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Modulation of the Optical Rotation of Polarized Light by Some Terpenes Depending on Solvents Properties

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Abstract—The data on the medium effect on the angle of polarized light rotation by optically active substances have been generalized by using the multiparametric linear free energy equations. It has been stated that along with the solvent polarity and polarizability, the specific solvation of the substrate is significant.

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Optical activity is characteristic of the compounds with the asymmetric atom(s) in the structure. It is known that the rotation angle of polarized light is dependent on the solvent nature; however, this effect (in particular, the influence of the solvent Kirkwood function [1] or Reinhardt electrophilic solvation parameters E_T [1, 2]) has not yet been quantified.

Analysis of $[\alpha]_D$ of propylene oxide in 35 solvents [1] showed [3], that for 24 media the $[\alpha]_D$ could be fitted well (multivariate correlation coefficient was R = 0.959) with the six-parametric Eq. (1), useful for generalization of data on the medium effect on the chemical kinetics or solubility [4]. This equation accounted for the following solvent parameters: polarizability and polarity, reflecting the ability to non-specific solvation; Palm basicity B and electrophilicity E_T, measures of possible specific solvation; Hildebrand solubility parameter δ, proportional to the cohesion energy; and the molar volume V_M.

$$[\alpha]_D = a_0 + a_1f(n^2) + a_2f(\varepsilon) + a_3B + a_4E_T + a_5\delta^2 + a_6V_M. \quad (1)$$

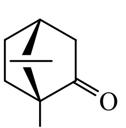
Further factor analysis of the Eq. (1) parameters [5] showed that propylene oxide $[\alpha]_D$ as a function of the solvent properties could be reasonably (R = 0.949) described by the simplified four-parametric Eq. (2) accounting only for the solvation processes.

$$[\alpha]_D = a_0 + a_1f(n^2) + a_2f(\varepsilon) + a_3B + a_4E_T. \quad (2)$$

The medium polarity was of less significance as well; for the tri-parametric equation $[\alpha]_D = f(n^2, B, E_T)$, R = 0.940. Elimination of any of the three remaining parameters led to poor correlation, with R < 0.9. However, the influence of the solvation factors on $[\alpha]_D$ of the optically active compounds was presumably dependent on the substrate chemical structure.

Indeed, analysis of the medium effect on the $[\alpha]_D$ of gel-like poly(propylene oxide) polymer with the average molecular weight of 3200 [6] showed that the following parameters were the most significant in that case: structural δ^2 and V_M, and polarizability n^2; the specific solvation parameters B and E_T being less important. The observed difference was likely due to different basicity of the epoxy (the monomer case) and ether (the polymer case) oxygen, and its restricted accessibility when in the polymer chain [3].

Inspired by the efficiency of multiparametric equations in generalizing the solvent effects on propylene oxide $[\alpha]_D$, we further extended the approach to the cases of other compounds. In particular, the optical activity was characteristic of many terpenes [7, 8]. In [9] the optical rotation angles were determined for 0.1 M solutions of six terpenes in seven solvents at 25°C. The Table shows the $[\alpha]_D$ for three cyclic terpenes containing the easily solvated carbonyl group in position 2 (cyclic ketones): camphor (**I**), fenchone (**II**), and verbenone (**III**), as well as the corresponding data for camphor quinone (**IV**) containing two carbonyl groups and for a couple of terpene hydrocarbons differing in the double bond position, α-pinene (**V**), endocyclic double bond, and β-pinene (**VI**), double bond in the side chain.



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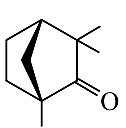

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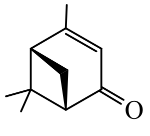

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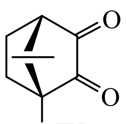

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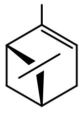
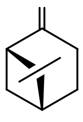


V



VI

With so much varied structures, it was assumed that for different terpenes different sets of Eq. (1) parameters would be the most significant, reflecting different types of the substrate solvation.

The correlation of experimental $[\alpha]_D$ values with those calculated in the frame of polarizable continuum model PCM [9] was reasonable in the cases of four solvents: cyclohexane, methanol, acetone, and acetonitrile; whereas in the cases of tetrachloromethane, benzene and chloroform the correlation was poor. As the PCM method accounted only for the electrostatic solvent–solute interactions, Menucci et al. concluded on the presence of other, nonelectrostatic effects. Thus, they attempted to correlate the $[\alpha]_D$ values for the studied terpenes with the E_T parameter of the solvents; however, no clear result was obtained. In the cases of fenchone and camphor, $[\alpha]_D$ was linear with E_T, whereas in the other cases the data for acetonitrile and acetone deviated from the plot. Moreover, in the cases of fenchone, β-pinene, camphor quinone, and verbenone $[\alpha]_D$ increased with growing E_T, while in the other cases $[\alpha]_D = f(E_T)$ was decreasing; this complicated the results interpretation in terms of specific solvation. The striking example was a pair of such similar compounds as β-pinene ($[\alpha]_D$ increased with E_T) and α-pinene ($[\alpha]_D$ decreased with E_T). Thus, the solvation effect was a complicated function of the solute structure.

It seemed reasonable to apply the multiparametric equation approach to the analysis of data from [9]. As the number of solvents was only higher by one than the number of Eq. (1) parameters, the equations obtained had $R \sim 1$ and were statistically unreliable. At the same time, the pairwise correlation coefficients for $[\alpha]_D$ and single parameters were in most cases quite low, not above 0.4–0.6 in most cases.

The factor analysis (by-turn elimination) according to [5] in the cases of all six terpenes gave statistically reliable equations with no more than three terms in most cases.

In the case of camphor, the electrophilic solvation of carbonyl oxygen with methanol or chloroform could be expected; however, the pairwise correlation coefficient r of $[\alpha]_D$ with the electrophilicity parameter E_T was low, only 0.524. The $[\alpha]_D$ values were well fitted by the triparametric Eq. (3) including factors of nonspecific solvation: polarizability, polarity, and the electrophilic factor.

$$\begin{gathered}[\alpha]_D = 187.12 - (345.24\pm 43.12)f(n^2) \\ - (32.84\pm 14.04)f(\varepsilon) - (1.17\pm 0.18)E_T, \\ R\ 0.971;\ s\ \pm 1.66.\end{gathered} \tag{3}$$

It is noteworthy that all solvation types decreased the optical anisotropy of the substrate reflected in $[\alpha]_D$. The polarity effect was relatively less significant: with $f(\varepsilon)$ eliminated, the multivariate correlation coefficient of the respective twoparametric equation only decreased to 0.944; whereas elimination of any of the

Experimental [9] and calculated according to Eq. (3) values of $[\alpha]_D$ for terpenes in different solvents

Растворитель	I			II	III	IV	V	VI
	$[\alpha]_{D\,exp}$	$[\alpha]_{D\,calc}$	$\Delta[\alpha]_D$					
Cyclohexane	57.10	55.62	–1.48	45.6	175.3	94.4	49.1	18.4
Tetrachloromethane	43.30	45.96	2.66	55.2	175.2	91.9	54.4	25.1
Benzene	38.30	38.03	–0.27	60.1	171.6	103.3	50.2	29.9
Chloroform	39.30	37.79	–1.51	62.1	185.5	97.6	58.1	18.1
Acetone	47.30	46.24	–1.06	51.3	179.8	117.1	54.2	15.2
Methanol	36.80	36.50	–0.30	60.9	169.6	–	56.3	15.9
Acetonitrile	42.60	44.55	1.95	55.7	42.6	111.6	59.9	12.9

two other parameters ruined the correlation. As was expected from the electrophilic character of the carbonyl group, the *B* term reflecting the solvent basicity, was less significant.

The $[\alpha]_D$ values calculated according to Eq. (3) in the case of camphor in various solvents are given in the Table, along with the experimental values. It is seen that the disagreement was in general within the accuracy limits, *s* ±1.66, noticeable deviations being observed in the cases of acetonitrile and tetrachloromethane (1.95 and 2.66, respectively).

In the case of another carbonyl-containing terpene, fenchone, the same solvation parameters were significant; however, the effect of solvation was the opposite, increasing the optical anisotropy. The data were reasonably fitted by the triparametric Eq. (4).

$$[\alpha]_D = -70.87 + (311.22\pm30.55)f(n^2) + (27.48\pm9.95)f(\varepsilon) + (1.01\pm0.13)E_T, \quad (4)$$
$$R\ 0.980;\ s\ \pm1.18.$$

The polarity factor was again of less significance: with this parameter excluded, for the resulting two-parametric equation $R = 0.95$. Probably, the difference in solvation effect direction was due to the features of fenchone structure, namely, screening of the carbonyl group with the spatially close isopropyl group.

The solvation of verbenone containing carbonyl group conjugated with the carbon–carbon double bond was even more sensitive to structural features. The $[\alpha]_D$ value in chloroform and methanol was only slightly different from that in cyclohexane. This was probably due to the possibility of both electrophilic and nucleophilic solvation in the case of this terpene.

Indeed, in the fitting Eq. (5) both of these factors were significant; however, their signs were opposite. The nonspecific solvation effect on $[\alpha]_D$ was negligible.

$$[\alpha]_D = 127.30 - (0.055\pm0.009)B + (2.24\pm0.21)E_T - (0.080\pm0.007)\delta^2, \quad (5)$$
$$R\ 0.983;\ s\ \pm1.01.$$

The medium basicity factor was relatively less important: with the *B* term excluded, $R = 0.873$. At the same time, the E_T factor and especially δ^2, characterizing the solvent self-association energy, were important: more associated was the medium, higher was its counteraction on the electrophilic solvation.

It is known that quinones are electron acceptors, capable of reacting with the electron-donor compounds with the formation of donor-acceptor complexes. Camphor quinone behavior was in line with this: in the electron-donor media, acetone, benzene, acetonitrile, the $[\alpha]_D$ value increase to 103–117 was observed, as compared with that in cyclohexane, 94.4.

Actually, the $[\alpha]_D$ of **IV** for 6 solvents could be fitted with a single-parametric equation ($R = 0.970$), the basicity factor *B* being the only parameter; additional accounting for the other factors did not improve much the correlation.

$$[\alpha]_D = 71.59 + (84.44\pm48.75)f(n^2) + (0.13\pm0.02)B, \quad (6)$$
$$R\ 0.982,\ s\ \pm1.91.$$

In contrast to terpenes containing an easily solvated carbonyl group, the solvent effects on the optical properties of terpene hydrocarbons, α-pinene and β-pinene, were less pronounced (see table); moreover, the major influencing factors were different. In the case of α-pinene, the most important factors were polarity and molar volume of the solvent (respective pairwise correlation coefficients *r* were 0.746 and 0.717).

In α-pinene carbonyl group, capable of the hydrogen bond formation, was absent. The solvent effect on $[\alpha]_D$ was reasonably fitted by four-parametric Eq. (7).

$$[\alpha]_D = 83.79 + (43.07\pm8.20)f(\varepsilon) - (0.05\pm0.01)B - (0.47\pm0.20)E_T - (0.27\pm0.07)V_M, \quad (7)$$
$$R\ 0.972;\ s\ \pm0.92.$$

The $[\alpha]_D$ increased with increase of the medium polarity, whereas the specific solvation factors decreased the optical anisotropy. Interestingly, with solvent molar volume increasing, $[\alpha]_D$ also decreased, probably due to steric hindrance. The electrophilicity factor was less significant: with the corresponding term being excluded from Eq. (7), for the resulting triparametric equation $R = 0.946$, close to the recommended $R \geq 0.95$.

In **V**, the solvated double bond was located in the cycle, whereas **VI** contained the double bond in the side chain, this determined a different solvation type and, thus, a different $[\alpha]_D$ behavior. In the case of **V**, $[\alpha]_D$ significantly increased in the solvating media ($CHCl_3$, CH_3OH, CH_3CN) as compared with that in cyclohexane, and changed only slightly in relatively inert CCl_4 and benzene. In the case of **VI**, $[\alpha]_D$ decreased in solvating media and increased in benzene and CCl_4. This was likely due to better accessibility of C=C towards interaction with a solvent. The significance of the single terms of Eq. (1) was also different in the case of **VI**: the pairwise correlation coefficient r of $[\alpha]_D$ and Hildebrand parameter was only 0.486, whereas the effects of polarity and polarizability factors was more prominent, $r = 0.780$ and 0.882, respectively. The electrophilicity parameter effect was negligible. Finally, the solvent effect on $[\alpha]_D$ was reasonably described by triparametric Eq. (8).

$$[\alpha]_D = -32.47 + (225.55\pm36.15)f(n^2) - (28.69\pm10.82)f(\varepsilon) + (0.07\pm0.01)B, \quad R\ 0.976;\ s\ \pm1.30. \tag{8}$$

In the cases of all studied solvents, $[\alpha]_D$ increased upon solvation, the opposite effect of polarity was relatively less important: excluding the corresponding term only slightly decreased R, to 0.948.

To conclude, the results of this work confirmed the outcome of [3]: the solvent effects on $[\alpha]_D$ of the optically active compounds could be generalized in the linear multiparametric equations. Such generalization allows to clarify the effects of separate solvation processes on $[\alpha]_D$ and determine the substrate structure effect. For example, in the cases of carbonyl-containing terpenes, the major factor affecting the optical properties was the electrophilic solvation of the carbonyl group.

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