Dipole Moments and Polarizabilities of Benzophenones Estimated from Spectroscopic Measurements *

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The effect of microenvironment on the absorption spectra of benzophenone and its amino-derivatives in n-heptane/n-butanol and n-heptane/benzene mixtures was investigated. The local dielectic constants, the composition of the solvatation shell, the Onsager cavity radius "a" and the values of α/a^3 (α — the polarizability of solute molecules) have been evaluated from the spectral shifts.

The electric and optical properties of molecules are commonly investigated by measurements of their absorption and fluorescence spectra, both in pure solvents of different polarities [1] and in mixed solvents [2]. The molecules benzophenone (BF), 2-aminobenzophenone (2ABF) and 4-aminobenzophenone (4ABF) investigated in this paper show no fluorescence at room temperature. Their absorption spectra, however, are shifted depending on the polarity of the solvent. Figure 1 shows the maxima of the absorption bands as functions of the content of n-butyl alcohol in n-heptane. In the case of benzophenone ($n \to \pi^*$ transition) an increase in the solvent polarity results in a shift of the spectrum to the short-wave side, whereas the absorption spectra of 2-aminobenzophenone and 4-aminobenzophenone ($\pi \to \pi^*$ transitions) are shifted to the long-wave side. Therefore measurements of absorption spectra in mixtures of polar and nonpolar solvents were carried out to determine the composition of the first coordination solvent shell, the Onsager cavity radius and the mean energy of interaction between the solvent and solute molecules in the ground state.

The absorption spectra at 293 K were measured using a Zeiss Specord UV VIS spectrofotometer. The refraction indices of solutions at 293 K were determined by means of an Abbe refractometer.

I. Solvent Shells

We assume, according to [3, 4], that the molecular radii and the refraction indices of solvents are equal ($a_s^{I} = a_s^{II} = a_s$ and $n_{I} = n_{II} = n$). The indices I and II refer to nonpolar (n-heptane) and polar (n-butanol) solvents, respectively. The mean filling-up degree of the solvent shell with molecules of the polar solvent in the first coordination sphere is de-

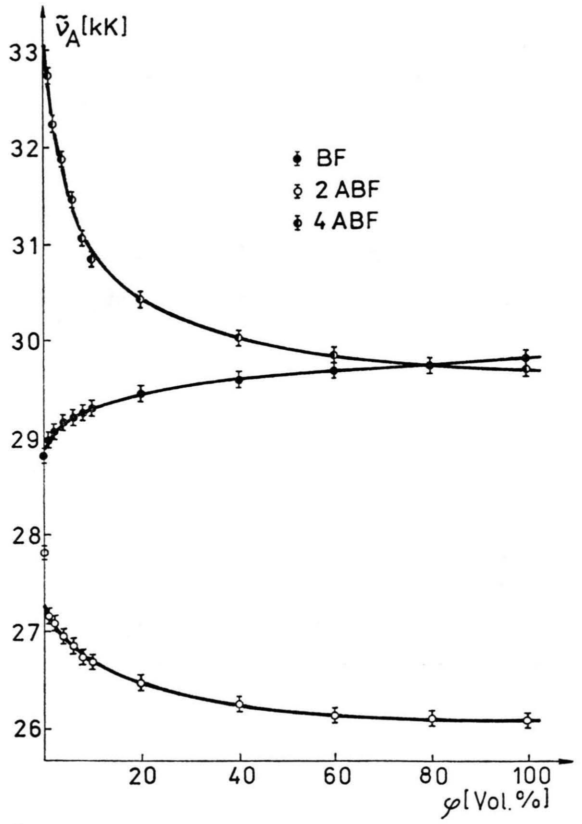

Fig. 1. Maxima of the absorption bands of BF, 2ABF and 4ABF as functions of content (in per cent) of n-butyl alcohol in n-heptane.

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fined as

$$\gamma \equiv \langle \gamma_{\mathrm{II}} \rangle = \frac{z_{\mathrm{I}}}{z_{\mathrm{I}} + z_{\mathrm{II}}}, \tag{1}$$

where z_{I} and z_{II} are the numbers of molecules of nonpolar and polar solvent in the solvent shell, respectively.

The shift of the absorption spectra in a binary solvent is [3, 5]

$$\begin{aligned} \delta \tilde{\nu}_{\mathrm{A}} &= \tilde{\nu}_{\mathrm{A}} - \tilde{\nu}_{\mathrm{A}}^{\mathrm{I}} \qquad (2) \\ &= -C_{\mathrm{A}} \left(\frac{2n^2+1}{n^2+2} \right) \left(\frac{\langle \varepsilon_1 \rangle - 1}{\langle \varepsilon_1 \rangle + 2} - \frac{n^2-1}{n^2+2} \right), \end{aligned}$$

where $\tilde{\nu}_{\mathrm{A}}$ is the wave number maximum of the absorption band for the mixed solvent and $\tilde{\nu}_{\mathrm{A}}^{\mathrm{I}}$ for the nonpolar solvent, and $C_{\mathrm{A}} = \frac{1}{2}(m_2 - m_1)$. The parameters m_1 and m_2 are connected with the dipole moments of the solute molecules in the ground and excited states (see [1]). In this work the values of C_{A} for BF, 2ABF and 4ABF were experimentally obtained using the theory of Kawski and Bilot [1]. From (2) we obtain values of $\langle \varepsilon_1 \rangle$ [9]:

$$\langle \varepsilon_1 \rangle = \frac{n^2 - 2\Delta\tilde{\nu}_{\mathrm{A}}}{1 + \Delta\tilde{\nu}_{\mathrm{A}}}, \tag{3}$$

where

$$\Delta\tilde{\nu}_{\mathrm{A}} = \frac{\delta\tilde{\nu}_{\mathrm{A}}}{C_{\mathrm{A}}} \frac{(n^2+2)^2}{3(2n^2+1)}. \tag{4}$$

For the mixed solvents, it was assumed [5] that the local dielectric constant $\langle \varepsilon_1 \rangle$ of the solvent shell is defined by the following dependence between the dielectric constant of the nonpolar (ε_{I}) and polar ($\varepsilon_{\mathrm{II}}$) solvents:

$$\langle \varepsilon_1 \rangle \approx \varepsilon_{\mathrm{I}} \gamma_{\mathrm{I}} + \varepsilon_{\mathrm{II}} \gamma_{\mathrm{II}}. \tag{5}$$

From (1) and (5) follows

$$\gamma = \frac{\langle \varepsilon_1 \rangle - \varepsilon_{\mathrm{I}}}{\varepsilon_{\mathrm{II}} - \varepsilon_{\mathrm{I}}}. \tag{6}$$

The values of $\langle \varepsilon_1 \rangle$ and γ calculated from (3) and (6) are given in Table I.

II. Determination of the Onsager Cavity Radius

The Onsager cavity radius "a" of the solute molecule can be determined from absorption spectra measured in mixtures of polar and nonpolar solvents. According to Gorodyskii and Bakhshiev [2] the value "a" of the absorbing molecule can be determined from the relative absorption shift

$$\Delta\tilde{\nu}_{\mathrm{A}}^{\mathrm{rel}} = \frac{\tilde{\nu}_{\mathrm{A}}^{\mathrm{I}} - \tilde{\nu}_{\mathrm{A}}}{\tilde{\nu}_{\mathrm{A}}^{\mathrm{I}} - \tilde{\nu}_{\mathrm{A}}^{\mathrm{II}}} = \frac{x}{(1-x)\exp(-B) + x}, \tag{7}$$

where x is the mole fraction of the polar solvent in nonpolar/polar mixtures

$$\begin{aligned} B = {} & \frac{\mu_{\mathrm{g}}^2}{a^3} \frac{C_{\mathrm{II}} - C_{\mathrm{I}}}{kT} - l \frac{\langle \mu_{\mathrm{s}}^{\mathrm{II}} \rangle^2}{a_{\mathrm{s}}^3} \frac{C_{\mathrm{II}}}{kT} \\ & + l \frac{\langle \mu_{\mathrm{s}}^{\mathrm{I}} \rangle^2}{a_{\mathrm{s}}^3} \frac{C_{\mathrm{I}}}{kT} \end{aligned} \tag{8}$$

contains the Onsager radius a.

The constants

$$C_{\mathrm{I,II}} = \frac{\varepsilon_{\mathrm{I,II}} - 1}{\varepsilon_{\mathrm{I,II}} + 2}, \tag{9}$$

μ_{g}, the ground-state dipole moment of the solute, $\langle \mu_{\mathrm{s}}^{\mathrm{I}} \rangle$ and $\langle \mu_{\mathrm{s}}^{\mathrm{II}} \rangle$, the average dipole moments of the solvent molecules I and II (for their determination

Table 1.

φ [%]	ε [4]	Benzenophenone [BF]			2-Aminobenzenophenone [2ABF]			4-Aminobenzenophenone [4ABF]		
		$\Delta\tilde{\nu}_{\mathrm{A}}^{\mathrm{rel}}$	$\langle \varepsilon_1 \rangle$	γ [%]	$\Delta\tilde{\nu}_{\mathrm{A}}^{\mathrm{rel}}$	$\langle \varepsilon_1 \rangle$	γ [%]	$\Delta\tilde{\nu}_{\mathrm{A}}^{\mathrm{rel}}$	$\langle \varepsilon_1 \rangle$	γ [%]
0	1.918	0.0000	1.918	0.00	0.0000	1.918	0.00	0.0000	1.918	0.00
1	1.962	0.1224	2.610	4.36	0.0833	2.220	1.90	0.0898	2.237	2.01
2	1.970	0.2653	2.993	6.78	0.1499	2.468	3.47	0.2275	2.808	5.61
4	2.008	0.3469	3.445	9.63	0.2500	2.915	6.29	0.3593	3.520	10.10
6	2.063	0.3980	3.773	11.69	0.3500	3.462	9.74	0.4730	4.329	15.20
8	2.128	0.4592	4.220	14.51	0.4417	4.083	13.65	0.5988	5.555	22.93
10	2.198	0.5102	4.650	17.23	0.4750	4.345	15.30	0.6557	6.278	27.50
20	2.698	0.6429	6.108	26.42	0.6667	6.434	28.48	0.7844	8.574	41.97
40	5.170	0.8163	9.002	44.80	0.8499	10.268	52.65	0.9072	12.375	65.94
60	8.980	0.8979	12.019	63.37	0.9417	13.983	76.08	0.9581	14.892	81.81
80	13.550	0.9592	14.987	82.41	0.9666	15.401	85.02	0.9850	16.622	92.72
100	17.750	1.0000	17.750	100.00	1.0000	17.750	100.00	1.0000	17.750	100.00

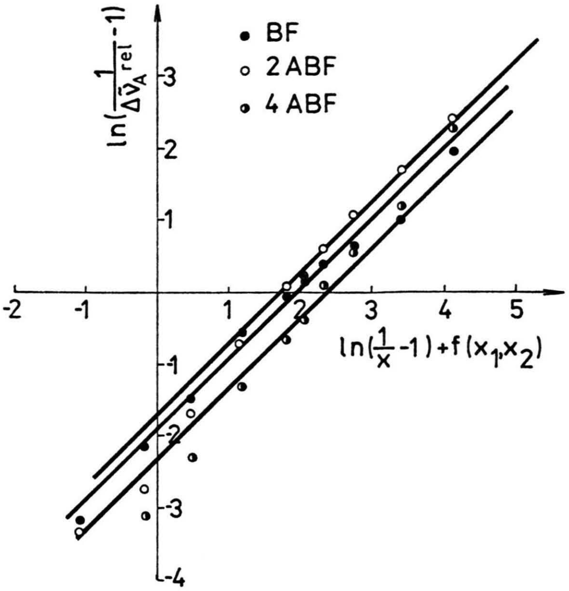

Fig. 2. $\ln\left(\frac{1}{\Delta\tilde{\nu}_A^{\rm rel}}-1\right)$ vs. $\ln\left(\frac{1}{x}-1\right)+f(x_1,x_2)$, according (7).

see [2]), and l, an empirical parameter ($l \approx 1$), have known values.

Plotting $\ln(1/\Delta\tilde{\nu}_A^{\rm rel}-1)$ vs.

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

according to (7) the value $\frac{\mu_g^2}{a^3}\,\frac{C_{\rm II}-C_{\rm I}}{kT}$ can easily be found. Figure 2, where

$$f(x_1,x_2)\equiv\frac{l}{a_s^3\,kT}\left(\langle\mu_s^{\rm II}\rangle^2 C_{\rm II}-\langle\mu_s^{\rm I}\rangle^2 C_{\rm I}\right),$$

shows this dependence for BF, 2ABF and 4ABF. Hence we obtained values of $\frac{\mu_g^2}{a^3}\,\frac{C_{\rm II}-C_{\rm I}}{kT}$ for these molecules, and using known μ_g values it was possible to determine the Onsager cavity radii [6] (Table II).

Table 2.

Substance	μ_g[D]	a[Å]	α/a^3	$-\Delta F_{\rm m}$[cm^{-1}]
BF	2.98 [12]	4.04	0.46	52
2ABF	2.65*	4.00	0.55	21
4ABF	4.73 [13]	5.16	0.75	128

* The dipole moment μ_g for 2-Aminobenzenophenone calculated by vectorial summation of μ_g of benzenophenone and μ of the substituted group [14].

III. Determination of α/a^3

According to the theory of Schuyer [7] and Bakhshiev [8] the values of α/a^3 for absorbing molecules can be determined. This requires the measurement of the integrated absorption spectra of the molecules studied in the mixtures of two nonpolar solvents with different refractive indices. In this case we have

$$\left(g\,\frac{\int K_\nu\,{\rm d}\nu}{\int K_\nu^0\,{\rm d}\nu}\right)^{-1/2}=A^{-1/2}\left(1-\frac{2\alpha}{a^3}\,\frac{n^2-1}{2n^2+1}\right),$$

where

$$g=\frac{(2n^2+1)^2}{9n^3}\quad\text{and}\quad A=\frac{f\pi e^2}{3m_c\int K_\nu^0\,{\rm d}\nu}. \qquad (10)$$

K_ν is the molar extinction coefficient of the solute molecules in the solvent mixture, K_ν^0 refers to the solvent with the highest refractive index n. e is electric charge, m the mass of an electron, c the velocity of light in vacuum and f the oscillator strength. Plotting $(g\int K_\nu{\rm d}\nu/\int K_\nu^0\,{\rm d}\nu)^{-1/2}$ as a function of $(2n^2-2)/(2n^2+1)$ (for the mixture) we obtain a straight line which cuts the ordinate axis at a point $A^{-1/2}$ and the slope of which is $\alpha/a^3 A^{-1/2}$ [9]. Figure 3 shows the curves plotted according to (10) for BF, 2ABF and 4ABF. The values of α/a^3 obtained from these curves are given in Table II. It seems possible that the high value of α/a^3 for 4ABF molecules (highest dipole moment in the

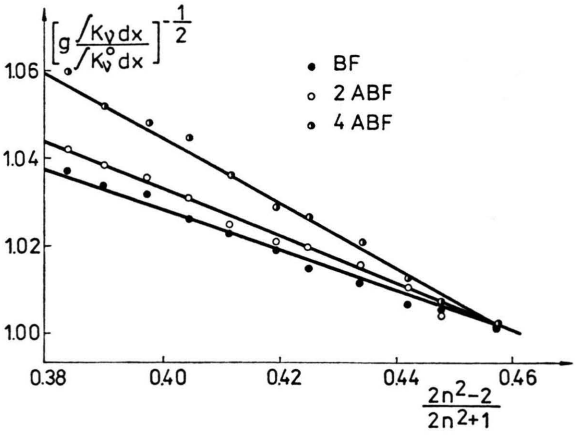

Fig. 3. $(g\int K_\nu{\rm d}\nu/\int K_\nu{}^0\,{\rm d}\nu)^{-1/2}$ as a function of $(2n^2-2)/(2n^2+1)$ for benzophenones in mixtures of n-heptane and benzene.

ground state) results from the difference between the dielectric constants of n-heptane and benzene.

IV. Mean Energy of Interaction

The statistical model of Masurenko [10] for ternary solvents was applied to determine the mean energy of interaction between the solute molecules and the binary solvent. The relative filling-up degree $\gamma \equiv \theta$ [9] of the solvent shell with the molecules of the polar solvent is given by

$$\frac{\gamma}{1-\gamma} = \frac{x}{1-x} \exp\left(-\frac{\Delta F_{\mathrm{m}}}{kT}\right). \tag{11}$$

γ is related to the spectroscopics quantities by the expression

$$\gamma = \frac{(n^2+2)}{(\varepsilon_{\mathrm{II}} - \varepsilon_{\mathrm{I}}) \left[\dfrac{1}{\Delta \tilde{\nu}_{\mathrm{A}}} - 1\right]}. \tag{12}$$

(12) was obtained [11] by taking into account the polarizability of the solute molecule. Plotting $\ln[\gamma/(1-\gamma)]$ vs. $\ln[x/(1-x)]$ (Fig. 4) we obtain straight lines the slopes of which are 1. On the ordinate axis they cut a segment corresponding to the energy of interaction $-\Delta F_{\mathrm{m}}$. The energies of interaction between molecules of BF, 2ABF, 4ABF and the solvent are given in Table 2

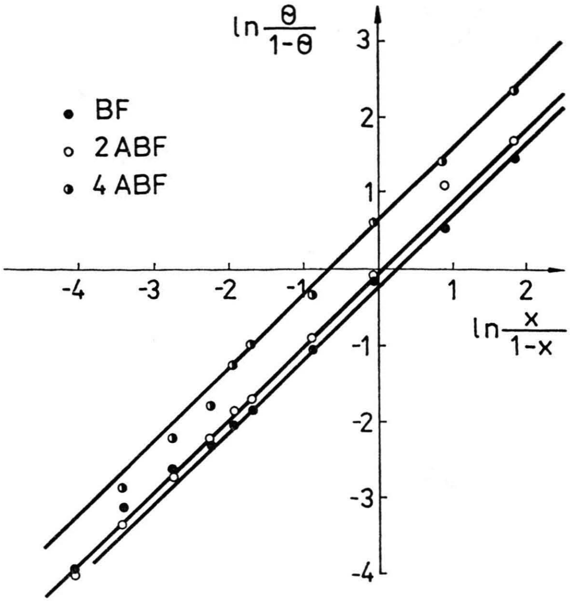

Fig. 4. Plott of $\ln\frac{\theta}{1-\theta}$ vs. $\ln\frac{x}{1-x}$ for benzophenones, see (11).

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