[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CATHOLIC UNIVERSITY, PEIPING, CHINA]

Dielectric Studies. VII. Dipole Moment of Acetonitrile in Solvents of Unknown Molecular Weights

BY NORMAN C. C. LI[1] AND TING-LI CHU

A search of the existing dipole moment literature shows that no studies have been made using solvents of unknown molecular weights. To find the dipole moment of a polar substance the usual method has been to dissolve it to low concentrations in a non-polar solvent of known molecular weight. The molar polarization P_2 of the solute molecules for each concentration is then calculated by means of the equation

$$P_{12} = \frac{E-1}{E+2}\frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2 \qquad (1)$$

in which P_{12} is the total polarization of the solution, E the measured dielectric constant and d the density of the solution; f_1 and f_2 are the mole fractions of the non-polar solvent and polar solute, respectively, whose molecular weights are M_1 and M_2; P_1 and P_2 are the molar polarizations of solvent and solute, respectively. It is seen from this equation that the molecular weight of the non-polar solvent used must be known before a dipole moment value can be given for the solute.

During the last four years the senior author of this paper and his students have examined over ten compounds of widely different nature dissolved in non-polar solvents of unknown molecular weights and have found the dielectric constant of the mixture $E_{1,2}$ and density of the mixture $d_{1,2}$ to be linear functions of the weight fraction of solute w in every case as long as w is less than about 0.08.[1a] The following expressions may therefore be written

$$E_{1,2} = E_1\,(1 + aw_2) \qquad (2)$$

$$d_{1,2} = d_1\,(1 + bw_2) \qquad (3)$$

where E_1 and d_1 are the dielectric constant and density of the pure solvent, respectively, a and b the dielectric constant and density coefficients, respectively. The expression originally introduced by Le Fevre and Vine[2] may therefore be used to calculate the molar polarization at infinite dilution $P_{2(\infty)}$ of a solute dissolved in a solvent of unknown molecular weight. The equation is

$$P_{2(\infty)} = [p_1\,(1 - b) + CaE_1]M_2 \qquad (4)$$

where p_1 is the specific polarization of the solvent, ($p_1 = (E_1 - 1)/(E_1 + 2)d_1$) and $C = 3/d_1(E_1 + 2)^2$, M_2 is the molecular weight of the solute. It is readily seen from this equation that a knowledge of the molecular weight of the non-polar solvent used is not necessary in calculating molar polarization and dipole moment. In this paper we report dipole moment determinations of acetonitrile using gasoline, kerosene, and petroleum ether as non-polar solvents of unknown molecular weights and compare the values obtained with values calculated from published data for solutions of the same compound in benzene.

Experimental

Procedure and Apparatus.—The dielectric constants were obtained by determining the capacity difference between rotor positions of a variable cell by means of a heterodyne beat apparatus similar to one used by Li and Williams.[3] It consisted of a standard oscillator beating against a variable oscillator, the frequency of which was controlled by a variable condenser in parallel with the dielectric cell. The beats between these two oscillators reached a phone through a detector and amplifier circuit. The dielectric cell and precision condenser were made in the physics department of Yenching University and carefully calibrated. Purified benzene, the dielectric instant of which was assumed to be 2.273 at 25°, was used in calibrating the dielectric cell.

Refractive indices were measured with an Abbé refractometer with thermostat prisms. Densities were determined by the usual pycnometer method. All such measurements were made in a thermostat regulated to 25 ± 0.01°.

Materials.—Acetonitrile was prepared by interaction between phosphorus pentoxide and acetamide and purified in the usual manner; b. p. 81.6°, d^{25}_4 0.7772, n^{25}_D 1.3418. Kerosene was extracted twice with one-tenth its volume of 15% sodium hydroxide solution, washed with water, dried over calcium chloride and distilled. Gasoline and petroleum ether were of the colorless grade and were used without further purification. Benzene of C. P. "thiophene-free" grade was subjected to a rigorous purification according to Weissberger and Proskaer.[4]

TABLE I

ACETONITRILE IN GASOLINE

W_2	E	d	a	b
0.00000	2.023	0.7497		
.01371	2.329	.7501	11.04	0.0389
.02819	2.657	.7504	11.11	.0339
.03135	2.725	.7506	11.07	.0383
.05821	3.330	.7513	11.10	.0367
.06192	3.411	.7514	11.08	.0366
			Mean 11.08	Mean .0368

TABLE II

ACETONITRILE IN KEROSENE

w_2	E	d	aE_1	bd_1
0.00000	2.098	0.7994		
.01423	2.454	.7991	25.02	−0.0211
.02675	2.767	.7988	25.01	.0224
.03358	2.939	.7986	25.05	.0238
.04132	3.132	.7985	25.02	.0218
.05215	3.404	.7982	25.04	.0230
			Mean 25.03	Mean − .0224

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(1) Present address: Department of Chemistry, St. Louis University.

(1a) Some of these results are being published in *J. Chinese Chem. Soc.*

(2) Le Fevre and Vine, *J. Chem. Soc.*, 1805 (1937).

(3) Li and Williams, *J. Phys. Chem.*, **41**, 1171 (1937).

(4) Weissberger and Proskaer, "Organic Solvents," Clarendon Press, Oxford, 1935.

TABLE III

ACETONITRILE IN PETROLEUM ETHER

w_2	E	d	aE_1	bd_1
0.0000	2.031	0.6528		
.01236	2.277	.6543	19.90	0.121
.02151	2.458	.6558	19.85	.139
.02863	2.600	.6563	19.87	.122
.04211	2.868	.6580	19.87	.124
.05627	3.149	.6598	19.86	.124
			Av. 19.87	

TABLE IV

SOLVENT CONSTANTS

	Gasoline	Kerosene	Petroleum ether
$C(= 3/d_1(E_1 + 2)^2)$	0.2473	0.2235	0.2828
$p_1 = (E_1 - 1)/(E_1 + 2)d_1)$	.3392	.3354	.3918

The results of the experimental work are presented in Tables I, II, III and IV. The dielectric constant data are accurate to about 0.1%.

Taking the molecular weight of acetonitrile as 41.05 and using equation (4), the values of $P_{2(\infty)}$ are calculated to be 241, 243.8, 243.8 for acetonitrile dissolved in gasoline, kerosene and petroleum ether, respectively. For pure acetonitrile the deformation polarization

$$\left(P_{2D} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}\right)$$

is calculated to be 11.12. Dipole moments are calculated by the formula

$$\mu = 0.01273 \times 10^{-18}\sqrt{(P_{2(\infty)} - P_{2D})T}$$

and the values obtained are 3.33, 3.35 and 3.35 × 10^{-18} for acetonitrile dissolved in gasoline, kerosene and petroleum ether, respectively.

The value for the dipole moment of acetonitrile in benzene solution has been reported by Lewis and Smyth[5] to be 3.51 × 10^{-18}. We have recalculated their results using the extrapolation method of Hedestrand,[6] and found the dipole moment value to be 3.37 × 10^{-18},[7] in agreement with the results we obtained using gasoline, kerosene and petroleum ether as solvents. Hedestrand's method was used because we found the dielectric constants and densities of the series of acetonitrile solutions in benzene to vary linearly with concentration. The dipole moment of acetonitrile in toluene, another solvent of known molecular weight, at 25°, as interpolated from the data of Lewis and Smyth, is found to be 3.38, again in agreement with our values using three different solvents of unknown molecular weights.

Summary

Data obtained indicate that dielectric constant and density of dilute solutions of polar solute in non-polar solvents of unknown molecular weights are linear functions of weight fractions of the solute. This suggests the use of non-polar solvents of unknown molecular weights for dipole moment determinations. Dipole moment values obtained for solutions of acetonitrile in gasoline, kerosene and petroleum ether are in close agreement with values obtained using nonpolar solvents of known molecular weights.

[5] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[6] Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[7] Subsequently Professor Smyth informed the senior author of this paper of the correctness of the recalculated value.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Continuous Method for the Preparation of Cadet's Liquid[1]

BY REYNOLD C. FUSON AND WILLIAM SHIVE[2]

Cadet's liquid is for the most part a mixture of cacodyl oxide and cacodyl.[3] The original procedure[4] for its preparation, which has continued in use for nearly two centuries with little modification, consists in heating a mixture of potassium acetate and arsenic trioxide at temperatures in the neighborhood of 325° and affords yields of not more than 17%. We have found that much better yields can be obtained by passing a mixture of arsenic trioxide and acetic acid over an alkali metal acetate catalyst at temperatures of 300–400°. The new procedure has the additional advantage of being continuous except for occasional regeneration of the catalyst.

Experimental

Procedure.—The apparatus consisted of a Pyrex tube (60 cm. × 16 mm.) arranged and equipped as shown in Fig. 1. The catalyst was placed in the portion of the tube surrounded by the electrical heating unit and held in place by an asbestos plug. The arsenic trioxide was placed just above the heating unit and extending along the tube for about 20 cm. The jacket surrounding this portion of the tube was connected to a 200-ml. flask containing phenyl ether, which was maintained at a boiling rate sufficiently high to give condensing vapors in the condenser. After the entire apparatus was swept with carbon dioxide, heating of the arsenic trioxide and addition of acetic acid from a dropping funnel were begun simultaneously. When

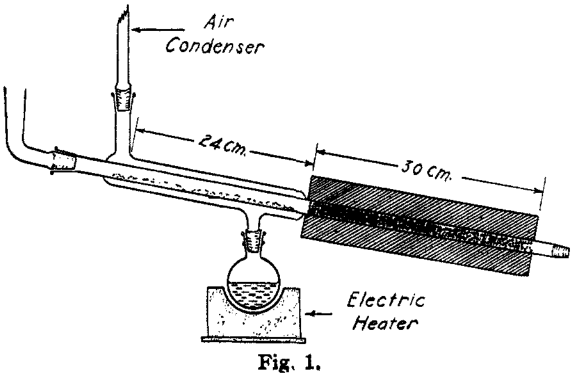

Fig. 1.

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[2] Present address: Department of Chemistry, University of Texas, Austin, Texas.

[3] Valeur and Gaillot, *Compt. rend.*, **185**, 956 (1927).

[4] Cadet de Gassicourt, *Mem. savants étrangers*, **3**, 633 (1760).