ISOTOPE EFFECT IN THE COMPRESSIBILITY AND ASSOCIATION OF DEUTEROALCOHOLS

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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ISOTOPE EFFECT IN THE COMPRESSIBILITY AND ASSOCIATION OF DEUTEROALCOHOLS

(Presented by Academician A. N. Frumkin, December 4, 1956)

In the present work we studied the velocity of ultrasound a and the density d in the interval from 10° to 60–80° for the following alcohols: CH_3OH and CH_3OD, C_2H_5OH and C_2H_5OD, $(CH_3)_2CHOH$ and $(CH_3)_2CHOD$, $CH_3(CH_2)_3OH$ and $CH_3(CH_2)_3OD$; $(CH_3)_2CHCH_2OH$ and $(CH_3)_2CHCH_2OD$, $C_2H_5CHOHCH_3$ and $C_2H_5CHODCH_3$, as well as D_2O (up to 95°). The adiabatic compressibility was calculated from the formula $\beta_{ad} = 1/a^2d$. In addition, the osmotic coefficients of the indicated alcohols in benzene solutions were measured cryoscopically in the interval 0.2–1.7 mol/kg of solvent.

Deuteroalcohols were obtained by hydrolysis with heavy water (99.6%) of the corresponding aluminum or magnesium alcoholates. All alcohols were thoroughly purified and dehydrated. The deuterium content in the hydroxyl of the D-alcohols, except for methyl alcohol, was about 99%. Deuteromethanol contained 30% of its hydrogen analogue. Considering this mixture ideal, we recalculated the measured values of the properties to pure CH_3OD. A stabilized generator of ultrasonic oscillations with a frequency of 3 MHz was used. The velocity of ultrasound was measured optically with an error of 1–2 m/sec. The cuvette was thermostated with an accuracy of 0.05°. As follows from the densities (Table 2), in the temperature interval studied the deuteroalcohols have a molar volume approximately 0.2% greater than their hydrogen analogues.

Table 1

Boiling points of alcohols (760 mm Hg)

Alcohol	t, °C	Alcohol	t, °C
CH_3OH	64.6	$CH_3(CH_2)_3OH$	117.8
CH_3OD	65.4	$CH_3(CH_2)_3OD$	118.2
C_2H_5OH	78.4	$(CH_3)_2CHCH_2OH$	108.0
C_2H_5OD	79.1	$(CH_3)_2CHCH_2OD$	108.2
$(CH_3)_2CHOH$	82.4	$C_2H_5CHOHCH_3$	99.5

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Alcohol	t, °C	Alcohol	t, °C
$(CH_3)_2CHOD$	83.0	$C_2H_5CHODCH_3$	99.7

The ratio of the cryoscopic molecular weight to the formula weight falls in the series: methyl, ethyl, *n*-butyl alcohol, and also in the series normal, iso-, secondary butyl alcohol. The indicated ratio for deuteroalcohols is 2-5% greater than for the corresponding hydrogen analogues (Fig. 1). Since benzene solutions of alcohols in the concentration region studied cannot be considered ideal, the ratios found of cryoscopic molecular weights to formula weights do not give exact values of the degree of association, but represent osmotic coefficients. It is clear, however, that the increase of this coefficient with increasing alcohol concentration is due to an increase in its degree of association.

There are also no grounds for doubting that the data presented in Fig. 1 indicate a decrease in the degree of association through hydrogen bonding in normal alcohols with an increase in the number of carbon atoms in the molecule, and also a greater degree of association of *n*-butyl alcohol than of its isomers. This corresponds to an increase in the shielding of the hydrogen bond

* K. G. Fedyakova took part in the cryoscopic experiments.

both as the radical lengthens and as the molecule branches, and also corresponds to the difference in the boiling temperatures and heats of vaporization of the butyl alcohols ([5]).

Thus, the results of the cryoscopic experiments mean that deuterioalcohols are associated by means of hydrogen bonds to a greater extent than their hydrogen analogs. This conclusion is confirmed by the fact that, as is seen from Table 1, the deuterioalcohols studied boil at higher temperatures than the corresponding hydrogen alcohols, and, as was shown earlier ([2]), replacement of hydrogen in the hydroxyl of an alcohol by deuterium leads to a lowering of its vapor pressure.

Fig. 1. Ratio of the cryoscopic molecular weight to the formula weight in benzene solution as a function of concentration.
1 –CH_3OH; 2 –CH_3OD; 3 –C_2H_5OH; 4 –C_2H_5OD; 5 –$(CH_3)_2CHOH$; 6 –$(CH_3)_2CHOD$; 7 –$CH_3(CH_2)_3OH$; 8 –$CH_3(CH_2)_3OD$; 9 –$(CH_3)_2CHCH_2OH$; 10 –$(CH_3)_2CHCH_2OD$; 11 –$C_2H_5CHOHCH_3$; 12 –$C_2H_5CHODCH_3$.

Fig. 2. Adiabatic compressibility:
1 –CH_3OD; 2 –CH_3OH; 3 –C_2H_5OD; 4 –C_2H_5OH; 5 –$(CH_3)_2CHOD$; 6 –$(CH_3)_2CHOH$; 7 –$CH_3CH_2CH_2OD$; 8 –$(CH_3)_2CHCH_2OH$; 9 –$C_2H_5CHODCH_3$; 10 –$C_2H_5CHOHCH_3$; 11 –$CH_3(CH_2)_3OD$; 12 –$CH_3(CH_2)_3OH$.

V. V. Tarasov ([6]) advanced the proposition that, in the case of alcohols having chain association by means of hydrogen bonds, compression occurs mainly not along the comparatively strong hydrogen bonds, but along the weaker van der Waals bonds between the chains (associates). The results of our compressibility determinations confirm this. As is seen from Fig. 2, in the homologous series of the alcohols studied the compressibility decreases from methyl to *n*-butyl (by 20%), although, as was mentioned, the degree of association by means of hydrogen bonds decreases in the same order (Fig. 1). This is explained by the fact that, with an increase in the number of carbon atoms in the molecule, the polarizability increases and, accordingly, the dispersive intermolecular interaction is enhanced ([7]).

Iso- and secondary butyl alcohols have greater compressibility than their normal primary analog. From a comparison of our data for isopropyl alcohol with Eucken' s results ([3]) for *n*-propyl alcohol it follows that the compressibility of the latter is less than that of its isomer. Finally,

Table 2

Density d (g/cm^3) and speed of ultrasound a (m/sec) in alcohols

	[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]	
t, °C	d	a	d	a	d	a	d	a	d	a	d	a	d	a	d	a	d	a	d	a	d	a	d	a
10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
20	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
30	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
40	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
50	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
60	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
70	–	–	–	–	[illegible]	[illegible]	[illegible]	[illegible]	–	989	–	973	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
80	–	–	–	–	–	–	–	–	–	–	–	–	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	1019	–	1012

I. G. Mikhailov ([8]) showed that *n*-hexyl alcohol has a lower compressibility than its isomers. Thus, alcohols with a branched chain of atoms in the molecule are characterized by greater compressibility than primary *n*-alcohols. This is explained by the fact that branching of the molecule leads to a decrease in the energy of intermolecular interaction both through a reduction in the degree of association by means of hydrogen bonding and through a decrease in the van der Waals interchain interaction, which is of decisive importance for compressibility.

All the deuterated alcohols studied have a speed of ultrasound 10–20 m/sec lower than that of the corresponding hydrogen analogues (see Table 2). The compressibility of deuteroalcohols is greater than that of their hydrogen analogues, with the isotope effect amounting to 1–2%, except for the secondary

butyl alcohols, for which the difference in compressibility is of the same order of magnitude as the error of determination (0.2%). For the isotopic analogues of methanol, a quite noticeable decrease in the relative difference in compressibility with increasing temperature is observed.

From the point of view described above, the isotope effect found in the compressibility means that, in deuteroalcohols, the interchain interaction (the van der Waals interaction between associates) is somewhat weaker than in their hydrogen analogues.

In Fig. 3 the speed of ultrasound, density, and compressibility of water and deuterium oxide are compared according to our data and also according to literature data. Up to 40°, the values of the speed reported by Lagemann et al. ([9]), as well as by Pankholi ([10]), agree with ours to within 1-2 m/sec. Pankholi' s data for higher temperatures are evidently greatly overestimated, and the conclusion following from them that the β—t curves for D_2O and H_2O intersect near 50° is untenable. Our results on the speed of ultrasound in D_2O in the interval 10-90° agree with Hoisinger' s data ([12]) to an accuracy of about 1 m/sec (0.07%). For the density of D_2O we used new literature data ([12]).

The existence in water of a minimum in the temperature curve of compressibility, like the existence of a maximum in density, is explained ([13]) by the superposition of two factors with increasing temperature: an increase in the intensity of thermal motion (increasing the compressibility) and the transition of water from a more associated state to a less associated one, with a more

by a denser packing of the molecules (a decrease in compressibility). The fact that the compressibility of D_2O is 2.5-3.5% greater, and that its minimum is observed 1° higher than in H_2O (65 and 64°), means, as we suppose, that the decrease in the degree of association in heavy water lags in temperature relative to ordinary water. This corresponds to a greater degree of association by means of hydrogen bonding, and also, apparently, to a smaller fraction of van der Waals interaction in D_2O as compared with H_2O. Such an interpretation of the question is consistent with the known isotope effect in the temperature of maximum density ([9]), in the thermal properties ([3,14]), and also in the solubility and solvent power of D_2O ([4]).

Table 3

Adiabatic compressibility
$\beta_{D_2O}\left(\frac{cm^2}{dyn}\cdot 10^{12}\right)$

t, °C	β	t, °C	β
10	49.40	65	43.05
20	47.00	70	43.10
30	45.35	80	43.45
40	44.20	90	44.20

t, °C	β	t, °C	β
50	43.50	95	44.65
60	43.15		

Fig. 3. Isotope effect in the density (d), ultrasonic velocity (a), and adiabatic compressibility (β_{ad}) of heavy water. On the curve a_{H_2O}: 1 –authors' data; 2 –Lagemann et al. ([9]); 3 –Huizinger ([11]); 4 –Pancholy ([10]).

The decrease in the ultrasonic velocity of the substances studied when hydrogen is replaced by deuterium is, to some extent, also directly caused by the increase in molecular weight ([15]).

The authors express their gratitude to Corresponding Member of the Academy of Sciences of the USSR A. I. Brodskii for consultation and discussion of the results.

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Received
1 IX 1956

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Note: Figure translations are in progress. See original paper for figures.