Isotope Effect in the Heat Capacity of Some Deuterium Compounds

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Isotope Effect in the Heat Capacity of Some Deuterium Compounds

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We have previously studied the effect of replacing hydrogen by deuterium on the density (ρ), the velocity of ultrasound, and the adiabatic compressibility (β_{ad}) of a number of liquids ([1–3]). In the present work we measured the heat capacity at constant pressure (c_p) and, using data on the magnitude of β_{ad} and the coefficient of thermal expansion (α), calculated the heat capacity at constant volume (c_v), the isothermal compressibility (β_{is}), the ratio (γ), and the difference ($c_p - c_v$) of heat capacities as functions of temperature for the following liquid isotopic substances: C_6D_6, C_6H_6; C_2H_5OD, C_2H_5OH; $CH_2OD{\cdot}CH_2OD$, $CH_2OH \cdot CH_2OH$; $CH_2OD \cdot CHOD \cdot CH_2OD$, $CH_2OH \cdot CHOH \cdot CH_2OH$.

The aim was to study the influence of isotopy on the heat capacity c_v, which until now had been done experimentally only for heavy water ([4]). Values of β_{is} were also necessary for judging the influence of replacing hydrogen by deuterium on intermolecular interaction. In addition, comparison of identical thermodynamic properties of ordinary ethyl alcohol, ethylene glycol, and glycerol was of independent interest.

The synthesis of the deuterium compounds is described in papers ([1–3]). The hydroxyl groups of the alcohols contained 97–98 at.% deuterium, and benzene 80%. All substances used were thoroughly purified, in particular dehydrated. Their densities and refractive indices corresponded to literature data ([5,6]). For heat-capacity measurements an adiabatic calorimeter of S. M. Skuratov's design ([7]) was used. Some improvements introduced by us and the procedure are described in ([8]). The error of an individual measurement of c_p was 0.3%. Table 1 gives graphically averaged values of c_p, whose error is 0.1%. These data were used to calculate other properties. The isothermal compressibility was calculated from the formula

$$\beta_{\mathrm{is}} = \beta_{\mathrm{ad}} + \frac{\alpha^2 TM}{c_p \rho}, \tag{1}$$

with an accuracy of 0.3–0.5%. The values of ρ and β_{ad} for all substances except ethylene glycol were taken from work ([1]). For the latter these quantities were determined by one of us and L. S. Zhilkin.* The value of α was calculated graphically from the density, with an accuracy of about 0.5%. Within this error the values of α for isotopic substances are identical. The values of c_v given in Table 1 were calculated from the formula

$$c_v = c_p \beta_{\text{ad}} / \beta_{\text{is}}, \qquad (2)$$

with an accuracy of 0.6–0.8%; for calculating the isotope effect in the value of c_v, graphically averaged values of it were taken. For the quantity γ the error is about 0.5%; for $(c_D/c_H)_v$ and γ_D/γ_H, about 1%. For benzene, Table 1 gives data referring to a content of 100 at.% deuterium. The corresponding extrapolation was made on the basis of additivity of the isotope effect. Our values of c_p for ordinary benzene agree within 0.3% with the results of the averaging of several works carried out in ([10]). Therefore, and since the purity of the pri–

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* The values of β_{ad} for ethylene glycol, determined from the velocity of ultrasound, are not given here, since they can be found by inverse calculation from the corresponding values of c_p, c_v, and β_{is} (Table 1). Our density values for the same alcohol agree, to an accuracy of $1 \cdot 10^{-4}$ g/cm^3, with the data of ([9]).

Table 1

Heat capacities and isothermal compressibilities

T, °C	c_p, cal/mol·deg, D	c_p, cal/mol·deg, H	c_v, cal/mol·deg, D	c_v, cal/mol·deg, H	$\beta_{\text{is}} \cdot 10^{12}$, cm^2/dyne, D	$\beta_{\text{is}} \cdot 10^{12}$, cm^2/dyne, H	$\alpha \cdot 10^4$, deg^{-1}	c_p, cal/mol·deg, D	c_p, cal/mol·deg, H	c_v, cal/mol·deg, D	c_v, cal/mol·deg, H	$\beta_{\text{is}} \cdot 10^{12}$, cm^2/dyne, D	$\beta_{\text{is}} \cdot 10^{12}$, cm^2/dyne, H	$\alpha \cdot 10^4$, deg^{-1}
	CH_2OD–$CHOD$–CH_2OD and CH_2OH–$CHOH$–CH_2OH	CH_2OD–CH_2OD and CH_2OH–CH_2OH												
10	53.1_0	50.5_4	48.5_5	45.9_2	23.5	23.1	4.63	35.9_9	34.5_6	31.8_4	30.3_8	35.7	35.4	6.28
15	53.8_1	51.0_7	49.1_3	46.3_4	23.9	23.5	4.70	36.4_1	34.9_0	32.2_0	30.6_6	36.4	36.1	6.31
20	54.5_2	51.6_1	49.8_6	46.7_4	24.2	23.8	4.76	36.8_2	35.2_8	32.5_5	30.9_8	36.9	36.6	6.33
25	55.2_1	52.1_4	50.2_9	47.1_8	24.6	24.2	4.84	37.2_7	35.5_5	33.0_0	31.2_6	37.7	37.4	6.36
30	55.9_2	52.7_0	50.7_4	47.8_0	25.0	24.6	4.92	37.7_4	35.9_8	33.5_6	31.6_1	38.4	38.1	6.38
35	56.6_2	53.2_6	51.2_2	48.0_0	25.4	25.0	4.99	38.2_4	36.3_2	33.9_8	31.9_5	39.0	38.7	6.41
40	57.3_3	53.8_5	51.8_1	48.4_8	25.8	25.5	5.06	38.8_8	36.7_3	34.4_0	32.3_2	39.5	39.5	6.43
45	58.0_2	54.4_8	52.5_3	48.8_8	26.2	25.9	5.13	39.3_9	37.1_8	34.9_0	32.7_2	40.4	40.0	6.46
50	58.7_1	55.1_4	52.9_8	49.2_7	26.6	26.3	5.21	39.9_5	37.6_6	35.4_4	33.1_8	41.2	41.0	6.48

T, °C	c_p, cal/mol·deg, D	c_p, cal/mol·deg, H	c_v, cal/mol·deg, D	c_v, cal/mol·deg, H	$\beta_{is}\cdot 10^{12}$, cm^2/dyne, D	$\beta_{is}\cdot 10^{12}$, cm^2/dyne, H	$\alpha\cdot 10^4$, deg^{-1}	c_p, cal/mol·deg, D	c_p, cal/mol·deg, H	c_v, cal/mol·deg, D	c_v, cal/mol·deg, H	$\beta_{is}\cdot 10^{12}$, cm^2/dyne, D	$\beta_{is}\cdot 10^{12}$, cm^2/dyne, H	$\alpha\cdot 10^4$, deg^{-1}
55	59.4_3	55.8_3	53.4_4	49.6_9	27.1	26.7	5.29	40.5_0	38.1_8	35.9_8	33.5_9	41.9	41.7	6.51
	C_2H_5OD and C_2H_5OH	C_6D_6 and C_6H_6												
10	26.6_2	25.6_9	22.4_2	21.4_3	108.9	107.8	10.77	35.8_5	31.5_6	26.1_0	21.7_2	86.8	86.4	11.94
15	27.2_1	26.2_3	22.9_3	21.9_3	112.3	111.2	10.93	36.0_2	31.8_0	26.4_0	22.0_7	89.8	89.2	
20	27.7_1	26.8_8	23.4_4	22.4_4	116.1	114.9	11.05	36.1_8	32.0_4	26.7_0	22.4_2	93.2	92.3	
25	28.3_1	27.3_9	23.9_7	22.9_5	120.0	118.9	11.20	36.4_4	32.2_2	27.0_1	22.7_7	96.5	95.6	
30	28.9_7	27.7_9	24.4_8	23.4_5	124.5	123.2	11.36	36.6_2	32.5_0	27.3_0	23.1_0	99.0	98.0	
35	29.5_5	28.3_9	25.0_0	23.9_4	129.0	127.6	11.37							
40	30.1_1	28.9_5	25.5_0	24.4_8	134.0	132.5	11.55							
45	30.6_6	29.5_3	26.0_3	24.9_8	139.4	137.4	11.74							
50	31.2_8	30.1_0	26.5_5	25.5_0	144.8	143.0	11.94							

the changing deutero-benzene and the deuterium content in it raise no doubt; we believe that the data in Table 1 for C_p (C_6D_6) are reliable to within a few tenths of a percent. Then the corresponding data of Ziegler and Andrews ([10]) are low by approximately 2%.*

For the deuterium compounds studied by us, the heat capacity c_v is considerably greater than for the corresponding ordinary substances (Table 1). Earlier ([4]) it was also established that $c_v(D_2O) > c_v(H_2O)$. Qualitatively this can be explained as follows. When a light isotope is replaced by a heavy one, the component of the heat capacity due to translational motion becomes larger as a result of the increase in molecular mass; the rotational component also increases because of the increase in the moments of inertia, while the vibrational components increase because of the decrease in the frequencies of molecular and atomic vibrations. Since, upon replacement by deuterium of hydrogen forming a hydrogen bond, the dissociation energy of the latter and the degree of association increase ([11]), the associative component of the heat capacity should probably also increase in this case.

The isotopic difference in heat capacity, $100[(c_D/c_H)_v - 1]$, for glycerol and ethylene glycol has similar values: 6.0–

* Our data on the value of c_p of ordinary alcohols are smaller than some and larger than other corresponding data in the literature ([12,9,5]) by 0.5–1.5%.

–7.5 and 5.5–8.0, respectively (Fig. 1). This corresponds to the fact that, for both substances, deuteration in the hydroxyl groups is associated with an almost identical relative increase in molecular weight (3.25%) and with approximately the same fraction of atomic bonds at which isotopic substitution occurs (in glycerol, at 3 bonds out of 13; in glycol, at 2 out of 9). For C_2H_5OD, relative to C_2H_5OH, the value of c_v is greater by 4.5–4.0%, but this is associated with an increase in molecular weight of only 2.18% and isotopic substitution at one bond out of 8. For C_6D_6, the heat capacity c_v is 20–18% (between 10 and 30°C) greater than the heat capacity of C_6H_6; however, in this case the molecular weights differ by 7.73%, and isotopic substitution occurs at 6 bonds out of 15. Judging from the data described, the component of the heat capacity due to association is probably not the determining factor for the isotopic difference in the value of c_v of the alcohols studied.

(Figure: Fig. 1)

Fig. 1. Ratio of heat capacities at constant volume of isotopic compounds:
1 –C_6D_6/C_6H_6;
2 –$CH_2OD \cdot CHOD \cdot CH_2OD/CH_2OH \cdot CHOH \cdot CH_2OH$;
3 –$CH_2OD \cdot CH_2OD/CH_2OH \cdot CH_2OH$;
4 –C_2H_5OD/C_2H_5OH.

The following feature is observed in the temperature dependence of the isotopic effect (Fig. 1). With increasing temperature the ratio $(c_D/c_H)_v$ for benzene decreases distinctly; for ethyl alcohol it decreases, but within the limits of error; for ethylene glycol and glycerol, on the contrary, it increases somewhat. Possibly this means that in the interval 10–55°C, with increasing temperature, the role of the heat-capacity component determined by the energy of rupture of hydrogen bonds increases; this component is larger in deuterated alcohols than in ordinary ones ([11]). However, the same feature may also be caused by an increase in another component of the heat capacity, in particular the vibrational one (c_E), or by the character of the temperature dependence of the derivative $\partial c_E/\partial \nu$, where ν is the frequency of vibrations. An increase in the ratio $(c_D/c_H)_p$ with increasing temperature was established earlier for methyl alcohol ([13]) in the interval 90–150°K (solid state) and 180–270°K (liquid), for ice ([14]) between 60 and 200°K, and for solid benzene ([10]) in the interval 100–250°K.

It is of interest to compare the isothermal compressibility of the three alcohols studied. At 25°C, for example, its values for ethyl alcohol, ethylene glycol, and glycerol are related as 4.75 : 1.5 : 1, respectively. The increase in β_{is} between 15 and 55°C is 32.5, 15.5, and 13.5%, respectively. Such a sharp difference in the behavior of ethyl alcohol, on the one hand, and ethylene glycol and glycerol, on the other, should, of course, be attributed to differences in intermolecular interaction, as well as to structural factors of these substances, especially in the temperature range studied.

Replacement of hydrogen by deuterium in the substances investigated causes an increase in isothermal compressibility by 0.5–1.5%. Since the accuracy of the values of β_{is} is a few tenths of a percent, the direction of the isotopic effect in this quantity is beyond doubt. It has the same sign as the isotopic effect in adiabatic compressibility, but is smaller than the latter—the difference in the value of β_{ad} at 20°C for C_6D_6 and C_6H_6 is 6%, while for the corresponding deuterated and ordinary alcohols it is 1.5-2%. According to the calculation made in ([1]), at 20°C $\beta_{is}(D_2O)$ is greater than $\beta_{is}(H_2O)$ by 3%, and $\beta_{ad}(D_2O)$ is greater than $\beta_{ad}(H_2O)$ by 4%.

Owing to the identity of the composition and structure of the molecule and of the types of intermolecular forces, apparently, in the region of moderate temperatures the structure of isotopic substances in the liquid phase is the same for the heavy and ordinary versions.

water has been shown experimentally [(15)]. Therefore the isotopic difference in compressibility should be explained by the difference in intermolecular interaction. For benzene this means that replacement of hydrogen by deuterium causes a weakening of the dispersion interaction of the molecules. This agrees with the data [(6,17)]. Since the energy of association by means of a hydrogen bond increases when the hydrogen forming it is replaced by deuterium [(11)], for ethanol the increase in compressibility as a result of the indicated isotopic substitution must be explained by a weakening of the dispersion interaction of the associates. This corresponds to the opinion of V. V. Tarasov [(16)] concerning the compressibility of monohydric alcohols. For glycerin and ethylene glycol we explain the relation $\beta_D > \beta_H$ by the fact that replacement of hydrogen by deuterium in the hydroxyl groups causes an increase in the degree of order of the spatial molecular network (a decrease in the number of broken hydrogen bonds), which corresponds to a certain decrease in the density of the distribution of molecules and an increase in the molecular volume [(1)].

(Figure: Figure 2)

Fig. 2. Ratio of heat capacity at constant pressure to heat capacity at constant volume:
1 $-C_6H_6$; 2 $-C_6D_6$; 3 $-C_2H_5OH$; 4 $-C_2H_5OD$; 5 $-CH_2OH \cdot CH_2OH$; 6 $-CH_2OD \cdot CH_2OD$; 7 $-CH_2OH \cdot CHOH \cdot CH_2OH$; 8 $-CH_2OD \cdot CHOD \cdot CH_2OD$.

For glycerin a peculiarity is observed in the temperature dependence of γ. For benzene this quantity decreases by approximately 4% in the interval $10 \div 30$°C; for ethyl alcohol, between 15 and 55°, it increases by 1.5%; for ethylene glycol its change is within the limits of error, while for glycerin the same quantity in the interval $10 \div 55°$ increases by 2% (Fig. 2). This is connected with the difference in the temperature dependence of the quantities c_v and $(c_p - c_v)$. For benzene the first of these increases, while the second decreases with increasing temperature; for ethylene glycol both quantities increase at approximately the same rate; for ethyl alcohol c_v increases faster than $(c_p - c_v)$, while for glycerin the opposite takes place (Table 1).

In connection with the dependences set forth above, the influence of replacing hydrogen by deuterium on the heat capacity c_p is qualitatively analogous to its influence on the quantity c_v, but for c_p the isotopic effect is smaller.

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

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