[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOYOLA UNIVERSITY OF CHICAGO AND THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY]

THE EFFECT OF THE DIELECTRIC CONSTANT OF THE SOLVENT ON THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME NON-AROMATIC KETONES

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In the past three decades, numerous workers (1–18) have been concerned with the effects of the solvent on the positions and intensities of absorption of the maxima of various molecules. Some correlations and generalizations have been made, but, in essence, no simple over-all picture can be drawn.

In view of the past work in this field, it seems highly unlikely that *any* simple explanation could be found to organize the entire subject into one of order and regularity. For this reason, it seems that information would be significant if obtained in various simple systems using solvent pairs, or possibly other combinations. Then, it should be possible to correlate a series of experiments in which a compound is dissolved in a system whose dielectric constant can be varied without causing much change in the chemical nature of the solvent. In this way, we would eliminate the effects of wide divergence in the chemical constitution of the various solvents.

To this end we chose the simple non-aromatic ketone series, using acetone (dimethyl ketone, DMK), methyl ethyl ketone (MEK), methyl *n*-propyl ketone (MPK), methyl isobutyl ketone (MIBK), and methyl cyclopropyl ketone (MCPK), and chose as the solvents, water, dioxane, and convenient mixtures of water-dioxane, for which the dielectric constants are known (19).

Table I shows a list of the physical properties of these ketones and Table II shows the positions of the maxima and the intensities of absorption of the maxima in water, dioxane, and 75:25, 50:50, 25:75 water-dioxane gram-weight mixtures of known dielectric constant. Fig. 1 shows a plot of log ϵ of the maxima of the ketones *vs.* the dielectric constant of the medium and Fig. 2 shows a plot of the λ_{max} of the ketones *vs.* the dielectric constant of the medium.

DISCUSSION

In the λ_{max} *vs.* dielectric constant plot, we see that there is a general trend in every case with the λ_{max} diminishing as the polarity of the solvent increases. It is probable that the dipoles associated with the solvent molecules tend to become associated with the non-binding electrons of the carbonyl group. Since excitation of these electrons is probably responsible for the main absorption at approximately 280 mμ by the carbonyl group, it seems likely that solvent interaction would cause a shift towards shorter wave lengths by making it necessary to supply a greater amount of energy to excite these partially bound electrons.

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TABLE I

PROPERTIES OF THE KETONES USED IN THIS WORK

	DMK[a]	MEK	MPK	MCPK	MIBK
B.P., °C.	54.8	76.9–77.1	101.0	110.1–110.3	112.4–112.6
PRESSURE, MM.	742	746	745	747	737
n_D^{25}	1.3560	1.3762	1.3861	1.4224	1.3933
d_4^{25}	0.7850	0.8014	0.8023	0.8938	0.7964

[a] The ketones used were: acetone (DMK), methyl ethyl ketone (MEK), methyl *n*-propyl ketone (MPK), methyl cyclopropyl ketone (MCPK), and methyl isobutyl ketone (MIBK).

TABLE II

ABSORPTION MAXIMA OF KETONES IN SOLVENT MIXTURES

SOLVENT	D	DMK[a]		MEK		MPK		MCPK		MIBK	
		log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}
H_2O, 100%	78.5	1.27	265.0	1.30	267.5	1.35	271.0	1.50	261.0	1.46	271.0
H_2O, 75% Dioxane, 25%	57.0	1.18	265.5	1.28	268.0	1.33	272.5	1.45	264.0	1.43	273.0
H_2O, 50% Dioxane, 50%	34.0	1.17	270.0	1.26	270.5	1.31	273.5	1.42	267.0	1.38	275.0
H_2O, 25% Dioxane, 75%	14.4	1.16	273.0	1.24	273.0	1.30	275.5	1.37	271.0	1.33	278.0
Dioxane, 100%	2.1	1.15	277.0	1.23	277.0	1.29	279.0	1.33	275.0	1.31	281.0

[a] Abbreviations for ketones are the same as in Table I.

The degree of bonding with the solvent molecules would be proportional to the strength of the solvent dipoles, which, in turn, is related to the value of the dielectric constant. Therefore, as the dielectric constant increases, in this case, it might be expected that the main absorption band would be shifted to shorter wave lengths.

The curves in Fig. 2 are in the general order of increasing molecular weights, DMK, MEK, MPK, and MIBK, with MCPK decidedly out of order, as it is below DMK. It is interesting to note that whereas, in pure water, the log ε for acetone is apparently abnormal, the λ_{max} is *not* and follows the general trend shown by all the ketones examined in this work.

In the log ε *vs.* D plot, the slopes for the straight-chain ketones, DMK, MEK, and MPK are almost identical, whereas the slopes for the branched-chain ketone, MIBK and the alicyclic ketone, MCPK, are quite similar, but different from that of the straight-chain ketones.

It is also interesting to note that there is, in general a direct relationship between the molecular size of the ketone and the intensity of absorption, being in the order of DMK, MEK, MPK, MIBK, and MCPK. In this regard, MCPK seems somewhat out of place.

Also, it seems that in the case of DMK, although there is linearity over a

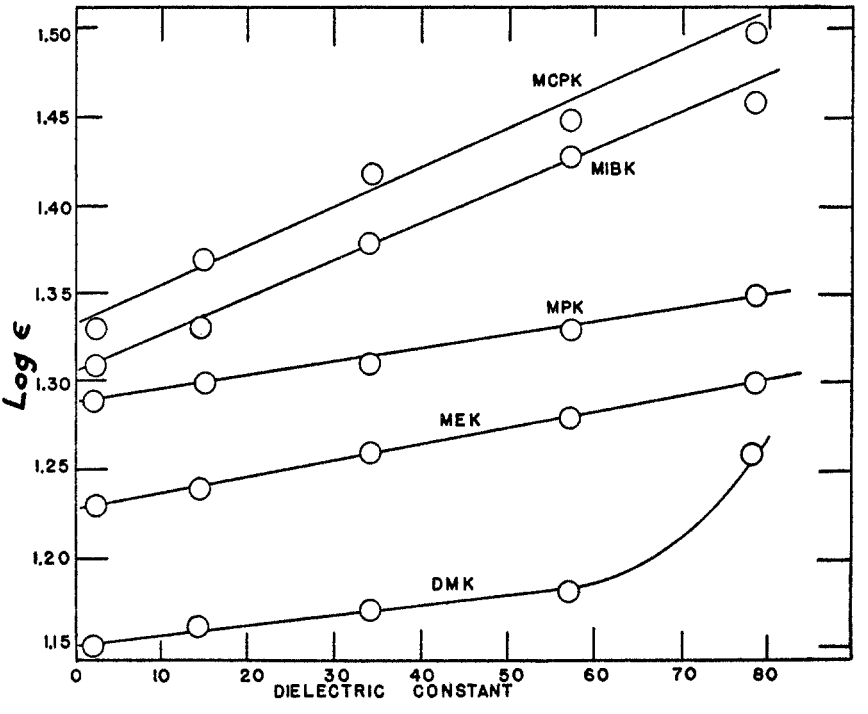

FIG. 1

wide range of dielectric constant, the log ϵ of acetone in pure water is distinctly out of line.

A word of caution should be given about over-extending the picture. For example, in the case of MIBK, figures (11) for isoöctane (D = 1.96) as a solvent show the λ_{max} = 283 mμ and log ϵ = 1.30, and for ethanol as a solvent (D = 25.0) figures show that λ_{max} = 279 mμ and log ϵ = 1.35. These figures fall reasonably well on the curves shown in Figs. 1 and 2. However, in the case of MCPK, figures for isoöctane as a solvent show that λ_{max} = 277 mμ and log ϵ = 1.28 and for ethanol as a solvent, λ_{max} = 271 mμ and log ϵ = 1.37, and these figures are distinctly and uniformly *off* the curves in Figs. 1 and 2.

Since in all the compounds tested, CH_3COR, we have a methyl ketone group, and since the chief variation in structure is the nature of the R group, the effects of the various changes in the structure of the R group should be correlated with the changes in the polarity of the solvent. One of the important factors is the orientation of the ketone molecules amongst the solvent molecules, and this depends on the size and nature of the R groups. It may be that as the solvent changes drastically from water-dioxane combinations to pure ethanol or pure isoöctane, the various R groups reorganize or reorient themselves with respect to the different sized and constituted solvent dipoles and this causes varying degrees of stability of the ground and excited states, thus resulting in the fluctuations observed by the various workers. It may be that while working in only a

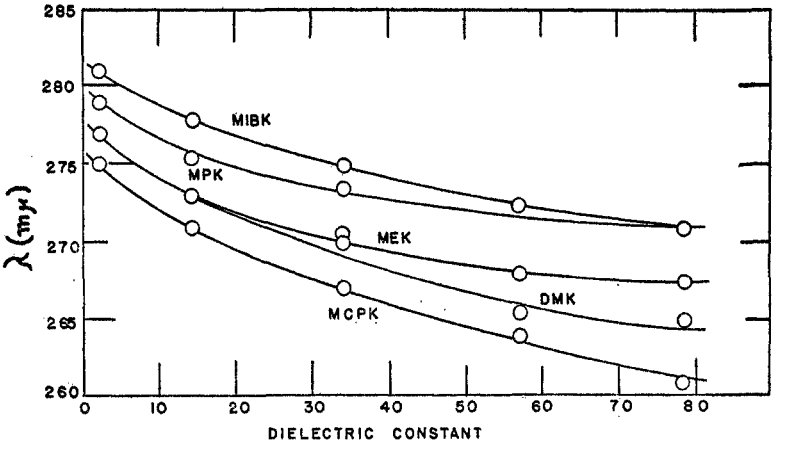

FIG. 2

variable solvent-pair combination, we are avoiding any drastic solvent solute orientation effect, which although not of tremendous value is appreciable and can be observed.

In the case of the effects of the cyclopropyl group, perhaps the unusual spectral properties of the three-membered ring may be attributed to its particular rigidity and the resultant difficulty of the solvent molecules to orient themselves or slip past this ring structure.

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EXPERIMENTAL

Ketones. Samples of the ketones were obtained from commercial sources and were carefully purified by distillation through a 70-plate Podbielniak column. Distillation was carried out for a period of time sufficient to reach equilibrium at reflux ratios of from 100:1 to 400:1. The boiling temperatures recorded were maintained for 15 minutes prior to collecting the sample. The samples were kept under anhydrous conditions.

Solvents. Dioxane. The dioxane was purified by the method of Weissberger (20), which consisted in refluxing a mixture of dioxane and sodium for 10 hours. The distilled material was stored under nitrogen. The m.p. of the dioxane was 10.5°.

Water. A dilute solution of potassium permanganate was refluxed for several hours and then distilled. Carbon dioxide was excluded from the system with potassium hydroxide.

Method. Spectra were determined with a Beckman spectrophotometer, model DU. The concentration of the ketones was 2×10^{-2} M. The water and dioxane were weighed in large quantities and then mixed to give the desired ratios. All solutions were stored under nitrogen. Extinction coefficients were calculated from the equation

$$E = d/cl$$

where c is the concentration of the solute, in moles per liter; l is the thickness of the cell, in centimeters; and $d = \log_{10} (I_0/I)$. I_0 is the intensity of light passing through the solvent, and I is the intensity of light passing through the solution.

SUMMARY

The ultraviolet absorption maxima of acetone, and methyl ethyl, methyl *n*-propyl, methyl isobutyl, and methyl cyclopropyl ketones were determined in water, dioxane, and water-dioxane mixtures of known dielectric constant. There is a linear relationship between log ϵ of these non-aromatic ketones and the dielectric constant, (acetone in pure water seems to be an anomalous case). There also are definite trends of the λ_{max} of the ketones as the dielectric constant of the medium is changed.

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