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Estimation of hydrogen bond energy in *n*-alkanols from the gas chromatography data

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The retention factors of C_1—C_9 *n*-alkanols on a capillary column with the SE-30 nonpolar phase were determined for temperatures between 320 and 400 K. From the temperature dependence of the free energy change, variations in the enthalpy of sorption of *n*-alkanols on the SE-30 polymethylsiloxane phase were calculated. The difference between the enthalpies of condensation and sorption was used to estimate the contribution of hydrogen bonding to self-association of pure liquid alcohols. The calculated energies of hydrogen bonds in liquid *n*-alkanols are in good agreement with the published data.

Key words: capillary gas chromatography, *n*-alkanols, SE-30 stationary phase, enthalpy of sorption.

The structure and properties of *n*-alkanols are largely governed by their ability for self-association in pure liquids through hydrogen bonding. Liquid alkanols are complex systems in which monomers coexist with linear and cyclic associates. The change of enthalpy of alkanols due to hydrogen bond formation is usually determined by investigating the properties of binary mixtures of *n*-alkanols C_1—C_{12}) and hydrocarbons C_6—C_{12}) at ambient temperature or at elevated (up to 60 °C) temperatures by various physicochemical methods.[1—7] Numerous theoretical models taking account of the composition and structure of associated liquids and the nature of intermolecular interaction (IMI) occurring in the liquids have been proposed.[8—13] The criterion of applicability of models is the agreement between the association parameters calculated in terms of these models and those obtained by calorimetric measurements. All the measurements are fairly laborious and the resulting values of the enthalpy change upon hydrogen bond formation in alcohols are varied over a broad range (16—27 kJ mol^{-1}). The purpose of this present work is to determine thermodynamic characteristics of sorption of *n*-alkanols on a capillary column with the SE-30 nonpolar phase by gas chromatography and to use the results for estimating the energy of hydrogen bond formation in a pure liquid consisting of associated alkanol molecules.

Experimental

Gas chromatographic analysis of *n*-alkanols (C_1—C_9) was conducted on a Micromat 412 chromatograph (Finland) with a quartz capillary column (25 m × 0.32 mm) with SE-30 (Nordian Instr.) as the stationary phase (SP); the SP layer thickness was d_f = 1.0 μm. The temperature of the flame ionization detector and the injector was 200 °C. The measurements were performed under isothermal conditions at temperatures of 48, 58, 66, 100, 110, 120, and 130 °C. Helium was used as a carrier gas, the split ratio at the inlet of the column was 1 : 100. The sample volume was 0.5—1.0 μL of a vaporous mixture of *n*-alkanols. The hold-up time needed to calculate the retention factor *k'* was determined as retention time of methane injected into the column simultaneously with the sample. The *k'* values for *n*-alkanols at various temperatures are given in Table 1.

The differential molar free energy of *n*-alkanols for GC sorption was calculated from the relation[15]

$$\Delta G_S{}^T = -RT\ln(k' \cdot \beta), \qquad (1)$$

where *R* is the universal gas constant, equal to 8.314 kJ (mol K)$^{-1}$; *T*/K is the temperature of analysis; β is the phase ratio calculated as follows:[16]

$$\beta = (d_c - 2d_f)^2/4(d_c d_f - d_f{}^2), \qquad (2)$$

where d_c is the internal diameter of the column.

Table 1. Values of *k'* for *n*-alkanols on a capillary column with the SE-30 stationary phase

n-Alkanol	*k'* at *T*/K						
	321	331	339	373	383	393	403
Methanol	0.161	0.140	0.118	—	—	—	—
Ethanol	0.368	0.285	0.231	—	—	—	—
Propanol	1.015	0.749	0.592	0.229	0.190	0.159	0.136
Butanol	2.699	1.901	1.450	0.481	0.384	0.313	0.260
Pentanol	6.895	4.692	3.443	0.975	0.755	0.597	0.481
Hexanol	—	—	—	1.933	1.451	1.116	0.871
Heptanol	—	—	—	3.795	2.762	2.057	1.561
Octanol	—	—	—	7.390	5.197	3.762	2.774
Nonanol	—	—	—	14.300	9.738	6.743	4.901

Note. The difference between the minimum and maximum *k'* values over five—seven measurements was 0.2—0.4% for C_2—C_9 *n*-alkanols and 1.5—2.0% for methanol.

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The change in enthalpy ΔH_S and entropy ΔS_S of *n*-alkanols upon sorption were determined using the equation

$$\Delta G_S{}^T = \Delta H_S - T\Delta S_S \qquad (3)$$

for narrow temperature ranges, 321—339 K and 373—403 K.

The ΔH_V values needed to calculate the contribution of hydrogen bonding to the enthalpy of *n*-alkanols were taken from a handbook[17] or calculated using the Clapeyron—Clausius equation for liquid—vapor systems.[18]

$$\Delta H_V{}^T = RT^2(\Delta \ln p^\circ/\Delta T). \qquad (4)$$

The vapor pressures at saturation p° were taken from a handbook.[19]

Results and Discussion

During GC analysis, the monomeric alkanol molecules occur under conditions of infinite dilution in the mobile and stationary phases. We suggested that the nonspecific interactions between the monomeric alkanol molecules and the SP simulate the IMI component caused by dispersion forces in pure alkanols. In this case, GC determination of the changes in the thermodynamic characteristics of alcohols upon sorption could be used for indirect estimation of the energy of hydrogen bonds in alkanol associates. The use of capillary columns permits relatively easy determination of the thermodynamic characteristics of sorption, and the use of quartz columns minimizes the possible distortion of results due to the adsorption on the column walls.

The differential molar free energy of sorption of a compound ($\Delta G_S{}^T$) is known to be the sum of the differential molar free energies of condensation of the monomers in the stationary phase (ΔG_V) and the molar excess energy of mixing (ΔG_E) of the substance with the stationary phase[14]

$$-\Delta G_S{}^T = -\Delta G_V + \Delta G_E. \qquad (5)$$

Equation (5) is valid for substances whose molecules exist as monomers both in pure liquid and in the vapor.

For the compounds under study, which are capable of forming associates, the free energy of evaporation of one mole of substance $\Delta G_V{}'$ can be represented by the sum

$$\Delta G_V{}' = \Delta G_{ass} + \Delta G_{Vm}, \qquad (6)$$

where ΔG_{ass} is the differential molar free energy of decomposition of one mole of the associate into individual molecules; ΔG_{Vm} is the differential molar free energy of evaporation of monomeric molecules from pure liquid, which is a mixture of monomers and associates. In the case of alkanols whose molecules are associated through the formation of intermolecular hydrogen bonds, we obtain

$$\Delta G_V{}' = \Delta G_{Vm} + \Delta G_{H\text{-}b}, \qquad (7)$$

where $\Delta G_{H\text{-}b}$ is the differential molar free energy for the cleavage of hydrogen bonds. Similarly, the change in the enthalpy upon evaporation from pure liquid ΔH_V for associated alkanols is described by the equation

$$\Delta H_V = \Delta H_{Vm} + \Delta H_{H\text{-}b}, \qquad (8)$$

where ΔH_{Vm} is the differential molar enthalpy of evaporation of monomeric alkanol molecules from a mixture of monomers and associates, and $\Delta H_{H\text{-}b}$ is the molar enthalpy of hydrogen bond cleavage.

In a chromatographic process, the alkanol molecules, which occur under conditions close to infinite dilution by the carrier gas, interact with the stationary phase as monomers; thus, Eq. (5) assumes the form

$$-\Delta G_S{}^T = -\Delta G_{Vm} + \Delta G_E. \qquad (9)$$

The differential molar enthalpy of sorption of monomeric alkanol molecules by the SP (ΔH_S) is expressed by the equation

$$\Delta H_S = -\Delta H_{Vm} + \Delta H_E, \qquad (10)$$

where ΔH_E is the differential excess molar enthalpy of mixing. Under conditions of GC analysis, the contribution of this term is usually small and, hence, it can be neglected. Thus,

$$\Delta H_S \approx -\Delta H_{Vm}. \qquad (11)$$

Table 2. Values of $\Delta G_S{}^T$ for sorption of *n*-alkanols on the SE-30 stationary phase

n-Alkanol	$-\Delta G_S{}^T$/kJ mol^{-1} at T/K						
	321	331	339	373	383	393	403
Methanol	6.8	6.6	6.3	—	—	—	—
Ethanol	9.0	8.6	8.2	—	—	—	—
Propanol	11.7	11.2	10.8	9.0	8.6	8.3	8.0
Butanol	14.3	13.8	13.4	11.3	10.9	10.5	10.1
Pentanol	16.8	16.3	15.8	13.5	13.0	12.6	12.2
Hexanol	—	—	—	15.6	15.1	14.6	14.2
Heptanol	—	—	—	17.7	17.2	16.6	16.1
Octanol	—	—	—	19.8	19.2	18.6	18.1
Nonanol	—	—	—	21.2	21.2	20.5	20.0

Table 3. Characteristics of the linear dependencies of $\Delta G_S{}^T$ on the number of carbon atoms in the *n*-alkanol molecule

Parameter	321 K	331 K	339 K	373 K	383 K	393 K	403 K
a	−3.8	−3.5	−3.2	−2.8	−2.5	−2.3	−2.1
b	−2.6	−2.6	−2.5	−2.1	−2.1	−2.0	−2.0
r	0.99984	0.99988	0.99983	0.99981	0.99981	0.99971	0.99976
sd	0.06	0.05	0.06	0.09	0.09	0.10	0.09

Note. r is the correlation coefficient, sd is the standard deviation for the equation $\Delta G_S{}^T = a + bn$.

Taking into account the fact that ΔH_S and ΔH_V for the sorption have opposite signs, it follows from Eqs. (8) and (11) that

$$\Delta H_{\text{H-b}} = \Delta H_V - |\Delta H_S|, \tag{12}$$

where ΔH_V is the enthalpy of evaporation of alkanol from pure liquid found by an independent method, *e.g.*, by calorimetry.

In order to verify the method proposed for the estimation of the $\Delta H_{\text{H-b}}$ values for *n*-alkanols in pure liquid, the $\Delta G_S{}^T$ values for the sorption of C_1—C_9 *n*-alkanols were calculated from the retention factors *k'* (see Table 1) on a quartz capillary column with SE-30. As follows from Table 2, the $\Delta G_S{}^T$ values obey a linear dependence on the number of C atoms in the alkanol molecule and gradually decrease with an increase in the temperature of analysis. It was shown in some experiments that the coefficients *b* characterizing the free energy of sorption of a methylene unit are close for the homologous series of *n*-alkanols and *n*-alkanes and decrease within the same limits as the temperature increases from 351 to 403 K. This indicates that the crucial role in the interaction of alkanols with the SE-30 nonpolar phase is played by dispersion interactions.

The temperature dependence of $\Delta G_S{}^T$ allows one to determine the ΔH_S values as well as the entropy changes (ΔS_S) for the sorption of alkanols. Tables 4 and 5 shows the resulting ΔH_S and ΔS_S values and the coefficients of linear equations relating the enthalpy and entropy of sorption of *n*-alkanols to the number of C atoms (*n*) in the molecule. As the temperature increases, the ΔH_S and ΔS_S values decrease in magnitude; however, the contribution of the entropy constituent ($T\Delta S_S$) to the free energy for the sorption of alkanols by the nonpolar phase somewhat increases.

Table 4. Values ΔH_S (kJ mol^{-1}) and ΔS_S (J (mol K)$^{-1}$) for *n*-alkanols

n-Alkanol	321—339 K		373—403 K	
	$-\Delta H_S$	$-\Delta S_S$	$-\Delta H_S$	$-\Delta S_S$
Methanol	15.6	27.4	—	—
Ethanol	23.4	44.9	—	—
Propanol	27.2	48.3	21.7	34.2
Butanol	31.3	52.7	25.7	38.6
Pentanol	34.8	56.0	29.5	42.9
Hexanol	—	—	33.2	47.2
Heptanol	—	—	37.0	51.7
Octanol	—	—	40.8	56.3
Nonanol	—	—	44.8	61.7

Note. In the 321—339 K range, the linear dependences refer to n = 2—5 because the ΔH_S and ΔS_S for methanol are determined with great uncertainty (see the note to Table 1).

The ΔH_S and ΔH_V values given in Table 4 were used to calculate the enthalpies of hydrogen bond formation $\Delta H_{\text{H-b}}$. The calculated $\Delta H_{\text{H-b}}$ values, together with the ΔH_V values used in the calculations are listed in Table 6. The ΔH_V values for the C_1—C_5 *n*-alkanols in the 321—339 K temperature range were found by interpolation using the linear dependences $\Delta H_V = a + bT$ plotted on the basis of the heats of evaporation taken from a handbook.[17] The ΔH_V values for the C_3—C_9 *n*-alkanols at higher temperatures, which are not available from the handbook,[17] were calculated for the 373—403 K range using the Clapeyron—Clausius equation and the vapor pressures at saturation.[19] Analysis of the data given in Table 6 shows that in the case of *n*-nonanol, the regular pattern of variation of ΔH_V upon the change in the number of C atoms in the alkanol molecule is violated in this temperature range. At ambient temperature, the linear correlation holds over the homologous series of C_1—C_{14} *n*-alkanols.[20] The underestimated ΔH_V value found for *n*-nonanol appears to be due to inaccuracy of the handbook values for the saturated vapor pressure for this substance.

The analysis of published data shows that the change in enthalpy upon the formation of hydrogen bonds in alkanol associates ($\Delta H_{\text{H-b}}$) virtually does not depend on

Table 5. Relating the *a* and *b* coefficients for the dependences $y = a + bn$* for ΔH_S and ΔS_S on the number of carbon atoms (*n*) in the *n*-alkanol molecule

Parameter	321—339 K		373—403 K	
	$-\Delta H_S$	$-\Delta S_S$	$-\Delta H_S$	$-\Delta S_S$
a	−15.8	−37.3	−10.3	−20.4
b	−3.8	−3.8	−3.8	−4.5
r	0.99971	0.99829	0.99994	0.99935
sd	0.12	0.28	0.09	0.35

Note. See Table 2.

Table 6. Values of ΔH_V and $\Delta H_{H\text{-}b}$ (in kJ mol^{-1}) for *n*-alkanols

n-Alkanol	321 K		331 K		339 K		298 K	373—403 K	
	$\Delta H_V{}^a$	$-\Delta H_{H\text{-}b}$	$\Delta H_V{}^a$	$-\Delta H_{H\text{-}b}$	$\Delta H_V{}^a$	$-\Delta H_{H\text{-}b}$	$-\Delta H_{H\text{-}b}{}^{298\ b}$	$\Delta H_V{}^c$	$-\Delta H_{H\text{-}b}$
Methanol	36.2	20.6	35.6	20.0	35.2	19.5	21.9	—	—
Ethanol	41.0	17.5	40.3	16.8	39.7	16.3	19.1	—	—
Propanol	46.2	19.0	45.2	17.9	44.3	17.1	21.5	40.8	19.1
Butanol	51.1	19.8	49.9	18.6	49.0	17.7	22.5	44.6	18.9
Pentanol	54.7	19.9	53.6	18.8	52.7	17.9	22.4	46.5	17.0
Hexanol	—	—	—	—	—	—	—	51.4	18.1
Heptanol	—	—	—	—	—	—	—	56.4	19.4
Octanol	—	—	—	—	—	—	—	61.5	20.7
Nonanol	—	—	—	—	—	—	—	60.9	16.1

[a] The values were obtained by interpolation of reference data.[17]

[b] The values were obtained by extrapolation of the $\Delta H_{H\text{-}b}$ values for 321—339 K to 20 °C.

[c] The values were calculated from reference data for saturated vapor pressures.[19]

the number of C atoms in the *n*-alkanol and *n*-alkane molecule used as the inert diluent. The $\Delta H_{H\text{-}b}$ values for C_1—C_5 *n*-alkanols extrapolated to ambient temperature are in good agreement with the results obtained previously[21—23] (see Table 6). The value of $\Delta H_{H\text{-}b}{}^{298}$ = 19.1 kJ mol^{-1} that was found for ethanol coincides with the enthalpy of dimerization of pure ethanol, $\Delta H_{H\text{-}b}$ = 19.0 kJ mol^{-1}, determined using the data on static dielectric constants.[15]

Published data on the influence of temperature on the strength of associates[21,22] show that the energy of hydrogen bonding in *n*-alkanols decreases somewhat with an increase in temperature. For example, as the temperature is raised from 298 to 308 K, the enthalpy of formation of hydrogen bonds in ethanol decreases from 23.2 to 22.2 kJ mol^{-1}.[22] When the temperature increases from 303 to 333 K, the $\Delta H_{H\text{-}b}$ value for EtOH decreases from 23.6 to 22.9 kJ mol^{-1}.[24] Chromatographic analysis allows one to follow the temperature dependence of the enthalpy of alkanol association over a broader range. For example, it follows from Table 6 that on passing from ambient temperature to the 373—403 K temperature range, the $\Delta H_{H\text{-}b}$ values for Pr^{n}OH, Bu^{n}OH, and *n*-pentanol diminish by 2.5, 3.6, and 5.4 kJ mol^{-1}, respectively.

The method proposed for the estimation of the energy of hydrogen bonding in pure liquids is facile and convenient as compared to methods described in the literature, which are labor-consuming and often expensive, and provides nearly the same results on the energy of hydrogen bond formation.

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