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Pair-wise interactions by gas chromatography VII. Interaction free enthalpies of solutes with secondary alcohol groups

András Dallos[a,*], Attila Sisak[b], Zita Kulcsár[a], Ervin sz. Kováts[a,c]

[a]*Department of Physical Chemistry, University of Veszprém, P.O. Box 158, H-8200 Veszprém, Hungary*
[b]*Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém, Hungary*
[c]*Pavillon A, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

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Abstract

A polar type liquid having a secondary alcohol substituent on a branched alkane skeleton, SOH, was used as stationary phase. The molecules of this stationary phase are nearly isomorphous and isochor with those of the branched alkane, C_{78}, elected as standard, i.e., the molecules of both solvents have nearly the same form and the same size. Partition properties of 158 chosen molecular probes were measured by gas chromatography on SOH and on an SOH–C_{78} mixture having a volume fraction of $\varphi_{SOH}=0.5$. Based on the resulting data an interaction free enthalpy could be calculated, i.e., the additional effect of the secondary alcohol to partition. Comparison with data determined earlier on another member of this solvent family, POH, having a primary alcohol as interacting group gives information about the effect of steric hindrance on polar type solute–solvent interaction free energies. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the present report are given partition properties of 158 molecular probes, *j*, between the ideal gas phase and the melt of the secondary alcohol, P=SOH, and its mixtures with the alkane, A≡C_{78}, with structures depicted in Fig. 1. The data are presented as standard chemical potential differences, $\Delta\mu$, related to the molal Henry coefficient, *g*, by Eq. (1):

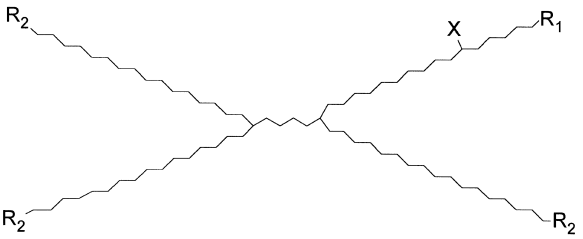

Fig. 1. Structures of the applied stationary phases: A≡C_{78}: X=H, $R_1=CH_2CH_3$, $R_2=CH_2CH_3$; SOH: X=OH, $R_1=CH_3$, $R_2=CH_2CH_3$. For the structures of the other members of the isomorphous, isochor family, consult Table 1.

*Corresponding author. Fax: +36-88-423-409.
E-mail addresses: dallos@almos.vein.hu (A. Dallos), ervin.kovats@epfl.ch (E.sz. Kováts).

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$$\Delta\mu_j^{\mathrm{L}} = RT \ln (g_j^{\mathrm{L}} / \mathrm{atm\ kg\ mol^{-1}}) \quad (1)$$

where R (=1.9872 cal mol^{-1} K^{-1}) is the universal gas constant and T (K) is the absolute temperature (1 cal=4.184 J; 1 atm=101 325 Pa). The superscript L denotes the stationary liquid which may be A or P or for an A–P mixture. Note, that throughout this paper the acronym SPOT will be used for the standard chemical potential difference (≡the standard molar Gibbs energy difference). The particular SPOT defined in Eq. (1) with the ideal gas phase as reference will be referred to as gSPOT.

Partition coefficients were deduced from gas chromatographic measurements performed at several temperatures in the temperature range of 90–210°C. Contribution to solute retention by adsorption at the interfaces was reduced to a negligible minimum by applying column packings with high liquid loading on an adequately deactivated support of low specific surface area [1]. The working technique developed in former projects [1–6] has been applied for the collection of data. It consisted of calculating gSPOTs of *n*-alkanes as a function of temperature with the average of data acquired over the whole project period and to characterize solutes by their retention indices. Latter data were then reconverted to gSPOTs by interpolation between the adequate *n*-alkanes (for details see below).

Data of this same set of molecular probes have been determined on all polar stationary phases, L=P, listed in Table 1 as well as on the alkane L=A≡C_{78} and on their mixtures, L=A–P.

Using the information listed in Table 1, inspection of Fig. 1 shows that the alkane C_{78} and all mono- and tetrafunctional ''solvents'', P, have as closely as possible the same form and that their molecules have nearly the same size (compare the molar volumes). In fact, in a first study gas chromatographic measurements on a series of five high-molecular-mass alkanes ($C_{59}H_{120}$–$C_{103}H_{208}$ of the Apolane series) have indicated [7] that data indeed depend on the *size* of the solvent molecule. The gSPOT of a solute is, as a first approximation, linearly proportional to the inverse of the molar volume of the alkane

Table 1
The members of the isomorphous isochor stationary phase family[a]

Symbol L	Polar interacting group (PIG)	R_1	R_2	X	$v^{\dagger}$ (cm^3 mol^{-1})	Ref.
The standard alkane						
C_{78}	–	CH_2CH_3	CH_2CH_3	H	1420.9	[1]
Dipolar endgroups						
MTF	(Mono)trifluoromethyl	CH_2CF_3	CH_2CH_3	H	1451.8	[4]
TTF	Tetrakis-trifluoromethyl	CH_2CF_3	CH_2CF_3	H	1495.7	[4]
PCl	Primary chloro	CH_2Cl	CH_2CH_3	H	1414.2	[5]
PBr	Primary bromo	CH_2Br	CH_2CH_3	H	1419.3	[5]
Hydrogen bond acceptors						
MMO	Monomethoxy	OCH_3	CH_2CH_3	H	1412.2	[6]
TMO	Tetramethoxy	OCH_3	OCH_3	H	1393.3	[6]
Hydrogen bond donor/acceptors with different steric environments						
POH	Primary alcohol	CH_2OH	CH_2CH_3	H	1404.2	[1]
SOH	Secondary alcohol	CH_3	CH_2CH_3	OH	1413.8	This work
Specific phases						
PSH	Primary thiol	CH_2SH	CH_2CH_3	H	1415.7	[6]
PCN	Primary cyano	CH_2CN	CH_2CH_3	H	1414.7	[6]
Furthermore						[7]
Alkanes of the Apolane series:	$C_{59}H_{120}$, $C_{67}H_{136}$, $C_{75}H_{142}$, $C_{87}H_{176}$, $C_{103}H_{208}$					

[a] For the symbols R_1, R_2 and X see Fig 1; $v^{\dagger}$ is the molar volume of the melt at the standard temperature $T^{\dagger}$=130+273.15=403.15 K.

solvent. Comparison of these same data with those of different alkanes from the literature has indicated that the effect of the *shape* of the solvent molecule is of secondary importance. Based on these conclusions the partition equilibrium of a solute between the standard alkane stationary phase, $A=C_{78}$ and an isomorphous, isochor, monofunctional polar stationary phase, P, may be considered as a measure of the additional interaction forces between the solute and the polar interacting group, PIG, of the polar solvent, P. The corresponding standard chemical potential difference is given in Eq. (2):

$$\Delta\!\!\!-\mu_j^{\mathrm{P}} = \Delta\mu_j^{\mathrm{P}} - \Delta\mu_j^{\mathrm{A}} \tag{2}$$

Obviously, for the specific SPOT, $\Delta\!\!\!-\mu_j^{\mathrm{P}}$, as defined in Eq. (2), the reference state is the ideal dilute solution of the solute in the apolar standard, A, hence it shell be referred to as aSPOT.

In this discussion the melt of a monofunctional solvent, P, was considered as if it was a (near 0.7 molar) ''solution of the polar interacting group, PIG, in the standard alkane solvent'' ([PIG]≈0.7 *M*). In order to control the validity of this primitive picture tetrafunctional derivatives have been prepared of two of the monofunctional solvents: MTF and MMO [3]. In fact, the aSPOT (and of course the gSPOT) data of solutes on the monofunctional ''solvent'' and on the tetrafunctional derivative adequately ''diluted'' with the alkane C_{78} (a 1:3 mixture) were shown to be the same [4,6]. Based on this observation a method has been proposed for the determination of a measure of the interaction of a standalone solute molecule with a unit concentration of standalone functional groups as follows. First, aSPOTs of a given solute are determined for a series of A–P mixtures, i.e., as a function of the concentration of the PIG, in the melt of L. From the results a quadratic equation is then fitted with the functional group concentration, [PIG], as variable. The slope of this function at zero concentration gives the necessary information for the calculation of an aSPOT in a hypothetical solvent with no interaction between its functional groups:

$$\Delta\!\!\!-'\mu_j^{\mathrm{idPIG}} \equiv \left(\partial\Delta\!\!\!-\mu_j^{\mathrm{A-P}} / \partial[\mathrm{PIG}]\right)_{T,[\mathrm{PIG}]=0} \tag{3}$$

This special aSPOT ''measured'' in a 1 molar ideal dilute solution of the given PIG, and the ideal dilute solution of the solute in the standard $A\equiv C_{78}$, is referred to by the special symbol $\Delta\!\!\!-'$ and will be designated by the acronym idSPOT. Its value is considered as the (additional) *interaction free enthalpy of the solute with a standalone polar interacting group, idPIG, in question*.

This work shall complete a unique data bank (based on about 40 000 retention measurements) [1–6] and represent an advanced version of that of McReynolds [8,9] (based on about 2000 retention measurements). It will hopefully permit prediction of partition data based either on structural details of the solute, *j*, and those of the solvent [10] or based on gSPOTs determined on a few selected standard stationary phases [11–14]. In fact, this has been the subject of many research projects since the introduction of gas chromatography (GC).

In a first paper on this subject Wehrli et al. have suggested that partition data with the ideal dilute solution in an alkane as reference state (ΔI values or aSPOT data) may be interpreted as a measure of polar type interactions. They have shown in Ref. [10] that the ''ΔI value'' may be calculated as a sum of additive increments (as proposed for thin-layer data by Schauer and Bulrisch [15–17]). A few years later Rohrschneider demonstrated in his classical paper [11] that ΔI values can be calculated by a method which is called today the ''linear free energy relationship''. A solvent (i.e., a stationary phase) is first characterized by partition data (ΔI values) of a necessary number, ν, of test solutes. The resulting ensemble of ν numbers are the elements of the property vector of the solvent. A similar property vector can be calculated for a given solute on the basis of its ΔI values on a limited number of stationary phases. The sum of the pair-wise multiplied terms of the two vectors gives the ΔI value of the solute. On the basis of data of some 22 stationary phases Rohrschneider has concluded [11] that the number of the necessary vector elements is $\nu=5$. On the basis of data of 200 stationary phases McReynolds has found [8,9] that the necessary number is $\nu=7$.

In the following years the paper of Rohrschneider has been subject to refinements and/or reinterpretation either in terms of ΔI values or in terms of the analogous aSPOT data. Snyder separated the effects

due to dispersion and polar interaction forces [18] and defined a polarity index corrected for the molecular masses for both of the solvent and of the solute. Karger et al. [19] have shown the relationship between the method of Rohrschneider and Hildebrand's solubility parameter. Kamlet et al. [20,21] have named the method ''linear solvation energy relationship'' (LSER) and have shown the relationship with other empirical descriptors, such as solvatochromic parameters (see also Ref. [22]). New parameters (for solutes and solvents) have been introduced by Abraham et al. [23] by using among others the McReynolds' data set for the demonstration of their utility [24]. Carr and co-workers [25,26] have proposed a similar model with an empirical polarizability term. An alternative approach is due to Poole and co-workers [27,28]. Based on molecular orbital methods Famini et al. developed a theoretical basis [29,30] for a priori prediction of the value of the elements of the property vectors.

In summary, we present a data bank with aSPOTs of 158 solutes between an ideal dilute solution in a stationary phase which is a ''solution of nonvolatile interacting groups in a standard alkane solvent'' and the ideal dilute solution of the molecular probes in the standard alkane as reference. Also given are idSPOT data in a hypothetical ''ideal dilute solution of polar interacting groups'', i.e., where these functional groups interact with solute molecules but not with each other. Let us insist, that (contrary to the McReynolds data set) care has been taken to present data based on partition measurements free from the influence of interfacial adsorption.

2. Theoretical

In the following are presented the most important relationships. For details see Refs. [1] and [5].

The relationship between the molal Henry coefficient, g_j^{L}, of a solute, j, in a liquid, L (the stationary phase) and the specific retention volume, $V_{\mathrm{g},j}^{\mathrm{L}}$, is given in Eq. (4):

$$g_j^{\mathrm{L}} = \Re T/(1000V_{\mathrm{g},j}^{\mathrm{L}}) \tag{4}$$

where $\Re$ (cm^3 atm mol^{-1} K^{-1}) is the universal gas constant and L may be A ($\equiv \mathrm{C}_{78}$) or P (any of the polar phases) or any A–P mixture. Use of the resulting molal Henry coefficient in Eq. (1) permits calculation of the corresponding gSPOT.

By supposing that the difference of the partial molar heat capacity of the solute between two standard states is constant in the experimental temperature domain, the temperature dependence of the corresponding SPOT is given by Kirchhoff's approximation. In the case of gSPOT with constant $\Delta C_{\mathrm{p},j}^{\mathrm{L}}$ (cal mol^{-1} K^{-1}) Eq. (5a) holds:

$$\Delta\mu_j^{\mathrm{L}} = \Delta H_j^{\mathrm{L}} - T\Delta S_j^{\mathrm{L}} + \Delta C_{\mathrm{p},j}^{\mathrm{L}} \cdot \left[T - T^{\dagger} - T \ln\left(\frac{T}{T^{\dagger}}\right) \right] \tag{5a}$$

where the regression coefficients are interpreted as follows: ΔH_j^{L} (cal mol^{-1}) and ΔS_j^{L} (cal mol^{-1} K^{-1}), are the difference of the partial molar enthalpy and entropy, respectively at an arbitrary standard temperature, $T^{\dagger}$. The temperature dependence of the aSPOT, $\mathbb{\Delta}\mu_j^{\mathrm{P}}$ is given by the analogous Eq. (5b):

$$\mathbb{\Delta}\mu_j^{\mathrm{P}} = \mathbb{\Delta}H_j^{\mathrm{P}} - T\mathbb{\Delta}S_j^{\mathrm{P}} + \mathbb{\Delta}C_{\mathrm{p},j}^{\mathrm{P}} \cdot \left[T - T^{\dagger} - T \ln\left(\frac{T}{T^{\dagger}}\right) \right] \tag{5b}$$

The mixture of the isomorphous and isochor liquid phases, $\mathrm{A} = \mathrm{C}_{78}$ and P is certainly a regular mixture. Hence, the aSPOT of the solute, j, as a function of the volume fraction, φ, is given by Eq. (6):

$$\mathbb{\Delta}\mu_j^{\mathrm{A-P}} = \varphi_{\mathrm{P}}\mathbb{\Delta}\mu_j^{\mathrm{P}} + \varphi_{\mathrm{A}}\varphi_{\mathrm{P}} m_j^{\mathrm{A-P}} \tag{6}$$

where $\mathbb{\Delta}\mu_j^{\mathrm{P}}$ is the aSPOT of the solute in pure P ($\varphi_{\mathrm{P}} = 1$). The factor $m_j^{\mathrm{A-P}}$ in the second term accounts for the excess SPOT. Its temperature dependence may be given as shown in Eq. (7):

$$m_j^{\mathrm{A-P}} = h_j - Ts_j \tag{7}$$

where the symbols h and s are enthalpic and entropic contributions, respectively.

The specific volume of an A–P mixture can certainly be approximated as a linear combination of those of the individual components (no excess volume of mixing). In such binary mixtures the molar concentration of the polar interacting group, [PIG], is given by Eq. (8):

$$[\mathrm{PIG}] = \varphi_{\mathrm{P}}[\mathrm{P}]^{\circ} = \varphi_{\mathrm{P}} 1000/v_{\mathrm{P}} \tag{8}$$

where v_P (cm^3 mol^{-1}) is the molar volume and [P]° is the molar concentration of the pure polar stationary phase, P, in the mixture at the temperature T.

Eq. (6) gives the necessary information for the calculation of the idSPOT by use of the relationship of Eq. (3). Consequently, partial derivation of Eq. (6) with respect to the molar concentration of the PIG, gives Eq. (9) for the interaction free enthalpy of the solute j at infinite dilution with a standalone interacting polar group, ''idPIG'' in the A–P mixture also at ideal dilution:

$$\begin{aligned}\Delta\mu_j^{\mathrm{idPIG}} &\equiv \left(\frac{\partial\Delta\mu_j^{\mathrm{A-P}}}{\partial[\mathrm{PIG}]}\right)_{T,[\mathrm{PIG}]=0}\\ &= \left(\frac{\partial\Delta\mu_j^{\mathrm{A-P}}}{\partial\varphi_P}\right)_{T,\varphi_P=0}\cdot\left(\frac{\partial\varphi_P}{\partial[\mathrm{PIG}]}\right)_T\\ &= \left(\Delta\mu_j^{P} + m_j^{\mathrm{A-P}}\right)v_P/1000 \qquad (9)\end{aligned}$$

The interaction free enthalpy given in Eq. (9) represents the net solute–solvent polar interaction contribution to the solvation free enthalpy, without any influence by the solute–solute interactions.

Chromatographic data of solutes other than n-alkanes were determined on the retention index scale. Let us recall that the retention index of a solute, j, is a measure of its gSPOT (or aSPOT) on a scale of fixed points given by the corresponding gSPOT of the n-alkanes, C_zH_{2z+2}, as given in Eq. (10):

$$\begin{aligned}I_j^{L} &= 100\cdot\frac{\Delta\mu_j^{L}-\Delta\mu_z^{L}}{\Delta\mu_{z+1}^{L}-\Delta\mu_z^{L}} + 100z\\ &= 100\cdot\frac{\delta\mu_{j/z}^{L}}{\delta\mu_z^{L}} + 100z \qquad (10)\end{aligned}$$

where δ designates the difference between the gSPOTs of two solutes. Retention indices can be given in A–P mixtures as a function of composition and temperature by the approximation given in Eq. (11):

$$I_j^{\mathrm{A-P}} = I_j^{A} + \varphi_P\Delta I_j^{P} + \varphi_A\varphi_P i_j^{\mathrm{A-P}} \qquad (11)$$

where

$$I_j^{A} = I_{130,j} + A_{T,j}\Delta T + A_{TT,j}\Delta T^2 \qquad (12)$$

$$\Delta I_j^{P} = \Delta I_{130,j} + \Delta A_{T,j}\Delta T + \Delta A_{TT,j}\Delta T^2 \qquad (13)$$

$$i_j^{\mathrm{A-P}} = A_{L,j} + A_{LT,j}\Delta T \qquad (14)$$

with $\Delta T = T - T^{\dagger}$ where $T^{\dagger} = 403.15$ K.

Let us insist that, strictly speaking, the retention index is not a linear function of the composition in mixed liquid stationary phases even if the mixture is ideal. However, the retention index difference of the solute j in the hypothetical ideal A–P mixture, at infinite dilution of the interacting polar atomic group, ''idPIG′'', is of theoretical and practical interest, because it is related to the polar solute–solvent interactions. Its value can be calculated, as given in Ref. [5]:

$$\Delta' I_j^{\mathrm{idPIG}} = \left(\Delta I_j^{P} + i_j^{\mathrm{A-P}}\right)\cdot\frac{v_P[\mathrm{PIG}]}{1000(1+[\mathrm{PIG}]\kappa)} \qquad (15)$$

with $\kappa = (\delta'\mu_z^{\mathrm{idPIG}} - \delta'\mu_z^{A})/\delta\mu_z^{A}$, where $\delta'\mu_z^{A}$ and $\delta'\mu_z^{\mathrm{idPIG}}$ are the slopes of the function $\delta\mu_z^{\mathrm{A/idPIG}}([\mathrm{PIG}])$ at [PIG] = 0 and 1 mol l^{-1}, respectively. In the case of C_{78}–SOH mixtures, the value of κ is of the order of -0.02 l mol^{-1}, consequently the value of the correcting factor in Eq. (15) is of the order of 1.02.

3. Experimental

3.1. General

The n-alkanes used as reference solutes for gas chromatography were from Merck (Darmstadt, Germany) with stated purity better than 99.5%. All other solutes used as molecular probes for gas chromatographic measurements (listed in Table 4) were research-grade compounds from Fluka (Buchs, Switzerland). The helium carrier (quality 6.0) and the ''insoluble solute'', neon (5.0), were from Messer-Griessheim (Krefeld, Germany). The synthesis of the alkane 19,24-dioctadecyldotetracontane, $C_{78}H_{158}$, used as the nonpolar standard stationary phase (C_{78}) has been reported in Ref. [3]. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were recorded on a spectrometer from Varian (Palo Alto, CA, USA; Model Unity 300), using hexamethyldisiloxane as internal standard. Gas chromatographic analyses of synthetic intermediates in the preparation of the stationary phase SOH (see below) were made with an instrument from Hewlett-Packard

(Palo Alto, CA, USA; Model 5830 A) using a methylsilicone stationary phase (SPB-1; capillary column of length $L=30$ m; initial temperature $t_i=150°C$; temperature gradient: 10 K min^{-1}), or from Shimadzu (Duisburg, Germany; Model GC 14/A) using a methylsilicone stationary phase (OV-17; capillary column, $L=10$ m; $t_i=100°C$; gradient 10 K min^{-1}). GC–mass spectrometry (MS) measurements were performed on an instrument from Hewlett-Packard (Model 5890 Series II GC–MSD) using the stationary phase SPB-1 in a 30 m capillary column ($t_i=150°C$; gradient 10 K min^{-1}).

3.2. The stationary phase SOH

Several reaction steps in the preparation of 18,23-dioctadecyl-7-hentetracontanol (stationary phase with secondary alcohol groups: SOH) are analogous to those described in Ref. [3] for the preparation of 18,23-dioctadecyl-1-hentetracontanol (stationary phase with primary alcohol groups: POH). Manipulations involving air-sensitive compounds were carried out in an Ar atmosphere using deoxygenated, dry solvents. The starting products: 10-undecenal (**1**; >95% purity) and 1-bromohexane (**2**) were from Aldrich and Fluka (Sigma–Aldrich, Budapest, Hungary). The preparation of the C_{60}-ketone, 24-octadecyl-19-dotetracontanone (**7**) has been reported in Ref. [3].

The abbreviations used below are as follows: abs.: absolute; *M*: mol l^{-1}; m.p.: melting point; RT: room temperature; sat.: saturated; aq.: aqueous; for the description of the NMR spectra: s: singlet; d: doublet; t: triplet; m: multiplet.

3.2.1. Synthesis of 7-benzyloxy-16-heptadecyne (*6*, see reaction scheme in Fig. 2)

3.2.1.1. 16-Heptadecen-7-ol (*3*)

In a 500-ml three-necked round-bottom flask equipped with a reflux condenser, a magnetic stirrer, an Ar gas inlet and a dropping funnel was placed 5.21 g (220 mmol) of Mg. In an Ar atmosphere the Mg was covered with 170 ml of freshly distilled tetrahydrofuran (THF) then 4.1 g (23 mmol) of 1,2-dibromoethane was added in one portion (activation of the surface). Under vigorous stirring a solution of 25.3 g (0.153 mol) of 1-bromohexane (**2**)

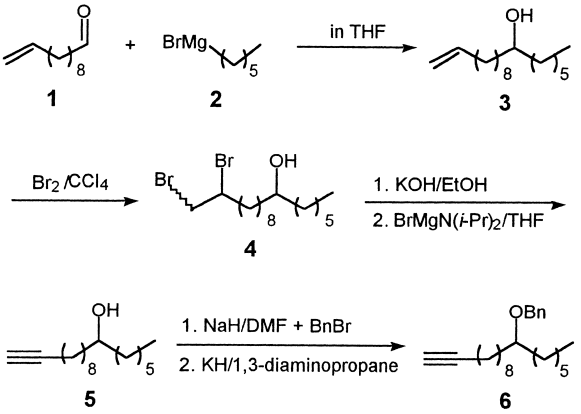

Fig. 2. Synthesis of 7-benzyloxy-16-heptadecyne.

in 100 ml of THF was introduced from the dropping funnel at a rate as to maintain a gentle reflux (ca. 40 min). After completed addition the reaction mixture was refluxed for a further period of 1.0 h, then cooled and the ready-to-use Grignard reagent was transferred to a 500-ml dropping funnel. The funnel was attached to a 1-l three-necked round-bottom flask equipped with a reflux condenser, an Ar gas inlet and a thermometer. In this flask was placed a solution of 25.0 g (141 mmol) of 10-undecenal (**1**; >95% purity) in 120 ml of THF. The flask was immersed in an ice–salt bath and the Grignard reagent was added drop-wise while maintaining the temperature below 0°C (ca. 90 min), then the mixture was allowed to warm up to RT (ca. 90 min). After hydrolysis of the Mg compound with sat. aq. NH_4Cl, hexane (50 ml) was added then the aqueous phase was extracted with further hexane (2×50 ml). The combined organic phase was dried over Na_2SO_4 and the solvent was removed in a rotary evaporator. Chromatography of the yellowish, oily residue on silica gel (200 g) gave with hexane (1.0 l) a first fraction, which was discarded. The second fraction, eluted with hexane–Et_2O (1:1; 800 ml), afforded after evaporation of the solvent and recrystallization in hexane at −18°C 32.1 g of 16-heptadecen-7-ol (**3**; GC: 98.0%) as a white crystalline solid (88% of the theory); m.p.: 36–37°C.

^{1}H-NMR [C^2HCl_3–tetramethylsilane (TMS)]: $\delta=$ 0.87 (m, 3 H), 1.29 (m, 18 H), 1.41 (m, 6 H), 2.04 (q, 2 H, $J=6.7$), 3.56 (m, 1 H), 4.93 (ddt, 1 H,

$J=10.0$, 2.2, 1.2), 4.99 (ddt, 1 H, $J=16.9$, 2.2, 1.2), 5.81 (ddt, 1H, $J=16.9$, 10.0, 6.7).

*3.2.1.2. 16,17-Dibromo-7-heptadecanol (**4**)*

In a 250-ml three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser a solution of 16-heptadecen-7-ol (**3**), (9.6 g; 37.0 mmol) in CCl_4 (170 ml) was cooled to 0°C (ice bath). A solution of Br_2 (6.2 g; 38.9 mmol) in CCl_4 (25 ml) was then added dropwise within 90 min. After stirring for an additional period of 15 min at 0°C the excess of Br_2 was reduced by shaking with 5% aq. $Na_2S_2O_3$ (30 ml). The organic phase was washed with sat. aq. $NaHCO_3$ (2×30 ml) then dried over Na_2SO_4. The solvent was removed in a rotary evaporator and the solid residue was recrystallized twice in 170 ml of hexane at −10°C to give colorless crystals: 14.0 g (90% of the theory) of 16,17-dibromo-7-heptadecanol (**4**); m.p.: 18–20°C. The product was used in the next step without further purification.

^{1}H-NMR (C^2HCl_3–TMS): $\delta=0.88$ (m, 3 H), 1.28 (m, 18 H), 1.41 (m, 6 H), 1.80 (m, 1 H), 2.15 (m, 1 H), 3.56 (m, 1 H), 3.63 (t, 1 H, $J=10.1$), 3.85 (dd, 1 H, $J=10.1$, 4.6), 4.17 (ddt, 1 H, $J=10.1$, 7.0, 4.4).

*3.2.1.3. 16-Heptadecyn-7-ol (**5**)*

In a 2-l three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser was placed a solution of 14.0 g (33.8 mmol) of the dibromoalcohol (**4**) and 27.1 g (48 mmol) of KOH in abs. EtOH (300 ml) and the reaction mixture was heated to reflux. After 16 h the mixture was cooled, water (70 ml) was added and 200 ml of EtOH was distilled off. The concentrated solution was cooled to RT and extracted with cyclohexane (2×80 ml) and Et_2O (2×50 ml). The combined organic phase was dried (Na_2SO_4) and the solvent was removed in a rotary evaporator. The residue (10.3 g) was transferred to a 1-l three-necked round-bottom flask containing a solution of $BrMgN(i\text{-}Pr)_2$ in 550 ml of anhydrous THF {prepared by reacting butyl-MgBr (145 mmol) with $(i\text{-}Pr)_2NH$ (2.4 g; 23.8 mmol) see Ref. [3]}. The reaction mixture was refluxed during 5.0 h, cooled to RT, then hydrolyzed with brine (100 ml). The aqueous phase was extracted with Et_2O (2×50 ml), the combined organic phase was washed with sat. aq. $NaHCO_3$ (2×50 ml) then dried (Na_2SO_4) and the solvent was removed in a rotary evaporator. Chromatography of the residue on silica gel (100 g) with benzene–cyclohexane (1:4; 1.0 l) afforded 8.0 g of a colorless, oily product consisting (GC–MS) of the ynol (**5**) (81%) and 17-bromo-16-heptadecen-7-ol (10%) besides some unknown minor components. This product was used in the next step without further purification.

^{1}H-NMR (C^2HCl_3–TMS): $\delta=0.88$ (m, 3 H), 1.28 (m, 18 H), 1.41 (m, 6 H), 1.53 (m, 2 H), 1.93 (t, 1 H, $J=2.7$), 2.18 (dt, 2 H, $J=7.0$, 2.7), 3.57 (m, 1 H).

*3.2.1.4. 7-Benzyloxy-16-heptadecyne (**6**)*

In a 500-ml three-necked round-bottom flask equipped with a reflux condenser (connected to a gas outlet), a thermometer and a magnetic stirrer was placed 1.03 g (42.5 mmol) of NaH (20% in mineral oil) in an Ar atmosphere. The oil was removed by washing with hexane (3×15 ml) then the hydride was covered with anhydrous dimethylformamide (DMF) (120 ml), cooled to −20°C (ice–salt bath) and at this temperature a solution of 10.2 g of the crude ynol (**5**), prepared in the previous step in anhydrous DMF (50 ml) was added within 1.5 h then the mixture was stirred for further 1.5 h. A solution of benzyl bromide (7.4 g; 3.3 mmol) in anhydrous DMF (50 ml) was now introduced within 7 h, the mixture was allowed to warm up slowly to RT (ca. 2 h) and the solution was stirred for additional 8 h. After hydrolysis with sat. aq. NH_4Cl (100 ml) and 15% aq. H_2SO_4 (70 ml) hexane (100 ml) was added to the mixture. The aqueous phase was extracted with Et_2O (2×50 ml) and hexane (2×80 ml). The combined organic phase was dried over Na_2SO_4 and evaporated in a rotary evaporator to give 12.8 g of a yellowish, oily product.

GC–MS analysis of the crude product showed the following components: 16-heptadecyn-6-ene (and isomers): 15%; 16-heptadecyn-7-ol (**5**) and isomers: 28%; isomers of **6**: 44%; 7-benzyloxy-17-bromo-16-heptadecyne (and isomers): 7%; unknown components: 6%.

The product was dissolved in hexane (150 ml) and cooled to −25°C. After 3 days 3.5 g of a white crystalline mass was filtered containing (**5**) and its isomers [GC: 83%; N.B.: The yield could be improved by repeated working up of the recovered

alcohol (**5**)]. After evaporation of the solvent the residue was heated in an Ar stream at 100°C/$2\cdot10^{-2}$ Torr where the main part of the 16-heptadecyn-6-ene isomers was removed by evaporation (1 Torr = 133.322 Pa). Chromatography of the residue (7.7 g) on silica gel (100 g) with cyclohexane (1.0 l) afforded 5.1 g (40% of the theory) of a mixture of the 17-yne (**6**), and its 15-yne isomer (GC: together 96.1%) as a white, oily material.

In a 250-ml three-necked round-bottom flask equipped with a magnetic stirrer, a thermometer and a reflux condenser was placed 1,3-diaminopropane (70 ml) then a suspension of 5.0 g (25.0 mmol) of KH (20% in mineral oil) was slowly introduced within a period of 20 min at RT. After stirring for additional 1.0 h a solution of 5.1 g (14.3 mmol) of the mixture of **6** and its 15-yne isomer in 1,3-diaminopropane (20 ml) was added within 5 min then after a further 5 min period, water (25 ml) was added. The aqueous layer was extracted with hexane (3×50 ml), the combined organic phase was washed with 15% aq. H_2SO_4 (25 ml), sat. aq. $NaHCO_3$ (2×25 ml) and dried over Na_2SO_4. The solvent was removed in a rotary evaporator and the residue was chromatographed on silica gel (80 g). Hexane (200 ml) eluted the mineral oil originating from the KH suspension. Elution with benzene–cyclohexane (1:4; 500 ml) afforded 4.5 g (88% of the theory) of 7-benzyloxy-16-heptadecyne (**6**, GC: 97.0%) as a white, oily material.

^{1}H-NMR (C^2HCl_3–TMS): $\delta = 0.88$ (m, 3 H), 1.28 (m, 18 H), 1.41 (m, 6 H), 1.51 (m, 2 H), 1.93 (t, 1 H, $J = 2.6$), 2.17 (dt, 2 H, $J = 7.0$, 2.6), 3.36 (m, 1 H), 4.49 (s, 2 H), 7.32 (m, 5 H). ^{13}C-NMR (C^2HCl_3–TMS): $\delta = 14.05$, 18.33, 22.60, 25.28, 28.43, 28.68, 29.01, 29.42, 29.48, 29.72, 31.82, 33.78, 70.66, 78.97, 84.68, 127.28, 127.67, 128.19. MS: $m/z = 342$ (M^+), 205, 131, 117, 92, 91 (base peak), 55.

3.2.2. Synthesis of 18,23-dioctadecyl-7-hentetracontanol (SOH, see reaction scheme in Fig. 3)

*3.2.2.1. 7-Benzyloxy-18,23-dioctadecyl-16-hentetracontyn-18-ol (**8**)*

In a 500-ml three-necked round-bottom flask equipped with a reflux condenser, a magnetic stirrer, an Ar gas inlet and a dropping funnel a solution of

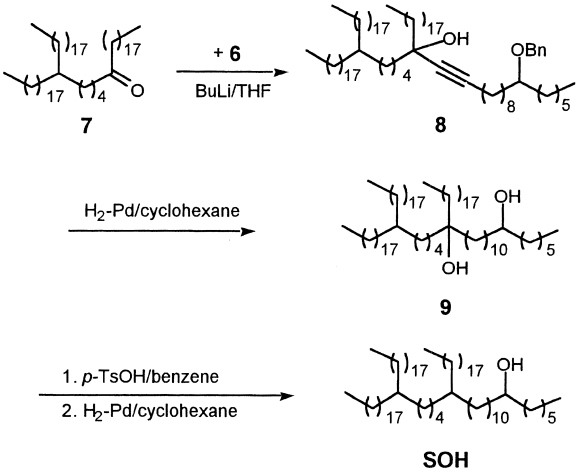

Fig. 3. Synthesis of 18,23-dioctadecyl-7-hentetracontanol.

the yne **6** (4.5 g; 12.8 mmol) in anhydrous THF (200 ml) was cooled to −20°C (ice–salt bath) and butyllithium (14.4 mmol, 2.5 *M* in hexane) was added within 10 min. The mixture was allowed to warm up to RT then the solid ketone **7** (10.0 g; 11.6 mmol) was added within 10 min. The mixture was stirred for additional 30 min while the initial white suspension turned to a clear solution, which was allowed to stand at RT for 5 h. After hydrolysis with sat. aq. NH_4Cl (80 ml) and addition of Et_2O (130 ml) the organic phase was dried over Na_2SO_4. After evaporation of the solvent in a rotary evaporator crystallization of the residue in Et_2O–MeOH (3:2; 300 ml) gave 13.3 g (95% of the theory) of 7-benzyloxy-18,23-dioctadecyl-16-hentetracontyn-18-ol (**8**, m.p.: 33–35°C). Reaction of a 0.1 g sample of **8** with 2,4-dinitrophenylhydrazine reagent (0.1 *M* in EtOH–H_3PO_4, 1:1) showed the absence of ketone (**7**).

*3.2.2.2. 18,23-Dioctadecyl-7,18-hentetracontanediol (**9**)*

In a 1-l stainless steel autoclave 13.2 g (11.0 mmol) of **8** in cyclohexane (550 ml) was placed together with 1.3 g of 10% Pd–C catalyst. The reaction mixture was shaken at 50°C and 80 bar H_2 pressure for 20 h then it was allowed to cool to RT and the catalyst was filtered. The crude 18,23-dioctadecyl-7,18-hentetracontanediol (**9**) was recrystal-

lized in ethyl acetate (100 ml) to give 11.5 g (94%) of pure **9**; m.p.: 55–58°C.

3.2.2.3. 18,23-Dioctadecyl-7-hentetracontanol (SOH)

In a round-bottom flask equipped with Dean–Stark trap 11.5 g (10.3 mmol) of the diol **9** and 0.4 g (2.1 mmol) of *p*-toluenesulfonic acid monohydrate were dissolved in benzene (500 ml). The reaction mixture was refluxed for 5 h, allowed to cool to RT and washed successively with water (2×200 ml) and sat. aq. $NaHCO_3$ (200 ml), finally dried over Na_2SO_4. The solvent was removed in a rotary evaporator. The residue was hydrogenated (see above) in cyclohexane (550 ml) in the presence of a 10% Pd–C catalyst (0.50 g) at 40°C and 15 bar H_2 pressure for 20 h. The catalyst was filtered and the solvent was evaporated in a rotary evaporator. Recrystallization of the residue in Et_2O–MeOH (3:2; 300 ml) afforded 10.2 g (89% of the theory) of pure SOH; m.p.: 62°C.

^{13}C-NMR (C^2HCl_3–TMS): δ=14.05, 22.55, 22.63, 25.56, 25.61, 26.64, 27.07, 29.31, 29.60, 29.65, 30.10, 31.78, 31.87, 33.62, 37.31, 37.43, 71.90. Anal.: $C_{77}H_{156}O$ (1098.02 g mol^{-1}): found: C: 84.42; H: 14.92%; calculated: C: 84.23; H: 14.32%.

3.3. Density of SOH

The density of liquid 18,23-dioctadecyl-7-hentetracontanol (SOH) was measured at 5 K intervals in the temperature range of 80–200°C on a sample of about 1 g using a precision digital densitometer from Anton Paar (Graz, Austria; Model DMA 55) with an external vibrating-tube remote cell for high pressure and temperature (Model DMA 512). The measuring cell consists of a U-tube, which is set into oscillation by an electronic excitation system. The characteristic frequency of the oscillating U-tube depends on the density of the sample contained in the tube. The calibration of the apparatus was performed by using 19,19-diethyl-14,24-ditridecylheptatriacontan (Apolane-67, $C_{67}H_{136}$) as described in Ref. [7]. Error in density is guaranteed to be less than $\pm 5\cdot 10^{-5}$ g cm^{-3}. On the experimental points Eq. (16) was fitted by linear regression:

$$\ln \rho_{SOH} = \ln M_{SOH} - \ln v_{SOH} = \ln \rho^{\dagger}_{SOH} - \alpha^{\dagger}_{SOH}\Delta T - B_{SOH}\Delta T^2 \quad (16)$$

where the M_{SOH} is the molar mass, v_{SOH} the molar volume, $\rho^{\dagger}_{SOH}$ the liquid density, $\alpha^{\dagger}_{SOH}$ is the isobaric coefficient of thermal expansion at the standard temperature $T^{\dagger}$=403.15 K. Finally, $B_{SOH}=(1/2)(d\alpha_{SOH}/dT)$ is the temperature coefficient of thermal expansion. The numerical values of the coefficients of Eq. (16) are listed in Table 2. Standard deviations are also reported in Table 2, calculated from the fitting errors obtained on the logarithmic scale.

3.4. Columns for gas chromatographic data

3.4.1. Support

The column support was prepared by deactivating the commercial Chromosorb G from Supelco (Bellefonte, PA, USA) as follows. In a 1.0-l ampoule was placed in an argon atmosphere 100 g of Chromosorb G and 2.5 g trimethyl(dimethylamino)silane. The ampoule was sealed, then heated to 250°C for 24 h.

Table 2
Physical properties of the liquid stationary phases A≡C_{78} [1] and SOH[a]

L	Formula	m.p. (°C)	M (g mol^{-1})	$v^{\dagger}$ (cm^3 mol^{-1})	$\rho^{\dagger}$ (g cm^{-3})	$\alpha^{\dagger}\cdot 10^4$ (K^{-1})	$B\cdot 10^7$ (K^{-2})	Δ_{95} (regression) (g cm^{-3})
C_{78}	$C_{78}H_{156}$	69–75	1096.1	1420.9	0.7714	7.62	1.26	±0.0008
SOH	$C_{77}H_{156}O$	62–64	1098.1	1413.8	0.7767	7.77	2.32	±0.0002
Δ_{95}					$\pm 5\cdot 10^{-5}$	$\pm 2\cdot 10^{-5}$	$\pm 9\cdot 10^{-4}$	

[a] Symbols: m.p. is melting point, M is the molar mass and $v^{\dagger}$ is the molar volume at the reference temperature $T^{\dagger}$=403.15 K. The density, ρ, of the melt, L, in the temperature range 80–200°C is given by Eq. (16) with the coefficients: $\rho^{\dagger}$ and $\alpha^{\dagger}$ (the density and the isobaric coefficient of thermal expansion, both at $T^{\dagger}$=403.15 K), further $B=(1/2)(d\alpha/dT)$ (the temperature coefficient of thermal expansion). The symbol Δ_{95} is for the confidence limit at the 95% confidence level of the corresponding coefficients or around the regression.

After cooling to RT, the silylated support was washed with Et_2O and dried in vacuum at 150°C.

3.4.2. Column packing

The desired amounts of the solid stationary phases, C_{78} and SOH were dissolved in cyclohexane to give together a ~3.0% (m/m) solution. To this solution was added the weighed amount of the deactivated support then the solvent was evaporated in a rotary evaporator [e.g., for the packing 1/1a: 1.0263 g SOH + 1.0563 g of C_{78} (together 2.0826 g) in 70 g of cyclohexane; 32.919 g of support]. The product was transferred to a cylindrical glass vessel and was heated in a slow argon stream first at 80°C for 4 h then at 130°C during 10 h. Properties of the prepared column packings are summarized in Table 3.

3.4.3. Columns

The packing material was filled into a coiled Pyrex tube of $L = 330$ cm, I.D. = 0.40 cm. The mass difference before and after the packing permitted calculation of the mass of the stationary phase in the column. Two columns were prepared with pure SOH: 0/1a and 0/1b and with a 1:1 mixture of C_{78}–SOH: 1/1a and 1/1b, one column was prepared with each of the mixtures of 1:3 and 3:1. Columns were stored filled with argon.

3.5. Apparatus

For details see Ref. [1]. In summary: for the determination of absolute retention data a modified double-column gas chromatograph from Packard (Delft, The Netherlands; Model 439) was used, equipped with thermal conductivity detectors. The temperature in the oven was measured with a platinum resistance thermometer (100 Ω, DIN 43710) in measuring devices from Systemteknik (Lidingoe, Sweden; Model S 1221) with a precision better than ±0.05 K. The platinum sensors were calibrated at the Hungarian National Bureau of Standards (Budapest, Hungary) between 273 K and 500 K with a precision of ±0.01 K. The mean column temperature was calculated by considering the temperature gradient indicated by chromel–alumel thermocouples at seven points in the oven. The experimental temperature did not change by more than 0.2 K during a working day. The inlet pressure of the helium carrier gas was controlled by a precision pressure regulator from Air Liquide (Liège, Belgium; Model DLRS No. 7) connected in series to a flow controller from Brooks (Veenendaal, The Netherlands; Model 5850 EM). The inlet pressure of the column was measured with a pressure gauge from Heise (Bassweiler, Germany; Model 710B) with a precision of ±1 mbar. Inlet pressures never exceeded 1.5 bar, and it was assumed that gas-phase imperfections were negligible. The outlet (atmospheric) pressure was measured with an accuracy of ±0.1 mbar by a digital barometer from Almemo (Holzkirchen, Germany; model 2290-3) equipped with a pressure transducer with temperature compensation (Model FD 8214). At the system outlet (ambient pressure and temperature) the carrier was first passed through a short column filled with wet cotton then the flow rate of the saturated carrier (typically 10 cm^3 min^{-1}) was measured by using a soap film flow meter. Chromatograms were recorded with an integrator from Hewlett-Packard (Palo Alto, CA, USA; Model 3390A) and the retention time was determined at the peak maximum. Fig. 4 shows a typical gas chromatogram of primary alcohols obtained on SOH as stationary phase.

Table 3
Characteristics of the chromatographic columns used in the present project[a]

Column, C_{78}–SOH	$\varphi^{\dagger}_{SOH}$	w_L (g)	P_L (%, m/m)
0/1a	1	1.842	6.06
0/1b	1	3.137	8.54
1/3	0.257	2.277	7.56
1/1a	0.491	1.837	5.95
1/1b	0.495	3.350	10.70
3/1	0.762	2.320	7.75

[a] Symbols: $\varphi^{\dagger}_{SOH}$ is the volume fraction of SOH at 130°C in the L = C_{78}–SOH mixture, w_L is the mass of the stationary liquid in the column and P_L the mass percent of L in the total packing material (liquid loading: $100w_L$/total mass).

3.6. Retention data

The retention time of neon was used as the hold-up time for the calculation of net retention times. The overall reproducibility of the retention volume of neon was better than 1% and was not affected by the amount of the gas injected. Retention data of the *n*-alkanes were measured on all columns between 90

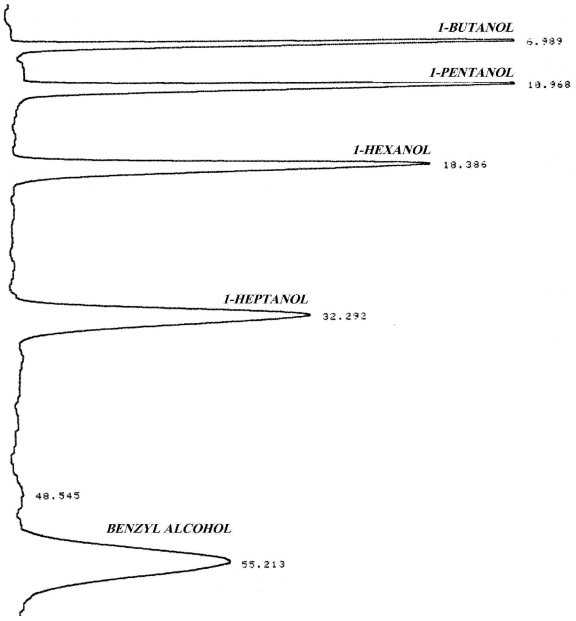

Fig. 4. Example of a typical gas chromatogram of a mixture of primary alcohols on the packed column No 0/1a (see Table 3) with the C_{77} secondary alcohol, SOH, as stationary phase. Experimental conditions: column temperature: $t_c = 130.2°C$; mobile phase: helium; quantity of mixture injected ≈0.3 μl.

and 210°C at 20 K intervals. Retention indices of the 158 molecular probes were determined on the columns 0/1a and 1/1a by using in the calculations the net retention times of the *n*-alkanes measured under the same conditions on the same working day.

4. Results

4.1. Standard chemical potentials of the n-alkanes

As explained in the Introduction, chromatographic data of all molecular probes were determined relative to those of the *n*-alkanes. Hence, on the quality of the gSPOT data of *n*-alkanes depended the quality of absolute data listed in Table 5. Therefore, for this specific group of solutes gSPOTs were determined with special care by the following procedure.

The chromatograph was equipped with two columns one with pure SOH ($\varphi_{SOH} = 1$) the second prepared with a SOH–A (1:1) mixture ($\varphi_{SOH} = 0.5$) as stationary phase. Gas chromatographic data were determined at seven temperatures between 90 and 210°C at 20 K intervals. Every working day *n*-alkanes with $z = 5$–14 were injected on both columns. Specific retention volumes were determined and converted to gSPOTs (Eqs. (4) and (1)), i.e., the ideal gas phase as reference. With the aid of gSPOTs on the stationary phase A from Refs. [1] and [5] these data were then corrected to give aSPOTs as indicated in Eq. (2). At the end of the project period the average of the daily results was calculated (see Ref. [4]) and data for C_{78} ($\varphi_{SOH} = 0.0$) were included. The latter are obviously zero at all conditions. The final data set of the average aSPOTs of six *n*-alkanes, C_zH_{2z+2} with $z = 6$–11, at seven temperatures on the three stationary phases with $\varphi_{SOH} = 0$, 0.5 and 1 gave a data table with $3 \times 6 \times 7 = 126$ data points (data for pentane were based partly on too short chromatograms). This basic data table was used for the variance analysis to determine the influence of the factors *T* (temperature), *L* (liquid phase composition) and *Z* (carbon number of the *n*-alkane) on the standard chemical potential differences of *n*-alkanes, $\Delta\mu_z^{A-P}$.

The result of the variance analysis is shown in Table 4. The analysis refers to the description of the experimental space by the multilinear Eq. (17), where $P_X^{(i)}$ an orthogonal polynomial of the degree *i* (1 for linear, 2 for quadratic, etc.) related to the effect $X = T$, *L* or *Z*. $b_X^{(i)}$ denotes the corresponding regression coefficient:

$$\begin{aligned}\Delta\mu_z^{A-P} &= b_L^{(1)}P_L^{(1)} + b_{L,Z}^{(1,1)}P_L^{(1)}P_Z^{(1)} + b_{T,L}^{(1,1)}P_T^{(1)}P_L^{(1)} \\ &\quad + \underline{b_{T,L,Z}^{(1,1,1)}P_T^{(1)}P_L^{(1)}P_Z^{(1)}} + b_{T,L}^{(2,1)}P_T^{(2)}P_L^{(1)} \\ &\quad + b_{T,L,Z}^{(2,1,1)}P_T^{(2)}P_L^{(1)}P_Z^{(1)} + b_L^{(2)}P_L^{(2)} + b_{L,Z}^{(2,1)}P_L^{(2)}P_Z^{(1)} \\ &\quad + b_{T,L}^{(1,2)}P_T^{(1)}P_L^{(2)} + b_{T,L,Z}^{(1,2,1)}P_T^{(1)}P_L^{(2)}P_Z^{(1)} \qquad (17)\end{aligned}$$

It is seen in Table 4 that the residual variance in the subspace *TL* (first res.) is significantly higher than the residual variance after deduction of all significant contributions. In fact, a higher error is introduced by adjusting a new temperature or by working with a new column compared to the error between a series of *n*-alkanes included in a same chromatogram. Consequently, effects in the *TL* subspace were tested against what is called the ‘‘first res.’’ and the remaining effects against the ‘‘second res.’’ (cf. the analogous variance analysis in Ref.

Table 4
Variance analysis of aSPOT data, $\underline{\Delta}\mu_z^{A-P}$, of *n*-alkanes in SOH–$C_{78}$ mixtures at 126 combinations of the levels of the factors *T*, *L* and *Z*[a]

Source		SQ	Φ	V'	F	Significance level (%)	$b_X^{(i)}$	Function
X	(i)							
$\underline{\Delta}\bar{\mu}$	(0)						24.675	$\Delta\mu_0^{\dagger,A}$
T	(1)	2391.04	1	2391.04	99.84	$1.82\cdot10^{-5}$	−2.178	ΔS_0^A
	(2)	88.62	1	88.62	3.70	7.66	0.242	$\Delta C_{P,0}^A$
	(res. T*	164.27	4	41.07	1.71	20.76)		
L	(1)	19 965.51	1	19 965.51	833.65	$3.55\cdot10^{-11}$	15.417	$\underline{\Delta}\mu_0^{\dagger,P}$
	(2)	21 598.40	1	21 598.40	901.83	$2.11\cdot10^{-11}$	−27.774	$m_0^{\dagger,A-P}$
	(res. L*	0.0	0	–	–	–)		
TL	(1,1)	2207.95	1	2207.95	92.19	$2.88\cdot10^{-5}$	−2.563	$\underline{\Delta}S_0^P$
	(1,2)	149.68	1	149.68	6.25	2.66	−1.156	s_0^{A-P}
	(2,1)	73.84	1	73.84	3.08	10.28	0.271	$\underline{\Delta}C_{P,0}^P$
	(res. TL*	147.08	9	16.34	0.68	71.51)		
First res.[b]	($=\Sigma X$*)	311.34	13	23.95				
Z	(1)	2421.90	1	2421.90	1248.62	$7.97\cdot10^{-55}$	2.567	$\delta\mu_z^{\dagger,A}$
	(2)	10.89	1	10.89	5.61	1.98	0.052	
	(res. Z**	44.35	3	14.78	7.62	0.01)		
TZ	(1,1)	17.92	1	17.92	9.24	0.31	0.110	δS_z^A
	(2,1)	112.45	1	112.45	57.98	$1.84\cdot10^{-9}$	0.160	$\delta C_{P,z}^A$
	(res. TZ**	62.76	28	2.24	1.16	29.17)		
LZ	(1,1)	822.49	1	822.49	424.04	$5.40\cdot10^{-35}$	1.832	$\delta\mu_z^{\dagger,P}$
	(2,1)	396.96	1	396.96	204.65	$1.56\cdot10^{-23}$	−2.205	$\delta m_z^{\dagger,A-P}$
	(res. LZ**	28.96	8	3.62	1.87	7.36)		
TLZ	(1,1,1)	1.36	1	1.36	0.70	40.49	0.037	δS_z^P
	(2,1,1)	46.64	1	46.64	24.04	$3.84\cdot10^{-4}$	0.126	$\delta C_{P,z}^P$
	(1,2,1)	15.73	1	15.73	8.11	0.54	−0.219	δs_z^{A-P}
	(res. TLZ**	50.15	57	0.88	0.45	99.93)		
Second res.[c]	($=\Sigma X$**)	186.21	96	1.94				

[a] Every datum is the average of 10–35 experimental determinations. The factors relate to temperature, *T*, (90, 110, 130, 150, 170, 190, 210°C), composition of the stationary liquid, *L*, ($\varphi_{SOH}=0$, 0.5, 1.0) and the carbon number of the *n*-alkane, *Z*, (6, 7, 8, 9, 10, 11) to give a data set at $7\times3\times6=126$ experimental conditions. Symbols: $X^{(i)}$ is the systematic polynomial variation of $\underline{\Delta}\mu_z^{A-P}$, on the effects *T*, *L* and *Z*; the subscripts in parentheses refer to the degree of the polynomial: (1) linear; (2) quadratic; SQ is the sum of squares, Φ the number of degrees of freedom, and $V'=V(\text{res.})+\nu_X V(X)$ is the combined variance to be analyzed by Fisher's *F* (ν_X is the number of statistical units in one datum of the subset used for the evaluation of the effect). The values of the coefficients $b_x^{(i)}$ of the orthogonal polynomial are also listed along with the corresponding thermodynamic functions. (For the symbols of thermodynamic functions see the text). The abbreviation ''res.'' denotes residual variance.

[b] Sum of the residuals marked by one asterisk.

[c] Sum of the residuals marked by two asterisks.

[1]). The results in Table 4 indicate that all the terms in Eq. (17) are significant with the exception of that underlined.

The aSPOT, $\underline{\Delta}\mu_z^{A-P}$, may also be expressed in terms of thermodynamic functions, by developing the relationship of Eq. (6) for $\underline{\Delta}\mu_z^{A-P}$ around the standard temperature, $T^\dagger$, by introducing $\Delta T=T-T^\dagger$, and by approximating the logarithmic function

multiplying ΔC_p, by the first two terms of its Taylor series and finally, by accepting a linear dependence of all functions on the carbon number of the *n*-alkanes, *z*, as follows:

$$\begin{aligned}\Delta\mu_z^{A-P} &= \varphi_P\cdot\left(\Delta\mu_0^{\dagger,P} + m_0^{\dagger,A-P}\right)\\ &+ \varphi_P z\cdot\left(\delta\mu_z^{\dagger,P} - \mu_z^{\dagger,A} + \delta m_z^{\dagger,A-P}\right)\\ &- \Delta T\varphi_P\Delta S_0^P - \underline{\Delta T\varphi_P z\cdot\left(\delta S_z^P - \delta S_z^A\right)}\\ &- \Delta T^2\varphi_P\Delta C_{p,0}^P/(2T^\dagger)\\ &- \Delta T^2\varphi_P z\cdot\left(\delta C_{p,z}^P - \delta C_{p,z}^A\right)/(2T^\dagger) - \varphi_P^2 m_0^{\dagger,A-P}\\ &- \varphi_P^2 z\delta m_z^{\dagger,A-P} + \Delta T\varphi_P^2 s_0^{A-P} + \Delta T\varphi_P^2\delta s_z^{A-P}\end{aligned} \quad (18)$$

The relation of the coefficients, $b_X^{(i)}$, to thermodynamic functions is listed in the last column of Table 4. The nonsignificance of the underlined term in Eqs. (17) and (18) is interpreted in terms of thermodynamic functions: there is no difference between the entropy term of the ''methylene increment'', δS_z^P, on the stationary phases C_{78} and SOH.

In the analysis of variance the term corresponding to the quadratic dependence of $\Delta\mu_z^{C_{78}-SOH}$ on liquid phase composition was found to be significant. It indicates that the dependence of the aSPOT on L (i.e., on φ_{SOH}) is not linear. From a thermodynamic viewpoint the sense of the observed curvature is not logical. Hence we supposed that the apparent divergence from linearity was due to measuring errors (±1%) and the restricted data set analyzed. Therefore, two additional columns were prepared with C_{78}–SOH mixtures of volume ratios $\varphi_{SOH}=0.25$ and 0.75 (1:3 and 3:1, see Table 3). On these columns a series of gSPOTs of *n*-alkanes were measured at a restricted number of temperatures. Fig. 5 illustrates the example of octane at 90°C that the dependence of $\Delta\mu_z^{C_{78}-SOH}$ on composition may be considered as linear.

The complete aSPOT data set, $\Delta\mu_z^{C_{78}-SOH}$, of the *n*-alkanes (C_zH_{2z+2} with $z=6$–11) on three C_{78}–SOH mixtures and at seven temperatures was now approximated by a thermodynamic function justified by the results of the variance analysis. A multiple regression was performed by assuming linearity of the thermodynamic functions of *n*-alkanes with carbon number and solvent composition and that the

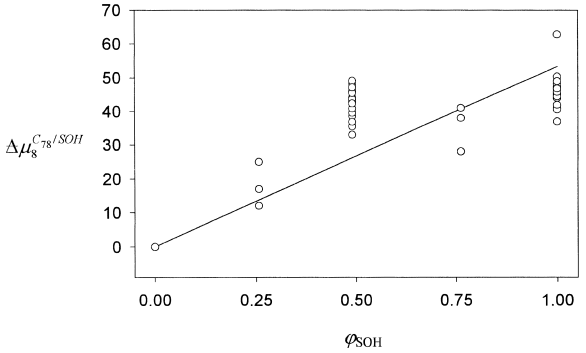

Fig. 5. An example of the dependence of the standard chemical potential difference, aSPOT, of an *n*-alkane in SOH–A mixtures as a function of the volume fraction of SOH, φ_{SOH}: octane ($z=8$) at $T=90.0+273.15$ K.

temperature dependence may be described by Kirchhoff's approximation:

$$\begin{aligned}\Delta\mu_z^{C_{78}-SOH} &= \varphi_{SOH}\cdot\left\{\left(\Delta H_0^{SOH} + z\delta H_z^{SOH}\right)\right.\\ &- T\cdot\left(\Delta S_0^{SOH} + z\delta S_z^{SOH}\right)\\ &\left.+\left(\Delta C_{p,0}^{SOH} + z\delta C_{p,0}^{SOH}\right)\cdot\left[T - T^\dagger - T\ln(T/T^\dagger)\right]\right\}\end{aligned} \quad (19)$$

The resulting regression coefficients in Eq. (19) are as follows: $\Delta H_0^{SOH}=91.05$ cal mol^{-1}; $\delta H_z^{SOH}=7.39$ cal mol^{-1}; $\Delta S_0^{SOH}=0.1876$ cal mol^{-1} K^{-1}; $\delta S_z^{SOH}=0.0099$ cal mol^{-1} K^{-1}; $\Delta C_{p,0}^{SOH}=3.196$ cal mol^{-1} K^{-1}; $\delta C_{p,z}^{SOH}=-0.503$ cal mol^{-1} K^{-1}. Eq. (19) was used for the calculation of the thermodynamic parameters for *n*-alkanes (ΔH, ΔS, ΔC_p), listed in columns 20–22 of Table 5, where it was supposed that the regression equation permitted extrapolation for lower ($z=5$) and higher ($z=12$–14) *n*-alkanes.

Data for the ideal dilute stationary phase, idSOH, were calculated as follows. Using the coefficients listed in Table 5 together with the molar volume of SOH (Eq. (16)) the slope, $\Delta'\mu_z^{idSOH}$, was calculated with the aid of Eq. (9), for 10 K intervals in the temperature range 90–210°C for a given alkane with $m_z^{C_{78}-SOH}=0$. Equations analogous to Eqs. (5a) and (5b) were fitted to the points $\Delta'\mu_z^{idSOH}$ of each alkane. The resulting regression coefficients, ($\Delta'H_z$, $\Delta'S_z$, $\Delta'C_{p,z}$) are given in columns 25–27 of Table

Table 5
Retention indices and thermodynamic data for 152 solutes in pure SOH and in an ideal dilute solution of SOH in the standard alkane A=C_{78} [a]

No.	Compound	n	Temp. range (°C)	Retention index on SOH; reference: C78													σ
				C78		SOH - C78			Mixture		id SOH([OH]=1) - C78						
				I_{130}	10 × A_T (K^{-1})	ΔI_{130}	10 × ΔA_T (K^{-1})	100× ΔA_{TT} (K^{-2})	A_L	10 × A_{LT} (K^{-1})	$\Delta' I_{130}$ (l mol^{-1})	10 × $\Delta' A_T$ (K^{-1}l mol^{-1})	100× $\Delta' A_{TT}$ (K^{-2}l mol^{-1})				
HYDROCARBONS																	
n-Alkanes																	
00.05	Pentane	94	90-210	500	def.												
00.06	Hexane	94	90-210	600	def.												
00.07	Heptane	94	90-210	700	def.												
00.08	Octane	94	90-210	800	def.												
00.09	Nonane	94	90-210	900	def.												
00.10	Decane	88	90-210	1000	def.												
00.11	Undecane	42	90-210	1100	def.												
00.12	Dodecane	16	130-210	1200	def.												
00.13	Tridecane	16	130-210	1300	def.												
00.14	Tetradecane	16	130-210	1400	def.												
Isoalkanes																	
10.01	2,2-Dimethylbutane	14	90-210	540.8	+ 0.93	+ 0.6^{s}	+0.03**	—**	+ 0.4**	+0.13**	+ 1.4	+0.24	—**	0.83
10.02	2,3-Dimethylbutane	14	90-210	573.2	+ 0.92	+ 1.2	+0.07	—**	- 0.1**	- 0.12**	+ 1.5	- 0.06	—**	0.23
10.03	2,2-Dimethylpentane	14	90-210	627.7	+ 0.85	+ 0.6	- 0.07**	—**	+ 0.5**	- 0.12**	+ 1.5	- 0.28	—**	0.61
10.04	2,3-Dimethylpentane	14	90-210	679.4	+ 0.98	+ 0.9	+0.07	—**	+ 0.2**	+0.11**	+ 1.7	+0.28	—**	0.30
10.05	2,4-Dimethylpentane	14	90-210	628.9	+ 0.53	+ 0.8	- 0.05**	—**	+ 1.4	- 0.08**	+ 3.1	- 0.17	—**	0.41
10.06	2,2-Dimethylhexane	14	90-210	719.4	+ 0.75	+ 0.5	- 0.06*	—**	+ 0.1**	- 0.02**	+ 0.9	- 0.12	—**	0.46
10.07	2,3-Dimethylhexane	14	90-210	765.6	+ 0.86	+ 0.9	+0.06	—**	- 0.2**	+0.10**	+ 1.0	+0.25	—**	0.29
10.08	2,4-Dimethylhexane	14	90-210	733.5	+ 0.54	+ 0.3	+0.13	—**	- 0.8*	+0.11**	- 0.8	+0.35	—**	0.30
10.09	3,4-Dimethylhexane	14	90-210	780.3	+ 1.07	+ 0.8	+0.14	—**	- 0.3**	+0.38	+ 0.7	+0.78	—**	0.27
10.10	2,2,3-Trimethylbutane	14	90-210	652.0	+ 1.30	+ 1.0	+0.50	—**	- 0.1**	+0.98	+ 1.5	+2.22	—**	0.32
10.11	2,2,4-Trimethylpentane	14	90-210	694.9	+ 0.95	+ 0.3**	+0.25	—**	- 0.4**	+0.51	- 0.1	+1.13	—**	0.61
10.12	2,3,4-Trimethylpentane	14	90-210	765.1	+ 1.35	+ 0.6	+0.34	—**	- 0.5**	+0.90	+ 0.3	+1.85	—**	0.76

[a] The reference data for pure C_{78} were taken from Ref. [5]. The symbol *n* denotes the number of data points used for regression. Constants and functions: *Y*, preceded by Δ refers to the reference state in C_{78}, i.e., $\Delta Y(P)=Y(P)-Y(C_{78})$; Δ′ values are for an "ideal dilute solution" of SOH. Retention indices: I_{130} is the retention index at the reference temperature $T^{\dagger}=130+273.15$ K; for the meaning of the coefficient, *A*, see Eqs. (12)–(14). Thermodynamic functions: *H* and *S* are partial molar enthalpy and entropy at $T^{\dagger}$, *C* is the mean partial molar heat capacity in the temperature range indicated; for the meaning of the coefficients *h* and *s* see Eq. (7). Errors: the symbol σ is the standard deviation around the regression, Data marked by the superscript, s, are significant at the 10–15% significance level if tested against σ. Data marked with one asterisk are at the 15–20% significance level, those marked by a double asterisk are under this limit. Note that *linearity* of the thermodynamic functions (ΔH, ΔS, ΔC_p, $\Delta' H$, $\Delta' S$, $\Delta' C_p$) of *n*-alkanes with carbon number and solvent composition was imposed by the regression function. This is the reason for the relatively high standard deviation given for the standard chemical potential of *n*-alkanes around the regression.

No.	Thermodynamic data on SOH; reference: C78												
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC_p (cal mol^{-1} K^{-1})	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC_p (cal mol^{-1} K^{-1})	h (cal mol^{-1})	s (cal mol^{-1} K^{-1})	$\Delta' H$ (cal l mol^{-2})	$\Delta' S$ (cal l mol^{-2} K^{-1})	$\Delta' C_p$ (cal l mol^{-2} K^{-1})	(cal mol^{-1})
HYDROCARBONS												
n-Alkanes												
00.05	- 5 507	- 16.043	+ 6.2	+ 128	+ 0.237	+ 0.7**			+ 167	+ 0.301	+ 1.2	22.0
00.06	- 6 505	- 17.131	+ 7.8	+ 135	+ 0.246	+ 0.2**			+ 175	+ 0.309	+ 0.5	15.2
00.07	- 7 517	- 18.341	+ 10.7	+ 143	+ 0.258	- 0.3**			+ 185	+ 0.322	- 0.3	16.4
00.08	- 8 517	- 19.540	+ 12.3	+ 150	+ 0.267	- 0.8**			+ 193	+ 0.330	- 1.0	17.1
00.09	- 9 531	- 20.792	+ 14.4	+ 158	+ 0.276	- 1.3**			+ 202	+ 0.337	- 1.7	18.1
00.10	- 10 539	- 22.035	+ 15.8	+ 165	+ 0.288	- 1.8**			+ 210	+ 0.351	- 2.5	19.8
00.11	- 11 561	- 23.322	+ 19.1	+ 172	+ 0.297	- 2.3**			+ 218	+ 0.359	- 3.2	23.0
00.12	- 12 569	- 24.581	+ 20.5	+ 180**	+ 0.306**	- 2.8**			+ 227	+ 0.366	- 3.9	27.3
00.13	- 13 576	- 25.840	+ 21.9	+ 187**	+ 0.318**	- 3.3**			+ 236	+ 0.379	- 4.7	29.9
00.14	- 14 583	- 27.099	+ 23.3	+ 194**	+ 0.327**	- 3.8**			+ 244	+ 0.387	- 5.4	33.7
Isoalkanes												
10.01	- 5 708	- 15.977	+ 6.0	+ 104	+ 0.179	+ 2.0	+ 51	+ 0.132**	+ 208	+ 0.412	+ 3.2	4.1
10.02	- 6 029	- 16.322	+ 6.4	+ 135	+ 0.263	+ 0.5s	- 20	- 0.048**	+ 151	+ 0.274	+ 1.0	1.4
10.03	- 6 602	- 17.009	+ 7.0	+ 92	+ 0.137	+ 2.1	- 4**	- 0.002**	+ 111	+ 0.160	+ 3.2	2.9
10.04	- 7 101	- 17.578	+ 8.9	+ 142	+ 0.268	+ 0.4**	+ 33	+ 0.089**	+ 234	+ 0.471	+ 0.9	1.6
10.05	- 6 686	- 17.208	+ 8.7	+ 113	+ 0.202	- 0.1**	- 47	- 0.093**	+ 84	+ 0.129	- 0.1	1.9
10.06	- 7 551	- 18.180	+ 10.4	+ 108	+ 0.176	+ 0.3**	- 18	- 0.036**	+ 113	+ 0.163	+ 0.5	1.8
10.07	- 7 991	- 18.678	+ 11.2	+ 142	+ 0.263	- 0.7	+ 5	+ 0.011**	+ 191	+ 0.347	- 0.7	1.2
10.08	- 7 741	- 18.467	+ 10.7	+ 167	+ 0.318	- 0.4**	+ 38	+ 0.081**	+ 270	+ 0.517	- 0.3	1.5
10.09	- 8 101	- 18.761	+ 10.3	+ 160	+ 0.302	+ 0.5	+ 110	+ 0.273**	+ 366	+ 0.774	+ 1.3	1.2
10.10	- 6 762	- 17.092	+ 8.1	+ 235	+ 0.501	- 0.1**	+ 214	+ 0.526**	+ 620	+ 1.416	+ 0.8	1.5
10.11	- 7 260	- 17.772	+ 9.7	+ 162	+ 0.306	+ 0.8	+ 95	+ 0.232**	+ 347	+ 0.721	+ 1.7	1.9
10.12	- 7 894	- 18.441	+ 9.6	+ 183	+ 0.352	+ 1.7	+ 231	+ 0.568**	+ 569	+ 1.259	+ 3.3	2.6

Table 5. Continued

No.	Compound	n	Temp. range (°C)	Retention index on SOH; reference: C78															σ
				C78		SOH - C78			Mixture		id SOH([OH]=1) - C78								
				I_{130}	$10\times A_T$ (K^{-1})	ΔI_{130}	$10\times \Delta A_T$ (K^{-1})	$100\times \Delta A_{TT}$ (K^{-2})	A_L	$10\times A_{LT}$ (K^{-1})	$\Delta' I_{130}$ ($l\ mol^{-1}$)	$10\times \Delta' A_T$ ($K^{-1} l\ mol^{-1}$)	$100\times \Delta' A_{TT}$ ($K^{-2} l\ mol^{-1}$)						
1-Alkenes																			
11.05	1-Pentene	17	90-210	485.0	+ 0.46	+ 2.7**	- 0.23	— **	- 1.9*	- 0.53*	+ 1.0	- 1.12	— **						0.82
11.06	1-Hexene	18	90-210	585.9	+ 0.49	+ 3.1	- 0.24	— **	- 2.2s	- 0.21**	+ 1.2	- 0.66	— **						0.93
11.07	1-Heptene	18	90-210	685.0	+ 0.41	+ 3.6	- 0.13*	— **	- 1.4**	- 0.07**	+ 3.1	- 0.26	— **						1.03
11.08	1-Octene	18	90-210	784.9	+ 0.45	+ 3.2	- 0.15s	— **	- 2.3**	- 0.04**	+ 1.3	- 0.28	— **						1.15
11.09	1-Nonene	18	90-210	885.0	+ 0.39	+ 3.3	- 0.07**	— **	- 1.5**	- 0.13**	+ 2.5	- 0.28	— **						1.25
11.10	1-Decene	18	90-210	985.0	+ 0.35	+ 3.3	- 0.05**	— **	- 2.4**	+0.06**	+ 1.4	+0.02	— **						1.34
1-Alkynes																			
12.05	1-Pentyne	24	90-210	484.4	- 0.20	+12.2	+0.24	— **	+ 0.8**	+0.54s	+18.6	+1.32	— **						0.91
12.06	1-Hexyne	24	90-210	587.3	+ 0.08	+12.7	+0.08**	— **	+ 0.6**	+0.56s	+19.1	+1.13	— **						0.92
12.07	1-Heptyne	23	90-210	687.3	+ 0.05	+13.1	+0.12s	— **	+ 0.4**	+0.65	+19.4	+1.32	— **						0.89
12.08	1-Octyne	24	90-210	787.5	+ 0.16	+12.8	+0.06**	— **	+ 0.4**	+0.38**	+19.0	+0.83	— **						1.11
12.09	1-Nonyne	22	90-210	887.9	+ 0.22	+12.9	+0.01**	— **	- 0.3**	+0.32**	+18.0	+0.65	— **						1.05
12.10	1-Decyne	23	90-210	987.9	+ 0.18	+13.1	+0.03**	— **	+ 1.4	+0.50	+20.8	+0.98	— **						0.60
Alkynes																			
13.01	2-Hexyne	14	90-210	642.0	- 0.19	+10.8	- 0.16	— **	+ 0.3**	- 0.09**	+15.9	- 0.23	— **						0.58
13.02	3-Hexyne	14	90-210	619.8	- 0.57	+10.3	- 0.18	— **	+ 0.5**	- 0.15**	+15.4	- 0.35	— **						0.65
13.03	4-Octyne	14	90-210	809.9	- 0.19	+ 9.2	- 0.18	— **	- 0.3**	- 0.08**	+12.6	- 0.27	— **						0.36
Monocyclic hydrocarbons																			
14.05	Cyclopentane	17	90-210	587.7	+ 2.29	+ 0.6**	- 0.14**	— **	- 3.2*	- 0.17**	- 3.7	- 0.49	— **						1.19
14.06	Cyclohexane	20	90-210	693.6	+ 3.09	+ 0.8	+0.21	— **	- 2.3**	+0.39**	- 2.1	+0.88	— **						1.17
14.07	Cycloheptane	18	90-210	837.5	+ 4.15	+ 1.1	+0.28	— **	- 0.7**	+0.33**	+ 0.6	+0.91	— **						0.81
14.08	Cyclooctane	16	90-210	965.8	+ 4.96	+ 1.5	+0.44	— **	- 0.1**	+0.26**	+ 2.1	+1.06	— **						0.70
14.10	Cyclodecane	10	130-210	1179.0	+ 6.89	+ 4.0	- 0.19s	— **	+ 0.0**	+0.24**	+ 5.8	+0.13	— **						0.69
Bicyclic hydrocarbons																			
15.01	*cis*-Hydrindane	10	130-210	1035.6	+ 5.92	+ 2.0	- 0.01**	— **	- 3.0*	+0.46**	- 1.4	+0.66	— **						0.53
15.02	*trans*-Hydrindane	9	130-210	1001.9	+ 5.29	+ 1.2**	+0.23**	— **	- 0.6**	+1.85**	+ 1.1	+3.11	— **						1.61
15.03	*cis*-Decalin	9	130-210	1152.9	+ 7.04	+ 3.3	+0.08**	— **	- 1.8**	+0.82s	+ 2.3	+1.35	— **						0.55
15.04	*trans*-Decalin	9	130-210	1112.4	+ 6.60	+ 2.0	- 0.05**	— **	- 4.7*	+0.32**	- 3.8	+0.38	— **						0.73
Methylcyclohexanes (MCH)																			
16.01	Methylcyclohexane	14	90-210	758.3	+ 3.24	+ 0.9	+0.16	— **	- 0.7**	+0.42**	+ 0.3	+0.87	— **						0.81
16.02	*cis*-1,2-Di MCH	13	90-210	868.2	+ 3.91	+ 1.3	+0.13	— **	- 1.1**	- 0.13**	+ 0.3	+0.01	— **						0.47
16.03	*trans*-1,2-Di MCH	12	90-190	837.8	+ 3.54	+ 0.9	+0.16	— **	- 1.2	- 0.02**	- 0.5	+0.21	— **						0.32
16.04	*cis*-1,4-Di MCH	13	90-210	838.2	+ 3.38	+ 1.3	- 0.15	— **	- 2.5s	+0.36**	- 1.8	+0.31	— **						0.81
16.05	*trans*-1,4-Di MCH	11	90-190	816.7	+ 3.12	+ 1.0	+0.15	— **	+ 0.1**	+0.44**	+ 1.6	+0.88	— **						0.64

No.	Thermodynamic data on SOH; reference: C78												
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC$_p$ (cal mol^{-1} K^{-1})	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC$_p$ (cal mol^{-1} K^{-1})	h (cal mol^{-1})	s (cal mol^{-1} K^{-1})	Δ'H (cal l mol^{-2})	Δ'S (cal l mol^{-2} K^{-1})	Δ'C$_p$ (cal l mol^{-2} K^{-1})	(cal mol^{-1})
1-Alkenes												
11.05	- 5 235	- 15.522	+ 5.1	+ 40	+ 0.005**	+ 0.8**	- 135	- 0.467**	- 174	- 0.753	+ 0.7	4.4
11.06	- 6 244	- 16.679	+ 8.3	+ 48	+ 0.076*	- 1.2**	- 80	- 0.239**	- 61	- 0.269	- 1.9	5.2
11.07	- 7 271	- 17.932	+ 12.2	+ 79	+ 0.154	- 2.8	- 89	- 0.245**	- 29	- 0.163	- 4.2	5.4
11.08	- 8 276	- 19.138	+ 12.5	+ 89	+ 0.158	- 0.9**	- 70	- 0.200**	+ 10	- 0.101	- 1.4	6.1
11.09	- 9 298	- 20.404	+ 14.0	+ 98	+ 0.167	- 0.7**	- 28	- 0.089**	+ 81	+ 0.068	- 1.0	6.4
11.10	- 10 314	- 21.663	+ 15.0	+ 99	+ 0.161	- 0.3**	+ 32	+ 0.047**	+ 165	+ 0.241	- 0.2	6.8
1-Alkynes												
12.05	- 5 391	- 15.969	+ 7.1	+ 58	+ 0.231	- 0.5**	+ 71	+ 0.175**	+ 199	+ 0.612	- 0.4	5.1
12.06	- 6 358	- 16.945	+ 8.6	+ 19**	+ 0.135	- 0.6**	+ 77	+ 0.197**	+ 152	+ 0.512	- 0.5	4.9
12.07	- 7 380	- 18.168	+ 11.9	+ 40	+ 0.176	- 1.9	+ 80	+ 0.196**	+ 182	+ 0.556	- 2.4	4.6
12.08	- 8 365	- 19.325	+ 12.9	+ 39^s	+ 0.157	- 1.6^s	+ 55	+ 0.141**	+ 143	+ 0.447	- 2.1	5.9
12.09	- 9 368	- 20.544	+ 15.3	+ 28*	+ 0.119	- 2.1	+ 24	+ 0.053**	+ 80	+ 0.259	- 2.9	5.2
12.10	- 10 385	- 21.811	+ 17.0	+ 42	+ 0.152	- 3.1	+ 46	+ 0.132**	+ 134	+ 0.425	- 4.3	3.3
Alkynes												
13.01	- 6 977	- 17.758	+ 9.3	- 24	- 0.014**	+ 1.6	- 15	- 0.028**	- 44	- 0.031	+ 2.4	1.9
13.02	- 6 829	- 17.675	+ 8.8	- 27	- 0.030**	+ 1.9	- 30	- 0.070**	- 72	- 0.121	+ 2.7	2.5
13.03	- 8 664	- 19.779	+ 13.0	+ 34	+ 0.093	- 1.1	- 9	- 0.029**	+ 35	+ 0.091	- 1.6	1.7
Monocyclic hydrocarbons												
14.05	- 5 857	- 15.694	+ 6.3	+ 24**	- 0.028**	+ 2.5	- 61	- 0.196**	- 74	- 0.371	+ 3.4	4.1
14.06	- 6 796	- 16.639	+ 9.4	+ 135	+ 0.249	- 0.7**	+ 13	+ 0.001**	+ 189	+ 0.300	- 0.8	5.1
14.07	- 8 036	- 17.876	+ 10.6	+ 171	+ 0.329	- 2.1	+ 2**	- 0.008**	+ 224	+ 0.404	- 2.8	3.8
14.08	- 9 178	- 19.086	+ 10.2	+ 207	+ 0.406	- 0.7**	+ 41	+ 0.100**	+ 330	+ 0.667	- 0.5	3.2
14.10	- 11 068	- 21.115	+ 16.3	+ 97	+ 0.155^s	- 3.1	+ 9	+ 0.032**	+ 134	+ 0.226	- 4.5	1.7
Bicyclic hydrocarbons												
15.01	- 9 800	- 19.749	+ 14.7	+ 286	+ 0.598	- 6.1	+ 82	+ 0.162**	+ 489	+ 0.996	- 8.4	2.4
15.02	- 9 564	- 19.587	+ 14.1	+ 274*	+ 0.565**	- 4.9**	+274	+ 0.677**	+ 751	+ 1.697	- 6.1	7.5
15.03	- 10 660	- 20.434	+ 13.0	+ 89*	+ 0.131**	- 1.7**	+114	+ 0.270**	+ 267	+ 0.520	- 2.2	2.6
15.04	- 10 411	- 20.311	+ 14.4	+ 178	+ 0.330^s	- 3.7	+ 46	+ 0.067**	+ 286	+ 0.483	- 5.1	3.2
Methylcyclohexanes (MCH)												
16.01	- 7 415	- 17.342	+ 9.1	+ 116	+ 0.190	+ 0.9	+ 52	+ 0.118**	+ 219	+ 0.390	+ 1.6	1.6
16.02	- 8 403	- 18.392	+ 7.9	+ 134	+ 0.227	+ 2.3	+ 53	+ 0.124**	+ 246	+ 0.451	+ 3.7	1.4
16.03	- 8 172	- 18.202	+ 7.8	+ 158	+ 0.286	+ 2.0	+ 47	+ 0.103**	+ 271	+ 0.500	+ 3.3	1.6
16.04	- 8 205	- 18.281	+ 9.2	+ 120	+ 0.206	- 1.2*	+ 85	+ 0.177**	+ 267	+ 0.482	- 1.4	3.6
16.05	- 8 031	- 18.123	+ 10.0	+ 149	+ 0.273	- 1.0**	+ 55	+ 0.131**	+ 270	+ 0.526	- 1.1	3.3

Table 5. Continued

No.	Compound	n	Temp. range (°C)	Retention index on SOH; reference: C78														σ
				C78		SOH - C78			Mixture		id SOH([OH]=1) - C78							
				I_{130}	$10\times A_T$ (K^{-1})	ΔI_{130}	$10\times \Delta A_T$ (K^{-1})	$100\times \Delta A_{TT}$ (K^{-2})	A_L	$10\times A_{LT}$ (K^{-1})	$\Delta' I_{130}$ ($l\ mol^{-1}$)	$10\times \Delta' A_T$ ($K^{-1} l\ mol^{-1}$)	$100\times \Delta' A_{TT}$ ($K^{-2} l\ mol^{-1}$)					
Cyclohexenes																		
17.01	Cyclohexene	14	90-210	705.0	+ 3.04	+ 4.3	+0.12^{s}	— **	- 0.8**	+0.30**	+ 5.0	+0.66	— **					0.76
17.02	1,3-Cyclohexadiene	13	90-210	689.6	+ 2.97	+ 7.6	+0.26	— **	- 1.6^{s}	+0.09**	+ 8.6	+0.60	— **					0.49
17.03	1,4-Cyclohexadiene	13	90-210	725.3	+ 2.96	+ 8.0	- 0.03**	— **	- 1.6**	- 0.01**	+ 9.1	+0.03	— **					0.68
Alkylbenzenes																		
18.00	Benzene	16	90-210	677.2	+ 2.68	+11.4	+0.56	— **	- 1.0**	+1.01	+15.1	+2.46	— **					0.63
18.01	Toluene	14	90-210	784.0	+ 2.75	+13.0	+0.50	— **	+ 2.1	+0.97	+21.9	+2.38	— **					0.59
18.02	Ethylbenzene	14	90-210	875.4	+ 3.08	+11.0	+0.39	— **	- 1.2**	+0.88	+14.2	+2.01	— **					0.59
Miscellaneous																		
19.01	Adamantane	10	130-210	1136.9	+ 7.87	+ 2.2	+0.39	— **	+ 2.1**	+0.55*	+ 6.4	+1.45	— **					0.52
19.02	Naphtalene	10	130-210	1214.1	+ 7.78	+20.3	- 0.23*	— **	- 1.7**	+0.65**	+26.7	+0.87	— **					0.95
19.03	Azulene	8	150-210	1326.0	+ 8.92	+23.8	+0.14**	— **	+20.5*	- 3.13**	+63.0	- 3.86	— **					2.41
ALKANE DERIVATIVES																		
1-Fluoroalkanes																		
20.05	1-Fluoropentane	16	90-210	555.9	+ 0.09	+12.7	+0.02**	— **	+ 0.6**	+0.02**	+19.0	+0.23	— **					1.15
20.06	1-Fluorohexane	16	90-210	656.8	+ 0.07	+12.9	+0.02**	— **	+ 0.9**	+0.13**	+19.8	+0.41	— **					0.93
20.07	1-Fluoroheptane	16	90-210	757.4	+ 0.07	+13.1	+0.03**	— **	+ 0.9**	+0.21**	+20.2	+0.54	— **					0.78
20.08	1-Fluorooctane	16	90-210	857.9	+ 0.08	+13.3	+0.02**	— **	+ 0.8**	+0.12**	+20.3	+0.39	— **					0.64
1-Chloroalkanes																		
21.04	1-Chlorobutane	14	90-210	639.0	+ 1.69	+13.2	- 0.03**	— **	- 0.1**	+0.01**	+18.8	+0.15	— **					0.59
21.05	1-Chloropentane	14	90-210	742.2	+ 1.48	+13.1	+0.29	— **	- 0.2**	+0.56	+18.6	+1.42	— **					0.47
21.06	1-Chlorohexane	13	90-210	843.7	+ 1.69	+13.0	+0.19	— **	- 1.1**	+0.56	+17.2	+1.27	— **					0.48
1-Bromoalkanes																		
22.04	1-Bromopropane	14	90-210	627.7	+ 2.32	+13.9	+0.28	— **	+ 0.9**	+0.64	+21.3	+1.57	— **					0.54
22.05	1-Bromobutane	12	90-210	731.4	+ 2.55	+13.6	+0.23	— **	+ 0.4**	+0.47	+20.1	+1.22	— **					0.58
22.06	1-Bromopentane	14	90-210	833.8	+ 2.66	+13.5	+0.24	— **	- 0.1**	+0.46	+19.3	+1.22	— **					0.49
1-Cyanoalkanes																		
24.02	Cyanoethane	12	90-210	492.6	+ 0.69	+40.8	- 0.31^{s}	+0.04*	- 1.7**	+0.09**	+55.7	+0.13	+0.08					1.18
24.03	1-Cyanopropane	15	90-210	587.9	+ 1.17	+43.0	- 0.63	+0.04	+ 2.3*	+0.27**	+64.7	- 0.01	+0.08					0.94
24.04	1-Cyanobutane	15	90-210	692.9	+ 1.35	+44.4	- 0.65	+0.06	+ 4.5	+0.43^{s}	+69.8	+0.25	+0.10					0.68
24.05	1-Cyanopentane	15	90-210	794.7	+ 1.44	+45.1	- 0.64	+0.06	+ 5.4	+0.47^{s}	+71.9	+0.34	+0.11					0.72

No.	Thermodynamic data on SOH; reference: C78												
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC_p	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC_p	h (cal mol^{-1})	s (cal mol^{-1} K^{-1})	$\Delta' H$ (cal l mol^{-2})	$\Delta' S$ (cal l mol^{-2} K^{-1})	$\Delta' C_p$	(cal mol^{-1})
Cyclohexenes												
17.01	- 6 926	- 16.812	+ 7.7	+ 73	+ 0.132	+ 2.0	+ 65	+ 0.153**	+ 186	+ 0.381	+ 3.2	1.6
17.02	- 6 781	- 16.650	+ 6.9	+ 86	+ 0.210	+ 1.6	+ 72	+ 0.162**	+ 222	+ 0.521	+ 2.7	1.5
17.03	- 7 152	- 17.113	+ 8.3	+ 56	+ 0.143	- 0.4**	+ 23	+ 0.040**	+ 109	+ 0.253	- 0.4	3.3
Alkylbenzenes												
18.00	- 6 729	- 16.685	+ 8.2	+ 145	+ 0.413	- 0.9**	+220	+ 0.529**	+ 522	+ 1.350	- 0.4	3.2
18.01	- 7 802	- 17.954	+ 10.9	+ 134	+ 0.377	- 2.8	+150	+ 0.351**	+ 404	+ 1.038	- 3.4	3.0
18.02	- 8 649	- 18.918	+ 11.9	+ 122	+ 0.332	- 2.6	+148	+ 0.350**	+ 383	+ 0.965	- 3.1	2.8
Miscellaneous												
19.01	- 10 548	- 20.340	+ 17.9	+ 429	+ 0.947	- 9.3	+ 15**	+ 0.069**	+ 605	+ 1.382	- 12.9	4.0
19.02	- 11 301	- 21.266	+ 17.9	+ 72**	+ 0.294**	- 7.3	+ 71	+ 0.190**	+ 221	+ 0.728	- 10.3	5.3
19.03	- 12 443	- 22.642	+ 21.9	+ 674**	+ 1.715**	- 18.1**	- 655	- 1.435**	+ 53	+ 0.465	- 26.5	12.5
ALKANE DERIVATIVES												
1-Fluoroalkanes												
20.05	- 6 043	- 16.603	+ 9.5	- 34^{s}	+ 0.003**	+ 0.3**	- 100	- 0.243**	- 173	- 0.298	+ 0.2	4.4
20.06	- 7 067	- 17.791	+ 11.2	- 12**	+ 0.043**	- 0.1**	- 50	- 0.114**	- 72	- 0.064	- 0.2	3.4

Table 5. Continued

No.	Compound	n	Temp. range (°C)	Retention index on SOH; reference: C78												
				C78		SOH - C78			Mixture		id SOH([OH]=1) - C78			
				I_{130}	$10\times A_T$ (K^{-1})	ΔI_{130}	$10\times \Delta A_T$ (K^{-1})	$100\times \Delta A_{TT}$ (K^{-2})	A_L	$10\times A_{LT}$ (K^{-1})	$\Delta' I_{130}$ ($l\ mol^{-1}$)	$10\times \Delta' A_T$ ($K^{-1} l\ mol^{-1}$)	$100\times \Delta' A_{TT}$ ($K^{-2} l\ mol^{-1}$)	σ
1-Nitroalkanes														
25.02	Nitroethane	22	90-210	566.5	+ 1.34	+39.8	- 0.73	+0.06	+ 0.4**	+0.56*	+57.2	+0.22	+ 0.11	1.09
25.03	1-Nitropropane	22	90-210	660.5	+ 1.74	+39.0	- 0.67	+0.04	+ 1.7**	+0.43**	+58.0	+0.11	+ 0.07	0.95
25.04	1-Nitrobutane	22	90-210	763.8	+ 2.02	+38.7	- 0.75	+0.06	+ 1.0**	+0.48*	+56.6	+0.07	+ 0.10	0.94
25.05	1-Nitropentane	22	90-210	865.9	+ 2.15	+38.8	- 0.65	+0.05	+ 1.3**	+0.44**	+57.1	+0.17	+ 0.10	0.95
1-Acetoxyalkanes														
26.03	1-Acetoxypropane	14	90-210	637.6	- 0.63	+30.8	- 0.96	+0.08	+ 2.6*	- 0.08**	+47.6	- 1.10	+ 0.11	0.87
26.04	1-Acetoxybutane	14	90-210	739.4	- 0.53	+31.5	- 0.92	+0.06	+ 2.6	- 0.15**	+48.6	- 1.15	+ 0.09	0.73
26.05	1-Acetoxypentane	14	90-210	840.0	- 0.40	+31.3	- 0.97	+0.07	+ 2.9	- 0.47**	+48.8	- 1.67	+ 0.10	0.69
1-Alkanols														
27.04	1-Butanol	19	90-210	594.5	+ 0.75	+49.6	- 3.96	+0.28	- 5.0s	+1.60	+63.5	- 2.84	+ 0.41	1.78
27.05	1-Pentanol	20	90-210	698.3	+ 0.78	+50.2	- 3.91	+0.31	- 2.6**	+1.61	+67.8	- 2.70	+ 0.46	2.06
27.06	1-Hexanol	20	90-210	800.0	+ 1.02	+51.5	- 4.14	+0.31	- 2.6**	+1.24s	+69.6	- 3.55	+ 0.46	1.93
27.07	1-Heptanol	20	90-210	901.4	+ 1.02	+52.8	- 4.23	+0.32	- 2.5**	+1.47	+71.6	- 3.34	+ 0.48	2.05
2-Alkanols														
28.04	2-Butanol	12	90-210	545.9	+ 0.46	+39.5	- 3.36	+0.34	- 4.2	+0.70**	+50.2	- 3.36	+ 0.50	1.00
28.05	2-Pentanol	12	90-210	644.5	+ 0.41	+41.4	- 3.25	+0.32	- 2.4s	+0.96	+55.4	- 2.79	+ 0.47	0.74
28.06	2-Hexanol	12	90-210	744.5	+ 0.60	+42.9	- 3.38	+0.30	- 1.1**	+0.88	+59.6	- 3.06	+ 0.45	0.71
28.07	2-Heptanol	12	90-210	844.5	+ 0.72	+43.9	- 3.45	+0.30	- 0.4**	+0.61**	+62.0	- 3.53	+ 0.43	0.88
2-Methyl-2-alkanols														
29.04	2-Methyl-2-propanol	20	90-210	472.1	+ 0.32	+37.7	- 3.03	+0.25	- 4.5	+0.33**	+47.3	- 3.46	+ 0.35	1.02
29.05	2-Methyl-2-butanol	21	90-210	597.5	+ 1.01	+37.8	- 2.79	+0.21	- 2.6**	+0.18**	+50.1	- 3.31	+ 0.30	1.40
29.06	2-Methyl-2-pentanol	21	90-210	690.2	+ 0.86	+38.3	- 2.79	+0.22	- 2.3**	+0.44**	+51.3	- 2.92	+ 0.31	1.53
29.07	2-Methyl-2-hexanol	16	90-210	785.7	+ 0.90	+39.0	- 2.83	+0.21	- 3.4**	+0.53**	+50.6	- 2.86	+ 0.30	1.81
1-Thiols														
30.04	1-Butanethiol	13	90-210	716.6	+ 3.09	+15.1	- 0.51	—**	- 1.6**	- 1.10	+19.1	- 2.21	—**	0.79
30.05	1-Pentanethiol	14	90-210	818.9	+ 3.26	+15.3	- 0.51	—**	- 1.0**	- 1.29	+20.3	- 2.50	—**	1.14
30.06	1-Hexanethiol	14	90-210	920.4	+ 3.32	+15.1	- 0.50	—**	- 1.4**	- 1.07	+19.4	- 2.16	—**	0.88
2-Alkanones														
31.04	2-Butanone	26	90-210	537.6	+ 0.63	+33.1	- 1.19	+0.05	- 0.9**	- 1.45	+45.9	- 3.41	+ 0.06	1.39
31.05	2-Pentanone	26	90-210	628.5	+ 0.75	+34.6	- 1.16	+0.06	+ 2.8	- 0.80	+53.4	- 2.38	+ 0.07	0.98
31.06	2-Hexanone	26	90-210	730.1	+ 0.83	+35.8	- 1.13	+0.06	+ 3.4	- 0.69	+55.9	- 2.15	+ 0.08	0.87
31.07	2-Heptanone	26	90-210	830.2	+ 0.91	+36.3	- 1.17	+0.06	+ 4.0	- 0.50*	+57.4	- 1.92	+ 0.09	0.87

No.	Thermodynamic data on SOH; reference: C78											
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH	ΔS	ΔC_p	ΔH	ΔS	ΔC_p	h	s	Δ'H	Δ'S	$\Delta' C_p$	
	(cal mol^{-1})	(cal mol^{-1} K^{-1})		(cal mol^{-1})	(cal mol^{-1} K^{-1})		(cal mol^{-1})	(cal mol^{-1} K^{-1})	(cal l mol^{-2})	(cal l mol^{-2} K^{-1})		(cal mol^{-1})
1-Nitroalkanes												
25.02	- 5 853	- 15.970	+ 10.0	- 440	- 0.640	- 0.7**	- 29	- 0.093**	- 588	- 0.849	- 1.7	6.7
25.03	- 6 746	- 16.954	+ 12.6	- 386	- 0.533	- 2.7	- 86	- 0.192**	- 591	- 0.833	- 4.5	5.8
25.04	- 7 735	- 18.076	+ 13.6	- 387	- 0.556	- 1.9	- 39	- 0.077**	- 529	- 0.712	- 3.3	5.5
25.05	- 8 744	- 19.282	+ 15.9	- 357	- 0.498	- 3.1	- 77	- 0.172**	- 544	- 0.774	- 5.2	5.4
1-Acetoxyalkanes												
26.03	- 7 008	- 17.893	+ 11.4	- 379	- 0.627	+ 2.0	- 142	- 0.323**	- 675	- 1.189	+ 2.1	4.2
26.04	- 8 021	- 19.088	+ 12.9	- 355	- 0.576	+ 1.7	- 101	- 0.217**	- 584	- 0.971	+ 1.8	3.5
26.05	- 9 005	- 20.249	+ 15.1	- 365	- 0.612	+ 0.8**	- 129	- 0.294**	- 642	- 1.140	+ 0.4	2.7
1-Alkanols												
27.04	- 6 259	- 16.592	+ 9.5	- 1239	- 2.517	+ 13.0	+ 186	+ 0.385**	- 1 395	- 2.782	+ 17.3	8.8
27.05	- 7 316	- 17.865	+ 12.9	- 1197	- 2.422	+ 12.4	+ 164	+ 0.364**	- 1 362	- 2.668	+ 16.5	10.6
27.06	- 8 295	- 18.990	+ 14.3	- 1237	- 2.524	+ 12.4	+ 102	+ 0.214**	- 1 506	- 3.024	+ 16.3	9.7
27.07	- 9 309	- 20.224	+ 17.4	- 1266	- 2.591	+ 10.8	+ 73	+ 0.134**	- 1 590	- 3.236	+ 13.7	10.3
2-Alkanols												
28.04	- 5 845	- 16.245	+ 10.1	- 1035	- 2.103	+ 14.0	+ 70	+ 0.096**	- 1 285	- 2.644	+ 18.9	3.9
28.05	- 6 862	- 17.438	+ 11.9	- 981	- 1.987	+ 12.9	+ 129	+ 0.270**	- 1 124	- 2.231	+ 17.5	3.1
28.06	- 7 838	- 18.568	+ 12.6	- 993	- 2.013	+ 12.8	+ 142	+ 0.331**	- 1 118	- 2.167	+ 17.4	3.6
28.07	- 8 825	- 19.744	+ 14.9	- 1005	- 2.046	+ 11.6	+ 76	+ 0.176**	- 1 228	- 2.434	+ 15.5	4.8
2-Methyl-2-alkanols												
29.04	- 5 085	- 15.379	+ 14.2	- 997	- 2.031	+ 4.5	- 138	- 0.460**	- 1 545	- 3.374	+ 4.3	7.7
29.05	- 6 223	- 16.464	+ 12.8	- 883	- 1.788	+ 5.3	- 104	- 0.322**	- 1 333	- 2.827	+ 6.0	7.4
29.06	- 7 206	- 17.696	+ 14.5	- 858	- 1.734	+ 5.9	- 25*	- 0.112**	- 1 184	- 2.450	+ 7.1	7.8
29.07	- 8 156	- 18.829	+ 16.5	- 856	- 1.731	+ 4.4	- 44	- 0.166**	- 1 211	- 2.530	+ 4.7	8.9
1-Thiols												
30.04	- 7 031	- 16.922	+ 6.9	- 148	- 0.279	+ 2.7	- 163	- 0.412**	- 424	- 0.938	+ 3.3	4.2
30.05	- 8 031	- 18.097	+ 10.1	- 113	- 0.194	- 1.0**	- 265	- 0.666**	- 523	- 1.184	- 2.3	5.6
30.06	- 9 042	- 19.330	+ 14.6	- 103	- 0.174	- 4.5	- 334	- 0.849**	- 611	- 1.430	- 7.6	4.3
2-Alkanones												
31.04	- 5 709	- 16.031	+ 10.1	- 491	- 0.833	- 0.5**	- 458	- 1.153**	- 1 278	- 2.651	- 2.5	7.8
31.05	- 6 622	- 17.063	+ 12.2	- 462	- 0.773	- 1.0**	- 323	- 0.768**	- 1 039	- 2.003	- 2.8	5.3
31.06	- 7 642	- 18.273	+ 13.5	- 445	- 0.735	- 0.6**	- 254	- 0.589**	- 916	- 1.695	- 2.1	4.6
31.07	- 8 636	- 19.462	+ 14.9	- 449	- 0.756	- 0.4**	- 212	- 0.474**	- 863	- 1.562	- 1.7	4.4

Table 5. Continued

| No. | Compound | n | Temp. range (°C) | Retention index on SOH; reference: C78 | | |

No.	Thermodynamic data on SOH; reference: C78													
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC$_p$ (cal mol^{-1} K^{-1})	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC$_p$ (cal mol^{-1} K^{-1})	h (cal mol^{-1})	s (cal mol^{-1} K^{-1})	Δ'H (cal l mol^{-2})	Δ'S (cal l mol^{-2} K^{-1})	Δ'C$_p$ (cal l mol^{-2} K^{-1})	(cal mol^{-1})
Aldehydes												
32.04	- 5 626	- 15.753	+ 6.0	- 378	- 0.637	+ 3.1	- 361	- 0.909**	- 993	- 2.057	+ 3.2	7.5
32.05	- 6 695	- 16.998	+ 10.1	- 341	- 0.553	+ 0.7**	- 228	- 0.558**	- 751	- 1.439	+ 0.0	5.2
32.06	- 7 732	- 18.258	+ 11.7	- 324	- 0.517	+ 0.7**	- 175	- 0.424**	- 653	- 1.198	+ 0.1	5.0
32.07	- 8 746	- 19.469	+ 14.1	- 304	- 0.495	- 0.5**	- 158	- 0.416**	- 612	- 1.187	- 1.5	3.8
Ethers												
33.06	- 7 070	- 17.803	+ 9.9	- 90	- 0.168	+ 1.2**	- 273	- 0.673**	- 502	- 1.162	+ 1.0	7.7
33.08	- 9 061	- 20.196	+ 13.8	- 41	- 0.077*	+ 0.0**	- 127	- 0.327**	- 236	- 0.566	- 0.3	4.5
Primary amines												
34.04	- 6 421	- 16.798	+ 6.7	- 932	- 1.914	+ 13.3	- 98	- 0.230**	- 1 374	- 2.829	+ 17.7	4.1
34.05	- 7 468	- 18.068	+ 10.0	- 1070	- 2.224	+ 14.0	+ 241	+ 0.539**	- 1 095	- 2.195	+ 19.2	2.0
34.06	- 8 470	- 19.259	+ 13.7	- 1013	- 2.095	+ 10.2	+ 118	+ 0.236**	- 1 195	- 2.452	+ 13.4	0.8
Secondary amines												
35.04	- 6 218	- 17.133	+ 10.4	- 1035	- 2.183	+ 19.1	+ 208	+ 0.544**	- 1 082	- 2.102	+ 26.8	10.2
35.06	- 7 858	- 18.658	+ 18.6	- 664	- 1.443	+ 2.4	- 316	- 0.851**	- 1 362	- 3.183	+ 1.4	5.0
Tertiary amines												
36.06	- 7 049	- 17.539	+ 15.1	- 397	- 0.850	- 2.7	- 466	- 1.142**	- 1 198	- 2.760	- 5.9	3.9
Halomethanes												
37.01	- 5 254	- 15.326	+ 4.1	- 51^s	+ 0.072**	+ 4.0	+ 298	+ 0.706**	+ 383	+ 1.183	+ 6.8	6.8
37.02	- 6 116	- 16.068	+ 7.7	- 150	- 0.190	+ 2.0	+ 129	+ 0.284**	- 2	+ 0.202	+ 3.1	4.5
37.03	- 6 641	- 16.422	+ 5.7	+ 26**	+ 0.035**	+ 3.0	+ 284	+ 0.682**	+ 432	+ 0.998	+ 5.1	7.6
37.04	- 5 078	- 15.274	+ 5.3	+ 24*	+ 0.081	+ 3.7	+ 60	+ 0.127**	+ 122	+ 0.300	+ 5.7	3.1
HALOBENZENES												
38.01	- 6 682	- 16.734	+ 11.6	+ 37	+ 0.193	- 3.5	+ 20	+ 0.031**	+ 93	+ 0.347	- 5.0	2.9
38.02	- 6 464	- 17.769	+ 10.8	- 7**	+ 0.075^s	- 1.2^s	- 130	- 0.320**	- 178	- 0.307	- 2.0	3.2
38.03	- 7 029	- 17.699	+ 10.2	+ 15*	+ 0.150	- 0.5**	+ 70	+ 0.157**	+ 138	+ 0.476	- 0.4	1.9
38.04	- 8 311	- 18.212	+ 11.7	+ 50	+ 0.195	- 2.5	+ 81	+ 0.178**	+ 191	+ 0.544	- 3.4	2.9
38.05	- 9 036	- 18.814	+ 10.2	+ 24^s	+ 0.138	- 0.5**	+ 199	+ 0.480**	+ 327	+ 0.904	- 0.2	3.5
38.06	- 9 504	- 18.533	+ 13.9	- 422	- 0.915	- 4.0	- 995	- 2.340^s	- 1 964	- 4.502	- 9.0	1.8

Table 5. Continued

No.	Compound	n	Temp. range (°C)	Retention index on SOH; reference: C78												σ
				C78		SOH - C78			Mixture		id SOH([OH]=1) - C78				
				I_{130}	$10\times A_T$ (K^{-1})	ΔI_{130}	$10\times \Delta A_T$ (K^{-1})	$100\times \Delta A_{TT}$ (K^{-2})	A_L	$10\times A_{LT}$ (K^{-1})	$\Delta' I_{130}$ ($l\ mol^{-1}$)	$10\times \Delta' A_T$ ($K^{-1} l\ mol^{-1}$)	$100\times \Delta' A_{TT}$ ($K^{-2} l\ mol^{-1}$)		
ALKYLPIRIDINES															
39.01	Pyridine	14	90-210	724.4	+ 3.43	+42.0	- 2.19	+0.13	+ 1.1**	+0.72**	+61.4	- 1.59	+ 0.20		1.73
39.02	2-Picoline	14	90-210	802.3	+ 2.84	+41.2	- 2.24	+0.14	+ 3.1**	+0.57**	+63.2	- 1.87	+ 0.21		1.60
39.03	3-Picoline	16	90-210	844.9	+ 3.49	+46.0	- 2.43	+0.17	+ 0.5**	+0.23**	+66.3	- 2.60	+ 0.24		0.56
39.04	4-Picoline	14	90-210	843.3	+ 3.72	+48.7	- 2.90	+0.20	+ 4.2	- 0.40**	+75.4	- 4.09	+ 0.27		1.15
39.05	2,3-Lutidine	14	90-210	934.3	+ 3.32	+45.0	- 2.47	+0.15	+ 4.9s	+0.51**	+71.0	- 2.22	+ 0.23		1.54
39.06	2,4-Lutidine	16	90-210	918.7	+ 2.89	+48.1	- 2.77	+0.17	+ 4.0	- 0.05**	+74.4	- 3.42	+ 0.24		0.70
39.07	2,5-Lutidine	14	90-210	919.1	+ 2.85	+44.9	- 2.66	+0.22	+ 6.3	+0.31**	+73.0	- 2.75	+ 0.32		1.44
39.08	2,6-Lutidine	14	90-210	872.0	+ 2.63	+34.9	- 2.28	+0.10	+ 3.1**	- 0.47**	+54.1	- 3.48	+ 0.14		1.54
39.09	3,4-Lutidine	14	90-210	986.2	+ 4.89	+54.7	- 3.64	+0.18	+ 2.9**	- 0.64**	+82.1	- 5.44	+ 0.24		1.83
39.10	3,5-Lutidine	16	90-210	963.5	+ 4.22	+52.1	- 3.53	+0.19	+ 3.8	- 1.08	+79.7	- 5.93	+ 0.25		0.62
39.11	2-Ethylpyridine	16	90-210	886.9	+ 3.33	+36.0	- 2.01	+0.11	+ 0.6**	- 0.32**	+52.2	- 2.91	+ 0.14		0.56
39.12	3-Ethylpyridine	12	90-210	938.6	+ 4.18	+45.6	- 2.99	+0.17	- 0.7**	- 0.96s	+64.0	- 5.12	+ 0.23		1.14
39.13	4-Ethylpyridine	14	90-210	941.1	+ 4.33	+49.2	- 3.22	+0.18	+ 1.1**	- 0.19**	+71.6	- 4.29	+ 0.25		0.97
39.14	2-Propylpyridine	14	90-210	976.5	+ 3.26	+34.1	- 1.89	+0.10	- 0.6**	- 0.40*	+47.8	- 2.89	+ 0.13		0.62
39.15	4-Propyl-pyridine	12	90-210	1032.3	+ 3.82	+48.9	- 2.41	+0.17	+ 1.4**	+1.15	+71.7	- 1.21	+ 0.26		0.77
39.16	2,3,6-Collidine	12	90-210	1000.5	+ 2.74	+36.0	- 2.03	+0.12	+ 3.5	- 0.73	+56.3	- 3.49	+ 0.15		0.80
39.17	2,4,6-Collidine	10	130-210	986.6	+ 2.28	+36.9	- 1.10	- 0.02**	+ 1.6**	- 0.43**	+54.9	- 1.75	- 0.03		0.54
39.18	4-tert-Butylpyridine	12	90-210	1067.3	+ 5.19	+51.5	- 3.46	+0.17	+ 6.3	- 1.42	+82.4	- 6.31	+ 0.21		0.65
39.19	3-Chloropyridine	16	90-210	884.5	+ 4.46	+33.6	- 1.12	+0.08	+ 0.6**	+0.08**	+48.6	- 1.09	+ 0.12		0.49
ORGANOSILICON COMPOUNDS															
40.01	Tetramethylsilane	18	90-210	428.1	- 0.46	+ 1.0s	+0.11**	—**	- 2.7**	- 1.11s	- 2.5	- 1.52	—**		1.82
40.02	Hexamethyldisilane	20	90-210	686.1	+ 0.32	+ 2.2	+0.10	—**	+ 0.4**	- 0.05**	+ 3.7	+0.11	—**		0.65
40.03	Hexamethyldisiloxane	18	90-210	597.4	- 2.47	+ 2.3	+0.05**	—**	- 0.2**	- 0.26**	+ 3.1	- 0.28	—**		0.79
MISCELLANEOUS															
41.01	Carbon disulphide	14	110-210	607.3	+ 4.19	+ 3.9	- 0.34	—**	- 2.2	- 0.55	+ 2.2	- 1.30	—**		0.24
41.02	Tetramethyltin	20	90-210	604.5	- 0.01	+ 2.9	+0.20	—**	- 2.0	+0.55	+ 1.4	+1.12	—**		0.70
41.03	Tetrahydrofuran	14	90-210	609.9	+ 2.12	+27.7	- 0.98	—**	+ 1.6**	- 0.70	+41.7	- 2.11	—**		0.74
41.04	1,4-Dioxane	13	110-210	670.1	+ 2.46	+34.2	- 0.92	—**	+ 1.0**	- 0.49	+50.2	- 1.63	—**		0.55
41.05	Thiophene	20	90-210	685.3	+ 2.98	+13.7	+0.54	—**	- 2.4	+1.31	+16.3	+2.91	—**		0.69
41.06	Cyclopentanone	14	90-210	741.1	+ 3.15	+42.7	- 1.37	+0.05	+ 2.0	- 0.50	+63.6	- 2.16	+ 0.08		0.49
41.07	Cyclohexanone	14	90-210	854.1	+ 4.10	+43.6	- 1.02	+0.10	+ 3.1	+0.30	+66.6	- 0.50	+ 0.16		0.32
41.08	Cyclohexanol	14	110-210	851.1	+ 4.17	+47.3	- 3.11	+0.20	+ 0.3**	+0.68	+67.9	- 2.91	+ 0.29		0.60
41.10	Piperidine	15	90-210	762.0	+ 3.00	+49.7	- 4.23	+0.27	- 1.7**	+2.38	+68.4	- 2.07	+ 0.40		1.25
41.11	Nitrobenzene	10	130-210	1049.4	+ 5.63	+37.1	- 0.19	+ —**	- 3.8	+0.77	+47.6	+1.30	+ —**		0.26
41.12	Benzyl alcohol	15	110-210	973.7	+ 4.34	+72.7	- 5.20	+0.35	- 3.5	+2.18	+98.6	- 3.49	+ 0.51		0.73
41.13	2-Phenylethanol	13	90-210	1054.4	+ 4.94	+64.9	- 3.86	+0.23	+ 4.8	- 0.11**	+99.3	- 4.87	+ 0.33		0.79
41.14	Anisole	14	90-210	909.0	+ 3.09	+21.6	- 0.22	+ —**	- 0.4**	- 0.18**	+30.2	- 0.32	+ —**		0.46
41.15	Phenetole	11	90-210	978.5	+ 2.37	+20.0	+0.04**	+ —**	- 1.6**	+0.33**	+26.4	+0.80	+ —**		0.47

No.	Thermodynamic data on SOH; reference: C78											
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC$_p$ (cal mol^{-1} K^{-1})	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	ΔC$_p$ (cal mol^{-1} K^{-1})	h (cal mol^{-1})	s (cal mol^{-1} K^{-1})	Δ'H (cal l mol^{-2})	Δ'S (cal l mol^{-2} K^{-1})	Δ'C$_p$ (cal l mol^{-2} K^{-1})	(cal mol^{-1})
ALKYLPYRIDINES												
39.01	- 7 032	- 16.839	+ 8.9	- 751	- 1.413	+ 6.1	+ 57	+ 0.177**	- 891	- 1.522	+ 8.0	7.9
39.02	- 7 948	- 18.105	+ 11.3	- 739	- 1.415	+ 5.4	- 8**	+ 0.022**	- 971	- 1.757	+ 6.8	7.1
39.03	- 8 242	- 18.314	+ 11.3	- 828	- 1.563	+ 6.6	- 42	- 0.054**	- 1 129	- 2.036	+ 8.3	2.6
39.04	- 8 199	- 18.219	+ 13.5	- 927	- 1.782	+ 5.4	- 251	- 0.558**	- 1 560	- 3.044	+ 5.9	4.6
39.05	- 9 255	- 19.678	+ 13.0	- 746	- 1.401	+ 5.6	+ 105	+ 0.318**	- 812	- 1.298	+ 7.4	6.9
39.06	- 9 182	- 19.679	+ 12.7	- 841	- 1.611	+ 7.0	+ 15	+ 0.063**	- 1 074	- 1.957	+ 9.0	3.1
39.07	- 9 237	- 19.807	+ 13.8	- 742	- 1.409	+ 7.4	+ 95	+ 0.276**	- 826	- 1.382	+ 9.9	6.0
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
39.09	- 9 535	- 19.747	+ 15.8	- 997	- 1.882	+ 4.2	- 55	- 0.068**	- 1 369	- 2.460	+ 4.5	7.8
39.10	- 9 413	- 19.719	+ 14.6	- 979	- 1.876	+ 5.8	- 164	- 0.334**	- 1 502	- 2.840	+ 6.7	2.0
39.11	- 8 770	- 19.065	+ 12.3	- 566	- 1.071	+ 3.5	- 80	- 0.191**	- 850	- 1.632	+ 4.1	2.0
39.12	- 9 136	- 19.324	+ 12.7	- 843	- 1.640	+ 6.2	- 117	- 0.308**	- 1 277	- 2.554	+ 7.5	5.0
39.13	- 9 071	- 19.133	+ 11.1	- 992	- 1.962	+ 8.6	- 56	- 0.124**	- 1 384	- 2.710	+ 10.9	4.6
39.14	- 9 609	- 20.024	+ 11.7	- 607	- 1.200	+ 5.3	- 97	- 0.239**	- 937	- 1.891	+ 6.6	3.0
39.15	- 10 169	- 20.708	+ 15.5	- 743	- 1.364	+ 5.1	+ 290	+ 0.709**	- 553	- 0.710	+ 7.1	3.1
39.16	- 10 063	- 20.842	+ 15.4	- 539	- 1.017	+ 3.0	- 96	- 0.215**	- 835	- 1.587	+ 3.4	3.1
39.17	- 9 982	- 20.818	+ 14.6	- 393	- 0.640	- 1.6**	- 93	- 0.210**	- 626	- 1.049	- 3.1	2.4
39.18	- 10 219	- 20.400	+ 14.7	- 1019	- 2.018	+ 6.3	- 286	- 0.631**	- 1 737	- 3.477	+ 6.9	2.7

No.	Thermodynamic data on SOH; reference: C78											
	C78			SOH - C78			Mixture		id SOH([OH]=1) - C78			σ
	ΔH	ΔS	ΔCp	ΔH	ΔS	ΔCp	h	s	Δ'H	Δ'S	Δ'Cp	
	(cal mol^{-1})	(cal mol^{-1} K^{-1})		(cal mol^{-1})	(cal mol^{-1} K^{-1})		(cal mol^{-1})	(cal mol^{-1} K^{-1})	(cal l mol^{-2})	(cal l mol^{-2} K^{-1})		(cal mol^{-1})
ERROR OF THE COEFFICIENTS (STANDARD DEVIATION)												
	3.4	0.0061	0.10	1.6	0.0042	0.09			4.5	0.0114	0.19	
	4.2	0.0102	0.49	16.5	0.0397	0.42			4.5	0.0114	0.19	
	6.3	0.0154	0.44	5.2	0.0130	0.22	2.3	0.6646	4.5	0.0114	0.19	
	18.3	0.0486	0.49	21.8	0.0525	0.53	2.9	0.7132	4.5	0.0114	0.19	
CONVERSIONS												
A	+555.5	+7.8161	+0.65	-2.2	+0.0072	-0.18	-1.4	0.0032	-2.9	0.0109	-0.26	
B	0	-0.0262	0	0	0	0	0	0	0	0	0	

4.2. Solution data of solutes other than n-alkanes

4.2.1. Retention indices

Retention indices of a given molecular probe were determined at temperature intervals of 20 K in the temperature range indicated in Table 5 on pure SOH ($\varphi_{SOH}=1$) and a C_{78}–SOH (1:1) mixture ($\varphi_{SOH}=0.5$). Retention data of the same solutes for the pure stationary phase C_{78} from Refs. [1] and [5] permitted calculation of the coefficients in Eqs. (13) and (14) by linear regression. If the quadratic term ΔA_{TT} was not significant even at the 20% significance level, a second regression was performed without the quadratic term. The fitted coefficients are presented in columns 7–11 of Table 5. The regression coefficients of Eqs. (13) and (14), the molar volume of SOH and the value of κ (evaluated using Eqs. (21) and (24)) at 10 K intervals were used in Eq. (15) to calculate the values $\Delta' I^{\mathrm{idSOH}}$ at every nominal temperature in the experimental domain. Quadratic regression of $\Delta' I^{\mathrm{idSOH}}$ values with temperature resulted in the coefficients $\Delta' I_{130}$, $\Delta' A_T$ and $\Delta' A_{TT}$ given in Table 5.

4.2.2. Thermodynamic data

For a given solute, j, experimental retention indices were converted one by one to standard chemical potentials by using Eq. (10) and thermodynamic data for n-alkanes calculated with coefficients listed in Table 5. The resulting gSPOTs, $\Delta\mu_j^{C_{78}-\mathrm{SOH}}$, were analyzed by multiple regression using Eqs. (5)–(7). Coefficients of Eqs. (5b) and (7) are given in columns 17–21 of Table 5. Finally, aSPOT values for the C_{78}–SOH system, $\Delta' \mu_j^{\mathrm{idSOH}}$, were calculated for each solute by following the same procedure as described for n-alkanes, using Eq. (9). Regression of $\Delta' \mu_j^{\mathrm{idSOH}}$ as a function of T gave the coefficients $\Delta' H_j^{\mathrm{idSOH}}$, $\Delta' S_j^{\mathrm{idSOH}}$ and $\Delta' C_{\mathrm{p},j}^{\mathrm{idSOH}}$, presented in columns 25–27 of Table 5.

4.2.3. Interconversion of thermodynamic data referring to different reference states

The relationship between standard chemical potentials related to the molal Henry coefficient, $\Delta\mu_j^{\mathrm{L}}$, and those related to the distribution coefficient, $\Delta\mu_j^{(\mathrm{D})\mathrm{L}}$, is given by:

$$\Delta\mu_j^{\mathrm{L}} - \Delta\mu_j^{(\mathrm{D})\mathrm{L}} = RT \ln\left[\Re T\rho_{\mathrm{L}}/(\mathrm{atm\ kg\ mol^{-1}})\right] \tag{25}$$

where ρ_{L} is the density of the stationary liquid. A data set, $\Delta\mu_j^{\mathrm{L}} - \Delta\mu_j^{(\mathrm{D})\mathrm{L}}$, was generated at 10 K intervals in the temperature range 90–120°C for the three solvents of the C_{78}–SOH system ($\varphi_{\mathrm{SOH}} = 0$, 0.5 and 1). Densities at 10 K intervals for pure solvents were calculated using Eq. (16) with coefficients given in Table 2. For density estimation of mixed solvents the ideal mixing rule for molar volume was applied. By fitting Eqs. (5)–(7) to the resulting density data set, the necessary corrections were obtained for the thermodynamic parameters, which are listed at the end of Table 5.

5. Discussion

In the family of our isomorphous, isochor stationary phases the stronger retention of a molecular probe on a polar solvent as compared with that on the standard alkane is a measure of the additional interaction of the PIG with an adhering zone of the probe. (The corresponding aSPOTs are designated by $\Delta\mu$). This is also true in the case of data obtained on the stationary phase with the standard alkane substituted by a secondary hydroxyl, SOH, and the isomorphous, isochor stationary phase POH with primary hydroxyl as substituent. The weaker additional interaction energy between a molecular probe on SOH (secondary hydroxyl) as compared with those on POH (primary hydroxyl) is certainly due to steric hindrance. On both stationary phases we dispose of data on the pure stationary phases, which may be considered as a 0.7 *M* solution of the hydroxyls as well as on a 1 *M* "ideal" stationary phase. The interacting groups of the hypothetical, ideal phase are in an ideal dilute state, i.e., they interact with the molecular probe but not with each other. (The corresponding aSPOTs are designated by $\Delta\mu'$).

Retention (partition) data may also be given by interpolation between fixed points which are marked by the gSPOTs of the *n*-alkanes, i.e., as retention indices. The main advantage of the retention index is a small temperature dependence contrary to that of SPOT data. Furthermore, the gSPOTs of the *n*-alkanes are slightly different in the isomorphous, isochor stationary phases due to differences in dispersion interaction forces between the interacting group and the *n*-alkane and due to the structure of the stationary phase by the presence of the polar interacting groups. A datum expressed as retention index will also be corrected for such differences. Because of these advantages retention data will be discussed in the following in terms of retention indices. The difference between the retention index on a polar stationary phase and the standard alkane will be designated as the ΔI value, $\Delta I_j^{\mathrm{P}} = I_j^{\mathrm{P}} - I_j^{\mathrm{C}_{78}}$, of the solute in question. The difference between the retention index of the solute, *j*, on a hypothetical stationary phase with ideal dilute polar interacting groups, I_j^{idP} and the standard alkane will be designated as the $\Delta I'$ value, $\Delta I_j^{\mathrm{idP}} = I_j^{\mathrm{idP}} - I_j^{\mathrm{C}_{78}}$, of the solute. Let us recall, that the calculation of the $\Delta I'$ value implies knowledge of the retention index on at least two stationary phase mixtures, e.g., on pure P and on an A–P (1:1) mixture. Consequently, the double amount of experimental effort must be invested for the determination of $\Delta I'$ values as compared with the determination of ΔI values.

Our project aims at the prediction of partition data of molecular probes in any solvent based on data published in Parts I–VI and in the present Part VII. Therefore, we put forward the question, whether the

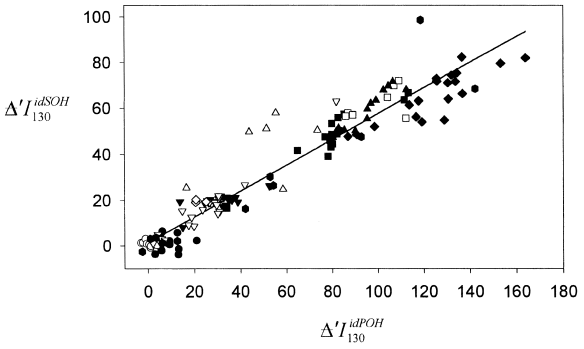

Fig. 6. $\Delta I'$ values at 130°C on the ideal dilute SOH stationary phase as a function of the analogous data on the ideal dilute POH. Data points: ○: isoalkanes; ●: cycloalkanes; ▽: alkenes, alkynes, aromatics; ▼: haloalkanes, halobenzenes; □: 1-cyano- and nitro-alkanes; ■: 1-acetoxy-alkanes, aldehydes, 2-alkanones, ethers, 1,4-dioxane, THF, cyclopentanone, cyclohexanone; △: amines; ▲: 1-alkanols, 2-alkanols, 2-Me-2-alkanols, cyclohexanol; ✦: pyridines; ◇: others. The solid line is the trace of the correlation function given in Eq. (26).

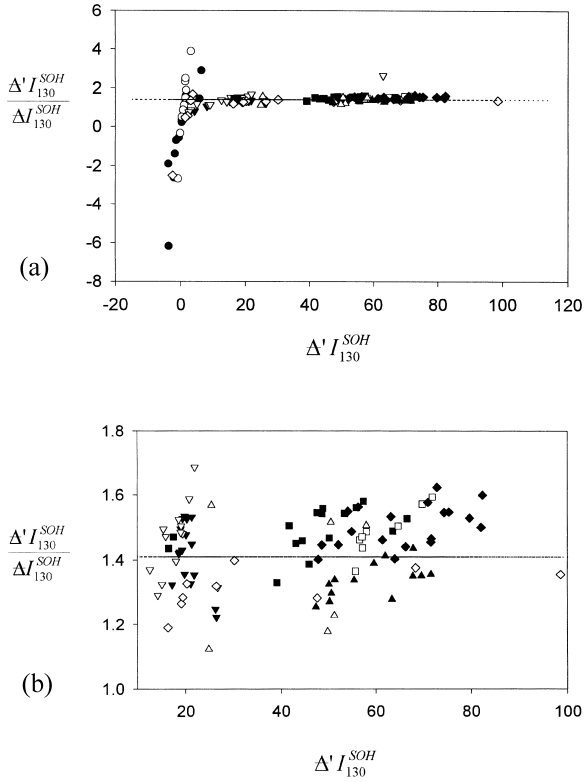

Fig. 7. (a) Ratio of the additional retention of solutes at 130°C on the ideal dilute and on pure SOH stationary phase expressed on the retention index scale as the ratio $\Delta' I_j/\Delta I_j$ as a function of the additional retention on the ideal dilute phase: $\Delta' I_j$. Symbols as in Fig. 5. The dotted line is the trace of the ratio of the concentration of the interacting group, SOH, in the ideal phase ([PIG]=1) and the melt of SOH (1.42=1/0.72). (b) Part of (a) without the outlier data point of azulene (enlarged).

data set determined on the stationary phase SOH gives new information or not. New information would mean that data on SOH have no correlation with formerly published data sets. As there must be a correlation with data on the stationary phase with primary alcohols, POH we hope that this correlation is not perfect. The second question is of economic nature. In fact, we hope that the use of ''ideal'' data is not necessary because of the additional work. Hence, we hope that there is a possibility permitting calculation of $\Delta' I$ values based on ΔI values determined on the pure stationary phase, SOH or on the 1:1 mixture. Obviously, a diluted phase is closer to the ideal dilute state but the additional retention on such a phase, i.e., the ΔI value is smaller, hence the error compared to the effect is higher.

Fig. 6 plots $\Delta' I$ values in the ideal dilute SOH stationary phase as a function of those measured on the POH phase at 130°C. There is a highly significant linear dependence between the data for the solutes ($n=139$) where data were available for both stationary phases. The linear correlation function is given in Eq. (26):

$$\Delta' I_{130}^{\mathrm{idSOH}} = 1.59(\pm 0.97) + 0.562(\pm 0.014)\Delta' I_{130}^{\mathrm{idPOH}} \quad (26)$$

The correlation coefficient is $r=0.962$. The constant in Eq. (26) is not significantly different from zero. The value of the slope differs significantly from unity ($0.562<1.0$) at a confidence limit $<<0.01\%$, indicating that the general effect of steric hindrance on retention data measured on SOH is highly significant. The specific information on steric hindrance of a given solute is obviously the deviation from the general trend. The standard deviation of $\sigma=\pm 7.2$ index units around the correlation is significantly higher than the experimental error of $\sigma \approx \pm 2$). Hence such a deviation may be interpreted as solute-specific information.

Fig. 7 plots ratios of the $\Delta' I$ value on the ideal SOH phase and the ΔI value of the molecular probe on the pure stationary phase SOH: $\Delta' I_{130}^{\mathrm{idSOH}}/\Delta I_{130}^{\mathrm{SOH}}$ as a function of the $\Delta' I$ values at 130°C. If the ''solution'' of the secondary hydroxyls in the stationary phase was ideal this ratio should be equal to the ratio of the SOH concentrations in the two phases, i.e., 1/[SOH]. The hydroxyl concentration in the pure SOH melt is $1000/v_{\mathrm{SOH}}$ mol l^{-1}. Using the value listed in Table 2 for the molar volume of SOH at 130°C, v_{SOH}, the value of the ratio is 1.4138 indicated in Fig. 7 as a dotted line. In the plot of Fig.

Table 6
Increments for the calculation of $\Delta' I$ values of alcohols on the stationary phases idSOH and idPOH

Methanol–methanol (basic value)	+176
Substituents:	
Methyl (C_1)	−9
C_2	−15
$<C_2$	−36

7 large deviations from this value are observed in the domain of $-5 < \Delta' I_{130}^{\mathrm{idSOH}} < +5$, i.e., in the domain where the $\Delta' I$ values and the experimental error are of the same order of magnitude. For other solutes the behavior of the pure stationary phase may be considered as a nearly ideal dilute solution of SOH groups.

On the basis of this discussion, the information content of the SOH data set may be useful for the prediction of partition data. This will be the subject of our last report.

It is now interesting to consider a special group of molecular probes, the alcohols. The ''adhering zone'' of this group of solutes is the same as the ''polar interacting group'' of the two stationary phases, POH and SOH. Some decades ago it has been proposed [10] that the ΔI value of an ''adhering zone'' can be calculated as a sum of a basic value of a sterically unhindered compound and negative increments for substituents of the basic compound. Unfortunately, in our data base $\Delta' I$ values of small alcohols such as methanol, ethanol, etc., are missing (too short retention in the experimental temperature domain). Nevertheless, it is interesting to note that the increments listed in Table 6 permit calculation of the $\Delta' I$ values of the alcohols on both stationary phases POH and SOH. Following Table 6 the solute methanol in a hypothetical stationary phase which a 1 *M* solution of nonvolatile methanol (as polar interacting group) would have a $\Delta' I$ value of $+176$. For C_3 and higher primary alcohols we calculate in POH a ΔI value of $+176-36-36=+104$. (exp. 99–105); and in SOH a ΔI value of $+176-36-36-36=+68$ (exp. 64–72). In the case of cyclohexanol it was proposed in Ref. [10] to consider the steric hindrance of the secondary alcohol to be similar to that of ''dimethylmethanol'' (i.e., 2-propanol) with a ΔI value on POH equal to $+176-36-9-9=+128$ in addition to the effect of the ''cyclohexane adhering zone'' to give $128+6=132$ (exp. 113). The same compound on SOH is $132-36=96$ (exp. 68). The system of increment additivity does not work for the interaction between highly substituted species: the ΔI value of two tertiary alcohols with long alkyl substituents would be $+176-(6\times 36)=-40$.

An interesting group of molecular probes is that of the pyridines. These compounds have been included as molecular probes as an example of Brønsted proton acceptors, which are at the same time hydrogen bond acceptors. No correlation was observed if ΔI values of pyridine derivatives were plotted as a function of the pK_a of the conjugate acid. In addition, we could not propose an increment system for the calculation of the individual data. In fact, alkyl substitution has certainly a serious effect on the polarity of the ring besides a steric effect. As an example, the ''steric hindrance'' of the nitrogen by α-methyl groups as shown by the ΔI values on SOH is contrary to expectation: pyridine: $+61$; α-methylpyridine: $+63$; α,α-dimethylpyridine: $+73$.

6. Nomenclature

Stationary phases (solvents)	
L	Any stationary liquid member of the isomorphous, isochor family or a mixture of them
$A \equiv C_{78}$	The reference alkane 19,24-dioctadecyldotetracontane, $C_{78}H_{158}$
P	A polar member of the family
A–P	Mixture of A and P
SOH and POH	P having secondary and primary interacting groups
Superscripts meaning ''in''	
L, A, P, A–P, SOH, POH, idPIG	The last symbol: ideal dilute solution of polar interacting groups
Subscripts meaning ''of''	
L, A, P, A–P, SOH, POH	Further of the solute *j* and of the *n*-alkane solute *z*
Acronyms	
SPOT	Standard chemical potential difference of *j* between the ideal dilute solution and a second reference state
gSPOT	Second reference is the ideal gas state at 1 atm
aSPOT	Second reference is the ideal dilute solution of *j* in A
idSPOT	First reference is the ideal dilute solution of *j* in a 1 *M* ideal solution of PIG, second reference the ideal dilute solution of *j* in A

PIG	The polar interacting group of L
idPIG	The polar interacting group of L at ideal dilution
Symbols (dimension)	
A (div.)	Coefficients in Eqs. (12)–(14)
α (K^{-1})	Isobaric coefficient of thermal expansion
$B=(1/2)$ ($d\alpha/dT$) (K^{-2})	Temperature coefficient of thermal expansion, α
ΔC_p (cal mol^{-1} K^{-1})	Partial molar heat capacity difference
δ	Difference between the property of two substances in the same solvent
Δ_{95} (div.)	Confidence limit at the 95% confidence interval
f (–)	Factor to give the standard deviation of a coefficient by multiplication of the standard deviation around the regression
F	Fischer's F
φ (–)	Volume fraction
Φ	Degrees of freedom
g (atm kg mol^{-1})	Molal Henry coefficient
h (cal mol^{-1})	Enthalpic coefficient in Eq. (7)
ΔH (cal mol^{-1})	Partial molar enthalpy difference at $T^{\dagger}$
i (–)	Coefficient in Eq. (14)
I (–)	Retention index
K_D (–)	Distribution coefficient
κ (–)	Coefficient in Eq. (15)
L	"Factor" in the variance analysis of Table 4 referring to the composition of the stationary phase
m	Coefficient in Eq. (7)
M (mol l^{-1})	Molar concentration
M (g mol^{-1})	Molar mass
$\Delta\mu$, $\Delta\!\!\!-\mu$ (cal mol^{-1}) and $\Delta\!\!\!-'\mu$ (cal mol^{-2})	Standard chemical potential differences, gSPOT, aSPOT and idSPOT
[PIG] (mol l^{-1})	Molar concentration of the polar interactive group in the liquid
R (cal mol^{-1} K^{-1}) or $\mathfrak{R}$ (cm^3 atm mol^{-1})	The universal gas constant
ρ (g cm^{-3})	Density
s (cal mol^{-1} K^{-1})	Entropic coefficient in Eq. (7)
ΔS (cal mol^{-1} K^{-1})	Partial molar entropy difference
σ (div.)	Standard deviation
T and $T^{\dagger}$ (K)	Temperature and standard temperature
T	"Factor" in the variance analysis of Table 4 referring to the temperature
v (cm^3 g^{-1})	Specific volume
V_g (cm^3 g^{-1})	Specific retention volume
w (g)	Mass of the stationary phase
z (–)	Carbon number of the n-alkane C_zH_{2z+2}
Z	"Factor" in the variance analysis of Table 4 referring to the effect of z.

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