Gas-chromatographic method of evaluation of *n*-alkanol ability for self-association in pure liquid

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The values of the gas-chromatographic indicator reflecting the capacity of analytes for self-association in pure liquids, $\delta T_{\rm b.p.}$, were estimated for C_1—C_9 and C_{11} *n*-alkanols by capillary gas chromatography on a nonpolar stationary phase under isothermal conditions. The $\delta T_{\rm b.p.}$ values of *n*-alkanols, found as the difference between the boiling points measured directly and those calculated from GC data, are correlated with thermodynamic characteristics of the formation of *n*-alkanol associates in pure liquids. Using *n*-alkanols as analytes with insignificant temperature increments of the retention indices, it was shown that the $\delta T_{\rm b.p.}$ values can be determined under conditions used in gas chromatography with temperature programming. In this way a single chromatographic run can be used to compare the capacities for self-association of analytes boiling over a wide temperature range. The C_2—C_9 *n*-alkanethiols, which are not associated in neat liquids, have negative $\delta T_{\rm b.p.}$ values. An interpretation of this finding is proposed.

Key words: capillary gas-chromatography, *n*-alkanols, *n*-alkanethiols, retention indices, temperature increments, gas-chromatographic indicator of self-association of analytes in pure liquids.

The capacity of *n*-alkanols for self-association and the properties of associates have long been attracting attention of researchers.[1—5] The structures of associates and the degrees of association of molecules are determined using various labor-consuming methods. Previously,[6,7] we proposed a simple gas-chromatographic (GC) procedure for evaluation of the capacity of heterocyclic nitrogen-containing compounds in pure liquids for self-association. The $\delta T_{\rm b.p.}$ value, defined as the difference between the boiling point of a pure substance measured directly $T_{\rm b.p.}$ and the "gas-chromatographic boiling point" $T_{\rm b.p.}{}^{\rm GC}$, calculated from the boiling points of *n*-alkanes and the retention index of the compound under study on a nonpolar column, was proposed as an indicator for self-association of substances in neat liquids. The $\delta T_{\rm b.p.}$ values were used to estimate the capacity for self-association of pure liquids of unsubstituted and alkyl-substituted five- and six-membered aromatic nitrogen-containing compounds with one to three N atoms in the ring.[7] Thermodynamic principles for the calculation of the GC indicator $\delta T_{\rm b.p.}$ was given and the enthalpies of self-association of nitrogenous heterocycles were found to correlate with $\delta T_{\rm b.p.}$. Since alkan-1-ols are the best studied class of compounds associated in pure liquids, they were chosen as the objects to investigate the variation of the $\delta T_{\rm b.p.}$ value as a function of the alcohol molecular weight and thermodynamic parameters of association.

The purpose of this study is to determine the $\delta T_{\rm b.p.}$ values of alkan-1-ols by capillary GLC and to compare them with $\delta T_{\rm b.p.}$ of alkane-1-thiols, incapable of self-association. An attempt was made to find correlations between the GC indicator of association, $\delta T_{\rm b.p.}$, and thermodynamic characteristics of alcohol self-associates in pure liquids and, finally, to use linear temperature programmed gas chromatography (TPGC) for estimating the capacity of alcohols for self-association based on the $\delta T_{\rm b.p.}$ values.

Experimental

Gas-chromatographic analysis of *n*-alkanols (C_1—C_9, C_{11}) was performed on a Micromat 412 chromatograph (Finland) using a fused silica capillary column (25 m × 0.32 mm) with SE-30 and a phase layer thickness d_f = 1.0 μm (Nordion Instr.). The flame ionization detector and the injector were kept at 200 °C. Analysis was carried out under isothermal conditions at temperatures of 48, 58, 66, 100, 110, 120, and 130 °C and under TPGC conditions at the initial temperature T_0 = 60 °C. All runs were programmed at rates of 2, 4, 6, and 8 K min^{-1}. The carrier gas (helium) pressure at the inlet of the column was 0.7 atm; the carrier gas split ratio was 1:100; a sample consisted of 0.5—1.0 μL of vapors of *n*-alkanol and *n*-alkane mixtures. Retention indices were calculated using C_4—C_{14} *n*-alkanes and the "dead time" was determined based on the retention of methane, which was injected into the column simultaneously with the mixture of alcohols and hydrocarbons. The retention indices obtained under isothermal conditions were calculated using the Kovats formula[8]; those derived in TPGC conditions were found using the Van den Dool and Kratz formula.[9] The $\delta T_{\rm b.p.}$ values for *n*-alkanols and *n*-alkanethiols were calculated using equations reported in a previous study.[6]

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Results and Discussion

The retention indices of alkan-1-ols for a nonpolar capillary column with SE-30 under TPGC conditions at chromatographic temperatures of 48—130 °C are listed in Table 1. It can be seen that the retention indices of *n*-alkanols slightly depend on the temperature of the analysis. For instance, when the column temperature increases from 48 to 130 °C, the temperature increment of the retention index ($\delta I/\delta T$) for *n*-propyl, *n*-butyl, and *n*-pentyl alcohols is, on the average, 0.184 index units (iu) per degree. Therefore, the retention indices determined under temperature programming conditions differ insignificantly from the isothermal values and the $\delta T_{\text{b.p.}}$ values can, apparently, be calculated from the data obtained under TPGC conditions.

The values for the GC indicator $\delta T_{\text{b.p.}}$ and the "gas-chromatographic boiling points" $\delta T_{\text{b.p.}}{}^{\text{GC}}$ for the compounds studied were calculated (according to Refs. 6 and 7) using the equations

$$\delta T_{\text{b.p.}} = T_{\text{b.p.}}(\text{X}) - T_{\text{b.p.}}{}^{\text{GC}}(\text{X}), \tag{1}$$

$$T_{\text{b.p.}}{}^{\text{GC}}(\text{X}) = T_{\text{b.p.}}(C_n) + \\ + \frac{T_{\text{b.p.}}(C_{n+1}) - T_{\text{b.p.}}(C_n)}{100}[I(\text{X}) - 100n], \tag{2}$$

where $T_{\text{b.p.}}(\text{X})$, $T_{\text{b.p.}}(C_n)$, and $T_{\text{b.p.}}(C_{n+1})$ are the boiling points of the compound under analysis and the *n*-alkanes used to calculate its retention index $I(\text{X})$, respectively.

Aliphatic alcohols are known to exist in the liquid state as linear associates, whose units are linked by H-bonds.[3,10,11] The number of units in the associates in liquid MeOH can vary from 6 to 20; each molecule is involved in the formation of two H-bonds at room temperature.[3] The energy of formation of the associates estimated by different methods is 17—26 kJ mol^{-1}.[1,3,12,13]

It is the additional consumption of energy needed to destroy the alcohol associates that accounts for the higher boiling points of these compounds. During GC analysis of *n*-alkanols, associates are destroyed in the injector of the chromatograph and monomeric molecules are evaporated from the liquid. Under conditions of infinite dilution in a chromatographic column, monomeric molecules are sorbed by the stationary phase. If the sorbent is a nonpolar phase, the sorbate—sorbent intermolecular interaction are mainly of the dispersion force type; the contribution of the induction component is less than 10% even for polar sorbates. The energy consumed for evaporation of a self-associated substance from the pure liquid (ΔG_{v}) is given by Eq. (3), while the energy evolved during GC sorption (ΔG_{s}) can be found from Eq. (4)[14]:

$$\Delta G_{\text{v}} = \Delta G_{\text{ass}} + \Delta G_{\text{vm}}, \tag{3}$$

$$\Delta G_{\text{s}} = \Delta G_{\text{vm}} + \Delta G_{\text{E}}. \tag{4}$$

The partial molar free energy of vaporization of molecules from a pure liquid (ΔG_{v}) comprises the energy of destruction of one mole of associates (ΔG_{ass}) and the energy of vaporization of monomeric molecules (ΔG_{vm}). The ΔG_{v} value is larger than the partial molar free energy of sorption (ΔG_{s}) associated with the transfer of one mole of a monomeric sorbate from the vapor phase into a nonpolar liquid phase (ΔG_{vm}) and its interaction with the liquid phase (ΔG_{E}) during chromatographic analysis. The term ΔG_{E} is the excess molar energy of mixing of a substance with the stationary phase. The ΔG_{s} value, in turn, is related to the partition coefficient K for the sorbate, which governs the sorbate distribution between the liquid and the stationary phase and depends on the vapor pressure p^0 above the sorbate pure liquid.[14,15]

$$K = \frac{RT\rho}{p^0\gamma^\infty M}, \tag{5}$$

where M is the molecular weight of the stationary phase; ρ is the density of the stationary liquid phase at the column temperature T; γ^∞ is the activity coefficient of the sorbate at infinite dilution; R is the gas constant. We

Table 1. Retention indices of alkan-1-ols on a capillary column with SE-30, obtained under isothermal conditions (I) and with linear temperature programming (I_{pr})

Alkan-1-ols	I/iu at T/°C							I_{pr}/iu
	48	58	66	100	110	120	130	
Methanol	400.0	400.0	400.0					400.0
Ethanol	463.6	459.2	457.4					444.7
Propanol	556.5	553.5	551.4	544.6	542.3	540.5	541.5	540.2
Butanol	661.9	659.2	657.3	650.0	648.9	647.7	647.6	647.1
Pentanol	766.0	763.4	761.5	754.6	753.5	752.7	752.2	751.9
Hexanol				857.4	856.6	856.0	855.3	856.8
Heptanol				959.5	959.0	958.2	957.7	959.5
Octanol				1060.9	1060.5	1059.9	1059.7	1061.7
Nonanol						1161.9	1161.3	1163.3
Undecanol						1363.0	1363.3	1364.6

Note. I_{pr} was determined at T_0 = 60 °C and a temperature programming rate of 4 K min^{-1}; iu are retention index units.

Table 2. Boiling points ($T_{b.p.}$),[15] calculated "gas-chromatographic boiling points" ($T_{b.p.}{}^{GC}$/°C) (I), and GC indicators of self-association ($\delta T_{b.p.}$/°C) (II) of alkan-1-ols on a capillary column with SE-30

Alkan-1-ols	$T_{b.p.}$ /°C	Isothermal conditions, T/°C														TPGC conditions*	
		48		58		66		98		107		117		126			
		I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Methanol	65.5	0	65.5	0	65.5	0	65.5									0	65.5
Ethanol	78.5	22.9	55.6	20.7	57.2	20.7	57.8									16.1	62.4
Propanol	97.4	54.6	42.8	53.0	43.7	53.0	44.4	50.7	46.7	50.0	47.4	49.4	48.0	49.7	47.7	49.3	48.1
Butanol	117.3	87.0	30.3	85.6	31.1	85.6	31.7	83.5	33.8	83.5	33.8	82.8	34.5	82.8	34.5	82.7	34.6
Pentanol	137.3	116.5	20.8	115.2	21.5	115.2	22.1	113.3	24.0	113.0	24.3	112.8	24.5	112.6	24.7	112.5	24.8
Hexanol	158.0							140.4	17.6	140.2	17.8	140.0	18.0	139.8	18.2	140.2	17.8
Heptanol	176.0							164.7	11.3	164.6	11.4	164.4	11.6	164.3	11.7	164.7	11.3
Octanol	194.5							187.4	7.1	187.3	7.2	187.2	7.3	187.1	7.4	187.6	6.9
Nonanol	213.5											208.4	5.1	208.3	5.2	208.7	4.8
Undecanol	243.0											245.7	−2.3	245.7	−2.7	246.0	−3.0

* T_0 = 60 °C, programming rate 4 K min^{-1}.

suggested that the difference between ΔG_v and the sum of ΔG_{vm} and ΔG_E plays the crucial role in the variation of ΔG_s for the compounds under study in gas chromatography under conditions of infinite dilution. The difference between ΔG_v and ΔG_s provides the possibility of gaining information on the capacity of a sorbate for self-association in the pure liquid using gas chromatography. The $T_{b.p.}{}^{GC}$ value of an alkan-1-ol can be found by modeling its behavior as that of a hypothetical hydrocarbon with a fractional number of C atoms, equal to I(X)/100. Unlike hydrocarbons, for which the boiling temperatures determined by gas chromatography on a nonpolar column virtually coincide with the experimental values, in the case of alcohols, $T_{b.p.}{}^{GC}$ is smaller than $T_{b.p.}$.

Table 2 presents the experimental $T_{b.p.}$ values,[16] the $T_{b.p.}{}^{GC}$ values, and the indicators of self-association in pure liquid $\delta T_{b.p.}$ for alkanols. It can be seen from Table 2 that the $\delta T_{b.p.}$ value for a given *n*-alkanol, like the retention index, depends slightly on the temperature of GC analysis. Therefore, TPGC conditions are suitable for determination of $\delta T_{b.p.}$ for all homologs in one experiment. The $\delta T_{b.p.}$ values obtained with temperature programming differ slightly from the corresponding values found under isothermal conditions. In our experiments programmed with rates of 2, 4, 6, and 8 K min^{-1}, we found that the $\delta T_{b.p.}$ values of alcohols virtually do not depend on the rate of programming. Thus, it can be concluded that TPGC conditions can be used to estimate the capacity for self-association in the pure liquid for any compounds having small temperature increments of the retention index ($\delta I/\delta T$).

The $\delta T_{b.p.}$ value is specific for each homolog; it decreases with an increase in the *n*-alkyl chain of the alcohol; the capacity of *n*-alkanols for self-association varies in a similar way. Methanol has the largest $\delta T_{b.p.}$ value, 65.5 °C. It is noteworthy that this value is close to the $\delta T_{b.p.}$ values for highly self-associated compounds such as imidazole and 1,2,4-triazole.[7] As the *n*-alkyl chain becomes longer, the proportion of self-associated alcohol molecules in the pure liquid diminishes. Thus for *n*-nonyl alcohol, $\delta T_{b.p.}$ is only 5° and for *n*-undecyl alcohol, it is −3°. *n*-Undecyl alcohol may form no associates in the pure liquid; in addition, the energy of its interaction with the nonpolar liquid phase might be greater than the energy of intermolecular interaction of identical molecules in the pure liquid. Yet another possible reason is inaccurate determination of $T_{b.p.}$ of high-boiling *n*-undecyl alcohol at atmospheric pressure. The decrease in the $\delta T_{b.p.}$ value in the homologous series is consistent with the decrease in the association constants (K_{ass}) of these compounds found by independent methods. For example, the association constant at 50 °C has been reported[17] to decrease 11-fold or, in another publication,[13] 4.8-fold on going from methanol to *n*-decyl alcohol. Although the K_{ass} values do not coincide, they still tend to decrease following an increase in the length of the *n*-alkyl chain, attesting to a decrease in the capacity of *n*-alkanols for self-association. The variation of the degree of association of alcohols as a function of the number of C atoms, derived from dielectric permittivity measurements,[12] is also correlated with the variation of $\delta T_{b.p.}$ in the homologous series of *n*-alkanols.

It seems of interest to compare the resulting GC indicators of association of *n*-alkanols with the corre-

Table 3. Experimental boiling points $T_{b.p.}$,[15] calculated "gas-chromatographic boiling points" $T_{b.p.}{}^{GC}$, and GC indicators of self-association $\delta T_{b.p.}$ for alkane-1-thiols

Alkane-1-thiols	$T_{b.p.}$/°C	$T_{b.p.}{}^{GC}$/°C*	$\delta T_{b.p.}$/°C
Ethanethiol	34.7	41.6	−6.9
Propanethiol	68.0	75.7	−7.7
Butanethiol	98.0	105.3	−7.3
Pentanethiol	126.0	133.0	−7.0
Hexanethiol	152.0	159.7	−7.7
Heptanethiol	174.5	180.8	−6.3
Octanethiol	198.5	202.4	−3.9
Nonanethiol	220.0	221.9	−1.9

* The calculation was performed using the retention indices presented in a previous study.[18]

sponding values for *n*-alkanethiols incapable of self-association through the formation of H-bonds in a pure liquid. Table 3 shows the experimental boiling points $T_{b.p.}$ for C_1—C_9 *n*-mercaptans, the $T_{b.p.}^{GC}$ values calculated from the retention indices on a nonpolar column, taken from a previous publication,[18] and the $\delta T_{b.p.}$ values calculated in this study. The GC indicators of *n*-mercaptans, unlike those of alcohols, are always negative and barely depend on the length of the *n*-alkyl chain at $n \le 7$. The negative $\delta T_{b.p.}$ values for mercaptans can be explained by assuming that the energy of interaction of these compounds with the nonpolar phase is greater than the energy of intermolecular interactions in liquid mercaptans. The decrease in the absolute magnitudes of $\delta T_{b.p.}$ in the case of *n*-octanethiol and *n*-nonanethiol indicates that under conditions of chromatographic analysis, the hydrocarbon chain determines the character of interactions of these molecules both with one another in the pure liquid and with the stationary phase.

The results obtained here demonstrate that the $\delta T_{b.p.}$ value is a sensitive indicator reflecting the capacity of organic compounds for self-association. The advantage of the gas-chromatographic method proposed here over other physicochemical methods is the fact that information on the capacity of various compounds for self-association in pure liquids can be obtained over a period of several minutes.

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