

Pair-wise interactions by gas chromatography

V. Interaction free enthalpies of solutes with primary chloro- and bromoalkanes[☆]

G. Défayes^a, K.S. Reddy^a, A. Dallos^b, E.sz. Kováts^{a,*}

^aLaboratoire de Chimie Technique, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

^bDepartment of Physical Chemistry, University of Veszprém, H-8201 Veszprém, Hungary

First received 5 December 1994; revised manuscript received 22 December 1994; accepted 5 January 1995

Abstract

Gas chromatographic data of ca. 140 molecular probes were measured on primary chloro and bromo derivatives of a C₇₈ branched alkane (C₇₈H₁₅₈) as stationary phases. Interaction free enthalpies between solutes and the dipolar chloroalkyl and bromoalkyl groups were nearly the same. Slight differences may be explained by the higher polarizability of the bromo substituent.

1. Introduction

The objective of our project, described in detail in Part I [1], is the determination of interaction free enthalpies between solutes at infinite dilution and an interacting group also at infinite dilution. The measuring system consists of a family of isosteric solvents shown in Fig. 1. Use of these solvents as stationary phases permits the easy determination of the gas chromatographic data of molecular probes and the derivation of the desired standard chemical potentials characterizing the interaction free enthalpies.

In this paper we report the interaction free enthalpies of a series of solutes with a primary chloroalkyl and bromoalkyl group, PCL and PBR, by using stationary phases with X = Cl and

Br. Data on these phases are of theoretical interest, as both interacting groups have about the same dipole moment ($\mu \approx 2.1$ D [2]) but not the same polarizability. Therefore, it was hoped that comparison of retention data in these solvents would teach us about the effect of the

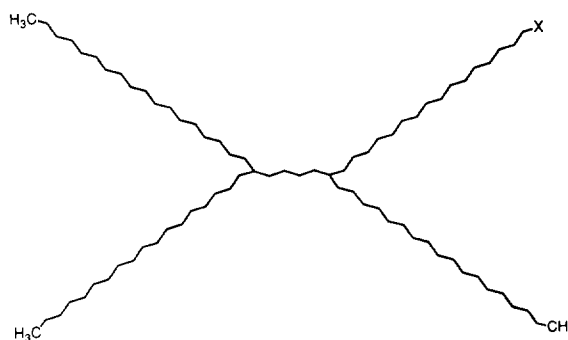


Fig. 1. Structure of the stationary phases: C₇₈, X = CH₂CH₃; PCL (primary chloro), X = CH₂Cl; PBR (primary bromo), X = CH₂Br.

* Corresponding author.

[☆] For Part IV, see Ref. [3]. Partly taken from the doctoral thesis of G.D., EPFL, No. 1212 (1994).

higher polarizability of the bromo substituent. Further information was sought from the comparison of these data with those obtained on a polar stationary phase, MTF (monotrifluoromethyl), where $X = CF_3$ [3]. The size of the trifluoromethyl group (diameter, $d \approx 4.1 \text{ \AA}$) is slightly larger than that of the chloro substituent ($d \approx 3.3 \text{ \AA}$) but its dipole moment is of the same order of magnitude [$\mu(CH_2CF_3) \approx 2.3 \text{ D}$]. Differences in the interaction energies in these two solvents should also be due to differences of polarizability.

2. Theoretical

The theory was given in detail in Ref. [1]. In the following is given a summary of the equations necessary for the understanding of the evaluation of data. First the molal Henry coefficient, g_j^L , is calculated from the specific retention volume, $V_{g,j}^L$, of solute j on the stationary liquid, $L = A, P$ or $A-P$ (mixture of A and P), by using

$$g_j^L = \frac{\mathcal{R}T}{1000V_{g,j}^L} \quad (1)$$

The related standard chemical potential difference between the ideal dilute solution of j in L and the vapour of j as ideal gas, $\Delta\mu_j^L$, is given by

$$\Delta\mu_j^L = RT \ln[g_j^L / (\text{atm kg mol}^{-1})] \quad (2)$$

where \mathcal{R} ($\text{cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$) or R ($\text{cal mol}^{-1} \text{ K}^{-1}$) is the universal gas constant. By supposing that the partial molar heat capacity, $\Delta C_{p,j}^L$, is constant in the experimental temperature domain (Kirchoff's approximation), the temperature dependence of the standard chemical potential can be described with adequate precision by

$$\Delta\mu_j^L = \Delta H_j^L - T \Delta S_j^L + \Delta C_{p,j}^L \left[T - T^+ - T \ln\left(\frac{T}{T^+}\right) \right] \quad (3)$$

where ΔH_j^L and ΔS_j^L are the partial molar

enthalpy and entropy difference, respectively, at the standard temperature T^+ . If the two stationary phases, $A = C_{78}$ and $P = \text{PCL}$, form a regular mixture, then the standard chemical potential of solute j in an $A-P$ system as a function of the volume fraction, φ , can be given by

$$\Delta\mu_j^{A-P} = \Delta\mu_j^A + \varphi_P \Delta\mu_j^P + \varphi_A \varphi_P m_j^{A-P} \quad (4)$$

where $\Delta\mu_j^P = \Delta\mu_j^P - \Delta\mu_j^A$ and $m_j^{A-P} = h - Ts$. In the absence of molar volume differences in the $A-P$ mixture (isosteric solvents), the factor m_j^{A-P} accounts for the effect of non-ideality of the $A-P$ mixture on the standard chemical potential of the solute. Its value as a function of temperature can be given as a combination of enthalpic, h , and entropic, s , contributions. Partial derivation of Eq. 4 with respect to concentration of the interacting group, X , gives Eq. 5, the necessary relationship for the calculation of the interaction free enthalpy of a solute at infinite dilution with an alone standing interacting polar group X in the $A-P$ mixture also at infinite dilution.

$$\begin{aligned} \Delta'\mu_j^{\text{idX}} &\equiv \left(\frac{\partial \Delta\mu_j^{A-P}}{\partial [X]} \right)_{T, [X]=0} \\ &= (\Delta\mu_j^P + m_j^{A-P}) v_p / 1000 \end{aligned} \quad (5)$$

where v_p ($\text{cm}^3 \text{ mol}^{-1}$) is the molar volume of P . Chromatographic data for 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 standard chemical potential on a scale given by the standard chemical potentials of the n -alkanes:

$$\begin{aligned} I_j^L &= 100 \cdot \frac{\Delta\mu_j^L - \Delta\mu_z^L}{\Delta\mu_{z+1}^L - \Delta\mu_z^L} + 100z \\ &= 100 \cdot \frac{\delta\mu_{j/z}^L}{\delta\mu_z^L} + 100z \end{aligned} \quad (6)$$

where δ designates the standard chemical potential difference between two substances in the same solvent. Retention indices, I_j^L , can be given in the $A-P$ mixture as a function of composition and temperature by the following approximation:

$$I_j^{A-P} = I_j^A + \varphi_P \Delta I_j^P + \varphi_A \varphi_P i_j^{A-P} \quad (7)$$

where

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

$$\Delta I_j^P = I_j^P - I_j^A$$

$$= \Delta I_{130,j} + \Delta A_{T,j} \Delta T + \Delta A_{TT,j} \Delta T^2$$

$$i_j^{A-P} = A_{L,j} + A_{LT,j} \Delta T$$

The symbol A is for a regression coefficient defined by its subscript and the other symbols are as before. Using Eq. 7, the retention index difference at infinite dilution of the interacting group, X , and of the solute j in A–P mixtures is given at the reference temperature by

$$\Delta' I_j^{\text{idX}} = (\Delta I_j^P + i_j^{A-P}) \frac{v_p[X]}{1000(1 + [X]\kappa)} \quad (8)$$

where $\kappa = (\delta' \mu_z^{\text{idX}} - \delta' \mu_z^A) / \delta \mu_z^A$ and $\delta' \mu_z^A$ and $\delta' \mu_z^{\text{idX}}$ is for the value of the slope of the function $\delta \mu_z^{\text{idX}}([X])$ at $[X] = 0$ and 1 mol l^{-1} , respectively. In the case of C_{78} –PCL mixtures, the value of κ is of the order of -0.02 l mol^{-1} and consequently the value of the correcting factor in Eq. 8 is of the order of 1.02.

3. Experimental

3.1. Materials

The stationary liquids, 19,24-dioctadecyldotetracontane ($C_{78} \equiv A$), 1-chloro-18,23-diocta-

decylhentetracontane (PCL) and 1-bromo-18,23-diotadecylhentetracontane (PBR), were synthesized in our laboratory [4,5]. The densities of the stationary liquids and the coefficients of Eq. 9 from Ref. [4] are given in Table 1, together with the temperature range of measurement:

$$\ln \rho_L = \ln M_L - \ln v_L = \ln \rho^\dagger - \alpha^\dagger \Delta T - B \Delta T^2 \quad (9)$$

where ρ^\dagger is the density and α^\dagger is the isobaric coefficient of thermal expansion at the standard temperature $T^\dagger = 403.15 \text{ K}$ and $B = (1/2)(d\alpha/dT)$. The ratio of the molar volume of the solvents PCL and PBR with reference to C_{78} is shown in Fig. 2 in Ref. [4]. All solutes were research-grade compounds from Fluka (Buchs, Switzerland). A batch of the same support, Chromosorb G HP from Supelco (Bellefonte, PA, USA), was used as for the measurements in Refs. [1] and [3]. Additional deactivation of the support by methylsilylation and the preparation of the columns were carried out as described in Ref. [1]. Three columns were prepared with pure PCL, one column with pure C_{78} and two columns with a 50:50 (v/v) mixture of C_{78} and PCL. The column characteristics are listed in Table 2.

3.2. Apparatus

The gas chromatograph was described in detail in Ref. [1]. Briefly, a Model 439 gas chromatograph from Packard-Becker (Delft, Netherlands)

Table 1
Physical properties of the stationary phases

L		Temperature range (°C)	M.p. (°C)	M (g mol ⁻¹)	ρ^\dagger (g cm ⁻³)	v^\dagger (cm ³ mol ⁻¹)	$\alpha^\dagger \cdot 10^4$ (K ⁻¹)	$B \cdot 10^7$ (K ⁻²)	σ (g cm ⁻³)
Symbol	Formula	(°C)							
C_{78}	$C_{78}H_{158}$	80–200	69–75	1096.1	0.7714	1420.9	7.62	1.26	0.0004
PCL	$C_{77}H_{155}Cl$	80–180	72–75	1116.6	0.7895	1414.2	7.60	1.26	0.0002
PBR	$C_{77}H_{155}Br$	80–170	73–76	1161.0	0.8180	1419.3	7.77	0.85	0.0004
Δ_{95}					± 0.00009	± 0.17	± 0.34	± 0.93	

M = molar mass; the symbols ρ^\dagger , α^\dagger and B are regression coefficients of Eq. 9 for the calculation of the density in the temperature range 80–210°C; v^\dagger is for the molar volume at the standard temperature $T^\dagger = 403.15 \text{ K}$. Data for PCL and PBR are from Ref. [4] those for C_{78} are from Ref. [6].

Table 2
Characteristics of the chromatographic columns

Column	Series	100 ϕ_p^+ (%)	w_L (g)	P_L (%)
C ₇₈			2.236	6.77
PBR			2.197	6.77
PCL	(a)		2.138	6.34
	(b)		2.167	6.37
	(c)		1.941	6.03
C ₇₈ -PCL	(a)	50.0	1.836	6.29
	(b)	50.0	1.751	6.29

ϕ_p^+ = Volume fraction of the polar solvent in the A-P mixture at 130°C; w_L = mass of the stationary liquid in the column and P_L = mass percentage of L in the packing (100 w_L /total mass).

was used, equipped with thermal conductivity detectors, a calibrated Pt sensor (100 Ω ; DIN 43710) with temperature-measuring device from Systemteknik (Lidingöe, Sweden) (Model S1220), a chromel-alumel thermocouple set to measure temperature gradient in the oven, a Model 5850 TR helium flow controller from Brooks (Veenendaal, Netherlands) and a Model 710B inlet pressure-measuring device from Heise (Bassweiler, Germany). Retention times are determined at the peak maximum with a Model 3396 A integrator from Hewlett-Packard (Palo Alto, CA, USA). In Ref. [1] are given details of the determination of absolute retention data under isothermal conditions.

3.3. Retention data

The mean experimental oven temperature, corrected for the temperature gradient in the oven, did not differ by more than 0.2 K from the desired nominal temperature. Retention data for *n*-alkanes determined at T_{exp} were corrected to data at T_{nom} as follows. On the PCL and C₇₈-PCL columns, retention volumes were measured every 15 K between 85 and 160°C and between 130 and 160°C for higher *n*-alkanes. After having measured all data on a given column, specific retention volumes were calculated from the neon retention as the starting point, then data were converted into standard chemical potentials by

using Eq. 2. Standard chemical potentials of a given alkane near a given nominal temperature were averaged to give an average data point at the average temperature, \bar{T}_{exp} . The temperature dependences of the averaged chemical potentials were obtained by fitting a quadratic polynomial to the data points. The first derivative of this function was then used to correct chemical potentials measured at \bar{T}_{exp} to T_{nom} . For details, see Ref. [1].

For all other solutes, only retention indices were determined and corrected for deviations from the nominal temperatures by an analogous iterative procedure. All successive calculations are based on these corrected data. They will be referred to as "experimental retention data". Retention data on PBR were measured at the standard temperature, $T^\dagger = 130^\circ\text{C}$ only. The difference between the experimental temperature and the nominal temperature, here $T_{nom} = T^\dagger$, never exceeded 0.1 K. Retention data at T_{exp} were corrected to T_{nom} using the results on the liquid PCL, the chromatographic behaviour of the two phases being very similar. Data on C₇₈ had to be corrected for the adsorption activity of the solid support used in this project, which was slightly different from that used earlier [1]. Therefore, retention indices were measured at 130°C on a C₇₈ column prepared with the actual support. These data were used for $I_{130}^{C_{78}}$ instead of those published in Ref. [1]. These same indices were converted into standard chemical potentials at 130°C with the aid of *n*-alkane data and used to correct partial molar enthalpies (see below). Corrected data are listed in Table 5. Corrections for weighing errors on PCL and C₇₈-PCL columns were made by using *n*-alkane data measured at 85, 115 and 130°C only, by assuming that specific retention volume differences on the two series of columns were due to weighing errors. With the aid of specific retention volumes, the factor $f = V_g^{(b)}/V_g^{(a)}$ was determined, which was assumed to be equal to the ratio of the mass of liquid in the columns, $f = w_L^{(a)}/w_L^{(b)}$. Differences between standard chemical potentials on the two columns are given by

$$RT \ln f = \Delta\mu_z^{(a)} - \Delta\mu_z^{(b)} \quad (10)$$

Table 3

Average ratio of specific retention volumes on columns of series (a) and (b), $f = V_g^{(b)}/V_g^{(a)}$, and the corresponding corrections to add to standard chemical potentials determined on columns of series (a)

<i>L</i>	<i>f</i>	0.5RT ln <i>f</i> (cal mol ⁻¹)					
		85°C	100°C	115°C	130°C	145°C	160°C
C ₇₈ -PCL	0.964	-12.9	-13.5	-14.1	-14.6	-15.1	-15.7
PCL	0.993	-2.4	-2.6	-2.7	-2.8	-2.9	-3.0

Table 4

Analysis of variance of the set of 108 standard chemical potentials of the *n*-alkane solutes with 5 ≤ *Z* ≤ 10 in the temperature range 85–160°C at three compositions of the C₇₈-PCL mixture

Source		<i>SQ</i>	Φ	<i>V'</i>	<i>F</i>	Sign. (%)	$b_X^{(i)}$	Function
<i>X</i>	(<i>i</i>)							
$\Delta\bar{\mu}$	(0)						34.2	$\Delta\mu_0^{+,A}$
<i>T</i>	(1)	0.3	1	id	0.01	–	0.03	ΔS_0^A
	(2)	23.8	1	id	0.46	–	-0.188	$\Delta C_{P,0}^A$
	(res. <i>T</i> [*])	289.1	3	96.4	1.86	20)		
<i>L</i>	(1)	69 440.2	1	id	$1.34 \cdot 10^3$	0.01	31.056	$\Delta\mu_0^{+,P}$
	(2)	2160.9	1	id	$4.16 \cdot 10^1$	0.1	-9.489	$m_0^{+,A-P}$
<i>TL</i>	(1,1)	35.1	1	id	0.68	–	-0.409	ΔS_0^P
	(1,2)	121.3	1	id	2.34	20	-1.316	s_0^{A-P}
	(2,1)	5.2	1	id	0.10	–	-0.108	$\Delta C_{P,0}^P$
	(res. <i>TL</i> [*])	229.7	7	32.8	0.63	–)		
1st res. ^a	(=Σ <i>X</i> [*])	518.9	10	51.9				
<i>Z</i>	(1)	4 950.8	1	id	$4.51 \cdot 10^2$	0.01	3.9	$\delta\mu_z^{+,A}$
	(2)	808.1	1	id	$7.35 \cdot 10^1$	0.01	-1.097	
	(3)	463.6	1	id	$4.22 \cdot 10^1$	0.1	0.630	
	(res. <i>Z</i> ^{**})	113.2	2	56.6	8.00	1)		
<i>TZ</i>	(1,1)	14.2	1	id	1.29	–	-0.124	δS_z^A
	(2,1)	5.7	1	id	0.51	–	-0.054	$\delta C_{P,z}^A$
	(res. <i>TZ</i> ^{**})	35.7	23	1.6	0.14	–)		
<i>LZ</i>	(1,1)	1 922.5	1	id	$1.75 \cdot 10^2$	0.01	3.026	$\delta\mu_z^{+,P}$
	(2,1)	554.6	1	id	$5.05 \cdot 10^1$	0.01	-2.816	$\delta m_z^{+,A-P}$
	(res. <i>LZ</i> ^{**})	695.5	8	86.9	7.91	1)		
<i>TLZ</i>	(1,1,1)	3.7	1	id	0.34	–	-0.078	δS_z^P
	(2,1,1)	3.0	1	id	0.27	–	-0.048	$\delta C_{P,z}^P$
	(1,2,1)	3.9	1	id	0.35	–	0.138	δs_z^{A-P}
	(res. <i>TLZ</i> ^{**})	34.8	47	0.7	0.10	–)		
2nd res. ^b	(=Σ <i>X</i> ^{**})	879.1	80	10.9				

The source of variance is related to orthogonal terms in Eq. 11. $X^{(i)}$ is the systematic polynomial variation of $\Delta\mu^{A-P}$ on the effects *T* (temperature), *L* (composition of the liquid stationary phase, 100φ_{PCL} = 0.0, 50.0 and 100.0%) and *Z* (carbon number of the solute). The subscripts in parentheses refer to the degree of the orthogonal polynomial: (1) linear; (2) quadratic; (3) cubic. *SQ* is the sum of squares, Φ is the number of degrees of freedom and $V' = V(\text{res.}) + \nu_X V(x)$ is the combined variance to be analysed 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) [7]. The coefficients $b_X^{(i)}$ in Eq. 11 are also listed along with the corresponding thermodynamic coefficients. The meanings of the symbols of thermodynamic functions are described in the text. Abbreviations: "res." = residual variance; "sign." = significance level; "id." means that $V' = SQ/\Phi$ is equal to the corresponding *SQ* ($\Phi = 1$).

^a Sum of the residuals marked by one asterisk.

^b Sum of the residuals marked by two asterisks.

Table 5

Retention indices and thermodynamic data for 140 solutes on pure C₇₈ and in C₇₈-PCL mixtures where data derived for idPCL are also given.

Index and chemical potential differences between PBR and C₇₈ are for 130°C. The symbol *n* is for the number of data points used for regression where points for pure C₇₈ were generated using the experimental data determined on the support used in this project at the reference temperature $T^* = 130 + 273.15$ K and the temperature coefficients from Refs. [1] and [3]. Constants and functions, *Y*, preceded by Δ refer to the difference between ideal dilute solution and ideal gas phase; Δ refer to those on C₇₈, i.e., $\Delta Y(P) = Y(P) - Y(C_{78})$; Δ' values are for an "ideal solution" of group X. Retention indices: I_{130} is for the retention index at T^* ; for the meaning of the coefficients, *A*, see Eq. 7. Thermodynamic functions: *H* and *S* are for partial molar enthalpy and entropy at T^* , *C_p* is for the mean partial molar heat capacity in the temperature range indicated; for the meaning of the coefficients *h* and *s*, see Eq. 4. At the end of the Table, additive corrections are listed to convert data, (A) to those related to the partition coefficients *K_D* and (B) to those where pressures are measured in units of bar (instead of atm). Errors: the symbol σ is for the standard deviation around the regression and at the end of the table are listed standard deviations of constants and functions in units of the standard deviation around the regression, $f(\text{coeff}) = \sigma(\text{coeff})/\sigma$. Data marked by a superscript *s* are significant at the 10% significance level if tested against σ . Data marked by one asterisk are at the 20% significance level those marked by double asterisks are under this limit. Note that linearity of the following thermodynamic functions of *n*-alkanes with carbon number was imposed by the regression function: ΔH , ΔS , ΔC_p , *h*, *s*, $\Delta'H$, $\Delta'S$ and $\Delta'C_p$.

No.	Compound	Temp. range (°C)	<i>n</i>	Retention index: C78/PCL						C78/PBR	
				C78	PCL - C78		id PCL - C78		σ	PBR - C78	
				I_{130}	$10 \times A_T$ (K ⁻¹)	ΔI_{130}	$10 \times \Delta A_T$ (K ⁻¹)	$\Delta' I_{130}$ (l mol ⁻¹)	$10 \times \Delta' A_T$ (K ⁻¹ l mol ⁻¹)		ΔI_{130}
HYDROCARBONS											
<i>n</i> -Alkanes											
00.05	Pentane	18	85-160	500	def.						
00.06	Hexane	18	85-160	600	def.						
00.07	Heptane	18	85-160	700	def.						
00.08	Octane	18	85-160	800	def.						
00.09	Nonane	18	85-160	900	def.						
00.10	Decane	18	85-160	1000	def.						
00.11	Undecane	12	115-160	1100	def.						
00.12	Dodecane	9	130-160	1200	def.						
00.13	Tridecane	9	130-160	1300	def.						
00.14	Tetradecane	9	130-160	1400	def.						
<i>Isoalkanes</i>											
10.01	2,2-Dimethylbutane	15	85-145	540.8	+0.93	+ 0.1**	-0.15*	+ 0.1	-0.21	0.24	- 0.3
10.02	2,3-Dimethylbutane	15	85-145	573.2	+0.92	+ 0.7	+0.01*	+ 1.0	+0.02	0.29	+ 0.6
10.03	2,2-Dimethylpentane	15	85-145	627.7	+0.85	+ 0.1**	-0.22	+ 0.1	-0.31	0.22	- 0.5
10.04	2,3-Dimethylpentane	15	85-145	679.4	+0.98	+ 0.6	+0.02**	+ 0.9	+0.03	0.13	+ 0.5
10.05	2,4-Dimethylpentane	15	85-145	628.9	+0.53	+ 0.0**	-0.15*	- 0.0	-0.21	0.24	- 0.1
10.06	2,2-Dimethylhexane	15	85-145	719.4	+0.75	- 0.1**	-0.23	- 0.2	-0.33	0.16	- 0.6
10.07	2,3-Dimethylhexane	15	85-145	765.6	+0.86	+ 0.5	+0.01**	+ 0.7	+0.02	0.13	+ 0.2
10.08	2,4-Dimethylhexane	15	85-145	733.5	+0.54	- 0.3	+0.07*	- 0.4	+0.09	0.17	- 0.3
10.09	3,4-Dimethylhexane	15	85-145	780.3	+1.07	+ 0.3	+0.12	+ 0.4	+0.18	0.13	+ 0.1
10.10	2,2,3-Trimethylbutane	15	85-145	652.0	+1.30	+ 0.4*	+0.51	+ 0.6	+0.73	0.34	- 0.2

No	Thermodynamic data: C78/PCL												C78/PBR	
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78	
	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)	ΔH (cal mol ⁻²)	ΔS (cal mol ⁻² K ⁻¹)	ΔC_P	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)	
HYDROCARBONS														
<i>n-Alkanes</i>														
00.05	- 5 507	-16.043	6.2	+102	+0.104	+ 3.1	-109	-0.355	- 50	-0.455	+ 4.1	3.6	+ 85.0	
00.06	- 6 505	-17.131	7.8	+105	+0.104	+ 2.7	-103	-0.355	- 41	-0.463	+ 3.5	3.1	+ 92.5	
00.07	- 7 517	-18.341	10.7	+107	+0.104	+ 2.3	- 98	-0.355	- 33	-0.471	+ 2.9	2.7	+ 95.7	
00.08	- 8 517	-19.540	12.3	+110	+0.104	+ 1.9	- 92	-0.355	- 25	-0.479	+ 2.3	2.6	+ 98.9	
00.09	- 9 531	-20.792	14.4	+113	+0.104	+ 1.5	- 87	-0.355	- 17	-0.487	+ 1.8	3.1	+102.8	
00.10	-10 539	-22.035	15.8	+115	+0.104	+ 1.2	- 81	-0.355	- 9	-0.495	+ 1.2	3.2	+106.3	
00.11	-11 561	-23.322	19.1	+117	+0.104	+ 0.8	- 76	-0.355	- 1	-0.503	+ 0.6	5.7	+112.2	
00.12	-12 569	-24.581	20.5	+120	+0.104	+ 0.4	- 70	-0.355	+ 7	-0.511	+ 0.0	6.1	+115.0	
00.13	-13 576	-25.840	21.9	+123	+0.104	+ 0.0	- 65	-0.355	+ 16	-0.520	- 0.5	8.9	+114.7	
00.14	-14 583	-27.099	23.3	+125	+0.104	- 0.4	- 59	-0.355	+ 24	-0.528	- 1.1	11.2	+137.2	
<i>Isoalkanes</i>														
10.01	- 5 708	-15.977	6.0	+ 57	-0.012**	+ 2.4	- 87 ^a	-0.289	- 81	-0.521	+ 3.0	1.1	+ 79.6	
10.02	- 6 029	-16.322	6.4	+ 98	+0.098	+ 2.8	-132	-0.400	- 85	-0.518	+ 3.6	1.0	+ 83.4	
10.03	- 6 602	-17.009	7.0	+ 55	-0.021**	+ 2.6	-210	-0.618	-263	-1.012	+ 3.0	0.6	+ 97.0	
10.04	- 7 101	-17.578	8.9	+120	+0.145	+ 3.5	- 98	-0.346	- 12	-0.391	+ 4.6	0.5	+ 93.0	
10.05	- 6 686	-17.208	8.7	+ 48	-0.036**	+ 0.4**	-112	-0.364	-133	-0.670	+ 0.2	0.5	+ 93.4	
10.06	- 7 551	-18.180	10.4	+ 57	-0.023*	+ 2.3	-177	-0.549	-217	-0.926	+ 2.7	0.4	+ 98.7	
10.07	- 7 991	-18.678	11.2	+122	+0.142	+ 3.1	-129	-0.439	- 57	-0.538	+ 4.0	0.6	+ 96.1	
10.08	- 7 741	-18.467	10.7	+100	+0.081	+ 0.9*	- 47	-0.235	+ 25	-0.341	+ 1.1	0.4	+ 98.6	
10.09	- 8 101	-18.761	10.3	+112	+0.116	+ 0.8	- 35	-0.212	+ 59	-0.259	+ 1.0	0.2	+ 97.6	
10.10	- 6 762	-17.092	8.1	+225	+0.402	+ 3.0	+117	+0.192	+441	+0.734	+ 4.6	0.6	+ 95.4	

(Continued on p. 138)

Table 5 (continued)

No.	Compound	n	Temp. range (°C)	Retention index: C78/PCL							C78/PBR	
				C78		PCL - C78		id PCL - C78		σ	PBR - C78	
				I_{130}	$\frac{10 \times}{A_T}$ (K ⁻¹)	ΔI_{130}	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹)	ΔI_{130}	$\frac{10 \times}{\Delta A_T}$ (l mol ⁻¹)			ΔI_{130}
10.11	2,2,4-Trimethylpentane	15	85-145	694.9	+0.95	- 0.1**	+0.18	- 0.1	+0.26	0.17	- 0.7	
10.12	2,3,4-Trimethylpentane	15	85-145	765.1	+1.35	+ 0.4*	+0.33	+ 0.6	+0.48	0.31	- 0.1	
<i>1-Alkenes</i>												
11.05	1-Pentene	15	85-145	485.0	+0.46	+ 1.4	-0.25*	+ 2.0	-0.34	0.51	+ 1.7	
11.06	1-Hexene	15	85-145	585.9	+0.49	+ 2.1	-0.22	+ 3.0	-0.29	0.32	+ 2.5	
11.07	1-Heptene	15	85-145	685.0	+0.41	+ 2.6	-0.07**	+ 3.8	-0.07	0.28	+ 3.0	
11.08	1-Octene	15	85-145	784.9	+0.45	+ 2.0	-0.17	+ 2.9	-0.22	0.20	+ 2.5	
11.09	1-Nonene	15	85-145	885.0	+0.39	+ 2.1	-0.07**	+ 3.0	-0.08	0.20	+ 2.9	
11.10	1-Decene	15	85-145	985.0	+0.35	+ 2.1	+0.07**	+ 3.0	+0.12	0.24	+ 2.6	
<i>1-Alkynes</i>												
12.05	1-Pentyne	15	85-145	484.4	-0.20	+ 7.1	+0.16	+10.3	+0.31	0.35	+ 7.5	
12.06	1-Hexyne	15	85-145	587.3	+0.08	+ 7.4	+0.01**	+10.7	+0.10	0.19	+ 7.4	
12.07	1-Heptyne	15	85-145	687.3	+0.05*	+ 7.9	+0.15	+11.5	+0.31	0.17	+ 7.8	
12.08	1-Octyne	15	85-145	787.5	+0.16	+ 7.5	+0.08*	+10.9	+0.20	0.16	+ 7.2	
12.09	1-Nonyne	15	85-145	887.9	+0.22	+ 7.6	+0.05**	+11.0	+0.16	0.16	+ 8.0	
12.10	1-Decyne	15	85-145	987.9	+0.18	+ 7.8	+0.18*	+11.3	+0.35	0.28	+ 7.8	
<i>Alkynes</i>												
13.01	2-Hexyne	15	85-145	642.0	-0.19	+ 6.3	+0.01**	+ 9.1	+0.09	0.14	+ 6.6	
13.02	3-Hexyne	15	85-145	619.8	-0.57	+ 5.5	-0.09**	+ 8.0	-0.06	0.31	+ 6.1	
13.03	4-Octyne	15	85-145	809.9	-0.19	+ 4.7	-0.02**	+ 6.8	+0.03	0.22	+ 5.6	
<i>Monocyclic hydrocarbons</i>												
14.05	Cyclopentane	18	85-160	587.7	+2.29	+ 1.4	-0.24	+ 2.0	-0.33	0.37	+ 2.5	
14.06	Cyclohexane	18	85-160	693.6	+3.09	+ 1.3	+0.09*	+ 1.9	+0.14	0.27	+ 2.8	
14.07	Cycloheptane	18	85-160	837.5	+4.15	+ 1.5	+0.13*	+ 2.3	+0.20	0.29	+ 2.9	
14.08	Cyclooctane	18	85-160	965.8	+4.96	+ 1.8	+0.31**	+ 2.6	+0.47	0.28	+ 3.3	
14.10	Cyclodecane	9	130-160	1179.0	+6.89	+ 4.4	-0.33	+ 6.3	-0.42	0.71	+ 3.1	
<i>Bicyclic hydrocarbons</i>												
15.01	cis-Hydrindane	9	130-160	1035.6	+5.92	+ 2.5	-0.17**	+ 3.6	-0.20	0.27	+ 4.0	
15.02	trans-Hydrindane	9	130-160	1001.9	+5.29	+ 2.0	-0.10**	+ 2.9	-0.12	0.30	+ 2.0	
15.03	cis-Decalin	9	130-160	1152.9	+7.04	+ 4.3	-0.13**	+ 6.2	-0.14	0.56	+ 3.4	
15.04	trans-Decalin	9	130-160	1112.4	+6.60	+ 1.7	+0.00**	+ 2.5	+0.02	0.21	+ 2.9	

No	Thermodynamic data: C78/PCL													C78/PBR
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78	
	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)	ΔH (cal mol ⁻²)	ΔS (cal mol ⁻² K ⁻¹)	ΔC_P	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)	
10.11	- 7 260	-17.772	9.7	+136	+0.175	+ 1.6	- 62*	-0.255	+ 59	-0.226	+ 2.1	0.8	+ 98.5	
10.12	- 7 894	-18.441	9.6	+173	+0.266	+ 1.7	+ 72	+0.053**	+297	+0.329	+ 2.6	0.5	+ 98.5	
<i>1-Alkenes</i>														
11.05	- 5 235	-15.522	5.1	+ 54*	+0.003**	+ 4.9	-322	-0.920	-421	-1.401	+ 6.0	2.4	+ 91.9	
11.06	- 6 244	-16.679	8.3	+ 59	+0.019**	+ 4.6	-250	-0.730	-310	-1.104	+ 5.8	1.6	+ 74.9	
11.07	- 7 271	-17.932	12.2	+ 95	+0.106*	+ 4.5*	-197*	-0.600	-184	-0.798	+ 5.8	1.3	+ 77.4	
11.08	- 8 276	-19.138	12.5	+ 66	+0.019**	+ 2.9*	- 78*	-0.327	- 64	-0.553	+ 3.7	1.0	+ 84.8	
11.09	- 9 298	-20.404	14.0	+ 49	-0.026**	- 0.1**	-121	-0.437	-152	-0.779	- 0.6	0.8	+ 87.4	
11.10	-10 314	-21.663	15.0	+ 96	+0.084*	+ 0.5**	-137	-0.509	-115	-0.741	+ 0.3	1.0	+ 93.2	
<i>1-Alkynes</i>														
12.05	- 5 391	-15.969	7.1	+ 88	+0.166	+ 4.4	-145	-0.476	-108	-0.506	+ 5.8	1.2	+ 25.1	
12.06	- 6 358	-16.945	8.6	+ 53	+0.076*	+ 4.2	-144	-0.462	-155	-0.611	+ 5.5	0.9	+ 49.0	
12.07	- 7 380	-18.168	11.9	+ 86	+0.153	+ 4.2	- 94	-0.349	- 40	-0.348	+ 5.6	0.7	+ 53.3	
12.08	- 8 365	-19.325	12.9	+ 53	+0.059	+ 2.1	- 24**	-0.187	+ 7	-0.265	+ 2.8	0.5	+ 60.7	
12.09	- 9 368	-20.544	15.3	+ 20	-0.028*	+ 0.0**	- 42	-0.244	- 69	-0.479	- 0.3	0.5	+ 60.8	
12.10	-10 385	-21.811	17.0	+ 70	+0.090*	+ 1.0**	- 2**	-0.160**	+ 55	-0.201	+ 1.3	1.5	+ 64.7	
<i>Alkynes</i>														
13.01	- 6 977	-17.758	9.3	+ 32	+0.003**	+ 1.9	- 27*	-0.159	- 22	-0.291	+ 2.5	0.4	+ 59.5	
13.02	- 6 829	-17.675	8.8	- 5**	-0.097*	+ 0.4**	-181	-0.565	-298	-1.024	- 0.0	1.3	+ 61.8	
13.03	- 8 664	-19.779	13.0	+ 34	-0.025*	+ 0.4**	- 53	-0.273	- 71	-0.530	+ 0.3	0.5	+ 70.7	
<i>Monocyclic hydrocarbons</i>														
14.05	- 5 857	-15.694	6.3	+ 29*	-0.062*	+ 2.4	-232	-0.677	-327	-1.145	+ 2.7	1.9	+ 75.8	
14.06	- 6 796	-16.639	9.4	+100	+0.105	+ 1.2*	- 74*	-0.302	- 8	-0.391	+ 1.5	1.3	+ 78.8	
14.07	- 8 036	-17.876	10.6	+105	+0.112	- 0.3**	- 47**	-0.250	+ 33	-0.318	- 0.6	1.4	+ 84.2	
14.08	- 9 178	-19.086	10.2	+146	+0.207	- 0.0**	- 7**	-0.137*	+149	-0.020	+ 0.0	1.2	+ 89.4	
14.10	-11 068	-21.115	16.3	- 66	-0.300	+ 5.3	- 78*	-0.321	-247	-0.987	+ 6.8	0.3	+ 81.1	
<i>Bicyclic hydrocarbons</i>														
15.01	- 9 800	-19.749	14.7	- 86	-0.365	+10.5	-125	-0.476	-349	-1.315	+13.8	0.4	+ 91.6	
15.02	- 9 564	-19.587	14.1	- 43	-0.263	+ 8.9	-349	-0.995	-600	-1.894	+11.3	0.1	+ 99.4	
15.03	-10 660	-20.434	13.0	- 10**	-0.163*	+ 4.2*	-178	-0.567	-310	-1.143	+ 5.2	0.5	+ 83.0	
15.04	-10 411	-20.311	14.4	+143	+0.187*	- 2.6**	- 1**	-0.192**	+137	-0.165	- 3.7	0.6	+ 95.7	

(Continued on p. 140)

Table 5 (continued)

No.	Compound	n	Temp. range (°C)	Retention index: C78/PCL						C78/PBR	
				C78		PCL - C78		id PCL - C78		PBR - C78	
				I_{130}	$\frac{10 \times}{A_T}$ (K ⁻¹)	ΔI_{130}	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹)	ΔI_{130} (l mol ⁻¹)	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹ l mol ⁻¹)	σ	ΔI_{130}
<i>Methylcyclohexanes (MCH)</i>											
16.01	Methylcyclohexane	15	85-145	758.3	+3.24	+ 1.0	-0.01**	+ 1.4	-0.00	0.24	+ 1.7
16.02	cis-1,2-Di MCH	15	85-145	868.2	+3.91	+ 1.4	+0.11	+ 2.0	+0.17	0.16	+ 2.8
16.03	trans-1,2-Di MCH	15	85-145	837.8	+3.54	+ 0.9	+0.17	+ 1.3	+0.25	0.20	+ 1.6
16.04	cis-1,4-Di MCH	15	85-145	838.2	+3.38	+ 1.4	+0.04**	+ 2.0	+0.07	0.12	+ 2.0
16.05	trans-1,4-Di MCH	15	85-145	816.7	+3.12	+ 1.0	-0.03**	+ 1.4	-0.03	0.22	+ 1.3
<i>Cyclohexenes</i>											
17.01	Cyclohexene	15	85-145	705.0	+3.04	+ 3.6	-0.02**	+ 5.2	+0.01	0.29	+ 4.9
17.02	1,3-Cyclohexadiene	15	85-145	689.6	+2.97	+ 6.2	+0.23	+ 9.0	+0.40	0.23	+ 7.0
17.03	1,4-Cyclohexadiene	15	85-145	725.3	+2.96	+ 6.5	-0.01**	+ 9.4	+0.06	0.28	+ 7.8
<i>Alkylbenzenes</i>											
18.00	Benzene	15	85-145	677.2	+2.68	+ 9.5	+0.58	+13.8	+0.94	0.52	+10.4
18.01	Toluene	15	85-145	785.7	+2.75	+ 9.5	+0.49	+13.8	+0.81	0.42	+10.7
18.02	Ethylbenzene	15	85-145	875.4	+3.08	+ 9.4	+0.32	+13.6	+0.57	0.35	+10.4
<i>Miscellaneous</i>											
19.01	Adamantane	9	130-160	1136.9	+7.87	+ 2.9	+0.67**	+ 4.2	+0.99	0.75	+ 3.5
19.02	Naphthalene	9	130-160	1214.1	+7.78	+17.4	+0.27**	+25.2	+0.59	1.21	+17.2
19.03	Azulene	9	130-160	1326.0	+8.92	+18.1	+1.27	+26.3	+2.03	0.50	+20.3
<i>ALKANE DERIVATIVES</i>											
<i>1-Fluoroalkanes</i>											
20.05	1-Fluoropentane	15	85-145	555.9	+0.09	+ 9.2	-0.17	+13.3	-0.14	0.18	+ 8.9
20.06	1-Fluorohexane	15	85-145	656.8	+0.07	+ 9.4	-0.06**	+13.6	+0.02	0.15	+ 9.1
20.07	1-Fluoroheptane	15	85-145	757.4	+0.07	+ 9.5	-0.03**	+13.8	+0.07	0.09	+ 9.2
20.08	1-Fluorooctane	15	85-145	857.9	+0.08	+ 9.6	-0.07	+13.9	+0.01	0.08	+ 9.3
<i>1,1,1-Trifluoroalkanes</i>											
21.08	1,1,1-Trifluorooctane	15	85-145	722.3	-2.27	+ 7.7	-0.07**	+11.1	-0.01	0.19	+ 6.3
21.10	1,1,1-Trifluorodecane	15	85-145	920.9	-2.28	+ 7.5	-0.16	+10.4	-0.14	0.17	+ 6.3
<i>1-Chloroalkanes</i>											
22.04	1-Chlorobutane	15	85-145	639.0	+1.69	+ 9.9	+0.01**	+14.3	+0.13	0.16	+10.4

No	Thermodynamic data: C78/PCL												C78/PBR	
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78	
	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)	ΔH (cal l mol ⁻²)	ΔS (cal l mol ⁻² K ⁻¹)	ΔC_P	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)	
Methylcyclohexanes (MCH)														
16.01	- 7 415	-17.342	9.1	+139	+0.189	+ 5.0	-131	-0.444	- 34	-0.474	+ 6.7	0.8	+ 88.2	
16.02	- 8 403	-18.392	7.9	+112	+0.124	+ 1.3	- 27*	-0.205	+ 70	-0.240	+ 1.7	0.4	+ 89.1	
16.03	- 8 172	-18.202	7.8	+125	+0.151	+ 1.1*	- 34**	-0.221	+ 78	-0.226	+ 1.4	0.7	+ 94.3	
16.04	- 8 205	-18.281	9.2	+118	+0.138	+ 2.8	- 94	-0.363	- 15	-0.438	+ 3.7	0.5	+ 91.4	
16.05	- 8 031	-18.123	10.0	+127	+0.156	+ 4.3	-184	-0.587	-129	-0.730	+ 5.6	0.5	+ 92.8	
Cyclohexenes														
17.01	- 6 926	-16.812	7.7	+118	+0.172	+ 6.0	-126	-0.422	- 49	-0.446	+ 8.1	0.8	+ 70.4	
17.02	- 6 781	-16.650	6.9	+105	+0.177	+ 3.3	- 8**	-0.138	+104	-0.028	+ 4.6	0.6	+ 59.4	
17.03	- 7 152	-17.113	8.3	+ 97	+0.156	+ 6.1	- 53	-0.253	+ 29	-0.219	+ 8.4	0.6	+ 55.9	
Alkylbenzenes														
18.00	- 6 729	-16.685	8.2	+150	+0.333	+ 3.3	+172	+0.308	+430	+0.843	+ 5.1	0.9	+ 39.4	
18.01	- 7 802	-17.954	10.9	+130	+0.275	+ 2.8	+ 86	+0.075**	+275	+0.418	+ 4.2	0.8	+ 41.6	
18.02	- 8 649	-18.918	11.9	+ 77	+0.135	+ 1.3	+ 65	+0.015**	+166	+0.126	+ 1.9	0.6	+ 47.3	
Miscellaneous														
19.01	-10 548	-20.340	17.9	+470	+1.008	-17.2	-134*	-0.454*	+418	+0.641	-23.5	0.7	+ 91.5	
19.02	-11 301	-21.266	17.9	+375	+0.944	-25.7	-447*	-1.188	-126	-0.406	-35.9	1.8	+ 15.7	
19.03	-12 443	-22.642	21.9	+ 42*	+0.130	+ 8.4	+369	+0.679	+549	+1.065	+12.3	0.2	+ 32.5	
ALKANE DERIVATIVES														
1-Fluoroalkanes														
20.05	- 6 043	-16.603	9.5	- 7**	-0.044*	+ 4.3	-184	-0.551	-290	-0.890	+ 5.5	0.8	+ 32.3	
20.06	- 7 067	-17.791	11.2	+ 33	+0.041	+ 4.9	-117	-0.395	-142	-0.558	+ 6.5	0.4	+ 44.9	
20.07	- 8 083	-19.012	12.5	+ 13*	-0.014**	+ 2.5	- 86	-0.329	-130	-0.553	+ 3.2	0.5	+ 49.9	
20.08	- 9 099	-20.255	14.3	+ 2**	-0.047	+ 2.1	- 63	-0.284	-117	-0.544	+ 2.6	0.3	+ 53.4	
1,1,1-Trifluoroalkanes														
21.08	- 8 196	-19.747	16.3	+ 39	+0.029**	+ 3.6	-113	-0.394	-135	-0.591	+ 4.7	1.0	+ 61.0	
21.10	-10 186	-22.163	20.2	+ 14**	-0.049*	+ 2.0	-141	-0.495	-219	-0.867	+ 2.3	0.8	+ 68.4	
1-Chloroalkanes														
22.04	- 6 540	-16.714	7.9	+ 33	+0.051*	+ 4.5	-106	-0.366	-125	-0.498	+ 6.0	0.7	+ 38.6	

(Continued on p. 142)

Table 5 (continued)

No.	Compound	n	Temp. range (°C)	Retention index: C78/PCL							C78/PBR	
				C78		PCL - C78		id PCL - C78		σ	PBR - C78	
				I_{130}	$\frac{10 \times}{A_T}$ (K ⁻¹)	ΔI_{130}	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹)	ΔI_{130} (l mol ⁻¹)	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹ l mol ⁻¹)			ΔI_{130}
22.05	1-Chloropentane	15	85-145	742.2	+1.48	+ 9.7	+0.35	+14.1	+0.61	0.37	+10.2	
22.06	1-Chlorohexane	15	85-145	843.7	+1.69	+ 9.7	+0.19	+14.1	+0.39	0.26	+10.2	
<i>1-Bromoalkanes</i>												
23.03	1-Bromopropane	15	85-145	627.7	+2.32	+10.5	+0.28	+15.2	+0.52	0.25	+11.4	
23.04	1-Bromobutane	15	85-145	731.4	+2.55	+10.4	+0.22	+15.1	+0.47	0.20	+11.4	
23.05	1-Bromopentane	15	85-145	833.8	+2.66	+10.4	+0.25	+15.1	+0.48	0.28	+11.5	
<i>1-Cyanoalkanes</i>												
24.02	Cyanoethane	15	85-145	492.6	+0.69	+28.6	-0.35	+41.4	-0.16	0.17	+27.9	
24.03	1-Cyanopropane	15	85-145	587.4	+1.17	+28.5	-0.09**	+41.3	+0.20	0.37	+28.5	
24.04	1-Cyanobutane	15	85-145	692.9	+1.35	+29.1	+0.07**	+42.2	+0.44	0.28	+29.2	
24.05	1-Cyanopentane	15	85-145	794.7	+1.44	+29.6	+0.10	+42.9	+0.49	0.26	+29.6	
<i>1-Nitroalkanes</i>												
25.02	Nitroethane	15	85-145	566.5	+1.34	+27.7	-0.46	+40.1	-0.33	0.52	+27.2	
25.03	1-Nitropropane	15	85-145	660.5	+1.74	+27.4	-0.05**	+39.7	+0.24	0.41	+26.7	
25.04	1-Nitrobutane	15	85-145	763.8	+2.02	+27.0	-0.09*	+39.1	+0.19	0.21	+26.8	
25.05	1-Nitropentane	15	85-145	865.9	+2.15	+27.0	-0.10**	+39.1	+0.17	0.26	+27.0	
<i>1-Acetoxyalkanes</i>												
26.03	1-Acetoxypropane	15	85-145	637.6	-0.63	+14.6	-0.11**	+21.1	+0.01	0.44	+13.3	
26.04	1-Acetoxybutane	15	85-145	739.4	-0.53	+14.6	-0.05**	+21.1	+0.10	0.30	+13.9	
26.05	1-Acetoxypentane	15	85-145	840.0	-0.40	+14.5	-0.19	+21.0	-0.10	0.28	+13.9	
<i>1-Alkanols</i>												
27.04	1-Butanol	15	85-145	594.5	+0.75	+17.1	-0.25	+24.7	-0.16	0.14	+17.3	
27.05	1-Pentanol	15	85-145	698.3	+0.78	+16.7	-0.07**	+24.2	+0.10	0.22	+17.2	
27.06	1-Hexanol	15	85-145	800.0	+1.02	+16.7	-0.13*	+24.2	+0.01	0.31	+18.0	
27.07	1-Heptanol	15	85-145	901.4	+1.02	+17.1	-0.03**	+24.8	+0.16	0.26	+18.5	
<i>2-Alkanols</i>												
28.04	2-Butanol	15	85-145	545.9	+0.46	+14.9	+0.35	+21.6	+0.68	0.39	+15.3	
28.05	2-Pentanol	15	85-145	644.5	+0.41	+14.8	+0.40	+21.5	+0.75	0.43	+15.4	
28.06	2-Hexanol	15	85-145	744.5	+0.60	+14.9	+0.13**	+21.6	+0.36	0.35	+15.6	
28.07	2-Heptanol	15	85-145	844.5	+0.72	+15.0	+0.04**	+21.7	+0.23	0.32	+15.7	

No	Thermodynamic data: C78/PCL												C78/PBR
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78
	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)	ΔH (cal mol ⁻²)	ΔS (cal mol ⁻² K ⁻¹)	ΔC_P	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)
22.05	- 7 642	-18.109	10.2	+103	+0.213	+ 3.2	+110	+0.157*	+275	+0.459	+ 4.7	0.9	+ 44.8
22.06	- 8 615	-19.234	12.1	+ 42	+0.054*	+ 1.1*	+ 24**	-0.077**	+ 61	-0.112	+ 1.5	0.7	+ 48.0
<i>1-Bromoalkanes</i>													
23.03	- 6 302	-16.268	6.3	+ 27	+0.045	+ 0.7*	+ 32*	-0.021**	+ 62	-0.018	+ 1.0	0.5	+ 35.4
23.04	- 7 299	-17.406	11.3	+ 25	+0.031*	+ 0.7**	+ 1**	-0.112*	+ 12	-0.177	+ 0.9	0.6	+ 35.1
23.05	- 8 318	-18.624	12.2	+ 40	+0.058*	+ 0.7**	+ 59	+0.014**	+110	+0.028	+ 1.0	0.7	+ 39.9
<i>1-Cyanoalkanes</i>													
24.02	- 5 258	-15.536	8.8	-251	-0.378	+ 4.5	-118	-0.364	-490	-0.970	+ 5.7	0.8	- 85.9
24.03	- 6 114	-16.339	11.2	-163	-0.182	+ 6.7	-151	-0.446	-415	-0.815	+ 8.8	1.5	- 67.9
24.04	- 7 164	-17.574	14.5	-147	-0.157	+ 4.6	- 10	-0.114	-199	-0.327	+ 6.2	1.0	- 60.2
24.05	- 8 174	-18.768	14.5	-175	-0.229	+ 2.1	+ 45	+0.008	-165	-0.266	+ 2.8	0.7	- 54.8
<i>1-Nitroalkanes</i>													
25.02	- 5 845	-15.970	10.0	-316	-0.554	+ 1.1**	-352	-0.955	-919	-2.071	+ 0.3	1.5	- 64.8
25.03	- 6 746	-16.954	12.6	-130	-0.130*	+ 6.6	-140*	-0.435	-361	-0.746	+ 8.7	1.7	- 48.8
25.04	- 7 735	-18.076	13.6	-159	-0.219	+ 3.9	- 48*	-0.227	-279	-0.597	+ 5.1	0.8	- 43.8
25.05	- 8 744	-19.282	15.9	-173	-0.264	+ 2.9	- 63**	-0.277*	-325	-0.743	+ 3.6	1.3	- 39.1
<i>1-Acetoxyalkanes</i>													
26.03	- 7 008	-17.893	11.4	- 29**	-0.044**	+ 5.3	-198	-0.630	-338	-0.996	+ 6.8	1.7	+ 22.1
26.04	- 8 021	-19.088	12.9	- 31*	-0.056**	+ 3.4	- 65*	-0.296	-154	-0.543	+ 4.4	1.2	+ 24.4
26.05	- 9 005	-20.249	15.1	- 71	-0.165	+ 2.4	- 65*	-0.313	-217	-0.732	+ 1.2	0.9	+ 28.0
<i>1-Alkanols</i>													
27.04	- 6 257	-16.592	9.5	-136	-0.268	+ 2.9	-186	-0.555	-459	-1.172	+ 3.3	0.6	+ 0.7
27.05	- 7 316	-17.865	12.9	- 74	-0.134	+ 2.9	-114	-0.397*	-276	-0.776	+ 3.6	1.2	+ 7.4
27.06	- 8 295	-18.990	14.3	- 82	-0.162	+ 2.7	- 36**	-0.234	-183	-0.602	+ 3.1	0.9	+ 7.2
27.07	- 9 309	-20.224	17.4	- 59	-0.106	- 2.3	+ 22**	-0.087**	- 71	-0.320	- 3.3	0.8	+ 9.5
<i>2-Alkanols</i>													
28.04	- 5 845	-16.245	10.1	+ 48*	+0.173	+ 3.9	+ 62**	+0.069**	+152	+0.334	+ 5.6	2.0	- 3.0
28.05	- 6 862	-17.438	11.9	+ 61	+0.183	+ 3.8	+154	+0.278	+294	+0.626	+ 5.7	0.9	+ 13.4
28.06	- 7 838	-18.568	12.6	+ 15**	+0.059*	+ 3.9	+ 87	+0.100**	+130	+0.189	+ 5.6	1.0	+ 16.6
28.07	- 8 825	-19.744	14.9	- 17**	-0.027**	+ 2.9	+ 90	+0.093**	+ 85	+0.047	+ 4.1	0.8	+ 20.9

(Continued on p. 144)

Table 5 (continued)

No.	Compound	n	Temp. range (°C)	Retention index: C78/PCL							C78/PBR	
				C78		PCL - C78		id PCL - C78			PBR - C78	
				I_{130}	$\frac{10 \times}{A_T}$ (K ⁻¹)	ΔI_{130}	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹)	ΔI_{130} (l mol ⁻¹)	$\frac{10 \times}{\Delta A_T}$ (K ⁻¹ l mol ⁻¹)	σ	ΔI_{130}	
2-Methyl-2-alkanols												
29.04	2-Methyl-2-propanol	15	85-145	472.1	+0.32	+12.9	-0.24	+18.7	-0.19	0.31	+13.3	
29.05	2-Methyl-2-butanol	15	85-145	597.5	+1.01	+13.4	-0.13*	+19.4	-0.03	0.30	+13.4	
29.06	2-Methyl-2-pentanol	15	85-145	690.2	+0.86	+13.3	-0.06**	+19.3	+0.07	0.35	+13.3	
29.07	2-Methyl-2-hexanol	15	85-145	785.7	+0.90	+13.2	-0.17	+19.1	-0.09	0.22	+13.6	
1-Thiols												
30.04	1-Butanethiol	15	85-145	716.6	+3.09	+10.4	-0.39	+15.0	-0.44	0.46	+11.7	
30.05	1-Pentanethiol	15	85-145	818.9	+3.26	+10.1	-0.59	+14.6	-0.73	0.40	+11.6	
30.06	1-Hexanethiol	15	85-145	920.4	+3.32	+10.5	-0.59	+15.2	-0.72	0.49	+11.5	
2-Alkanones												
31.04	2-Butanone	15	85-145	537.6	+0.63	+19.2	-0.49	+27.8	-0.48	0.43	+18.8	
31.05	2-Pentanone	15	85-145	628.5	+0.75	+19.5	-0.37	+28.2	-0.30	0.35	+18.9	
31.06	2-Hexanone	15	85-145	730.1	+0.83	+19.9	-0.22	+28.8	-0.08	0.16	+19.4	
31.07	2-Heptanone	15	85-145	830.2	+0.91	+19.9	-0.31	+28.8	-0.21	0.17	+20.2	
Aldehydes												
32.04	Butanal	15	85-145	542.1	+1.23	+17.3	-0.70	+25.0	-0.80	0.42	+18.2	
32.05	Pentanal	15	85-145	646.9	+1.32	+18.0	-0.37	+26.0	-0.32	0.23	+18.8	
32.06	Hexanal	15	85-145	748.4	+1.30	+18.1	-0.26	+26.2	-0.16	0.21	+18.7	
Ethers												
33.06	Dipropylether	15	85-145	656.0	-0.00**	+ 4.7	-0.16	+ 6.8	-0.17	0.22	+ 5.0	
33.08	Dibutylether	15	85-145	854.4	+0.07 ^s	+ 4.3	-0.14	+ 6.2	-0.15	0.16	+ 5.0	
Halogenomethanes												
37.01	Dichloromethane	15	85-145	506.3	+1.49	+13.3	+0.47	+19.3	+0.83	0.40	+14.5	
37.02	Trichloromethane	15	85-145	607.9	+2.27	+10.8	+0.34	+15.7	+0.61	0.35	+12.1	
37.03	Tetrachloromethane	15	85-145	680.5	+3.20	+ 4.8	+0.04**	+ 7.0	+0.11	0.14	+ 5.7	
37.04	CF ₂ Br ₂	15	85-145	479.0	+1.04	+ 4.2	+0.20	+ 6.1	+0.34	0.23	+ 5.2	
HALOGENOBENZENES												
38.01	Fluorobenzene	15	85-145	664.9	+2.25	+11.0	+0.20	+15.9	+0.42	0.27	+11.2	
38.02	Hexafluorobenzene	15	85-145	546.8	-2.14	+ 7.5	-0.03**	+10.9	+0.04	0.34	+ 5.0	

No	Thermodynamic data: C78/PCL												C78/PBR	
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78	
	ΔH (cal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔC_p	ΔH (cal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔC_p	f_i (cal mol ⁻¹)	s (cal mol ⁻¹ K ⁻¹)	ΔH (cal l mol ⁻²)	ΔS (cal l mol ⁻² K ⁻¹)	ΔC_p	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)	
2-Methyl-2-alkanols														
29.04	- 5 085	-15.379	14.2	- 17**	-0.015**	- 7.7	-146	-0.460	-247	-0.713	-11.1	0.8	- 7.3	
29.05	- 6 223	-16.464	12.8	- 13*	-0.017**	+ 6.8	- 56	-0.232	-108	-0.377	+ 9.2	0.6	+ 22.5	
29.06	- 7 206	-17.696	14.5	+ 12**	+0.037**	+ 6.3	- 42**	-0.225	- 59	-0.307	+ 8.5	0.8	+ 26.1	
29.07	- 8 156	-18.829	16.5	- 28	-0.071	+ 4.2	- 34**	-0.209	-107	-0.446	+ 5.5	0.8	+ 28.1	
1-Thiols														
30.04	- 7 031	-16.922	6.9	- 42	-0.137	+ 5.3	-350	-0.980	-578	-1.637	+ 6.4	0.9	+ 36.6	
30.05	- 8 031	-18.097	10.1	-101	-0.293	+ 3.7	-310	-0.888	-608	-1.737	+ 4.1	0.5	+ 40.3	
30.06	- 9 042	-19.330	14.6	- 97	-0.287	+ 3.3	-358	-1.023	-674	-1.929	+ 3.4	1.0	+ 42.5	
2-Alkanones														
31.04	- 5 709	-16.031	10.1	-202	-0.389	+ 3.4	-401	-1.092	-849	-2.086	+ 3.5	0.9	- 27.2	
31.05	- 6 622	-17.063	12.2	-142	-0.260	+ 5.2	-255	-0.724	-559	-1.386	+ 6.4	0.7	- 9.7	
31.06	- 7 642	-18.273	13.5	-117	-0.203	+ 3.9	-153	-0.491	-385	-0.988	+ 4.8	0.2	- 5.7	
31.07	- 8 636	-19.462	14.9	-133	-0.252	+ 3.8	-108	-0.389	-347	-0.921	+ 4.7	0.4	- 4.4	
Aldehydes														
32.04	- 5 626	-15.753	6.0	-255	-0.546	+ 2.0	-407	-1.116	-940	-2.359	+ 1.4	0.5	- 19.0	
32.05	- 6 695	-16.998	10.1	-164	-0.331	+ 2.8	-177	-0.550	-488	-1.259	+ 3.1	1.3	- 5.8	
32.06	- 7 732	-18.258	11.7	-126	-0.247	+ 2.7	-147	-0.481	-394	-1.049	+ 3.1	1.2	+ 0.1	
Ethers														
33.06	- 7 070	-17.803	9.9	+ 41	+0.001**	+ 3.7	-157	-0.506	-200	-0.805	+ 4.7	1.0	+ 89.1	
33.08	- 9 059	-20.196	13.8	+ 12 ^s	-0.086	+ 0.2**	- 85	-0.352	-148	-0.731	- 0.1	0.4	+ 75.7	
Halogenomethanes														
37.01	- 5 254	-15.326	4.1	+ 71	+0.210	+ 2.7	+181	+0.388	+353	+0.838	+ 4.2	0.7	- 6.3	
37.02	- 6 116	-16.068	7.7	+ 62	+0.136	+ 2.5	+114	+0.191	+231	+0.419	+ 3.7	0.6	+ 28.6	
37.03	- 6 641	-16.422	5.7	+ 49	+0.022**	+ 1.5	-114	-0.384	-126	-0.598	+ 1.7	0.5	+ 66.2	
37.04	- 5 078	-15.274	5.3	+ 72	+0.090	+ 1.1*	- 8**	-0.098**	+ 62	-0.082	+ 1.5	0.8	+ 36.8	
HALOGENOBENZENES														
38.01	- 6 682	-16.734	11.6	+ 40	+0.082 ^s	+ 2.9	- 23**	-0.174*	- 2	-0.185	+ 3.9	1.1	+ 32.7	
38.02	- 6 464	-17.769	10.8	+ 53*	+0.080**	+ 4.9	-124*	-0.392 ^s	-122	-0.494	+ 6.5	2.0	+ 51.9	

(Continued on p. 146)

Table 5 (continued)

No.	Compound	Temp. range (°C)	Retention index: C78/PCL							C78/PBR		
			n	C78		PCL - C78		id PCL - C78		σ	PBR - C78	
				I_{130}	$10\times$	ΔI_{130}	$10\times$	ΔI_{130}	$10\times$			ΔI_{130}
					A_T		ΔA_T		ΔA_T			
	(K^{-1})	(K^{-1})	(l mol^{-1})	(K^{-1} mol^{-1})								
38.03	Trifluoromethylbenzene	85-145	15	656.3	+0.24	+11.8	+0.37	+17.1	+0.67	0.25	+10.3	
38.04	Chlorobenzene	85-145	15	865.0	+4.21	+11.8	+0.21	+17.1	+0.44	0.32	+13.2	
38.05	Bromobenzene	85-145	15	960.0	+5.39	+12.9	+0.15	+18.7	+0.37	0.28	+14.5	
38.06	Iodobenzene	130-160	9	1079.6	+6.77	+14.4	+0.33	+20.9	+0.64	0.19	+16.4	
ALKYLPYRIDINES												
39.01	Pyridine	85-130	12	724.4	+3.43	+19.4	+0.23**	+28.1	+0.56	0.46	+22.1	
39.02	2-Picoline	85-130	12	802.3	+2.84	+16.3	+0.08**	+23.6	+0.31	0.45	+19.2	
39.03	3-Picoline	85-130	12	844.9	+3.49	+19.8	+0.24**	+28.7	+0.58	0.58	+23.4	
39.04	4-Picoline	85-130	12	843.3	+3.72	+21.6	+0.37*	+31.3	+0.78	0.62	+24.2	
39.05	2,3-Lutidine	85-130	12	934.3	+3.32	+17.9	+0.33*	+25.9	+0.68	0.46	+19.8	
39.06	2,4-Lutidine	85-130	12	918.7	+2.89	+18.9	+0.53 ^s	+27.4	+0.98	0.61	+20.5	
39.07	2,5-Lutidine	85-130	12	919.1	+2.85	+17.6	+0.38*	+25.5	+0.75	0.64	+19.5	
39.08	2,6-Lutidine	85-130	12	872.0	+2.63	+13.7	-0.39 ^s	+19.8	-0.40	0.46	+16.2	
39.09	3,4-Lutidine	85-130	12	986.2	+4.89	+21.3	-0.43*	+30.8	-0.37	0.39	+24.2	
39.10	3,5-Lutidine	85-130	12	963.5	+4.22	+21.5	-0.05**	+31.1	+0.18	0.74	+23.2	
39.19	3-Chloropyridine	85-130	12	884.5	+4.46	+16.9	-0.02**	+24.5	+0.17	0.18	+18.5	
ORGANOSILICON COMPOUNDS												
40.01	Tetramethylsilane	85-145	15	428.1	-0.46	+ 1.9	+0.22*	+ 2.8	+0.32	0.42	+ 0.4	
40.02	Hexamethyldisilane	85-145	15	686.1	+0.32	+ 0.7	-0.03**	+ 1.0	-0.03	0.17	+ 0.4	
40.03	Hexamethyldisiloxane	85-145	15	597.4	-2.47	- 0.5	-0.15	- 0.7	-0.22	0.23	- 2.2	
MISCELLANEOUS												
41.01	Carbondisulphide	85-160	18	607.3	+4.19	+ 4.8	-0.21	+ 6.9	-0.24	0.22	+ 7.8	
41.02	Tetramethyltin	85-145	15	604.5	-0.01**	+ 2.6	+0.53	+ 3.8	+0.79	0.47	+ 2.8	
41.03	Tetrahydrofuran	85-145	15	609.9	+2.12	+12.7	+0.03**	+18.4	+0.19	0.43	+13.7	
41.04	1,4-Dioxane	85-160	18	670.1	+2.46	+14.5	-0.17*	+21.0	-0.07	0.37	+15.4	
41.05	Thiophene	85-145	15	685.3	+2.98	+11.1	+0.84	+16.1	+1.33	0.69	+12.5	
41.06	Cyclopentanone	85-145	15	741.1	+3.15	+23.4	-0.01**	+33.9	+0.26	0.42	+24.6	
41.07	Cyclohexanone	85-145	15	854.1	+4.10	+24.2	+0.44 ^s	+35.1	+0.91	0.69	+25.1	
41.08	Cyclohexanol	85-160	18	851.1	+4.17	+17.1	-0.07**	+24.8	+0.10	0.21	+18.8	
41.11	Nitrobenzene	130-160	9	1049.4	+5.63	+28.2	-0.07**	+40.7	+0.23	0.38	+28.8	

No	Thermodynamic data: C78/PCL													C78/PBR
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78	
	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)	ΔH (cal mol ⁻²)	ΔS (cal mol ⁻² K ⁻¹)	ΔC_p	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)	
38.03	- 7 029	-17.699	10.2	+ 86	+0.204	+ 3.7	- 50**	-0.239	+ 31	-0.099	+ 5.1	1.0	+ 40.1	
38.04	- 8 311	-18.212	11.7	+ 42	+0.079	+ 2.5	+ 53	-0.013**	+106	+0.023	+ 3.5	0.6	+ 32.7	
38.05	- 9 038	-18.814	10.2	+ 33	+0.063*	+ 3.0	+ 46*	-0.028**	+ 85	-0.016	+ 4.2	0.9	+ 32.3	
38.06	- 9 504	-18.533	13.9	- 3**	-0.015**	+ 2.7	+ 63	-0.015**	+ 55	-0.117	+ 3.6	0.2	+ 5.8	
ALKYLPYRIDINES														
39.01	- 7 032	-16.839	8.9**	-247**	-0.536	- 6.7	-111*	-0.405*	-516	-1.355	- 9.9	3.4	- 22.8	
39.02	- 7 948	-18.105	11.3	-165	-0.376*	- 3.2**	- 84**	-0.358*	-374	-1.094	- 5.1	1.8	- 1.3	
39.03	- 8 242	-18.314	11.3*	-217	-0.466	- 5.7*	+ 40**	-0.044**	-265	-0.760	- 8.4	2.0	- 27.5	
39.04	- 8 199	-18.219	13.5	-257	-0.545	- 7.9	+145*	+0.247**	-166	-0.441	-11.2	1.8	- 27.1	
39.05	- 9 255	-19.678	13.0	- 31**	-0.033**	+ 0.0**	+ 68**	+0.018**	+ 34	-0.068	- 0.0	1.7	+ 3.1	
39.06	- 9 182	-19.679	12.7	-171	-0.372	- 7.6	+153	+0.235	- 45	-0.244	-10.7	0.6	+ 5.2	
39.07	- 9 237	-19.807	13.8	-203	-0.467	- 8.1	+165	+0.269	- 76	-0.336	-11.4	1.2	+ 11.6	
39.08	- 8 816	-19.387	14.8*	-132*	-0.330*	+ 1.2**	-260*	-0.795	-581	-1.657	+ 0.7	2.4	+ 13.3	
39.09	- 9 535	-19.747	15.8	-281	-0.615	- 1.8*	-343	-1.050	-905	-2.410	- 3.9	0.7	- 28.6	
39.10	- 9 413	-19.719	14.6	-430	-0.987	-12.0	-228	-0.705	-948	-2.437	-18.1	1.8	- 18.5	
39.19	- 8 455	-18.317	12.1	-136	-0.301	- 1.1*	-116	-0.428	-375	-1.076	- 2.1	0.4	+ 9.5	
ORGANOSILICON COMPOUNDS														
40.01	- 4 894	-15.508	0.5**	+162	+0.281	+ 5.1	-104**	-0.323*	+ 52	-0.134	+ 7.0	2.4	+ 61.2	
40.02	- 7 309	-18.009	11.7	+117	+0.140	+ 2.6	- 21**	-0.145	+ 95	-0.109	+ 3.5	0.5	+ 92.5	
40.03	- 7 037	-18.453	13.1	+127	+0.151	+ 5.9	- 96	-0.336	- 1	-0.368	+ 8.0	0.5	+ 99.6	
MISCELLANEOUS														
41.01	- 5 654	-14.938	7.5	+ 7**	-0.078	+ 3.7	-209	-0.618	-318	-1.065	+ 4.5	1.2	+ 47.5	
41.02	- 6 572	-17.231	5.0	+197	+0.365	+ 2.5	+188	+0.372	+508	+0.952	+ 4.1	0.9	+ 81.2	
41.03	- 6 157	-16.144	8.3	- 83*	-0.194	- 1.1**	- 41**	-0.181**	-188	-0.562	- 1.9	1.8	+ 20.0	
41.04	- 6 686	-16.674	9.4	- 19**	-0.017**	+ 5.2*	- 54**	-0.240**	-114	-0.390	+ 7.0	1.8	+ 12.3	
41.05	- 6 755	-16.646	9.2	+178	+0.422	+ 2.4	+327	+0.698	+693	+1.531	+ 4.2	0.6	+ 28.9	
41.06	- 7 281	-17.228	8.7	-183	-0.319	- 1.0**	+ 44**	-0.009**	-194	-0.458	- 1.7	1.7	- 28.9	
41.07	- 8 250	-18.189	7.0	- 90	-0.090**	- 1.0**	+284	+0.571	+274	+0.679	- 1.0	1.7	- 23.7	
41.08	- 8 187	-18.075	9.5	- 56	-0.097	+ 3.5	- 8**	-0.150*	-104	-0.384	+ 4.6	1.1	+ 6.2	
41.11	- 9 898	-19.828	12.5	-200*	-0.331*	+ 2.4**	- 32**	-0.223**	-323	-0.772	+ 2.9	1.2	- 31.8	

(Continued on p. 148)

Table 5 (continued)

No.	Compound	Temp. range n (°C)	Retention index: C78/PCL							C78/PBR	
			C78		PCL - C78		id PCL - C78		PBR - C78		
			I_{130}	$10\times$ A_T	ΔI_{130}	$10\times$ ΔA_T	ΔI_{130}	$10\times$ ΔA_T	σ	ΔI_{130}	
				(K^{-1})		(K^{-1})	(l mol^{-1})	($K^{-1} l$ mol^{-1})			
41.12	Benzyl alcohol	15	85-145	973.7	+4.34	+26.3	+0.07**	+38.1	+0.41	0.35	+28.1
41.13	2-Phenylethanol	9	130-160	1054.4	+4.94	+24.7	+0.70	+35.7	+1.29	0.32	+26.9
41.14	Anisole	15	85-145	909.0	+3.09	+15.7	+0.01**	+22.7	+0.20	0.16	+16.4
41.15	Phenetoic	15	85-145	978.5	+2.37	+14.3	+0.17*	+20.7	+0.41	0.34	+15.0

ERROR OF THE COEFFICIENTS (STANDARD DEVIATION)

$f(n\text{-alkanes})$	85-160	def.					
$f(\text{solutes})$	85-145	0.43	0.15	0.77	0.30	1.09	0.42

CONVERSIONS

A	Data related to K_D	0	0	0	0	0	0
B	Data related to 1 bar	0	0	0	0	0	0

Average values of $RT \ln f$ deduced from n -alkane data are given in Table 3. Alkane data on columns of series (a) were adjusted to the average of the two columns by adding $0.5RT \ln f$.

3.4. Standard chemical potentials of n -alkanes C_{78} -PCL. Pentane-decane

Standard chemical potential differences of n -alkanes, C_zH_{2z+2} with $z = 5-10$, were calculated on these two phases ($\varphi = 0.5$ and 1) with the alkane C_{78} as reference in the temperature range of 85–160°C at 15 K intervals. Inclusion of data from Ref. [1] for C_{78} gave a set of $6 \times 3 \times 6 = 108$ data points.

The variance analysis of the influence of the factors T , L and Z on $\Delta\mu^{A-P}$ is shown in Table 4. The analysis refers to the description of the experimental space by Eq. 11 where $P_X^{(i)}$ is an orthogonal polynomial of the degree i related to

the effect $X = T$, L and Z and $b_X^{(i)}$ is the corresponding regression coefficient (cf. the analogous variance analysis in Ref. [1]):

$$\begin{aligned} \Delta\mu^{A-P} &= \Delta\mu^{A-P} - \Delta\mu^{C_{78}} \\ &= b_L^{(1)} P_L^{(1)} + b_{L,Z}^{(1,1)} P_L^{(1)} P_Z^{(1)} \\ &\quad + b_{T,L}^{(1,1)} P_T^{(1)} P_L^{(1)} + b_{T,L,Z}^{(1,1,1)} P_T^{(1)} P_L^{(1)} P_Z^{(1)} \\ &\quad + b_{T,L}^{(2,1)} P_T^{(2)} P_L^{(1)} + b_{T,L,Z}^{(2,1,1)} P_T^{(2)} P_L^{(1)} P_Z^{(1)} \\ &\quad + b_L^{(2)} P_L^{(2)} + b_{L,Z}^{(2,1)} P_L^{(2)} P_Z^{(1)} \\ &\quad + b_{T,L}^{(1,2)} P_T^{(1)} P_L^{(2)} + b_{T,L,Z}^{(1,2,1)} P_T^{(1)} P_L^{(2)} P_Z^{(1)} \end{aligned} \quad (11)$$

The terms corresponding to $\varphi = 0$ are not significant, hence they are not included in Eq. 11 (see Table 4). The dependence of $\Delta\mu^{A-P}$ on T is not significant but $\Delta\mu^{A-P}$ varies significantly with Z at the three levels: linear, quadratic and cubic. The terms underlined in Eq. 11 are not signifi-

No	Thermodynamic data: C78/PCL												C78/PBR	
	C78			PCL - C78			Mixture		id PCL([Cl]=1) - C78				PBR - C78	
	ΔH (cal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔC_p	ΔH (cal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔC_p	\bar{h} (cal mol ⁻¹)	s (cal mol ⁻¹ K ⁻¹)	ΔH (cal mol ⁻²)	ΔS (cal l mol ⁻² K ⁻¹)	ΔC_p	σ (cal mol ⁻¹)	$\Delta\mu$ (cal mol ⁻¹)	
41.12	- 9 390	-19.512	10.6	- 94	-0.089**	+ 5.6	+ 1**	-0.149**	-130	-0.333	+ 7.6	1.1	- 34.5	
41.13	-10 164	-20.423	14.3	+ 34**	+0.206*	- 1.4**	+155 ^s	+0.215**	+258	+0.574	- 1.6	0.6	- 23.5	
41.14	- 9 029	-19.434	12.4	- 56	-0.117**	+ 1.2	- 39*	-0.224	-152	-0.527	+ 1.4	0.6	+ 20.9	
41.15	- 9 847	-20.587	13.4	- 25**	-0.062**	- 0.4**	+ 20**	-0.096**	- 33	-0.287	- 0.7	1.7	+ 30.8	

ERROR OF THE COEFFICIENTS (STANDARD DEVIATION)

3.4	0.0061	0.10	3.3	0.0094	1.24	14.6	0.0371	4.7	0.0013	1.75
6.3	0.0154	0.44	23.7	0.0586	1.31	40.2	0.1042	33.5	0.0829	1.85

CONVERSIONS

A	555	7.814	0.7	- 0.5	+0.045	- 0.05	- 1.2	-0.002	- 2.6	+0.062	- 0.07
B	0	-0.026	0	0	0	0	0	0	0	0	0

cant. The standard chemical potential, $\Delta\mu^{A-P}$, can also be expressed in terms of thermodynamic functions, by approximating the function multiplying ΔC_p by the first term of its Taylor series and introducing linear dependence of all functions on Z as follows:

$$\begin{aligned} \Delta\mu^{A-P} = & \varphi_p(\Delta\mu_0^{+,P} + m_0^{+,A-P}) \\ & + \varphi_p z(\delta\mu_z^{+,P} - \delta\mu_z^{+,A} + \delta m_z^{+,A-P}) \\ & - \Delta T \varphi_p \Delta S_0^P - \Delta T_p z(\delta S_z^P - \delta S_z^A) \\ & - \Delta T^2 \varphi_p \frac{\Delta C_{P,0}^P}{2T^+} - \Delta T^2 \varphi_p z \frac{\delta C_{P,z}^P - \delta C_{P,z}^A}{2T^+} \\ & - \varphi_p^2 m_0^{+,A-P} - \varphi_p^2 z \delta m_z^{+,A-P} \\ & + \Delta T \varphi_p^2 s_0^{A-P} + \Delta T \varphi_p^2 z \delta s_z^{A-P} \end{aligned} \quad (12)$$

Comparison of Eqs. 11 and 12 gives the necessary relationships between the coefficients, $b_X^{(j)}$, and thermodynamic functions (see last column of

Table 4). The non-significance of the underlined terms in Eq. 12 (line/term: 3/2, 4/1, 4/2 and 6/2) is interpreted as follows. There is no difference between the entropy of the "methylene increment", δS_z^P , on the stationary phases C₇₈ and PCL (3/2) and the same is true for the partial molar heat capacity of a hypothetical "nullane", $\Delta C_{P,0}^P$, (4/1) and for the heat capacity of the "methylene increment", $\delta C_{P,z}^P$, (4/2). The entropic contribution for the curvature is same for all n -alkanes, δs_z^{A-P} , (6/2).

C₇₈-PCL. Pentane-tetradecane

In addition to the data used for the analysis of variance, standard chemical potentials of higher alkanes, hendecane-tetradecane, were measured on PCL and C₇₈-PCL in the temperature range 130–160°C with C₇₈ as reference. The data set of $3 \times 3 = 9$ points for each higher alkane was evaluated on the basis of the results of the

variance analysis of the lower alkanes (Table 4) as follows. Analysis of the second-order effect LZ and the third-order effect TLZ with the aid of orthogonal polynomials shows that ΔH_z^P and h_z are linear functions of z , whereas $\Delta S_{z,s_z}^P$ and $\Delta C_{P,z}^P$ are independent of the carbon number, z . Imposing these constraints, a multiple regression was performed on the set of 108 (lower alkanes) + 36 (higher alkanes) = 144 data points of $\Delta\mu_z^{A-P}$. The regression coefficients are listed in columns 17–21 in Table 5. The functions ΔH_z^A , ΔS_z^A and $\Delta C_{P,z}^A$ for C_{78} from Ref. [1] are reproduced in columns 14–16 of Table 5. At this point it is important to note that the description of the experimental space for alkanes by Eqs. 11 and 12 was only used for discussing the significance of the terms and that the data listed in Table 5 are the result of fitting Eq. 4 to the experimental points.

Data for the ideal solvent, idPCL ($[Cl] = 1 \text{ mol l}^{-1}$), were calculated as follows. Using the coefficients listed in Table 5 together with the molar volume of PCL (Eq. 9), the slope $\Delta'\mu_z^{\text{idX}}$, was calculated with the aid of Eq. 5 for every 15 K interval in the temperature range 85–160°C for a given alkane. The data $\Delta'\mu_z^{\text{idX}}$ were analysed as a function of T and z and the resulting regression coefficients $\Delta'H_z$, $\Delta'S_z$ and $\Delta'C_{P,z}$ are given in columns 22–24 of Table 5.

PBR. Pentane–tetradecane.

Standard chemical potentials for n -alkanes (C_5 – C_{14}) were measured on PBR solvent only at the reference temperature. $\Delta\mu_z^P$ values are given in the last column of Table 5. On substitution of $\Delta\mu_z^P$ and the molar volume of PBR (Table 1) in Eq. 5 with $m_z^{A-P} = 0$ gives $\Delta'\mu_z^{\text{idX}}$ values for idPBR ($[Br] = 1 \text{ mol l}^{-1}$) at 130°C.

Numerical value of the “methylene increment”,

$\delta\mu_z$

Standard chemical potentials of n -alkanes (C_5 – C_{14}) for the system C_{78} –PCL can be represented as a function of ΔT , φ and a linear function of z by

$$\Delta\mu_z^{A-P} = 3465.8 - 510.49z + 9.712 \Delta T + \pm\sigma = \begin{matrix} 25.4 & 2.60 & 76 \end{matrix}$$

$$\begin{aligned} &+ 1.2379 \Delta Tz + 0.0043 \Delta T^2 - 0.00244 \Delta T^2z \\ &\quad \begin{matrix} 77 & 7 & 7 \end{matrix} \\ &+ 47.5\varphi_P + 2.55\varphi_{Pz} - 0.104 \Delta T\varphi_P \\ &\quad \begin{matrix} 4 & 4 & 19 \end{matrix} \\ &- 0.0062 \Delta T^2\varphi_P + 0.00048 \Delta T^2\varphi_{Pz} \\ &\quad \begin{matrix} 1 & 1 \end{matrix} \\ &+ 6.7\varphi_A\varphi_P + 5.52\varphi_A\varphi_{Pz} + 0.355 \Delta T\varphi_A\varphi_P \\ &\quad \begin{matrix} 3 & 3 & 57 \end{matrix} \end{aligned} \quad (13)$$

The partial derivative of Eq. 13 with respect to the variable z is the “methylene increment”; its value at $\varphi_P = 0$ and $\varphi_P = 1$ is given by Eqs. 14 and 15, respectively:

$$\delta\mu_z^A = -510.5 + 1.2379 \Delta T - 0.00244 \Delta T^2 \quad (14)$$

$$\pm\sigma = \begin{matrix} 2.6 & 77 & 7 \end{matrix}$$

$$\delta\mu_z^P = -507.9 + 1.2379 \Delta T - 0.00196 \Delta T^2 \quad (15)$$

$$\pm\sigma = \begin{matrix} 2.6 & 77 & 7 \end{matrix}$$

Similarly, the data for n -alkanes on the ideal stationary phase “idPCL” at $[Cl] = 1 \text{ mol l}^{-1}$ can be given as a function of ΔT and z by Eq. 16 and the “methylene increment” by Eq. 17:

$$\Delta'\mu_z^{\text{idX}} = 3516.2 + 10.127 \Delta T - 0.0044 \Delta T^2 \quad (16)$$

$$\pm\sigma = \begin{matrix} 25.4 & 76 & 9 \\ -497.0z + 1.2460 \Delta Tz - 0.00172 \Delta T^2z \\ 2.6 & 76 & 9 \end{matrix}$$

$$\delta'\mu_z^{\text{idX}} = -497.0 + 1.246 \Delta T - 0.0017 \Delta T^2 \quad (17)$$

$$\pm\sigma = \begin{matrix} 2.6 & 76 & 9 \end{matrix}$$

3.5. Solution data of solutes other than n -alkanes

Retention indices

Retention indices were determined at 15 K intervals in the temperature range indicated in Table 5 for the stationary phases PCL and C_{78} –PCL. Retention indices on the column packed with C_{78} on the new support were slightly lower than those reported in Ref. [1]. Therefore, retention indices were determined at 130°C on this column and retention indices at other temperatures were calculated by using these data

and the temperature coefficient from Ref. [1]. With the aid of this data set (fifteen points for every solute measured in the temperature range 85–145°C; nine points for those measured in the temperature range 130–160°C), coefficients of Eq. 7 were calculated. It was found that the retention index was a linear function of the composition and of the temperature. A second analysis has been made without considering the non-significant quadratic terms in the regression. The values of the coefficients $I^A \Delta I^P$ at 130°C and the linear temperature dependence of the coefficients are given in columns 5–8 of Table 5. Regression coefficients of Eq. 7 with $i = 0$, the values of κ (calculated using Eqs. 14 and 17) and the molar volume of PCL at 15 K intervals (using Eq. 9) were used in Eq. 8 to calculate the slopes $\Delta'I^{\text{idX}}$ at 15 K intervals in the experimental domain. Linear regression of $\Delta'I^{\text{idX}}$ with temperature resulted in the coefficients listed in columns 9 and 10 of Table 5.

Thermodynamic data

For a given solute, experimental retention indices on the stationary phases $\varphi = 0.5$ and 1 were converted one by one into standard chemical potentials by using Eq. 6 and thermodynamic data for n -alkanes listed in Table 5. Standard chemical potentials on C_{78} were calculated using the retention indices measured on the new C_{78} column at 130°C and the thermodynamic functions $\Delta H_j^{\dagger,A}$, $\Delta S_j^{\dagger,A}$ and $\Delta C_{P,j}^A$ reported in Ref. [1] as follows. For a given solute the retention index difference, $\delta I_j^{\dagger,A}$, was calculated between the new C_{78} column and data reported in Ref. [1] using the equation

$$\delta I_j^{\dagger,A} = I_j^{\dagger,A} (\text{Ref. [1]}) - I_j^{\dagger,A} (\text{new column}) \quad (18)$$

These $\delta I_j^{\dagger,A}$ values were then used together with n -alkane data from Ref. [1] to calculate the corrected standard chemical potentials at T^\dagger with the aid of the equation

$$\delta \mu_j^{\dagger,A} = \left(\frac{\Delta \mu_{z+1}^{\dagger,A} - \Delta \mu_z^{\dagger,A}}{100} \right) \delta I_j^{\dagger,A} \quad (z < j < z + 1) \quad (19)$$

By adding the correction term, $\delta \mu_j^{\dagger,A}$, to the

partial molar enthalpy from Ref. [1], $\Delta H_j^{\dagger,A}$, a corrected set of standard chemical potentials could be calculated for C_{78} by using Eq. 3. Standard chemical potentials on the stationary phases PCL and C_{78} -PCL and the corrected data on C_{78} were analysed together by multiple regression using Eq. 4. The results are given in columns 14–21 of Table 5. Finally, $\Delta'\mu_j^{\text{idX}}$ values were calculated for every solute by the same method as described under n -alkanes. Regression of $\Delta'\mu_j^{\text{idX}}$ as a function of T gave the coefficients $\Delta'H_j^{\text{idX}}$, $\Delta'S_j^{\text{idX}}$ and $\Delta'C_{P,j}^{\text{idX}}$ which are listed in columns 22–24 of Table 5.

Retention index and thermodynamic data of solutes on PBR

Retention indices of solutes measured at 130°C on the stationary phase PBR are given in column 12 of Table 5 as the retention index difference between PBR and C_{78} . Retention index data were converted into standard chemical potentials using Eq. 6 and thermodynamic data for n -alkanes listed in Table 5. Standard chemical potential differences between PBR and C_{78} are presented in column 26 of Table 5.

4. Results

In Table 5 are listed retention data for the molecular probes. As already mentioned, all regressions concerning retention indices are based on experimental retention index data and all thermodynamic functions are calculated from regressions based on experimental standard chemical potentials. The latter data were obtained by converting experimental retention indices point by point with the aid of standard chemical potentials of n -alkanes as fixed points. The separate treatment of the two data sets has the following consequences.

A first consequence of the separate treatment is that the conversion of retention indices calculated with coefficients listed in Table 5 into a given standard chemical potential will not give exactly the same result as the same standard chemical potential calculated with thermodynamic functions listed in the right-hand side of

Table 5 (and vice versa). The difference between the two results will be more important at higher deviations from the central temperature of the experimental temperature range of determination.

A second consequence of the separate treatment of the two types of retention data is that analogous regression coefficients may be significant in one experimental space and not significant in the other. Let us note that, at constant temperature, the standard chemical potential of a solute is approximately quadratic whereas the retention index is a linear function of the composition of the PCL–C₇₈ mixed stationary phase. (In Table 5 the non-significant regression coefficient, A_L , is not listed, contrary to the corresponding regression coefficients, \hat{h} and s , for the standard chemical potentials.) From this observation we conclude that the curvature of the function $\Delta\mu_j^{A-P}(\varphi_P)$ of a solute, characterized by $m_j^{A-P} = \hat{h} - Ts$, must be nearly the same as the curvature of the same function of an n -alkane having the same retention index as the solute, m_z^{A-P} . The value of the coefficient m_z^{A-P} as a function of the carbon number and the temperature difference, $\Delta T = T - T^+$, is given by the regression

$$m_z^{\text{PCL-A}} = 6.7 + 5.52z - 0.355 \Delta T \quad (20)$$

$$\pm \sigma = 0.3 \quad 0.03 \quad 0.057$$

Eq. 20 permits the calculation of the coefficient $m_z^{\text{PCL-A}}$ for any hypothetical alkane with fractional carbon numbers. In Fig. 2 are plotted experimental regression coefficients of solutes, $m_j^{\text{PCL-A}}$, as a function of the same coefficients of hypothetical n -alkanes, $m_z^{\text{PCL-A}}$, having the same retention index as the solutes, $z^* = I_j^A/100$. The correlation $m_j^{\text{PCL-A}}/m_z^{\text{PCL-A}}$ is satisfactory and can be given by

$$m_j^{\text{PCL-A}} = 3.6 + 0.905m_z^{\text{PCL-A}} + 0.108 \Delta T - 0.0029m_z^{\text{PCL-A}} \Delta T \quad (21)$$

$$\pm \sigma = 2.7 \quad 0.055 \quad 0.045 \quad 0.0006$$

Finally, let us recall that in Table 5 retention indices and partial molar enthalpies of the solutes at 130°C in the non-polar standard C₇₈ are slightly different from those reported in Ref. [1].

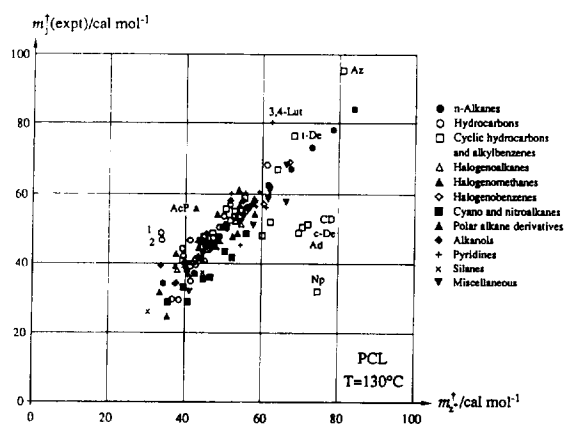


Fig. 2. Plot of experimental regression coefficients, m_j , in Eq. 4 of solute j ("curvature") as a function of those of hypothetical n -alkanes, m_z^* , calculated with Eq. 20, in C₇₈–PCL mixtures. Outliers: 1 = 1-pentene; 2 = 1-pentyne; CD = cyclodecane; c-De = *cis*-decalin; t-De = *trans*-decalin; Ad = adamantane; Np = naphthalene; Az = azulene; AcP = acetoxopropane; 3,4-Lut = 3,4-lutidine.

In fact, slight variations of the activity of the support do influence these data. For the sake of self-consistency, a C₇₈ column was prepared with the batch of support used in this study and retention indices of all solutes were determined at 130°C. Differences between values reported in Ref. [1] and this work are slightly positive and amount to 0–2 i.u. This difference was then converted into standard chemical potential difference and added to partial molar enthalpies reported in Ref. [1] to give those listed in Table 5.

5. Discussion

The main objective of this project was the study of the influence of the polarizability of the dipolar interacting group, X, on the interaction force between solute and the group X. The additional effect of the interacting group is best characterized by the $\Delta'I$ value of the molecular probe defined in Eq. 8. This value is the index difference of a solute in a hypothetical 1 M ideal solution of the interacting group X with reference of the solute in an isosteric alkane. Fig. 3 shows $\Delta'I$ -values in the ideal 1 M solution for X = PBR as a function of the $\Delta'I$ -value for X =

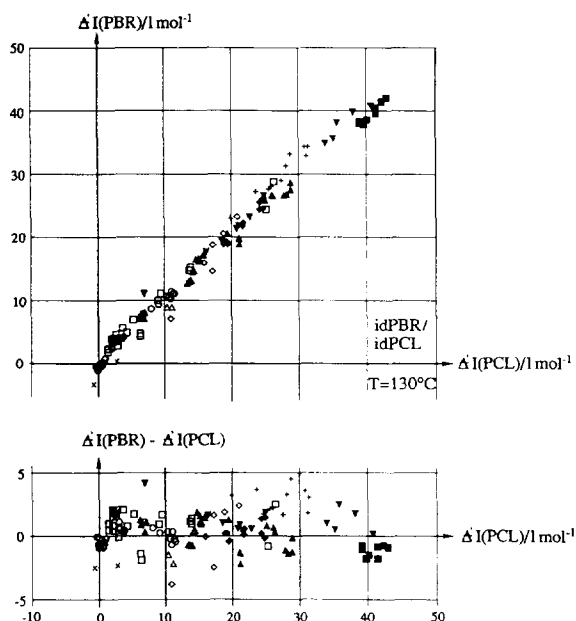


Fig. 3. Retention index difference of solutes in an ideal 1 *M* solution of the interacting groups PBR and in an ideal solution in C_{7N} ($\Delta'I$ values) as a function of the same difference in PCL and C_{7N} . At the bottom are shown the differences of their differences.

PCL. There is an excellent correlation between additional forces in the two solvents and, at first glance, the effect of the higher polarizability of the bromo substituent seems to be negligible. At the bottom of the figure are plotted differences between the $\Delta'I$ values of a solute in PBR and in PCL. The differences never exceed ± 5 i.u. and do not correlate with the amplitude of the $\Delta'I$ value in PCL.

In Fig. 4, these differences are compared with those measured in an ideal solution of trifluoromethylalkane groups. These interacting groups have a slightly higher dipole moment compared with that of the chloro- and bromoalkane groups (2.3 versus 2.1 D) but the group polarizability is smaller, i.e., it is a “harder” group. The plot in Fig. 4 shows that these interaction force differences correlate. Based on these comparisons, we propose that contributions due to polarizability are not negligible. However, it is certainly not a linear function of the parameter called polarizability measured by some classical characteristic number such as group polarizability. Some

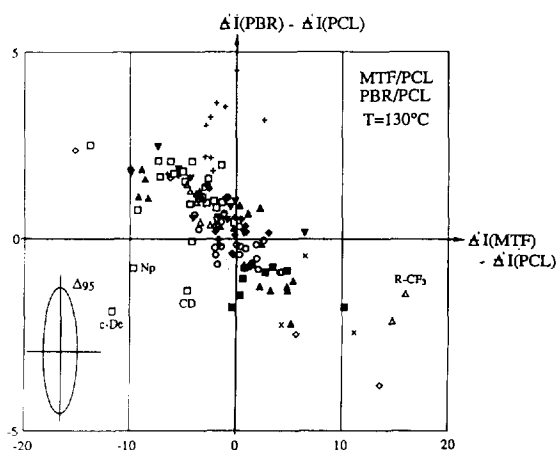


Fig. 4. Differences between the $\Delta'I$ values in ideal 1 *M* solutions of PBR–PCL as a function of those in the pair MTF–PCL. Outliers: CD = cyclodecane; c-De = *cis*-decalin; Np = naphthalene; R- CF_3 = trifluoroalkanes.

possible measures of group polarizability are shown in Fig. 5; the influence of additional polarizability in the MTF–PCL system is about four times greater than that with the PBR–PCL pair, whereas the polarizability is not four times different.

We did not succeed in correlating these MTF–PCL differences with molecular properties characteristic of the polarizability of the solute and the interacting group X. As a possible experimental measure of the interaction by polarizability we propose the coefficient A_X in

$R_X/cm^3 \text{ mol}^{-1}$	9.7	10.5	13.4
$\alpha_X/10^{-24} \text{ cm}^3$	3.83	4.16	5.31
$V_X/10^{-24} \text{ cm}^3$	52.4	36.3	40.9
α_X/V_X	0.073	0.115	0.130

Fig. 5. Comparison of molar refraction, R_X , [8] polarizability, α_X , and Van der Waals volume, V_X , [9] of the three polar groups, X = MTF, PCL and PBR. A possible measure of the “hardness” of the groups, α_X/V_X , is also given.

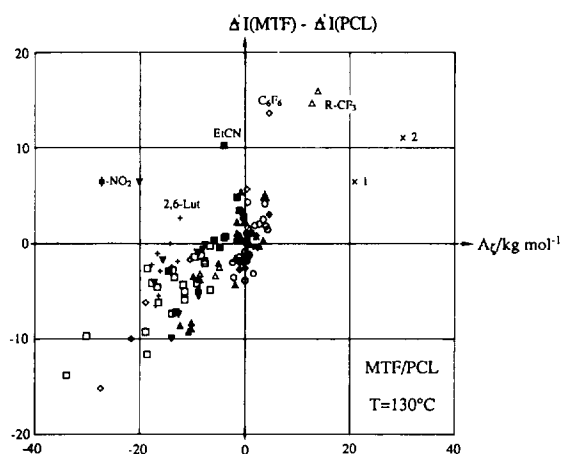


Fig. 6. Differences of the ΔI values between trifluoromethyl (MTF) and primary chloro (PCL) groups in ideal 1 M solutions as a function of the constant A_ζ of Eq. 22. The value of the coefficients are slightly different from those published in Ref. [11]. They are unpublished data determined on capillary columns coated with a C_{67} and C_{103} alkane from Ref. [17]. Outliers: R-CF₃ = trifluoroalkanes; EtCN = cyanoethane; C₆F₆ = hexafluorobenzene; 2,6-Lut = 2,6-lutidine; 1 = hexamethyldisilane; 2 = hexamethyldisiloxane.

the equation [10,11]

$$I = I_\infty + A_\zeta \zeta \quad (22)$$

where ζ is the inverse of the molecular mass of the alkane solvent. Actually, following London [12,13], in these solvents (no polarity) the interaction between a solute and solvent should be proportional to the polarizability of the interacting molecules. Eq. 22 can be interpreted in two ways. First, it can be assumed that the effect of the molecular mass (molar volume) of the alkane solvent on the retention index is purely entropic, as proposed by Flory [14,15] and Huggins [16]. Second, it can be assumed that the interaction between solute and alkane is proportional to the density of the interacting alkane solvent. It is obvious that density and the variable ζ are linearly correlated. Following the latter model the effect would be enthalpic and the first derivative of Eq. 22, the constant A_ζ , would be a measure of the change in the interaction force

with the polarizability of the solvent. Fig. 6 shows that there is a fair correlation between the difference in the ΔI values in the ideal MTF and PCL solutions and the coefficients A_ζ .

Acknowledgements

This paper reports part of a project supported by the Fonds National Suisse de la Recherche Scientifique. The authors gratefully acknowledge the help of Dr. R. Cloux in the synthesis of stationary liquids.

References

- [1] K.S. Reddy, J.-Cl. Dutoit and E.sz. Kováts, *J. Chromatogr.*, 609 (1992) 229.
- [2] R.C. Reid, J.M. Prausnitz and T.K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 3rd ed., 1977.
- [3] K.S. Reddy, R. Cloux and E.sz. Kováts, *J. Chromatogr. A*, 673 (1994) 181.
- [4] R. Cloux, G. Défayes, K. Fóti, J.-Cl. Dutoit and E.sz. Kováts, *Synthesis*, (1993) 909.
- [5] G.A. Huber and E.sz. Kováts, *Anal. Chem.* 45 (1973) 1155.
- [6] G. Körösi and E.sz. Kováts, *J. Chem. Eng. Data*, 26 (1981) 323.
- [7] R.A. Fisher and F. Yates, *Statistical Tables*, Oliver and Boyd, Edinburgh, 6th ed., 1963.
- [8] R.C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 67th ed., 1986, p. E-372.
- [9] A. Bondi, *Physical Properties of Molecular Liquids, Crystals and Glasses*, Wiley, New York, 1968.
- [10] D.F. Fritz and E.sz. Kováts, *Anal. Chem.*, 45 (1973) 1175.
- [11] G. Défayes, D.F. Fritz, T. Görner, G. Huber, Ch. de Reyff and E.sz. Kováts, *J. Chromatogr.*, 500 (1990) 139.
- [12] F. London, *Z. Phys.*, 62 (1930) 245.
- [13] J. Mahanty and B.W. Ninham, *Dispersion Forces*, Academic Press, London, 1976.
- [14] P.J. Flory, *J. Chem. Phys.*, 9 (1941) 660.
- [15] P.J. Flory, *J. Chem. Phys.*, 10 (1942) 51.
- [16] M.L. Huggins, *J. Chem. Phys.*, 9 (1941) 440.
- [17] P. Zeltner, G.A. Huber, R. Peters, F. Tátrai, L. Boksányi and E.sz. Kováts, *Helv. Chim. Acta*, 62 (1979) 2495.