[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Dielectric Studies. IX. Studies with Gasoline[1]

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In earlier papers[2] it was shown that dipole moment studies can be made using solvents of unknown molecular weights, such as gasoline, kerosene and petroleum ether, and that the dipole moment values so obtained are in close agreement with values obtained using non-polar solvents of known molecular weights. The assumption is made, of course, that gasoline, kerosene and petroleum ether are non-polar. In this study this assumption is put to rigorous experimental tests by determining the dipole moment of gasoline and its fractions.

Experimental

The dielectric constants were obtained by determining the capacity difference between rotor positions of a variable cell by means of a heterodyne beat apparatus. It consisted of two oscillators, "The Ferret Model 600" manufactured by the Coastwise Electronics, a Model 200 Signal Tracer manufactured by the Precision Electronics Inc. of Chicago, a precision condenser, Type 722-D, made by General Radio Co. and a dielectric cell. Purified benzene, the dielectric constant of which was assumed to be 2.273 at 25° and 2.254 at 35°, was used in calibrating the dielectric cell.

Refractive indices were measured with an Abbe refractometer with thermostated prisms. Densities were determined by the usual pycnometer method. All such measurements were made in thermostats regulated to 25° and 35°.

For dipole moment determinations the gasoline samples used were taken at random, had a yellowish color and were used without purification. Sample A was separated into eight fractions. The molecular weights of gasoline and the fractions were determined by the usual cryoscopic method in benzene of 5.4° f. p. A summary of the results is presented in Table I.

TABLE I

RESULTS ON GASOLINE AND FRACTIONS AT 25°

Temp., °C.	Mean values aE_1	b	$P_{2(\infty)}$	P_{2D}	$\mu \times 10^{18}$
Gasoline, sample A boiling fraction: below 60	−0.58	−0.34	21.3	21.3	0
60–70	.43	.30	24.8	24.3	.15
70–100	.42	.26	30.8	30.6	.09
100–120	.40	.25	35.1	33.9	.22
120–140	.37	.21	35.7	35.2	.15
140–160	.26	.12	38.2	38.3	0
160–190	.25	.14	39.9	39.3	.17
Above 190	.18	.13	43.3	41.3	.31
Gasoline, sample B, undistilled	.34	.20	43.4	42.8	.17

In Table I the constants a and b are the dielectric constant and density coefficients, respectively, in the expressions

$$E = E_1(1 + aw_2) \quad (1)$$

$$d = d_1(1 + bw_2) \quad (2)$$

where E_1 and d_1 are the dielectric constant and density of the pure solvent; E and d are the dielectric constant and density, respectively, of a mixture of gasoline of weight fraction w_2 dissolved in benzene. The weight fractions of the solute, gasoline, vary from 0 to about 0.08. $P_{2(\infty)}$ is the molar polarization at infinite dilution and is given by the equation

$$P_{2(\infty)} = (p_1(1 - b) + CaE_1)M_2 \quad (3)$$

where p_1 is the specific polarization of the solvent, $C = 3/d_1(E_1 + 2)^2$, and M_2 is the molecular weight of the solute.[3] The values of p_1 and C used in this paper are those for benzene and equal to 0.3412 and 0.1882, respectively.

As shown in Table I, with the exception of the highest boiling fraction which boils above 190°, the fractions from gasoline, sample A, have dipole moments ranging from 0 to 0.2×10^{-18} and are therefore essentially non-polar. The presence of the small apparent moment values in some of the fractions is understandable since the percentage error in $[P_{2(\infty)} - P_{2D}]$ is large when the difference is very small. Traces of polar impurities in the higher fractions, which are colored yellow, may also account for the small moments. In earlier papers where gasoline has been used for dipole moment determinations only the colorless grade was used and the assumption was made that it was non-polar. In this study we have used, for the first time, yellowish samples of gasoline and the result shows that the assumption is essentially correct and justifies the close agreement of dipole moments with those using non-polar solvents of known molecular weights.

The polarity of a compound is also indicated by the difference between the square of the refractive index and the dielectric constant. We have taken at random another sample of gasoline, fractionated it, determined the density, refractive index and dielectric constant of each fraction. The results are shown in Table II.

From the table it is seen that in three cases there is an exact equivalence between n^2_D and E and that the maximum difference between the two quantities is only 0.023 in the highest boiling fraction. This agrees with the results of Table I in

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(2) See for example Li and Chu, THIS JOURNAL, 69, 558 (1947); Li, An and Wu, *ibid.*, 69, 2558 (1947).

(3) For a discussion of these equations see ref. 1 of this paper.

TABLE II

DENSITY, SQUARE OF REFRACTIVE INDEX, DIELECTRIC CONSTANT OF GASOLINE AT 35°

Temp., °C.	d	n^2_D	E	$E - n^2_D$
Original sample of gasoline	0.7349	2.002	2.012	0.010
Boiling fraction: 60–90	.6782	1.909	1.909	0
90–100	.6933	1.937	1.937	0
100–120	.7164	1.960	1.960	0
120–140	.7257	1.987	1.990	0.007
140–160	.7449	2.008	2.021	.013
160–180	.7619	2.033	2.050	.017
Above 180	.7910	2.074	2.097	.023

that the highest boiling fraction has relatively the highest dipole moment of all fractions, namely, 0.31×10^{-18}. Benzene and carbon tetrachloride have frequently been used as non-polar solvents in dipole moment determinations. The difference in n^2_D and E for benzene and carbon tetrachloride at 25° are, however, 0.037 and 0.114, respectively. According to this criterion, gasoline should be more non-polar than benzene or carbon tetrachloride.

Table III lists the dipole moment values which have been obtained using gasoline and similar solvents of indefinite molecular weights and the values obtained for the same compounds using solvents of known molecular weights.

TABLE III

DIPOLE MOMENT AT 25°[a]

Castor oil	in gasoline 3.62×10^{-18}	in benzene 3.7×10^{-18}
Tung oil	kerosene 2.92	benzene 2.9
Di-*n*-butyl ether	kerosene 1.17	benzene 1.22
		toluene 1.13
Ethyl-*n*-butyl ether	kerosene 1.19	benzene 1.24
Acetone	gasoline 2.8	benzene 2.72
Chloroform	gasoline 1.16	benzene 1.15
Acetonitrile	gasoline 3.33	benzene 3.37
	kerosene 3.35	toluene 3.38
	petroleum ether 3.35	

[a] The values for castor oil and tung oil are taken from Li, *J. Chinese Chem. Soc.*, **13**, 8 (1946); the values for the ethers from Li and Hsü, *ibid.*, **13**, 11 (1946); the other values are from Ref. 1 of this paper.

Summary

Dipole moment can be measured using gasoline as solvent, a substance which has no definite molecular weight and whose physical properties may vary greatly with different samples. Experimental results indicate that gasoline and its fractions are essentially non-polar. A summary of the dipole moment values obtained using gasoline and similar solvents of indefinite molecular weights is given and shown to be in close agreement with values obtained using non-polar solvents of known molecular weights.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Catalytic Decomposition of Ethane and Ethane–Hydrogen Mixtures

BY CHARLES KEMBALL[1] AND HUGH STOTT TAYLOR

The work of Morikawa, Benedict and Taylor[2,3] and of Morikawa, Trenner and Taylor[4] showed that the exchange reactions between the lower hydrocarbons and deuterium on supported nickel catalysts could be brought about at lower temperatures than the decomposition reactions. The energy of activation for the breaking of the carbon–hydrogen bond was some 15 kcal./mole less in the case of propane, than that for the breaking of the carbon–carbon bond. There is little doubt that the exchange reaction involves dissociative adsorption of the hydrocarbon, *e. g.*, as ethyl radical and hydrogen atom, and re-evaporation of the ethyl with a deuterium atom. Much less can be conjectured about the decomposition reaction and it was considered worthy of further study. Morikawa and his co-workers showed that, over a certain range of composition, the rate of production of methane from ethane and hydrogen depended inversely on the 2.5 power of the hydrogen pressure. This point required further investigation because it is difficult to see the kinetic interpretation of such a dependence. Accordingly it was decided to extend their investigation to a wider range of composition for the reacting mixture and further to study the decomposition of ethane in the absence of hydrogen.

Experimental

Analysis.—The reaction was followed by the withdrawal of a sample of gas and analysis by means of a mass spectrometer. The height of the mass 30 peak was determined solely by the ethane concentration and the mass 16 peak was almost entirely due to the methane. A small correction was made for the mass 16 in the ethane pattern; this amounted to 0.004 of the height of the "30 peak." In order to allow for fluctuations in the behavior of the instrument and to avoid the difficulty of using a constant pressure behind the leak of the spectrometer, the ratio of the "16 peak" to the "30 peak" was always measured. A series of known mixtures of ethane, methane and hydrogen were used to obtain calibration curves giving the ratio methane/ethane in terms of the ratio "16 peak"/"30 peak." The curve was linear up to 0.7 for methane/ethane, and was not greatly affected by the presence of hydrogen in the mixture. It was possible to estimate the amount of methane in a mixture to closer than 2% in this manner. A static system was used to follow the reaction and checks were made that the samples withdrawn were representative of the whole reacting gas.

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(1) Commonwealth Fund Fellow, Princeton University, 1946–1947.

(2) Morikawa, Benedict and Taylor, THIS JOURNAL, **58**, 1445 (1936).

(3) Morikawa, Benedict and Taylor, *ibid.*, **58**, 1795 (1936).

(4) Morikawa, Trenner and Taylor, *ibid.*, **59**, 1103 (1937).