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Correlation of the Solubility of 4,4'-Isopropylidenediphenol with Solvent Properties

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Abstract — Data on the solubility of 4,4'-isopropylidenediphenol in organic solvents can be quantitatively correlated with a linear three-parameter equation. The parameters exerting a decisive effect on the solubility are the polarity and basicity of solvents, favoring formation of intermolecular hydrogen bonds. At the same time, an increase in the cohesion energy of the medium decreases the solubility of the title compound.

The solubility of substances in organic solvents was usually considered only on the qualitative level (the solubility is high if the solvent and solute are similar in nature), and only relatively recently it was established that, in the case of gases, the solubility is determined by the joint effect of both solvation factors and the energy required for formation of a cavity in the liquid medium [1–3]. Correspondingly, a quantitative relationship between the solubility and physicochemical characteristics of solvents can be obtained on the basis of the linear free energy relationship by using multiparameter equations taking into account both specific and nonspecific solvation effects. The following equation, which proved to be efficient in correlation of data on solubilities of various gases in organic solvents, was suggested in [1]:

$$\log N = a_0 + a_1 \frac{n^2 - 1}{n^2 + 2} + a_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + a_3 B + a_4 E_T + a_5 \delta^2, \tag{1}$$

where N is the gas solubility (mole fraction scale); n and ε, refractive index and dielectric permittivity of the solvent, determing its polarizability and polarity (the properties responsible for the capability for nonspecific solvation); B, Koppel–Palm basicity of the solvent [4]; E_T, Reichardt electrophilicity of the solvent [5] determining its capability for specific (acid–base) interactions; and δ^2, Hildebrand solubility parameter squared, the quantity proportional to the energy consumption for formation of a cavity in the liquid structure to accommodate the solute molecule.

The same equation appeared also to be suitable for the correlation of data on the solubility of fullerene C_{60} in 89 solvents. It was found that the solubility of this cyclic chemically neutral substance is determined by only three factors: polarizability of solvents, positively affecting the solubility, and their polarity and cohesion energy density, exerting a negative effect [6]. In the same paper, Eq. (1) was shown to be preferable over some other multiparameter equations [7, 8] involving other solvent characteristics.

Therefore, it seemed appropriate to check the suitability of Eq. (1) for correlating data on the solubility of other crystalline substances in organic solvents. As investigation object we chose 4,4'-isopropylidenediphenol 4-$HOC_6H_4C(CH_3)_2C_6H_4OH$-4 (**I**), as extensive and reliable data are available on its solubility in various media [9]. Our choice was also governed by the fact that this substance considerably differs in the properties from neutral fullerene C_{60} because of the presence of hydroxy groups. At the same time, both these substances can serve as models for describing the interactions of coals with organic solvents, simulating the unit cells of slightly (**I**) and deeply metamorphized coals. Finally, the main method for purification of compound **I** widely used in production of epoxy resins is its crystallization, and correlation of data on its solubility in various media may facilitate the choice of the optimal solvents.

Data on the solubility (wt %) of **I** in 20 solvents at 18°C, taken from [9], and the corresponding values on the mole fraction scale (N) are listed in the table. The solvent characteristics were taken from reviews [10, 11], and the calculation followed the recommendations of the Group for Correlation Analysis in Chemistry at IUPAC [12]. The solubilities cited in [9] from different patents in some cases appreciably disagree with each other, e.g., 0.61 and 0.90 wt % in benzene, 0.16 and 0.25 wt % in *m*-xylene, 0.86 and 1.50 wt % in CH_2Cl_2, 0.08 and 0.20 wt % in trichloroethylene, and 0.12 and 0.99 wt % in chlorobenzene. However, a check calculation shows that the lower values are underestimated. Therefore, in the table we

Experimental (taken from [9]) and calculated [by Eq. (3)] data on the solubility of 4,4'-isopropylidenediphenol (wt % and mole fraction N)

Solvent no.	Solvent	Experiment			Calculation	
		wt %	N	$\ln N$	$\ln N$	$\Delta\ln N$
1	*n*-Heptane	0.01	0.00004	–10.1266	–8.7246	1.4020
2	Cyclohexane	0.02	0.00008	–9.4335	–8.7556	0.6779
3	Benzene	0.90	0.00209	–6.1706	–7.6953	–1.5247
4	Toluene	0.30	0.00121	–6.7171	–7.2542	–0.5371
5	*m*-Xylene	0.16	0.00074	–7.2089	–7.0374	0.1714
6	Dichloromethane	0.86	0.00322	–5.7384	–4.9099	0.8285
7	Chloroform	1.10	0.00578	–5.1534	–5.9755	–0.8221
8	Tetrachloromethane	0.04	0.00028	–7.9866	–8.4633	–0.4767
9	1,2-Dichloroethane	3.50	0.01548	–4.1682	–4.3387	–0.1705
10	Vinylidene chloride	0.93	0.00397	–5.5290	–6.0340	–0.5050
11	Trichloroethylene	0.08	0.00046	–7.6843	–6.9807	0.7036
12	Chlorobenzene	0.12	0.00491	–5.3165	–5.2958	0.0207
13	Methanol	67.10	0.22254	–1.5026	–2.5576	–1.0550
14	Ethanol	60.00	0.23237	–1.4594	–1.4311	0.0283
15	2-Propanol	32.40	0.11202	–2.1891	–1.0278	1.1612
16	*n*-Butanol	77.50	0.52793	–0.6388	–1.0976	–0.4588
17	Acetone	52.00	0.21606	–1.5322	–0.9627	0.5695
18	Acetic acid	17.70	0.05354	–2.9273	–3.5147	–0.5873
19	Diethyl ether	56.0	0.29239	–1.2297	–0.9630	0.2667
20	Water	0.000028[a]	0.000028	–10.4833	–10.1760	0.3073

[a] Solubility in g l^{-1}.

give the values from patent [13], which are better consistent with those given by our equation. These values were used in the final calculation. Thus, we obtained five-parameter equation (2), correlating with a high degree of reliability the data on the solubility of **I**.

$$\ln N = -17.378 + (14.59 \pm 7.36) f(n^2) + (14.32 \pm 3.01) f(\varepsilon) - (5.48 \pm 0.60) \times 10^{-3} \delta^2 + (1.92 \pm 0.25) \times 10^{-2} B + (0.10 \pm 0.05) E_T, \qquad (2)$$

$$R\ 0.978,\quad S\ \pm 0.648.$$

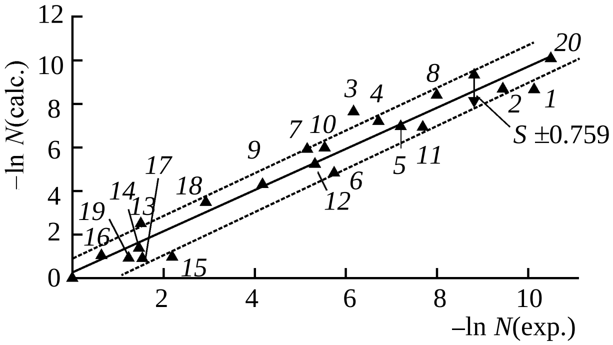
Since the pair correlation coefficients r, except that with δ^2, are within 0.2–0.25, the influence of separate parameters of Eq. (2) on $\ln N$ was evaluated, according to the recommendations from [12], by their alternate exclusion, with simultaneous determination of the multiple correlation coefficient R. This procedure showed that the factors of the solvent polarizability and electrophilicity are insignificant: Their exclusion decreases R insignificantly, to 0.974 and 0.973, respectively. Hence, the solubility of **I** is described with sufficient accuracy by three-parameter equation (3):

$$\ln N = -11.150 + (18.42 \pm 2.49) f(\varepsilon) - (4.76 \pm 0.46) \times 10^{-3} \delta^2 + (1.82 \pm 0.24) \times 10^{-2} B, \qquad (3)$$

$$R\ 0.970,\quad S\ \pm 0.759.$$

The solubility is positively affected by the solvent basicity and polarity (the correlation coefficients r with the corresponding parameters are 0.755 and 0.635, respectively), which agrees with the presence of hydrophilic phenolic groups in **I** and with the acidity of **I** (it dissolves in alkalis [9]). At the same time, in accordance with the above reasonings, the energy consumption for the formation of a cavity in the liquid structure (it is proportional to δ^2) decreases the solubility of **I**; however, the effect of this parameter is less significant [the corresponding coefficient r is 0.179, and exclusion of δ^2 from Eq. (3) decreases R only slightly].

The values of $\ln N$ calculated by Eq. (3) and their deviations $\Delta\ln N$ from the experimental values are given in the table. The correlation between the experimental and calculated [Eq. (3)] values of $\ln N$ is shown in the figure. The majority of $\ln N$ values fall within the error corridor $S \pm 0.759$ or are only slightly out of it.



Correlation between the experimental and calculated [Eq. (3)] sollubilities of 4,4'-isopropylidenediphenol at 18°C (mole fraction scale, *N*). Point numbers are solvent numbers in the table.

The high solubility of **I** in appreciably basic solvents (ether, acetone) and in polar alcohols suggests that the solubility will also be high in other solvents with high *B* (DMF, DMSO, amines, etc.), and the applicability of Eq. (1) to describing the solubilities of both fullerene C_{60} and compound **I** in various media suggests that it may be universally applicable to other crystalline organic compounds, although further check is required.

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