THE CAVITY RADIUS AND THE MEAN POLARIZABILITIES OF DIAZINES ESTIMATED FROM ELECTRONIC ABSORPTION MEASUREMENTS*

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The empirical values α/a^3 (α — the polarizability, a — the Onsager cavity radius) for pyrazine, pyrimidine and pyridazine were determined. From these values and for the cavity radius determined by spectroscopic measurements, the mean polarizabilities were calculated.

A knowledge of the cavity radius a of solute molecules and their polarizabilities are indispensable for investigations of the electrical and optical properties of these molecules In particular, a knowledge of these parameters is necessary to determine the dipole moments in various excited states [1–3]. Several reports on spectroscopic properties of diazines have recently appeared [4–6]. We have determined the cavity radius a for this class of molecules as the mean value of the cavity radius for pyrimidine and pyridazine. Based on this value and on the values α/a^3, the mean polarizability values α were found for the molecules studied.

Pyrazine and pyrimidine (Fluka AG) and pyridazine (Loba Chemie) were used as obtained. The solvents n-heptane, n-butanol, izopentane, cycloheptane were of spectral quality and were used without further purification. The absorption spectra at 20°C were measured using a Beckman Model 25 spectrophotometer. The refraction indexes of the solutions at 20°C were determined by means of an Abbe refractometer.

The Onsager cavity radius a of the solute molecule can be determined based from absorption spectra measurements in a mixture of polar and nonpolar solvents. According

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to Gorodyskii and Bakhshyev [7] the value a of the absorbing molecules can be determined from the relative absorption shift:

$$\Delta\tilde{\nu}_A^{rel} = \frac{\tilde{\nu}_A^I - \tilde{\nu}_A}{\tilde{\nu}_A^I - \tilde{\nu}_A^{II}} = \frac{x}{(1-x)\exp(-B)+x}, \tag{1}$$

where

$$B = \frac{\mu_g^2}{a^3}\frac{C_{II}-C_I}{kT} - l\frac{\langle\mu_s^{II}\rangle^2}{a_s^3}\frac{C_{II}}{kT} + l\frac{\langle\mu_s^{I}\rangle^2}{a_s^3}\frac{C_I}{kT}, \quad\text{and}\quad C_{I,II} = \frac{\varepsilon_{I,II}-1}{\varepsilon_{I,II}+2}.$$

Terms I and II refer to nonpolar and polar solvents respectively. μ_g is the ground-state dipole moment of the solute and $\langle\mu_s^I\rangle$ and $\langle\mu_s^{II}\rangle$ are the average values of dipole moments of the solvent molecules I and II (for their determination see [7]), a_s is the Onsager cavity radius of the solvent molecules, l an empirical parameter ($l = 1$), and x is the mole fraction of the polar solvent in nonpolar/polar mixtures. ε_I and ε_{II} are the dielectric constants of nonpolar and polar solvents, respectively.

Plotting $\ln\left(\dfrac{1}{\Delta\nu_A^{rel}} - 1\right)$ as a function of

$$\ln\left(\frac{1}{x}-1\right) + l\frac{\langle\mu_s^{II}\rangle^2}{a_s^3}\frac{C_{II}}{kT} - l\frac{\langle\mu_s^I\rangle^2}{a_s^3}\frac{C_I}{kT}$$

according to Eq. (1), the value $\dfrac{\mu_g}{a^3}\dfrac{C_{II}-C_I}{kT}$ can be easily found. Fig. 1 shows this dependence for pyridazine ($C = 10^{-3}$ M/l) in mixtures having various percentages of n-heptane
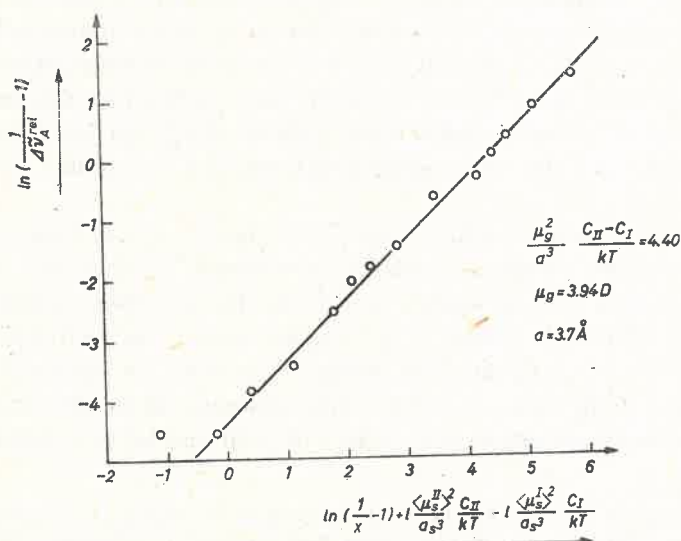

Fig. 1. The relative absorption shift $\ln\left(\dfrac{1}{\Delta\tilde{\nu}_A^{rel}} - 1\right)$ for pyridazine in n-heptane/n-butanol mixtures for different mole fractions x of n-butanol, according to Eq. (1)

and n-butanol. Hence, we have $\dfrac{\mu_g^2}{a^3}\dfrac{C_{II}-C_I}{kT} = 4.40$ that gives for $\mu_g = 3.94$ D [8] a value of 3.7 Å for the cavity radius.

The same method was used in [9] where for pyrimidine the cavity radius a was found to be 3.3 Å. The values of the Onsager cavity radius of pyrimidine and pyridazine should be similar because of the great similarity in their molecular structures. It seems reasonable for this class of molecules to assume the value of a equal to 3.5 Å, which is the mean value for pyrimidine and pyridazine. Based on the measurements of absorption and fluorescence band shifts for pyrimidine and pyridazine in various solvents, the following values of a were found to be 3.7 Å and 3.9 Å respectively [6], assuming that the dipole moments in the ground and excited states are parallel. The value of a could be overestimated especially in the case of pyrimidine because the above assumption is not precisely fulfilled ($\sphericalangle\, \vec{\mu}_e, \vec{\mu}_g = 75°$) [9].

According to the theory of Schuyer [10] and Bakhshyev [11] the values of α/a^3 of the absorbing molecules can be determined. In this case we have

$$\left(g\,\frac{\int K_v dv}{\int K_v^0 dv}\right)^{-\frac{1}{2}} = A^{-\frac{1}{2}} - \frac{\alpha}{a^3}A^{-\frac{1}{2}}\frac{2n^2-2}{2n^2+1}, \qquad (2)$$

where

$$g = \frac{(2n^2+1)^2}{9n^3} \quad \text{and} \quad A = \frac{f\pi e^2}{3mc\int K_v^0 dv}.$$

K_v is the molar extinction coefficient of the solute molecule, K_v^0 refers to the solvent having the biggest refractive index, n the refractive index of the solution, e the charge and m the mass of an electron, c is the light velocity in a vacuum, and f the oscillator-strength.
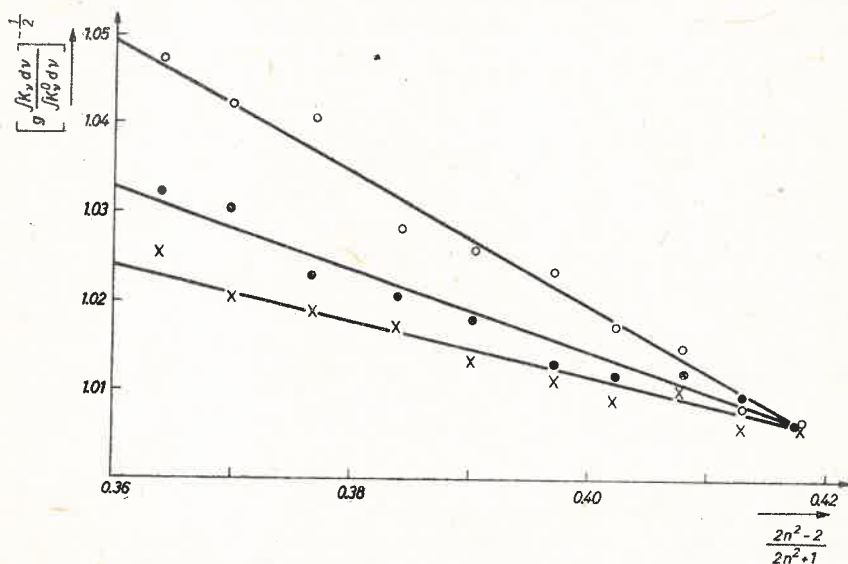

Fig. 2. $(g\int K_v dv/\int K_v^0 dv)^{-\frac{1}{2}}$ as function of $2n^2-2/2n^2+1$, for diazines ($\times$ — pyrazine, ● — pyrimidine, O — pyridazine (in isopentane/cycloheptane mixtures, according to Eq. (2)

Plotting $(g \int K_v d_v / \int K_v^0 dv)^{-\frac{1}{2}}$ as a function of $(2n^2 - 2)/(2n^2 + 1)$ a straight line is obtained which cuts the oridinate axis at the point $A^{-\frac{1}{2}}$ and whose slope is $\alpha/a^3 A^{-\frac{1}{2}}$. To obtain the largest range in the refractive index for a solution, mixtures of benzene and n-heptane were use most often. However, for high polar solute substances the band shift and its deformation in benzene in relation to n-heptane can be very large which can cause a false $\int K_v dv$ value. Therefore, other mixtures were applied [12]. In our investigations a mixture of cycloheptane ($n = 1.444$) and isopentane ($n = 1.354$) was used. Hence, a smaller change in the refractive index was observed than in the case of the benzene and n-heptane mixture. However, the position and shape of absorption bands for the diazines we studied do not change significantly when isopentane is replaced by cycloheptane. Fig. 2 shows the curves plotted according to Eq. (2) for pyrazine, pyrimidine and pyridazine. The values of a, α/a^3 and α obtained from these curves (Fig. 1 and 2) are given in Table I.

TABLE I

Compound	μ_g [D]	a [Å]	α/a^3	α [Å^3]
pyrazine	0		0.27	11.6
pyrimidine	2.40	3.5	0.38 0.40 [13]	16.3
pyridazine	3.94		0.56	23.9

It appears that the mean polarizabilities for diazines, similar to dipole moments, depend on the mutual position of nitrogen heteroatoms in the molecule.

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