid measurements increases from 2.02 to 2.04 over this range of temperature. The use of this value $P_E + P_A = 45.8$ to calculate the moment from the gas measurements gives a mean value 2.09. Since this is higher than the mean value 2.03 calculated in the same way from the empirically corrected solution values and since such deviations from the gas laws as may have occurred would tend to make the polarization and, hence, the moment values high, it seems reasonable to assign a value 2.07 ± 0.05 to the moment of heptyl bromide. The difference between this value and the accurate value 2.02 found for ethyl bromide vapor¹² is equal to the probable error in the determination.

The accurate values for butyl chloride in Table I show, as in the case of heptyl bromide, that the atomic polarization value 13.6 obtained from the variation of polarization in heptane solution with temperature⁸ was high and the moment value 1.88 correspondingly low. Calculation of the moment from these solution polarizations by subtraction of the molar refraction gives values rising from 1.98 at 183°K to 2.07

TABLE I. Polarizations and dipole moments.

<i>n</i> -Heptyl bromide			<i>n</i> -Butyl chloride	
<i>T</i> , °K	<i>P</i>	$\mu \times 10^{18}$	<i>T</i> , °K	<i>P</i> ₀
372.8	117.7	2.13	314.7	109.9
373.5	120.3	2.17	337.4	104.5
377.0	116.3	2.13	379.1	96.4
388.5	114.9	2.14	405.5	91.7
393.0	113.3	2.13	428.2	88.1 _s
395.5	115.5	2.17	479.6	82.0 _s
414.8	112.0	2.16	$a = 28.5, P_A = 3.6, \mu = 2.04 \times 10^{-18}$	
415.8	111.2	2.15		
423.3	110.0	2.16		
433.8	108.2	2.15		
Mean value = 2.15				

at 343°K. These values are close to those found by Parts,¹³ 1.97 at 283°K in benzene solution and the approximate value 2.00 calculated from a variation of polarization with temperature over a range of only 40°. Calculation of the polarizations in heptane to the vapor state by means of the Müller equation leads to moment values rising from 2.07 at 183°K to 2.13 at 343°K. If, however, the polarization values thus calculated to the vapor state are diminished by 3.0, the difference between the value of a in Table I and MR_D , the moment variation is reduced to a rise from 2.05 to 2.09 over this temperature range. These values are close to the accurate value 2.04 in Table I.

The identity of the moment of *n*-butyl chloride with the accurate value 2.04 found by Sängers¹⁴ for *n*-propyl chloride and the closeness of both values to the most accurate found for ethyl chloride, 2.05 by Fuchs¹⁵ and 2.02 by Sängers shows the absence of detectable increase in moment with increase in the length of the chain of the alkyl chloride beyond two carbons. The variation with temperature of the polarization of butyl bromide in solution in heptane⁸ gave a high atomic polarization 19.3 and a low moment 1.81. Calculation of the moment by subtracting the molecular refraction MR_D gives 1.97 at 183°K, identical with the value found by Parts at 283°K in benzene solution, and 2.08 at 343°K. Subtraction of an additional 3.5 to take care approximately of the atomic polarization and application of the Müller equation to these data

¹⁰ J. Errera and M. L. Sherrill, J. Am. Chem. Soc. **52**, 1993 (1930).

¹¹ C. P. Smyth, J. Chem. Phys. **1**, 247 (1933).

¹² C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **2**, 499 (1934).

¹³ A. Parts, Zeits. f. physik. Chemie **B7**, 327 (1930).

¹⁴ R. Sängers, Helv. Phys. Acta **3**, 161 (1930); Physik. Zeits. **32**, 20 (1931).

¹⁵ O. Fuchs, Zeits. f. Physik **63**, 824 (1930).

give 2.02 at 183°K and 2.09 at 343°K. The mean of these two values 2.06 is indistinguishable from the mean 2.07 found in similar fashion for butyl chloride. With the moment of ethyl bromide vapor 2.02,¹² it is probable that the moments of propyl and butyl bromide vapors differ by no more than 0.03 from 2.04, which differs by no more than the probable error from the value 2.07 here determined for heptyl bromide. The variation with temperature of the polarization of butyl iodide in solution⁸ gave a very high atomic polarization 21.9 and a correspondingly low moment value 1.59. Calculation of the moment from these data by use of the molecular refraction gives values rising from 1.80 at 193°K to 1.87 at 293°K. In view of the accurate value 1.90 for the moment of ethyl iodide vapor,¹² it is probable that the moments of *n*-propyl and of *n*-butyl iodide vapor differ from 1.93 by no more than 0.04.

It is evident from these calculations of apparent moment values at different temperatures in solution as well as from a tendency toward increase between values at 25° and 50° previously published² that, in many cases, the apparent value of the moment in solution increases with rising temperature. The change of polarization with temperature thus involved affects the slope of the $P-1/T$ curve so as to give too large a value of a and a correspondingly small value of b . Although the method of plotting polarizations in solution against $1/T$ has given satisfactory values for the moments in solution of chlorobenzene, chloroform¹⁶ and *tert*.-butyl chloride,¹⁷ it is evidently wholly unsatisfactory for the *n*-alkyl halides and cannot, therefore, be generally employed with safety.

In view of the dependence of the apparent polarization and moment of the solute upon the dielectric constant of the solvent found by

Müller,^{7, 18} it follows that the apparent value of a moment in solution should rise as the dielectric constant of the solvent decreases with rising temperature. Jenkins¹ has been able to account for increase in the apparent moment of nitrobenzene in solution in dekaline with rising temperature entirely by the effect of the decrease in the dielectric constant of the dekaline. However, the results of the calculations given in this paper show that in the case of heptyl bromide and butyl chloride, the effect of change in the dielectric constant of the solvent as calculated directly by Müller's equation accounts for only about one-third of the apparent variation. When allowance is made also for atomic polarization, the apparent variation is reduced to about one-half. The qualitative explanation previously given¹¹ for the incorrectness of the abnormally high atomic polarization values involves much the same fundamental idea as do these empirical equations for the effect of solvent. It may be said that the apparent moment found for a molecule in solution is influenced by the internal field acting on the molecule. Although the effect of this internal field, which decreases with rising temperature, is greatly reduced by extrapolation to infinite dilution and, sometimes, wholly eliminated by the further use of an empirical equation involving the dielectric constant of the solvent, a small error may yet remain in the moment values obtained from solution. As a matter of fact, this was shown by Müller's discovery that there were other substances in addition to those containing movable dipoles to which his equation did not apply. The failure to eliminate entirely this effect of the internal field may evidently have only a small influence upon the moment value determined at one temperature, but may seriously impair the accuracy of values determined from the variation of polarization with temperature.

¹⁶ C. P. Smyth and S. O. Morgan, *J. Am. Chem. Soc.* **50**, 1547 (1928).

¹⁷ C. P. Smyth and R. W. Dornte, *J. Am. Chem. Soc.* **53**, 545 (1931).

¹⁸ See also, H. O. Jenkins, *Nature* **133**, 106 (1934) and S. Sugden, *ibid.* **133**, 415 (1934).