Effect of H/D isotope substitution on polarizability of methanol molecules

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The electron polarizabilities ($\alpha_0 \cdot 10^{24}$/cm^3 molec.$^{-1}$) were estimated from the data on refractive indices and molar volumes of H/D isotopomers of methanol at 25 °C using the Lorentz—Lorentz formula: 3.265 (CH_3OH), 3.260 (CH_3OD), 3.235 (CD_3OH), and 3.231 (CD_3OD). A relationship between the isotope effects for α_0 and volume (packing) changes in the structure of liquid methanol induced by deuterosubstitution in the methanol molecule was proposed.

Key words: methanol, polarizability of molecules, H/D isotope effects.

It is known[1—3] that the electron polarizability α_0 of a nonelectrolyte molecule decreases when protons are replaced by deuterons. This seemingly anomalous effect can be explained[1] by a decrease in the zero-point energy of atomic vibrations in a deuterosubstituted molecule at a relatively unchanged potential curve of the electron energy and force constants of the bonds. Published data on the mechanism of the influence of polarizability of a heterofunctional molecule upon proton substitution by deuterons in different structural fragments are virtually lacking. Available information on the refractometric and volume properties of the liquid H/D isotopomers provides this estimation for the deuterosubstituted analogs of methanol.

In this work, we estimated the polarizability of D-isotopomers of methanol CH_3OD, CD_3OH, and CD_3OD at 25 °C and found a relationship between the isotope effect (IE) for this molecular characteristic and changes in the molar volume properties of the alcohol under the effect of deuterosubstitution.

Results and Discussion

The results of refractometric studies of deuterated methanols (as n_D values)* are known.[4] Some data on the IEs for the refractive index $\delta n_D(H \rightarrow D) = n_D(D) - n_D(H)$ for the substitutions $CH_3OH \rightarrow CH_3OD$ and $CH_3OH \rightarrow CD_3OD$ at standard temperature are also published.[2,3] Comparison of the results shows that the scatter of the primary $n_D(H)$ values reaches $2 \cdot 10^{-3}$, while the discrepancy between $\delta n_D(H \rightarrow D)$ at 25 °C is at most $2 \cdot 10^{-4}$ (which is commensurable with the error of experimental determination of n_D for methanol).

As found previously,[5,6] the IE values depend on the methodology of the experiment to a less extent than $n_D(H)$ or $n_D(D)$ do. For this reason, the method, which was good in studying[5,6] other properties of isotoposubstituted liquid systems, was used in this work to standardize n_D. The method is based on the summation of the averaged (by sampling of published[7,8] data) values $n_{D_{av}}(H) = 1.3267 \pm 0.0001$ at 25 °C and reliable[2—4] IE values $\delta n_D(H \rightarrow D)$: $\delta n_D(CH_3OH \rightarrow CH_3OD) \approx -0.0012 \pm 0.0002$, $\delta n_D(CH_3OH \rightarrow CD_3OH) \approx -0.0014 \pm 0.0002$, and $\delta n_D(CH_3OH \rightarrow CD_3OD) \approx -0.0027 \pm 0.0002$. The numerical values of $n_D = n_{Dav}(H) + \delta n_D(H \rightarrow D)$, molar volumes V of the methanol isotopomers, and polarizabilities α_0 of their molecules are given in Table 1. The α_0 values were calculated in the framework of the Langevin—Debye model[9,10] while ignoring the effect of H/D isotope substitution on the electric dipole moment of an alcohol mol-

Table 1. Refractive indices, polarizabilities of molecules, and molar volumes of the H/D isotopomers of methanol with the corresponding isotope effects at 25 °C

Isotopomer	n_D	α_0*	$-\delta\alpha_0(H \rightarrow D)$	V	$\delta V(H \rightarrow D)$
		10^{-24} cm^3 molec.$^{-1}$		cm^3 mol^{-1}	
CH_3OH	1.3267	3.265	—	40.744	—
CH_3OD	1.3255	3.260	0.005	40.810	0.066
CD_3OH	1.3253	3.235	0.030	40.529	−0.215
CD_3OD	1.3240	3.231	0.034	40.625	−0.119

* Based on the above standardization scheme for $n_D(D)$, the α_0 values were estimated with an error of $3 \cdot 10^{-27}$ cm^3 molec.$^{-1}$.

* The refractometric data on the spectral (yellow) D line of sodium ($\lambda_D = 5893 \cdot 10^{-8}$ cm) were used to analyze the refractive indices of the methanol isotopomers.

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ecule and dielectric constant of its medium using the known Lorentz—Lorentz formula

$$R_0 = [(n_D^2 - 1)/(n_D^2 + 2)]_0 V = (4/3)\pi N_A \alpha_0,$$

where R_0 is the molar refraction, and N_A is Avogadro´s number. Subscript "0" indicates a hypothetical state corresponding to the light energy with the zero-point energy. The V values of the alcohols under study are known.[6]

According to the data in Table 1, the substitution of protons by deuterons separately in each structural fragment (CH_3 or OH groups) of the methanol molecule is accompanied by similar effects of decreasing the refractive index of methanol. In this case, the IE $\delta n_D(CH_3OH \rightarrow CD_3OD)$ within the determination error is equal to the sum of the IEs for n_D induced by H/D substitutions in particular fragments. Similar additivity of the IEs is also retained for the summation of negatively charged $\delta\alpha_0(CH_3OH \rightarrow CH_3OD)$ and $\delta\alpha_0(CH_3OH \rightarrow CD_3OH)$. However, the influence of the nature of H/D isotope substitution on the polarizability of the methanol molecule has specific features: for the substitution OH → OD, the α_0 value decreases insignificantly, only by ~0.15% on the average, while its contraction reaches 1% when CH_3 is replaced by CD_3.

The IEs on the polarizability and molar volume of methanol are evidently related. The decrease in α_0 for the substitutions $CH_3OH \rightarrow CD_3OH$ is accompanied by the volume effects $\delta V(H \rightarrow D)$, which are negative in sign and whose absolute values are from two- to threefold greater than the positive IE for V caused by the replacement of protons by deuterons in the hydroxyl group of the methanol molecule (see Table 1). This experimental fact confirms the earlier (obtained by the results of Monte Carlo simulation[11] and NMR spectroscopy[12]) conclusions on a substantial contribution of van der Waals (mainly dispersion) interactions of the contacting methyl groups to the formation of the molecular packing of methanol.

At the same time, the observed inconsistency in signs of the IEs $\delta\alpha_0(H \rightarrow D)$ and $\delta V(H \rightarrow D)$ for the substitution $CH_3OH \rightarrow CH_3OD$ (see Table 1) suggests that specific interactions, which induce the loosening of the structure of deuterosubstituted alcohol (due to the formation of more extended and simultaneously more stable O...D—O bonds[1,5]), are predominant in a methanol medium.

Thus, the results obtained in this study show that the H/D isotope substitution in the methanol molecule induces the "additive-group" decrease in its electron polarizability, which is especially pronounced when protons are substituted by deuterons in the methyl group. The relationship between the IEs for the polarizability of alcohol molecules and the molar volume indicates a significant role of van der Waals interactions in the structural organization of even such a strongly associated (through H bonds) solvent (alcohol) as methanol.

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