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# Solvent Effects on the Absorption Spectrum of the Perylene-$SbCl_5$ Complex

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**Abstract**—The perylene–$SbCl_5$ complex is characterized by two absorption maxima, whose positions depend on the nature of the solvent. The maximum in the region of $19\times10^{-3}$ $cm^{-1}$ corresponds to the perylene cationic form and depends on the medium polarity, while another, in the region of $14\times10^{-3}$ $cm^{-1}$, corresponding to the perylene–$SbCl_5$ complex, is governed primarily by the ability of the solvent to the electrophilic solvation. However, the quantitative generalization of the data on the frequencies of absorption maxima is only possible using multiparameter equations that take into account various properties of the solvents.

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Antimony pentachloride is a strong electron acceptor and, naturally, complexing agent. The heat of interaction of a number of substances with $SbCl_5$, the so-called Gutman's donor numbers *DN* [1], have been proposed as a measure of their basicity (electron donor ability). On the other hand, polycyclic aromatic hydrocarbons are capable to release electrons in the presence of such acceptors, converting into positive ions [2]. Because of the possible solvation, the extent and energy of such interactions depend on the properties of solvents in which the complexation occurs.

In [3] to assess such a dependence the electron absorption spectra of $SbCl_5$–perylene complex in 16 solvents were considered. It was found that the spectra obtained in polar media contain a strong absorption maximum near 540 nm accompanied by a weak shoulder at 740 nm. Relevant data are given in Tables 1 and 2. Absorption peak at 540 nm was assigned by Kuroda et al. to the positively charged perylene ion since a similar peak was observed in the spectrum of the solution of perylene in sulfuric acid. At the same time, in a low-polarity media, with the Kirkwood function less than 0.3 this band is more diffuse and its maximum is shifted to higher frequencies. Simultaneously, a weak absorption that in the polar media is manifested as a shoulder at ~740 nm appears as a distinct, though less intense, absorption band with a maximum near ~710 nm. There is also a broad weak absorption band near 1200 nm. In [3] they were assigned to the absorption of the solvated perylene–$SbCl_5$ complex. Based on the general theory of the medium effect on the absorption spectra [4] Kuroda et al. [3] suggested that the peak at ~ 540 nm should depend on the polarizability and the polarity of the environment. However, at constructing the relationship between the absorption frequency ν and the function $(n^2 - 1)/(n^2 + 2)$ only an approximate linear relationship was found for the more polar media (nos. 8–16), while the absorption frequencies in the low-polarity solvents (nos. 1 –7) sharply deviate from this dependence (Fig. 1). Even less clear results were obtained at evaluating the polarity effect: At revealing a dependence of ν on $(\varepsilon - 1)/(2\varepsilon + 1)$ it was only found that the values of ν can be separated into two distinct groups, with no apparent dependence (Fig. 2). Kuroda et al. suggested that such features were the result of influence of specific interaction, but did not attempt to quantify it. They did not interpret also the medium effect on the position of absorption maximum at 740 nm.

It is accepted now that the characteristics of a substance behavior in solvents is determined by a set of effects of various solvation processes, and it also depends on the medium cohesion. Nature of the solvation can be determined using the principle of

**Table 1.** The values of the wavelengths $\lambda_1$ and the experimental and calculated with Eq. (3) frequencies $\nu_1$ of the light absorption of perylene cation

| Run no. | Solvent | $f(n)$ | $f(\varepsilon)$ | $\lambda_1$, nm | $\nu_{1exp}\times10^3$, cm$^{-1}$ | $\nu_{1calc}\times10^3$, cm$^{-1}$ | $\Delta\nu_1\times10^3$, cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | Heptane | 0.2304 | 0.186 | 504 | 19.841 | 19.774 | –0.067 |
| 2 | Cyclohexane | 0.2563 | 0.203 | 512 | 19.531 | 19.559 | 0.028 |
| 3 | $CCl_4$ | 0.2742 | 0.226 | 521 | 19.194 | 19.273 | 0.079 |
| 4 | Benzene | 0.2947 | 0.231 | 510 | 19.608 | 19.300 | –0.308 |
| 5 | Toluene | 0.2926 | 0.238 | 517 | 19.342 | 19.278 | –0.064 |
| 6 | Carbon disulfide[a] | 0.3567 | 0.261 | 508 | 19.685 | 18.532 | –1.153 |
| 7 | Trichloroethylene[a] | 0.2828 | 0.309 | 502 | 19.920 | 18.749 | –1.171 |
| 8 | Chloroform | 0.2941 | 0.359 | 545 | 18.349 | 18.561 | 0.212 |
| 9 | 1-Chloronaphthalene | 0.3569 | 0.365 | 558 | 17.921 | 17.986 | 0.065 |
| 10 | Bromobenzene | 0.3232 | 0.373 | 562 | 17.794 | 18.170 | 0.376 |
| 11 | Chlorobenzene | 0.3064 | 0.377 | 559 | 17.889 | 18.238 | 0.349 |
| 12 | Tetrachloroethane | 0.2911 | 0.413 | 547 | 18.282 | 18.096 | –0.186 |
| 13 | *cis*-Dichloroethylene | 0.2682 | 0.423 | 546 | 18.315 | 18.147 | –0.168 |
| 14 | *o*-Dichlorobenzene | 0.3193 | 0.436 | 560 | 17.857 | 17.806 | –0.051 |
| 15 | Nitrobenzene | 0.3215 | 0.479 | 556 | 17.986 | 17.610 | –0.376 |
| 16 | Acetonitrile | 0.2106 | 0.480 | 538 | 18.587 | 18.699 | 0.112 |

[a] Solvents excluded from the calculation.

**Table 2.** The values of the wavelengths $\lambda_2$ and the experimental and calculated with Eq. (5) frequencies $\nu_2$ of the light absorption of perylene–$SbCl_5$ complex

| Run no. | Solvent | $\lambda_2$, nm | $\nu_{1exp}\times10^3$, cm$^{-1}$ | $\nu_{1calc}\times10^3$, cm$^{-1}$ | $\Delta\nu_1\times10^3$, cm$^{-1}$ |
|---|---|---|---|---|---|
| 1 | Heptane[a] | 700 | 14.286 | 13.333 | –0.953 |
| 2 | Cyclohexane | 710 | 14.085 | 14.213 | 0.128 |
| 3 | $CCl_4$ | 700 | 14.286 | 14.268 | –0.018 |
| 4 | Benzene | 710 | 14.085 | 14.215 | 0.130 |
| 5 | Toluene | 710 | 14.085 | 13.912 | –0.173 |
| 6 | Carbon disulfide | 650 | 15.385 | 15.197 | –0.188 |
| 7 | Trichloroethylene[a] | 680 | 14.706 | 13.954 | –0.752 |
| 8 | Chloroform | 742 | 13.477 | 13.587 | 0.110 |
| 9 | 1-Chloronaphthalene | 755 | 13.245 | 13.212 | –0.033 |
| 10 | Bromobenzene | 748 | 13.369 | 13.633 | 0.264 |
| 11 | Chlorobenzene | 745 | 13.423 | 13.560 | 0.137 |
| 12 | Tetrachloroethane | 745 | 13.423 | 13.378 | –0.045 |
| 13 | *cis*-Dichloroethylene | 740 | 13.514 | 13.306 | –0.208 |
| 14 | *o*-Dichlorobenzene | 745 | 13.423 | 13.404 | –0.019 |
| 15 | Nitrobenzene | 740 | 13.514 | 13.258 | –0.256 |
| 16 | Acetonitrile | 735 | 13.609 | 13.777 | –0.168 |

[a] Solvents excluded from the calculation.

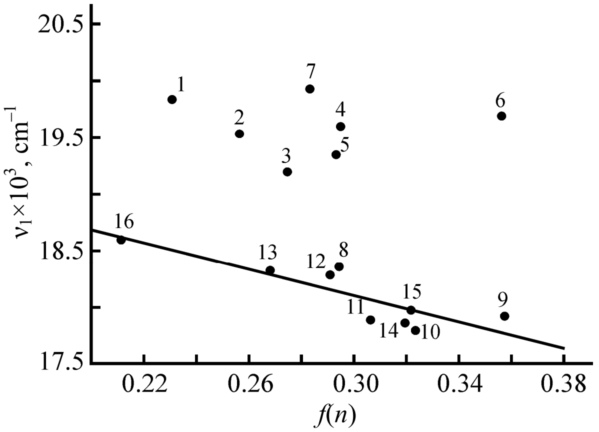

**Fig. 1.** Relation between the frequencies $\nu_1$ of absorption of the $SbCl_5$–perylene complex in various solvents and the function $(n^2 - 1)/(n^2 + 2)$. The point numbers correspond to Table 1.

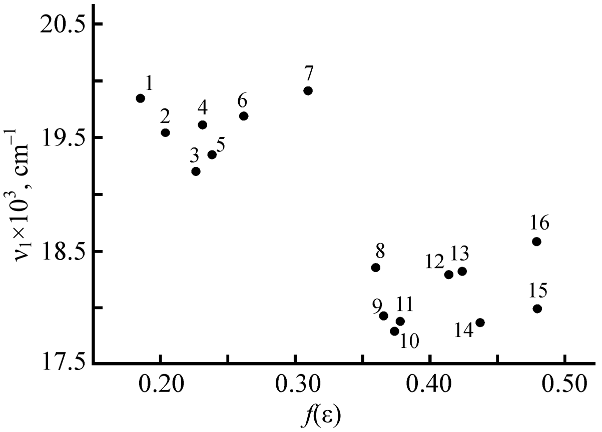

**Fig. 2.** Relation between the frequencies $\nu_1$ of absorption of the $SbCl_5$–perylene complex in various solvents and the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$. The point numbers correspond to Table 1.

linearity of free energies applying multiparameteric equations. This is applicable in particular to the spectral characteristics of individual compounds and complexes [5–7].

Given the above, it seems reasonable attempt to consider the data in [3] based on the principle of the free energy linearity using a six-parametric equation, in accordance with [7].

$$Y = \nu = a_0 + a_1(n^2 - 1)/(n^2 + 2) + a_2(\varepsilon - 1)/(2\varepsilon + 1) + a_3E_T + a_4B + a_5\delta^2 + a_6V_M. \quad (1)$$

In Eq. (1), $n$ is refractive index of solvent and $\varepsilon$ is its dielectric constant, determining its polarizability and polarity, respectively, and thus the ability to nonspecific solvation; $B$ is the solvent basicity by Palm and $E_T$ is its electrophilicity by Reichardt, which determine the ability of the solvent to acid–base interaction, that is, to specific solvation; $\delta^2$ is the squared Hildebrand solubility, which is proportional to the cohesion energy of the medium; $V_M$ is the molar volume of the solvent. As the calculations are based on the principle of free energy linearity, it is more convenient to perform them using the frequency rather than the wavelength of the absorption maximum. This approach was shown promising, for example, in the study of iodine absorption frequency in different media [9].

The calculation and testing the significance of individual terms in the equation were carried out in accordance with the IUPAC recommendations of the correlation analysis in chemistry [9]. The adequacy of these equations is confirmed by the determination of their Fisher criterion, which in all cases less than the tabulated values at a confidence level of 0.95 for the appropriate number of data.

Since the free energy linearity principle reflects the impact of individual energy effects on a measured parameter, the data of [3] are presented in Table 1 in the form of frequencies corresponding to both absorption maxima, $\nu\times10^{-3}$ cm$^{-1}$. We found that Eq. (1) generalizes the data on $\nu_1$ for absorption at the wavelength of 510 nm with unsatisfactorily low correlation factor: the value of multiple correlation coefficient $R$ is equal only to 0.897. But exclusion, in accordance with [9], of the most deviating data for trichlorethylene and $CS_2$ increases $R$ to 0.935 and 0.955 respectively. Thus, the obtained Eq. (2), which describes adequately the dependence of the absorption frequencies $\nu_1$ on the properties of solvents:

$$\nu_1\times10^3 = 21.868 - (5.896\pm2.733)f(n^2) - (6.391 \pm 3.370)f(\varepsilon) + (0.0510\pm0.0047)B + (0.025\pm0.080)E_T - (0.002\pm0.004)\delta^2 - (0.001\pm0.005)V_M. \quad (2)$$

The values of pair correlation coefficients $r$ between $\nu_1$ and individual parameters are, respectively, 0.578, 0,847, 0.182, 0,673, 0,654, 0.118, standard error of the equation $s = \pm0.219$.

Owing to low $r$ values, impossible to determine the significance of the influence of individual parameters, but large standard deviations of the coefficients of most terms in the equation indicate their insignificance. Therefore, we carried out, according to recommendations [9], testing the significance of individual members by their successive elimination, each time calculating $R$ for the equations with fewer terms. By this way the insignificance of the terms was established with $V_M$, as well as $\delta^2$ and $E_T$, despite the relatively high value of $r$, of the order of 0.65. Finally, the relationship between $\nu_1$ and characteristics of solvents is described adequately by three-parameteric Eq. (3):

$$\nu_1\times10^3 = 22.5543 - (6.670\pm1.824)f(n^2) - (6.338\pm0.773)f(\varepsilon) + (0.003\pm0.002)B, \quad R\ 0.954;\ s\ \pm0.222. \tag{3}$$

Effect of basicity, that is, possible competition with perylene for the interaction with $SbCl_5$ of more basic media also is not relatively important: exclusion of a term containing $B$ decreases $R$ only slightly, to 0.941. However, note that in [3] the measurements were carried out in the environments only with low and little differing basicity. The insignificance of the term with $E_T$, that is, lack of electrophilic solvation of the resulting perylene cation is also noteworthy. Thus, our analysis supports the opinion [3] that the decisive influence on the perylene–$SbCl_5$ interaction have the nonspecific solvation and the corresponding separation of solvents in two groups by significance (Figs. 1 and 2), but adequate overall picture can be obtained only by combined consideration of the factors of polarity, polarizability and, advisably, the basicity. Table 1 shows the $\nu_1$ values calculated with Eq. (3) and their differences with the experiment, $\Delta\nu_1$. Fig. 3 shows relations between the calculated from Eq. (3) and experimental $\nu_1$ values. As can be seen, most of the deviations do not exceed the limit $s = \pm0.222$, that is, they fall in the acceptable range of errors $\pm s$. More noticeable deviations that occurred in the cases of benzene, chlorobenzene, bromobenzene and nitrobenzene do not exceed $\pm2s$.

The values of the spectral shifts $\nu_2$ (Table 2) at ~740 nm attributed in [3] to the solvation of undissociated $SbCl_5$–perylene complex can also be generalized with Eq. (1). Like in the case of $\nu_1$ frequencies the $R$ value for all 17 solvents 0.879 is unsatisfactorily low, but the exclusion from the consideration of the data for heptane or trichlorethylene leads to an increase in $R$ up to 0.921 and 0.967, respectively.

Thus, we obtain generalized Eq. (4):

$$\nu_2\times10^3 = 19.876 + (2.444\pm2.086)f(n^2) + (0.547\pm2.261)f(\varepsilon) + (0.001\pm0.003)B - (0.159\pm0.051)E_T + (0.002\pm0.002)\delta^2 - (0.021\pm0.003)V_M \tag{4}$$

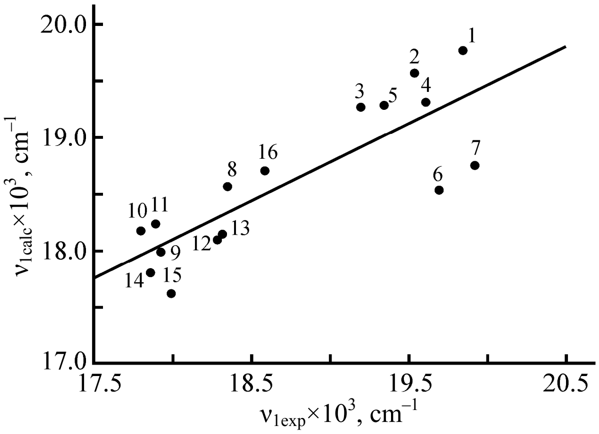

**Fig. 3.** Correspondence between calculated and experimental values of the absorption frequencies $\nu_1$ of the $SbCl_5$–perylene complex. The point numbers correspond to Table 1.

with $r$, respectively, 0.143, 0.666, 0.287, 0.617, 0.270 and 0.450; $R = 0.967$; $s = \pm0.144$.

It may be noted the lack of a clear separation of frequencies $\nu_2$ in two groups depending on the solvent polarity, in contrast to the frequency $\nu_1$. Like the case of $\nu_1$, the equation can be simplified to three-parameteric, but now the other parameters are significant:

$$\nu_2\times10^3 = 20.321 - (0.164\pm0.018)E_T + (0.003\pm0.001)\delta^2 - (0.018\pm0.002)V_M, \quad R\ 0.959;\ s\ \pm0.162. \tag{5}$$

The results of calculation with Eq. (5) of the theoretical $\nu_2$ values and their differences from the experimental data are listed in Table 2. As can be seen, in this case, the compilation of data on $\nu_2$ using a three-parameteric equation gives acceptable results.

The practical insignificance of the impact of nonspecific solvation parameters on the shift of the absorption frequency $\nu_2$ is noteworthy: Here the determining factors are the electrophilic solvation and the molar volume. The last effect is probably associated with a large volume of the perylene–$SbCl_5$ complex resulting in a loss of its contacts with solvent molecules of a large size. Both these factors reduce the frequency of light in the spectrum of complex (blue shift), that is, the energy of the corresponding electron transition.

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