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# Pair-wise interactions by gas chromatography
# IV. Interaction free enthalpies of solutes with trifluoromethyl-substituted alkanes

K.S. Reddy, R. Cloux, E.sz. Kováts*

*Laboratoire de Chimie Technique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

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**Abstract**

Two polar-type liquids were used as stationary phases, one being a mono(trifluoromethyl) (MTF) and the other a tetrakis(trifluoromethyl) (TTF) derivative of the parent branched alkane, $C_{78}H_{158}$ (C78). Gas chromatographic data for about 160 molecular probes were measured on pure MTF and on C78–TTF mixtures at several temperatures. It was found that data on MTF are the same as data on a C78–TTF mixture with $\varphi_{TTF} = 0.25$, both melts having the same molar concentration of trifluoromethyl groups. Interaction free enthalpies were calculated from data measured on C78–TTF mixtures between the probe and a trifluoromethyl group, both at infinite dilution.

## 1. Introduction

The objective of this 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 in an alkane solvent. A series of interacting groups are proposed for characterizing different types of intermolecular forces such as dispersion- and polar-type interactions. The measuring system consists of a family of isosteric and isomorphous solvents, L, shown in Fig. 1, having molecules of the same size and form, and suitable for use as stationary phases in gas chromatography. The family includes a standard paraffin, A = C78 ($C_{78}H_{158}$), and a series of polar compounds, P, in which a methyl or an ethyl group is substituted for an interacting group, X. The synthesis of members of this family was reported in Part III [2]. With these stationary phases at hand, the method consists in measuring gas chromatographic data for a solute on a series of A–P mixtures at several tempera-

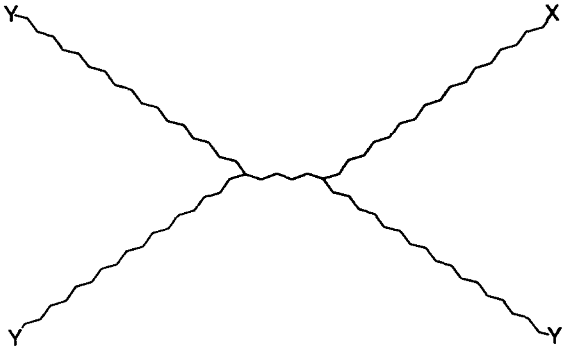

Fig. 1. Structure of the applied stationary phases: C78: X = Y = $CH_3$; MTF (monotrifluoromethyl): X = $CF_3$, Y = $CH_3$; TTF (tetrakistrifluoromethyl): X = Y = $CF_3$.

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* Corresponding author.

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tures, to convert these data into standard chemical potentials and to extrapolate the results to infinite dilution of the interacting group, $[X] \rightarrow 0$, with the aid of simple laws of regular mixtures [3,4]. In Part I the method was described in detail and was shown to give the desired data on the example of a stationary phase, P, having primary hydroxyl, POH, as an interacting group, X. The results have been shown (Part II) [5] to compare well with spectroscopic and calorimetric measurements of hydrogen bonding interactions.

In this paper we report the interaction free enthalpies of a series of chosen solutes at infinite dilution with an "alone-standing" trifluoromethylalkane "dissolved" in an alkane solvent. Such a group is thermostable and chemically inert. Bonded to an alkane chain, the group has a relatively high dipole moment (*ca.* 2.3 D [6]), hence it was hoped that such a stationary phase would measure the interaction of a solute with a permanent dipole [7–9]. It will be seen that the situation is more complicated and at present we cannot offer a satisfactory interpretation of the results.

Interaction free enthalpies between solutes and trifluoromethylalkane groups are considerably weaker than those between solutes and primary hydroxyl functions. Therefore, for this study we considered the question of whether a stationary phase substituted with more than one weakly interacting group, such as tetrakis(trifluoromethyl) (TTF) ($X = Y = CF_3$ in Fig. 1) may be applied for experimentation. In order to answer this question, data were measured on C78–TTF mixtures and the results were represented with the aid of Eq. 5 as a function of the composition. It will be shown that results on an appropriate C78–TTF mixture are very close to those measured on a pure mono(trifluoromethyl) (MTF) derivative ($X = CF_3$, $Y = CH_3$ in Fig. 1).

## 2. Theoretical

Detailed derivation of the necessary equations was given in Part I. A short summary of the essential equations is presented here for understanding the Experimental section and Table 6.

The molal Henry coefficient of a solute, $g_j$, can be calculated from the specific retention volume, $V_{g,j}$ (not reduced to 0°C) by using the equation

$$V_{g,j} = V_{N,j}/w_L = \mathcal{R}T/1000g_j \tag{1}$$

where $V_{N,j}$ is for the net retention volume at temperature $T$ (K), $w_L$ is the mass of the stationary liquid $L = A$, P or A–P, in the column, and $\mathcal{R}$ (cm$^3$ atm mol$^{-1}$ K$^{-1}$; 1 atm = 101 325 Pa) is the universal gas constant. The standard chemical potential of a solute, $j$, with reference to the (ideal) gas phase is given by

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

By assuming that the partial molar heat capacity difference of the solute between the liquid and gas phase, $\Delta C_{P,j}^L$, is constant in the experimental temperature domain of *ca.* 100 K (Kirchhoff's approximation), the temperature dependence of the standard chemical potential can be described with adequate precision by

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

where $\Delta H_j^L$ and $\Delta S_j^L$ are the partial molar enthalpy and entropy difference, respectively, at the standard temperature $T^\dagger$. The standard chemical potential difference of a solute, $j$, in a liquid, L, with reference to the ideal dilute solution in the standard alkane, $A = C78$, is given by

$$\boldsymbol{\Delta}\mu_j^L = \Delta\mu_j^L - \Delta\mu_j^A = \boldsymbol{\Delta}H_j^L - T\,\boldsymbol{\Delta}S_j^L + \boldsymbol{\Delta}C_{P,j}^L\left[T - T^\dagger - T\ln\left(\frac{T}{T^\dagger}\right)\right] \tag{4}$$

If the liquid, L, is a regular mixture of A and P, then the standard chemical potential of the solute, $j$, as a function of the composition is given by the relationship

$$\boldsymbol{\Delta}\mu_j^{A/P} = \varphi_P\,\boldsymbol{\Delta}\mu_j^P + \varphi_A\varphi_P m_j^{A/P} \tag{5}$$

where $\varphi_P$ is the volume fraction of P in the binary A–P mixture ($\varphi_A + \varphi_P = 1$) and $\boldsymbol{\Delta}\mu_j^P$ is the standard chemical potential of the solute in pure P ($\varphi_P = 1$) with reference to A ($\varphi_P = 0$). In mixtures of the isosteric solvents, A and P, the following relationship holds for the excess chemical potential $m_j^{A/P}$:

$$m_j^{A/P} = \hbar_j - Ts_j \qquad (6)$$

If the specific volume of an A–P mixture can be given as a linear combination of those of the individual components (no excess volume on mixing), the relationship between the volume fraction, $\varphi_P$, and the molar concentration of the interacting group, [X], is given by

$$\varphi_P = v_P[X]/1000n \qquad (7)$$

where $v_P$ (ml mol$^{-1}$) is the molar volume of P at temperature $T$ and $n$ is the number of interacting groups, X, in the molecule ($n = 1$ for MTF and $n = 4$ for TTF). Use of Eqs. 5 and 7 gives for the interaction free enthalpy of the solute $j$ in the A–P mixture at ideal dilution

$$\begin{aligned} \bar{\Delta}'\mu_j^{idX} &\equiv \left(\frac{\partial \bar{\Delta}\mu_j^{A/P}}{\partial[X]}\right)_{T,[X]=0} \\ &= \left(\frac{\partial \bar{\Delta}\mu_j^{A/P}}{\partial \varphi_P}\right)_{T,\varphi_P=0} \left(\frac{\partial \varphi_P}{\partial[X]}\right)_T \\ &= (\bar{\Delta}\mu_j^P + m_j^{A/P}) v_P/1000n \qquad (8) \end{aligned}$$

Eq. 8 is the necessary relationship for calculating the interaction free enthalpy of the group X at infinite dilution with a solute also at infinite dilution, with reference to the alkane solvent. The meaning and use of Eq. 8 are illustrated in Fig. 2 on the example of three solutes, $6 = n$-hexane, $7 = n$-heptane and $j$ = butyronitrile in mixtures of C78 and TTF. Note that in Fig. 2 chemical potentials are shown with reference to the gas phase ($\Delta$) and not with reference to the dilute solution in C78 ($\bar{\Delta}$).

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 by the standard chemical potentials of the $n$-alkanes:

$$\begin{aligned} I &= 100 \frac{\Delta\mu_j^L - \Delta\mu_z^L}{\Delta\mu_{z+1}^L - \Delta\mu_z^L} + 100z \\ &= 100 \frac{\delta\mu_{j/z}^L}{\delta\mu_z^L} + 100z \qquad (9) \end{aligned}$$

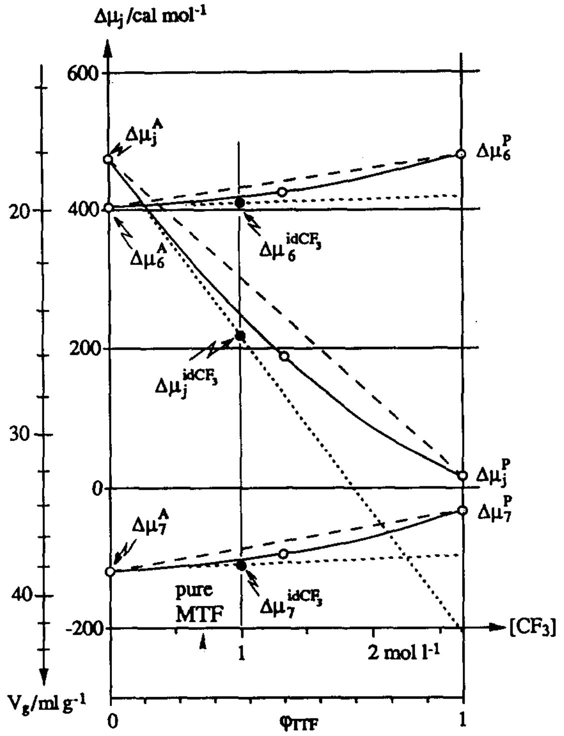

Fig. 2. Dependence of the standard chemical potential of a solute on composition in C78–TTF mixtures illustrated on the example of $6 = n$-hexane, $7 = n$-heptane and $j$ = butyronitrile at 130°C. $V_g$ is the specific retention volume, $\varphi_{TTF}$ is the volume fraction of TTF and [CF$_3$] is the molar concentration of trifluoromethyl groups in the liquid mixture applied as stationary phase. Reference state for all data: ideal gas in equilibrium with the stationary liquid. In Table 6 data are listed with reference to those in C78, *i.e.*, all data are equal to zero at $\varphi_{TTF} = [CF_3] = 0$.

where $\delta$ designates the difference between the standard chemical potential of two substances in the same solvent. In our mixtures of similar solvents the retention index can be given by the following approximation:

$$\bar{\Delta}I_j^{A/P} = I_j^{A/P} - I_j^A = \varphi_P \bar{\Delta}I_j^P + \varphi_A\varphi_P i_j^{A/P} \qquad (10)$$

where

$$\bar{\Delta}I_j^P = \bar{\Delta}I_{130,j} + \bar{\Delta}A_{T,j}\Delta T + \bar{\Delta}A_{TT,j}\Delta T^2 \qquad (11)$$

and

$$i_j^{A/P} = A_{L,j} + A_{LT,j}\Delta T \qquad (12)$$

and the other symbols are as before. Using Eqs. 7 and 10, the retention index difference of a solute at infinite dilution of the interacting group X in A is given by

$$\left(\frac{\partial \Delta I_j^{\mathrm{A/P}}}{\partial [\mathrm{X}]}\right)_{T,[\mathrm{X}]=0} = (\Delta I_j^{\mathrm{P}} + i_j^{\mathrm{A/P}})v_{\mathrm{P}}/1000n \qquad (13)$$

Note that, as shown in ref. 1, the retention index of solute, $j$, in a hypothetical ideal mixture of A and P is given by

$$\begin{aligned} I_j^{\mathrm{A/idX}} &= I_j^{\mathrm{A}} + \left(\frac{\partial \Delta I_j^{\mathrm{A/P}}}{\partial [\mathrm{X}]}\right)_{T,[\mathrm{X}]=0} \frac{[\mathrm{X}]}{1+[\mathrm{X}]\kappa} \\ &= I_j^{\mathrm{A}} + \Delta' I_j^{\mathrm{idX}} \qquad (14) \end{aligned}$$

with

$$\kappa = (\delta' \mu_z^{\mathrm{idX}} - \delta' \mu_z^{\mathrm{A}})/\delta \mu_z^{\mathrm{A}} \qquad (15)$$

where $\delta'\mu_z^{\mathrm{A}}$ and $\delta'\mu_z^{\mathrm{idX}}$ are the values of the slope of the function $\delta\mu_z^{\mathrm{A/idX}}([\mathrm{X}])$ at $[\mathrm{X}] = 0$ and 1 mol $\mathrm{l}^{-1}$, respectively. In the case of C78–TTF mixtures, the value of $\kappa$ is of the order of 0.02 l $\mathrm{mol}^{-1}$, and consequently the value of the correcting factor in Eq. 14 is of the order of 0.98.

## 3. Experimental

### 3.1. Materials

Solutes were research-grade compounds from Fluka (Buchs, Switzerland). The preparation of the stationary liquids, 19,24-dioctadecyldotetracontane (C78) and 1,1,1-trifluoro-19,24-dioctadecyldotetracontane (MTF) was reported previously [2,10]. The stationary liquid TTF was prepared from dimethyl adipate (from Fluka) and 18,18,18-trifluorooctadecyl bromide (synthesized following ref. 11) in an analogous procedure to that described previously [10] as follows.

*19,24-Bis(18,18,18-trifluorooctadecyl)-1,1,1,42,42,42-hexafluorodotetracontane-19,24-diol (TTF-diol)*

In a 250-ml three-necked round-bottomed flask, Mg (2.40 g, 100 mmol) was covered with tetrahydrofuran (THF) (20 ml) in an argon atmosphere, then 1,2-dibromoethane (0.94 g, 5.0 mmol) was added (activation of Mg). When evolution of ethylene had stopped, first a solution of 18,18,18-trifluorooctadecyl bromide (15.5 g, 40.0 mmol) in THF (40 ml) was added dropwise and the mixture was heated at reflux for 3.0 h. At this temperature, a solution of dimethyl adipate (1.57 g, 9.0 mmol) in THF (10 ml) was added dropwise (*ca.* 20 min.). The mixture was refluxed for a further 2.0 h and allowed to stand overnight at room temperature. After hydrolysis with saturated aqueous $NH_4Cl$ (50 ml), the aqueous phase was extracted with cyclohexane (100 ml), the combined organic phase was dried ($Na_2SO_4$) and the solvent was removed in a rotary evaporator. The residue (13.85 g) was dissolved in cyclohexane (40 ml) and filtered on silica gel (100 g). With cyclohexane (600 ml) as eluent, a mixture of 1,1,1-trifluorooctadecane and 1,1,1,36,36,36-hexafluorohexatriacontane was eluted (3.13 g), then with cyclohexane–diethyl ether (50:50) (500 ml) 10.39 g of crude TTF-diol. The latter fraction was recrystallized from ethanol–cyclohexane (90:10) (300 ml) at 5°C to give 9.70 g (80%) of pure TTF-diol as a white powder, m.p. 44–45.5°C. IR ($CCl_4$, $CS_2$): $\nu = 3620$, 2920, 2860, 1465, 1390, 1255, 1145, 840, 720, 655 $\mathrm{cm}^{-1}$. $^1$H NMR ($C^2HCl_3$, TMS): $\delta = 1.27$ (m, 126H), 1.55 (m, 12H), 2.06 ppm (m, 8 protons). $^{13}$C NMR ($C^2HCl_3$, TMS): $\delta = 21.84$ (q, $J = 2.7$), 23.52, 24.14, 28.71, 29.17, 29.35, 29.55, 29.68, 30.32, 33.76 (q, $J = 28$), 39.35, 74.40, 127.31 ppm (q, $J = 276$ Hz).

*19,24-Bis(18,18,18-trifluorooctadecyl)-1,1,1,42,42,42-hexafluorodotetracontane (TTF)*

In a 250-ml round-bottomed flask equipped with a Dean–Stark trap, TTF-diol (9.62 g, 7.16 mmol) and *p*-toluenesulphonic acid monohydrate (0.14 g, 0.74 mmol) were dissolved in benzene (100 ml). The reaction mixture was heated at reflux for 3.0 h, then it was allowed to cool to room temperature and the acid was extracted with saturated aqueous $NaHCO_3$ (50 ml). The aqueous phase was extracted with hexane (50 ml), the combined organic phase was dried ($Na_2SO_4$) and the solvent was removed in a rotary evaporator. The residue (9.37 g) was dissolved in hexane (50 ml) and filtered on a silica gel (100 g) column. With hexane (700 ml) were eluted 6.04 g of a mixture of 19,24-bis(18,18,18-trifluorooctadecyl)-1,1,1,42,42,42-hexafluorodotetraconta-A,B-dienes with A = 18 or 19 and B = 23 or 24. This TTF-dienes mixture was dissolved in cyclohexane (400 ml), transferred into a stainless-steel autoclave and 10% Pd–C (0.55 g) was added. The mixture was hydrogenated at 40°C and 10 bar $H_2$ pressure for 18 h. The catalyst was filtered on silica gel (20 g), then eluted with additional cyclohexane (100 ml). After removal of the solvent in a rotary evaporator, the crude TTF (6.04 g) was dissolved in a mixture of absolute ethanol (100 ml)–cyclohexane (40 ml) at 45°C and the product was crystallized at 5°C. The white crystalline powder was filtered, washed with a cold mixture of absolute ethanol (50 ml)–cyclohexane (20 ml) and finally dried in air to give 5.82 g (62%) of pure TTF, m.p. 54.5–57.5°C. IR ($CCl_4$, $CS_2$): $\nu = 2920, 2850, 1465, 1385, 1255, 1145, 840, 720, 655\ \text{cm}^{-1}$. $^1H$ NMR ($C^2HCl_3$, TMS): $\delta = 1.27$ (m, 126H), 1.56 (m, 12H), 2.06 ppm (m, 8 protons). $^{13}C$ NMR ($C^2HCl_3$, TMS): $\delta = 21.88$ (q, $J = 2.8$), 26.81, 27.24, 28.75, 29.21, 29.40, 29.59, 29.66, 29.75, 30.21, 33.80 (q, $J = 28$), 33.85, 37.52, 127.34 ppm (q, $J = 276$ Hz).

### *Densities*

Densities were measured on samples of about 2 g with an ASTM Model 941/78 pycnometer from Schmizo (Zofingen, Switzerland) at 10 K intervals in the temperature range 80–200°C. Eq. 16 was fitted on the experimental points, corrected for vacuum, by linear regression:

$$\ln \rho_L = \ln M_L - \ln v_L = \ln \rho^\dagger - \alpha^\dagger \Delta T - B \Delta T^2 \qquad (16)$$

where $\rho^\dagger$ is the density and $\alpha^\dagger$ is the isobaric coefficient of thermal expansion at the standard temperature $T^\dagger = 130.0 + 273.15 = 403.15$ K and $B = (1/2)(d\alpha/dT)$ [12]. Coefficients of Eq. 16 for the stationary liquids are listed in Table 1. Fig. 3 shows that the ratio of the molar volumes of the stationary phases C78–MTF and C78–TTF is reasonably near unity over the whole temperature range.

### *Support*

For the preparation of the support, a batch of Chromosorb G HP from Supelco (Bellefonte, PA, USA) was sieved and the fraction with particle diameter 150–180 μm was deactivated

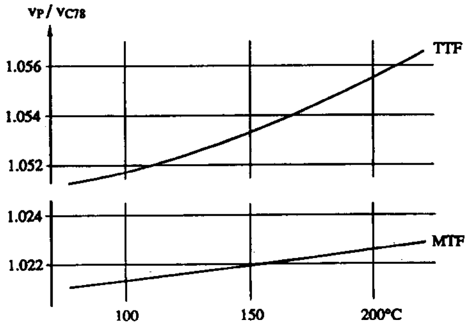

Fig. 3. Ratio of the molar volume of the P and C78 stationary phases as a function of temperature. P = MTF and TTF.

Table 1
Physical properties of the stationary phases

| L | | M.p. (°C) | $M$ (g mol$^{-1}$) | $\rho^\dagger$ (g cm$^{-3}$) | $v^\dagger$ (cm$^3$ mol$^{-1}$) | $\alpha^\dagger \cdot 10^4$ (K$^{-1}$) | $B \cdot 10^7$ (K$^{-2}$) | $\sigma$ |
|---|---|---|---|---|---|---|---|---|
| Symbol | Formula | | | | | | | |
| C78 | $C_{78}H_{158}$ | 69–75 | 1096.1 | 0.7714 | 1420.9 | 7.62 | 1.26 | 0.0004 |
| MTF | $C_{77}H_{155}CF_3$ | 69–74 | 1150.1 | 0.7922 | 1451.8 | 7.74 | 1.29 | 0.0007 |
| TTF | $C_{74}H_{146}(CF_3)_4$ | 54–58 | 1312.0 | 0.8772 | 1495.7 | 7.92 | 2.54 | 0.0008 |
| $\Delta_{95}$ | | | | ±0.00009 | ±0.17 | ±0.34 | ±0.93 | |

$M$ = Molar mass; $\rho^\dagger$, $\alpha^\dagger$ and $B$ = regression coefficient of Eq. 16 for the calculation of the density in the temperature range 80–210°C; $v^\dagger$ = molar volume at the standard temperature $T^\dagger = 403.15$ K. Data for C78 are from ref. 12.

by treatment with trimethyl(dimethylamino)silane (Fluka) at 250°C as described in ref. 1, where the preparation of column packings is also given. Columns (coiled Pyrex tubes, 330 cm × 0.40 cm I.D.) were weighed before and after packing; the mass difference gave the amount of stationary phase in the column. Column characteristics are given in Table 2. Columns were stored under argon. Two series of columns, (a) and (b), were prepared independently for each stationary liquid in order to estimate the importance of weighing errors.

### 3.2. Apparatus

Details of the gas chromatograph used for the determination of retention were presented previously [1,13]. In summary, a modified Packard-Becker (Delft, Netherlands) Model 439 gas chromatograph equipped with two thermal conductivity detectors was used. The temperature in the oven was measured with a Pt sensor (100 Ω; DIN 43710) and a measuring device from Systemteknik (Lidingoe, Sweden) Model S 1220. The Pt sensor was calibrated by the Eidg. Amt für Messwesen (Berne, Switzerland) between 0 and 400°C with a precision of ±0.1 K. The temperature gradient in the oven was measured with chromel–alumel thermocouples at eight points. The mean column temperature was calculated by considering the temperature gradient as described in ref. 14. IR spectra were recorded on a Perkin-Elmer (Norwalk, CT, USA) Model 684 spectrophotometer. $^1H$ NMR spectra were recorded at 200 MHz and $^{13}C$ NMR spectra were measured at 50 MHz on a Model AC-P 200 spectrometer from Bruker (Spectrospin, Fällanden, Switzerland).

Table 2
Characteristics of the chromatographic columns

| Column | Series | $100\varphi_P$ (%) | $w_L$ (g) | $P_L$ (%) |
|---|---|---|---|---|
| C78[a] | | | 2.101 | 6.81 |
| MTF | (a) | | 1.771 | 6.13 |
| | (b) | | 1.695 | 6.10 |
| C78–TTF | (a) | 50.0 | 1.946 | 6.04 |
| | (b) | 50.0 | 1.895 | 5.89 |
| TTF | (a) | | 1.889 | 6.12 |
| | (b) | | 1.819 | 5.97 |

$\varphi_P$ = Volume fraction of the polar solvent in the A–P mixture at 130°C; $w_L$ = mass of the stationary liquid in the column; $P_L$ = mass percentage of $L$ of the packing ($100w_L$/total mass).

[a] Data reported in Table 6 were measured on this column.

### 3.3. Retention data

Determination of retention data was described in detail previously [1,13]. In summary, the helium carrier flow was regulated with a Model 5850TR flow controller (Brooks, Veenendaal, Netherlands); flow-rates were measured by means of a soap-film flow meter; inlet and outlet pressures were measured with a Model 710B precision device (Heise, Bassweiler, Germany). Retention time was determined at the peak maximum with a Model 3396A integrator (Hewlett-Packard, Palo Alto, CA, USA). Neon was used for the determination of the hold-up time. Inlet pressures never exceeded 1.5 bar, and it was assumed that gas-phase imperfections were negligible. The overall reproducibility of the retention volume of neon was better than 1%. Retention data were measured at 20 K intervals between 90 and 210°C at experimental temperatures as near as possible to the envisaged nominal temperature. The experimental temperature did not change by more than 0.2 K during a working day. The first, last and the mid-day chromatograms of a working day were for a mixture of $n$-alkanes, $C_zH_{2z+2}$, always containing the alkanes with $z = 5$–$10$. Retention indices of all solutes were evaluated with the average net retention time of the alkanes if their individual values did not deviate by more than 1%. Otherwise, data for the working day were rejected.

#### Standard chemical potentials

After having measured all data on a given column, specific retention volumes of $n$-alkanes were converted into standard chemical potentials (see Eq. 2). With data determined near a given nominal temperature, the following average was calculated:

$$\Delta\mu_z(\bar{T}_{\mathrm{exp}}) = [\Delta\mu_z(T_{\mathrm{exp},1}) + \cdots + \Delta\mu_z(T_{\mathrm{exp},n})]/n \qquad (17)$$

where $T_{\mathrm{exp},i}$ is the experimental temperature of the $i$th determination near a nominal temperature, $n$ is the number of determinations and

$$\bar{T}_{\mathrm{exp}} = (T_{\mathrm{exp},1} + \cdots + T_{\mathrm{exp},n})/n \qquad (18)$$

A quadratic regression was now fitted to every data set for an alkane measured on the same stationary liquid to give the dependence of the chemical potential on temperature, $\Delta\mu_z(T)$. Chemical potentials measured at $\bar{T}_{\mathrm{exp}}$ were then corrected to $T_{\mathrm{nom}}$ by using the first derivative of the quadratic regression.

### *Retention indices*

Retention indices at nominal temperatures were calculated 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 MTF columns*

Specific retention volumes of $n$-alkanes were determined on both series of MTF columns; they were systematically lower on columns of series (b) by about 1% (weighing error). Experimental standard chemical potentials were calculated for both series of columns for every alkane at every nominal temperature and the average of the data obtained on both columns was used for further calculations.

### *Correction for weighing errors on TTF and C78/TTF columns*

On columns of series (a), data were determined at all temperatures. On columns of series (b), specific retention volumes of $n$-alkanes were determined at 90, 130 and 170°C only. Assuming that specific retention volumes differ on both series of columns owing to weighing errors by a factor $f = V_g^{(b)}/V_g^{(a)}$, the difference between the standard chemical potentials on the two columns is given by

$$RT \ln f = \Delta\mu_z^{(a)} - \Delta\mu_z^{(b)} \qquad (19)$$

The best values of $RT \ln f$ were deduced from alkane data at the three temperatures, then data on column of series (a) were corrected by $0.5RT \ln f$. Values of $RT \ln f$ are given in Table 3.

## *3.4. Solution data for n-alkanes as a function of the factors T (temperature), L (composition of the liquid stationary phase) and Z (carbon number of the n-alkane)*

### *C78-TTF: pentane-decane*

Standard chemical potentials of $n$-alkanes, $C_zH_{2z+2}$ with $z = 5$–10, were determined on two stationary phases ($\varphi = 0.5$ and 1) in the temperature range 90–210°C at 20 K intervals. Inclusion of data from ref. 1 for C78 gave a set of 6 × 3 × 7 = 126 data points. The variance analysis of the influence of the factors $T$, $L$ and $Z$ on the standard chemical potentials of $n$-alkanes is shown in Table 4. The analysis refers to the description of the experimental space by Eq. 20 where $P_X^{(i)}$ is an orthogonal polynomial of the

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)

| L | $f$ | $0.5RT \ln f$ (cal mol$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 90°C | 110°C | 130°C | 150°C | 170°C | 190°C | 210°C |
| C78-TTF | 0.992 | −2.8 | −2.9 | −3.1 | −3.2 | −3.4 | −3.5 | −3.7 |
| TTF | 1.014 | +4.9 | +5.2 | +5.5 | +5.7 | +6.0 | +6.3 | +6.6 |

Table 4
Analysis of variance of the set of 126 standard chemical potentials of the *n*-alkane solutes with $5 \leq z \leq 10$ in the temperature range 90–210°C at three compositions of the C78–TTF mixture

| Source | | $SQ$ | $\phi$ | $V'$ | $F$ | Sign. (%) | $b_X^{(i)}$ | Function |
|---|---|---|---|---|---|---|---|---|
| $X$ | $(i)$[a] | | | | | | | |
| $\Delta\bar{\mu}$ | (0) | | | | | | 22.0 | $\Delta\mu_0^{\dagger,\mathrm{A}}$ |
| $T$ | (1) | 68 516 332.2 | 1 | id | $4.45 \cdot 10^5$ | 0.01 | 368.71 | $\Delta S_0^{\mathrm{A}}$ |
| | (2) | 40 197.9 | 1 | id | $2.61 \cdot 10^2$ | 0.01 | −5.156 | $\Delta C_{\mathrm{P},0}^{\mathrm{A}}$ |
| | (res. $T$* | 1 430.1 | 4 | 357.5 | 2.32 | 20) | | |
| $L$ | (1) | 181 025.0 | 1 | id | $1.17 \cdot 10^3$ | 0.01 | 46.423 | $\Delta\mu_0^{\dagger,\mathrm{P}}$ |
| | (2) | 3 908.9 | 1 | id | $2.54 \cdot 10^1$ | 0.1 | 11.814 | $m_0^{\dagger,\mathrm{A/P}}$ |
| $TL$ | (1,1) | 439.8 | 1 | id | 2.85 | 10 | 1.144 | $\Delta S_0^{\mathrm{P}}$ |
| | (1,2) | 466.9 | 1 | id | 3.03 | 10 | −2.043 | $s_0^{\mathrm{A/P}}$ |
| | (2,1) | 186.2 | 1 | id | 1.21 | 20 | 0.430 | $\Delta C_{\mathrm{P},0}^{\mathrm{P}}$ |
| | (res. $TL$* | 573.1 | 9 | 63.7 | 0.41 | –) | | |
| 1st res.[a] | (=Σ $X$*) | 2 003.2 | 13 | 154.1 | | | | |
| $Z$ | (1) | 89 130 113.9 | 1 | id | $7.18 \cdot 10^6$ | 0.01 | −492.5 | $\delta\mu_z^{\dagger,\mathrm{A}}$ |
| | (2) | 14 911.3 | 1 | id | $1.20 \cdot 10^3$ | 0.01 | 4.361 | |
| | (3) | 65.6 | 1 | id | $5.28 \cdot 10^1$ | 5 | −0.220 | |
| | (res. $Z$** | 147.9 | 2 | 74.0 | 5.95 | 5) | | |
| $TZ$ | (1,1) | 722 289.8 | 1 | id | $5.82 \cdot 10^4$ | 0.01 | 22.166 | $\delta S_z^{\mathrm{A}}$ |
| | (2,1) | 4 374.4 | 1 | id | $3.52 \cdot 10^2$ | 0.01 | −0.996 | $\delta C_{\mathrm{P},z}^{\mathrm{A}}$ |
| | (res. $TZ$** | 666.8 | 28 | 23.8 | 1.92 | 5) | | |
| $LZ$ | (1,1) | 9 717.1 | 1 | id | $7.82 \cdot 10^1$ | 0.01 | 6.298 | $\delta\mu_z^{\dagger,\mathrm{P}}$ |
| | (2,1) | 492.9 | 1 | id | $3.97 \cdot 10^1$ | 0.01 | −2.454 | $\delta m_z^{\dagger,\mathrm{A/P}}$ |
| | (res. $LZ$** | 90.0 | 8 | 11.3 | 0.91 | –) | | |
| $TLZ$ | (1,1,1) | 13.6 | 1 | id | 1.10 | – | −0.118 | $\delta S_z^{\mathrm{P}}$ |
| | (2,1,1) | 6.7 | 1 | id | 0.54 | – | −0.048 | $\delta C_{\mathrm{P},z}^{\mathrm{P}}$ |
| | (1,2,1) | 92.5 | 1 | id | 7.45 | 1 | −0.534 | $\delta s_z^{\mathrm{A/P}}$ |
| | (res. $TLZ$** | 275.4 | 57 | 4.8 | 0.39 | –) | | |
| 2nd res.[b] | (=Σ $X$**) | 1 180.1 | 95 | 12.4 | | | | |

The source of variance is related to orthogonal terms in Eq. 20. $X^{(i)}$ is the systematic polynomial variation of $\Delta\mu$ on the effects $T$ (temperature), $L$ (composition of the liquid stationary phase, $100\varphi_{\mathrm{TTF}} = 0.0$, 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, $\phi$ 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 $F$ ($\nu_X$ is the number of statistical units in one datum of the subset used for the evaluation of the effect). The coefficients $b_X^{(i)}$ in Eq. 20 are also listed along with the corresponding thermodynamic coefficients. The meaning of the symbols of thermodynamic functions are described in the text. The abbreviation "res." is for residual variance, "sign." is for significance level and "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.

degree $i$ related to the effect $X = T$, $L$ and $Z$ and $b_X^{(i)}$ is the corresponding regression coefficient.

$$\begin{aligned}\Delta\mu_z^{\mathrm{A/P}} = {} & b^{(0)} + b_Z^{(1)} P_Z^{(1)} + b_T^{(1)} P_T^{(1)} + b_{T,Z}^{(1,1)} P_T^{(1)} P_Z^{(1)} \\ & + b_T^{(2)} P_T^{(2)} + b_{T,Z}^{(2,1)} P_T^{(2)} P_Z^{(1)} + b_L^{(1)} P_L^{(1)} \\ & + b_{L,Z}^{(1,1)} P_L^{(1)} P_Z^{(1)} + b_{T,L}^{(1,1)} P_T^{(1)} P_L^{(1)} \\ & + \underline{b_{T,L,Z}^{(1,1,1)} P_T^{(1)} P_L^{(1)} P_Z^{(1)}} + \underline{b_{T,L}^{(2,1)} P_T^{(2)} P_L^{(1)}} \\ & + \underline{b_{T,L,Z}^{(2,1,1)} P_T^{(2)} P_L^{(1)} P_Z^{(1)}} + b_L^{(2)} P_L^{(2)} \\ & + b_{L,Z}^{(2,1)} P_L^{(2)} P_Z^{(1)} + b_{T,L}^{(1,2)} P_T^{(1)} P_L^{(2)} \\ & + b_{T,L,Z}^{(1,2,1)} P_T^{(1)} P_L^{(2)} P_Z^{(1)} \qquad (20)\end{aligned}$$

It is seen that the residual variance in the subspace $TL$ (1st res.) is higher than the residual variance deduced from the third-order effect $TLZ$ (2nd res.). In fact, a higher error is introduced by adjusting a new temperature or by working with a new column compared to the error between alkanes injected on a given column at exactly the same temperature. Consequently, effects in the *TL* subspace were tested against the "1st res." and the remaining effects against the "2nd res." (*cf.*, the analogous variance analysis in ref. 1).

The results in Table 4 indicate that all the terms in Eq. 20 are significant with the exception of those underlined. In addition to the terms in Eq. 20, also the quadratic and cubic dependence of the standard chemical potential, $\Delta\mu_z^{A/P}$, on the carbon number were significant. The corresponding terms are not included in Eq. 20 in spite of the fact that the dependence of $\Delta\mu_z^{A/P}$ on carbon number, $z$, is not strictly linear. The relation of the coefficients $b_X^{(i)}$ to thermodynamic functions is listed in the last column in Table 4. This relationship was found by comparing coefficients in Eqs. 20 and 22. The latter equation was obained by developing the relationship of Eq. 3 for $\Delta\mu_z^{A/P}$ around the standard temperature, $T^\dagger$, by introducing $\Delta T = T - T^\dagger$, and by approximating the logarithmic expression multiplying the partial molar heat capacity, $\Delta C_p$, by the first term of its Taylor series and introducing a linear dependence on $z$ for the functions $Y = H_z$, $S_z$, $C_{P,z}$, $\hbar_z$ and $s_z$.

$$Y_z = Y_0 + z\,\delta Y_z \tag{21}$$

$$\begin{aligned}\Delta\mu_z^{A/P} &= \Delta\mu_0^{\dagger A} + z\,\delta\mu_z^{\dagger A} - \Delta T\,\Delta S_0^{A} - \Delta T z\,\delta S_z^{A}\\ &- \Delta T^2 \frac{\Delta C_{P,0}^{A}}{2T^\dagger} - \Delta T^2 z \frac{\delta C_{P,z}^{A}}{2T^\dagger} + \varphi_P(\Delta\mu_0^{\dagger,P} + m_0^{\dagger,A/P})\\ &+ \varphi_P z(\delta\mu_z^{\dagger,P} - \delta\mu_z^{\dagger,A} + \delta m_z^{\dagger,A/P}) - \Delta T\varphi_P\,\Delta S_0^{P}\\ &\underline{-\Delta T\varphi_P z(\delta S_z^{P} - \delta S_z^{A})}\,\underline{-\Delta T^2\varphi_P \frac{\Delta C_{P,0}^{P}}{2T^\dagger}}\\ &\underline{-\Delta T^2\varphi_P z \frac{\delta C_{P,z}^{P} - \delta C_{P,z}^{A}}{2T^\dagger}} - \varphi_P^2 m_0^{\dagger,A/P}\\ &- \varphi_P^2 z\,\delta m_z^{\dagger,A/P} + \Delta T\varphi^2 s_0^{A/P}\\ &+ \Delta T\varphi^2 z\,\delta s_z^{A/P}\end{aligned} \tag{22}$$

The visual arrangement of Eqs. 20 and 22 facilitates the identification of the corresponding coefficients. The non-significance of the three underlined terms in Eq. 22 is interpreted in terms of thermodynamic functions as follows. There is no difference between the entropy of the "methylene increment", $\delta S_z^P$, on the stationary phase C78 and TTF (1st term) and the same is true for the partial molar heat capacity of a hypothetical "nullane", $\Delta C_{P,0}^P$, (2nd term) and for the heat capacity of the "methylene increment", $\delta C_{P,z}^P$, (3rd term).

### *C78*

Retention index and thermodynamic data on C78 have been published previously [1]. New

Table 5
Retention indices and thermodynamic data of some solutes on the standard alkane C78

| No. | Compound | $n$ | Temperature range (°C) | Retention index (C78) | | | Thermodynamic data (C78) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $I_{130}$ | $A_T \cdot 10$ (K$^{-1}$) | $\sigma$ | $\Delta H$ (cal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta C_P$ (cal mol$^{-1}$ K$^{-1}$) | $\sigma$ (cal mol$^{-1}$) |
| 10.12 | 2,2-Dimethylhexane | 15 | 90–170 | 719.9 | +0.77 | 0.36 | −7 554 | −18.180 | +10.4 | 1.1 |
| 38.06 | Iodobenzene | 15 | 130–210 | 1 078.9 | +6.70 | 0.32 | −9 500 | −18.533 | +13.9 | 1.7 |
| 41.12 | Benzyl alcohol | 15 | 130–210 | 973.7 | +4.29 | 0.37 | −9 389 | −19.512 | +10.6 | 2.1 |
| 41.13 | 2-Phenylethanol | 15 | 130–210 | 1 054.5 | +4.83 | 0.31 | −10 164 | −20.423 | +14.3 | 1.7 |
| 41.16 | Aniline | 15 | 130–210 | 932.1 | +6.98 | 0.59 | −8 423 | −17.640 | + 8.0 | 3.3 |
| 41.17 | Cyclohexylamine | 15 | 130–210 | 860.2 | +3.88 | 1.06 | −8 380 | −18.432 | +11.2 | 6.2 |

$I_{130}$ is the retention index at the standard temperature, $A_T$ is the temperature coefficient of retention index; thermodynamic functions are the coefficients of Eq. 3; other symbols are as in Table 6. 1 cal = 4.184 J.

Table 6

Retention indices and thermodynamic data for 160 solutes; data in C78–TTF mixtures where data derived for $idCF_3$ are also given and on pure MTF with reference to those in C78

Data in the reference alkane C78 (not listed) are given in ref. 1 and in Table 5 of this paper. The symbol $n$ is the number of data points used for regression where points for pure C78 were taken from ref. 1 ($n/3$ for C78–TTF mixtures; $n/2$ for MTF). Constants and functions, $X$, preceded by $\Delta$ refer to those on C78, *i.e.*, $\Delta X = X - X$ (in C78); $\Delta'$ values are derivatives with respect of concentration $[CF_3]$. Retention indices: $I_{130}$ is the retention index at the reference temperature $T^{\dagger} = 130 + 273.15$ K; for the meaning of the coefficients $A$, see Eqs. 11 and 12. Thermodynamic functions $H$ and $S$ are partial molar enthalpy and entropy at $T^{\dagger}$ and $C_p$ is the mean partial molar heat capacity in the temperature range indicated; for the meaning of the coefficients $h$ and $s$, see Eq. 6. At the end of the Table additive corrections are listed to convert data (A) to those related to the partition coefficients $K_D$ (see Eq. 30) and (B) to those where pressures are measured in units of bar (instead of atm). Errors: the symbol $\sigma$ is 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, $f$ (coeff) $= \sigma$ (coeff)$/\sigma$. Data with a superscript s are significant at the 10% significance level if tested against $\sigma$. Data with one asterisk are at the 20% significance level and those marked with two 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: $\Delta H$, $\Delta S$, $\Delta C_p$, $h$, $s$, $\Delta'H$, $\Delta'S$ and $\Delta'C_p$.

| No. | Compound | Temp. range | Retention index : C78 / TTF | | | | | | | | C78 / MTF | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | n | TTF - C78 | | Mixture | | id([CF₃]=1) - C78 | | σ | n | MTF - C78 | | σ |
| | | (°C) | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | $A_L$ | 10 × $A_{LT}$ ($K^{-1}$) | $\Delta' I_{130}$ (l $mol^{-1}$) | 10 × $\Delta' A_T$ ($K^{-1}$ l $mol^{-1}$) | | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | |
| HYDROCARBONS | | | | | | | | | | | | | | |
| *n-Alkanes* | | | | | | | | | | | | | | |
| 00.05 | Pentane | 90-210 | 21 | | | | | | | | 14 | | | |
| 00.06 | Hexane | 90-210 | 21 | | | | | | | | 14 | | | |
| 00.07 | Heptane | 90-210 | 21 | | | | | | | | 14 | | | |
| 00.08 | Octane | 90-210 | 21 | | | | | | | | 14 | | | |
| 00.09 | Nonane | 90-210 | 21 | | | | | | | | 14 | | | |
| 00.10 | Decane | 90-210 | 21 | | | | | | | | 14 | | | |
| 00.11 | Undecane | 150-210 | 12 | | | | | | | | 8 | | | |
| 00.12 | Dodecane | 150-210 | 12 | | | | | | | | 8 | | | |
| 00.13 | Tridecane | 150-210 | 12 | | | | | | | | 8 | | | |
| 00.14 | Tetradecane | 150-210 | 12 | | | | | | | | 8 | | | |
| *Isoalkanes* | | | | | | | | | | | | | | |
| 10.01 | 2,2-Dimethylbutane | 90-170 | 15 | + 3.8 | -0.53 | + 1.7 | $+0.04^{**}$ | + 2.1 | -0.17 | 0.24 | 10 | + 1.4 | $+0.10^{**}$ | 0.32 |
| 10.02 | 2,3-Dimethylbutane | 90-170 | 15 | + 2.8 | -0.38 | $- 1.4^{**}$ | $-0.59^{**}$ | + 0.5 | -0.36 | 0.82 | 10 | + 0.7 | +0.10 | 0.15 |
| 10.03 | 2,2-Dimethylpentane | 90-170 | 15 | + 4.7 | -0.42 | + 1.1 | $-0.10^{**}$ | + 2.2 | -0.18 | 0.33 | 10 | + 1.5 | $-0.02^{**}$ | 0.41 |
| 10.04 | 2,3-Dimethylpentane | 90-170 | 15 | + 2.3 | -0.31 | $- 1.5^{*}$ | $-0.54^{*}$ | + 0.3 | -0.32 | 0.47 | 10 | + 0.9 | $+0.15^{**}$ | 0.53 |
| 10.05 | 2,4-Dimethylpentane | 90-170 | 15 | + 4.0 | -0.59 | $- 1.8^{*}$ | -1.07 | + 0.8 | -0.62 | 0.48 | 10 | + 1.3 | -0.19 | 0.08 |
| 10.06 | 2,3-Dimethylhexane | 90-170 | 15 | + 2.6 | -0.31 | $- 1.6^{s}$ | -0.66 | + 0.3 | -0.36 | 0.37 | 10 | + 0.7 | +0.14 | 0.13 |
| 10.07 | 2,4-Dimethylhexane | 90-170 | 15 | + 4.0 | $-0.30^{s}$ | $- 0.4^{**}$ | $-0.39^{**}$ | + 1.4 | -0.25 | 0.44 | 10 | + 1.5 | $+0.09^{s}$ | 0.18 |
| 10.08 | 3,4-Dimethylhexane | 90-170 | 15 | + 2.1 | -0.28 | - 1.9 | $-0.14^{**}$ | - 0.0 | -0.16 | 0.25 | 10 | + 0.9 | $+0.18^{*}$ | 0.41 |
| 10.09 | 2,2,3-Trimethylbutane | 90-170 | 15 | + 7.1 | $+0.16^{*}$ | + 2.1 | $+0.51^{s}$ | + 3.5 | +0.28 | 0.29 | 10 | + 3.4 | $+0.25^{s}$ | 0.51 |
| 10.10 | 2,2,4-Trimethylpentane | 90-170 | 15 | + 7.0 | $-0.02^{**}$ | + 1.6 | $+0.06^{**}$ | + 3.2 | +0.04 | 0.26 | 10 | + 2.8 | +0.28 | 0.38 |
| 10.11 | 2,3,4-Trimethylpentane | 90-170 | 15 | + 3.4 | $+0.11^{**}$ | $+ 0.0^{**}$ | $+0.21^{**}$ | + 1.6 | +0.13 | 0.35 | 10 | + 1.2 | +0.32 | 0.33 |

| No. | Thermodynamic data : C78 / TTF | | | | | | | | | C78 / MTF | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TTF - C78 | | | Mixture | | id([$CF_3$]=1) - C78 | | | σ | MTF - C78 | | | σ |
| | $\Delta H$ (cal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$K$^{-1}$) | $\Delta C_P$ (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$^{-1}$) | $\Delta H$ (cal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta C_P$ (cal mol$^{-1}$ K$^{-1}$) | (cal mol$^{-1}$) |
| HYDROCARBONS | | | | | | | | | | | | | |
| *n-Alkanes* | | | | | | | | | | | | | |
| 00.05 | + 49 | -0.026 | - 1.9 | - 236 | -0.412 | - 69 | -0.161 | -0.8 | 4.8 | - 69 | -0.113 | -1.7 | 4.4 |
| 00.06 | + 61 | -0.026 | - 1.7 | - 230 | -0.412 | - 65 | -0.166 | -0.8 | 4.5 | - 62 | -0.107 | -1.6 | 4.2 |
| 00.07 | + 72 | -0.026 | - 1.6 | - 225 | -0.412 | - 60 | -0.171 | -0.7 | 4.5 | - 56 | -0.101 | -1.5 | 4.9 |
| 00.08 | + 83 | -0.026 | - 1.5 | - 219 | -0.412 | - 56 | -0.176 | -0.7 | 4.1 | - 49 | -0.095 | -1.3 | 5.3 |
| 00.09 | + 94 | -0.026 | - 1.4 | - 214 | -0.412 | - 52 | -0.181 | -0.7 | 4.9 | - 43 | -0.089 | -1.2 | 4.6 |
| 00.10 | + 106 | -0.026 | - 1.3 | - 208 | -0.412 | - 47 | -0.186 | -0.6 | 4.3 | - 36 | -0.083 | -1.0 | 5.2 |
| 00.11 | + 117 | -0.026 | - 1.2 | - 202 | -0.412 | - 43 | -0.191 | -0.6 | 3.6 | - 29 | -0.077 | -0.9 | 3.1 |
| 00.12 | + 128 | -0.026 | - 1.1 | - 197 | -0.412 | - 39 | -0.195 | -0.5 | 4.5 | - 23 | -0.071 | -0.8 | 3.5 |
| 00.13 | + 139 | -0.026 | - 1.0 | - 191 | -0.412 | - 34 | -0.200 | -0.5 | 4.3 | - 16 | -0.065 | -0.6 | 2.7 |
| 00.14 | + 151 | -0.026 | - 0.8 | - 185 | -0.412 | - 30 | -0.205 | -0.5 | 4.6 | - 10 | -0.059 | -0.5 | 2.9 |
| *Isoalkanes* | | | | | | | | | | | | | |
| 10.01 | - 104 | -0.369 | + 2.1 | - 249 | -0.424 | -128 | -0.286 | +0.6 | 1.0 | - 62 | -0.082$^{*}$ | +2.9$^{*}$ | 1.8 |
| 10.02 | - 52$^{*}$ | -0.273 | + 6.1$^{s}$ | - 364 | -0.754 | -154 | -0.381 | +2.0 | 3.5 | - 53 | -0.073 | +4.5 | 0.8 |
| 10.03 | - 72 | -0.310 | + 3.2 | - 271 | -0.501 | -126 | -0.297 | +1.0 | 1.5 | - 84 | -0.144 | +2.7$^{*}$ | 2.1 |
| 10.04 | - 19 | -0.226 | + 4.8 | - 331 | -0.689 | -132 | -0.346 | +1.6 | 1.5 | - 40 | -0.048$^{**}$ | +3.1$^{**}$ | 2.7 |
| 10.05 | - 98 | -0.382 | + 3.0$^{s}$ | - 443 | -0.961 | -202 | -0.502 | +0.8 | 1.9 | -113 | -0.218 | -1.3 | 0.4 |
| 10.06 | - 11$^{**}$ | -0.224 | + 2.7 | - 346 | -0.739 | -137 | -0.369 | +0.8 | 1.5 | - 33 | -0.042$^{s}$ | +1.7 | 0.7 |
| 10.07 | - 27 | -0.235 | + 2.3$^{*}$ | - 306 | -0.622 | -126 | -0.324 | +0.7 | 1.9 | - 51 | -0.074 | +0.1$^{**}$ | 0.9 |
| 10.08 | - 0$^{**}$ | -0.202 | + 0.1$^{**}$ | - 239 | -0.482 | - 94 | -0.267 | -0.1 | 1.8 | - 26$^{**}$ | -0.025$^{**}$ | +2.5$^{*}$ | 2.1 |
| 10.09 | + 23$^{**}$ | -0.044$^{**}$ | - 0.5$^{**}$ | - 148$^{s}$ | -0.187$^{**}$ | - 43 | -0.077 | -0.2 | 2.0 | - 43$^{*}$ | -0.019$^{**}$ | -0.9$^{**}$ | 2.6 |
| 10.10 | - 8 | -0.137 | + 1.5$^{**}$ | - 232 | -0.406 | - 87 | -0.196 | +0.4 | 1.9 | - 32$^{*}$ | -0.006$^{**}$ | +3.3$^{s}$ | 2.0 |
| 10.11 | + 56 | -0.042$^{**}$ | + 3.4 | - 187 | -0.326$^{s}$ | - 50 | -0.141 | +1.2 | 1.5 | - 6$^{**}$ | +0.029$^{**}$ | +6.8 | 1.7 |

(Continued on p. 192)

Table 6 (*continued*)

| *No.* | *Compound* | *Temp. range* | *Retention index : C78 / TTF* | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *n* | *TTF - C78* | | *Mixture* | | *id([CF$_3$]=1) - C78* | | *σ* | *n* | *MTF - C78* | | *σ* |
| | | *(°C)* | | $\Delta I_{130}$ | *10 ×* $\Delta A_T$ *(K$^{-1}$)* | $A_L$ | *10 ×* $A_{LT}$ *(K$^{-1}$)* | $\Delta' I_{130}$ *(l mol$^{-1}$)* | *10 ×* $\Delta' A_T$ *(K$^{-1}$l mol$^{-1}$)* | | | $\Delta I_{130}$ | *10 ×* $\Delta A_T$ *(K$^{-1}$)* | |
| 10.12 | 2,2-Dimethylhexane | 90-170 | 15 | + 4.1 | -0.32 | - 0.3$^{**}$ | -0.13$^{**}$ | + 1.4 | -0.17 | 0.36 | 10 | + 0.9 | +0.18$^{*}$ | 0.39 |
| *1-Alkenes* | | | | | | | | | | | | | | |
| 11.06 | 1-Hexene | 90-170 | 15 | + 4.7 | -0.09$^{**}$ | - 1.0$^{**}$ | +0.51$^{s}$ | + 1.4 | +0.17 | 0.36 | 10 | + 0.8$^{*}$ | -0.12$^{**}$ | 0.40 |
| 11.07 | 1-Heptene | 90-170 | 15 | + 5.6 | +0.04$^{**}$ | - 0.3$^{**}$ | +0.79 | + 1.9 | +0.32 | 0.26 | 10 | + 1.6 | +0.08$^{**}$ | 0.42 |
| 11.08 | 1-Octene | 90-170 | 15 | + 5.5 | +0.00$^{**}$ | - 0.0$^{**}$ | +0.62 | + 2.1 | +0.25 | 0.25 | 10 | + 1.2 | +0.04$^{**}$ | 0.32 |
| 11.09 | 1-Nonene | 90-170 | 15 | + 6.0 | +0.01$^{**}$ | + 0.8$^{**}$ | +0.57 | + 2.6 | +0.24 | 0.29 | 10 | + 1.5 | +0.13$^{*}$ | 0.38 |
| 11.10 | 1-Decene | 90-170 | 15 | + 5.8 | +0.07$^{**}$ | + 1.1 | +0.35 | + 2.6 | +0.18 | 0.19 | 10 | + 1.3 | +0.25 | 0.35 |
| *1-Alkynes* | | | | | | | | | | | | | | |
| 12.05 | 1-Pentyne | 90-170 | 15 | + 19.3 | +0.12$^{**}$ | + 4.8 | +1.44 | + 9.1 | +0.67 | 0.81 | 10 | + 7.3 | +0.19$^{*}$ | 0.44 |
| 12.06 | 1-Hexyne | 90-170 | 15 | + 19.3 | -0.02$^{**}$ | + 3.4 | +0.89 | + 8.6 | +0.40 | 0.38 | 10 | + 6.4 | -0.17$^{**}$ | 0.80 |
| 12.07 | 1-Heptyne | 90-170 | 15 | + 19.9 | +0.05$^{**}$ | + 4.2 | +0.95 | + 9.2 | +0.46 | 0.30 | 10 | + 6.6 | -0.03$^{**}$ | 0.62 |
| 12.08 | 1-Octyne | 90-170 | 15 | + 20.2 | -0.02$^{**}$ | + 4.0 | +0.77 | + 9.2 | +0.36 | 0.29 | 10 | + 6.3 | +0.03$^{**}$ | 0.42 |
| 12.09 | 1-Nonyne | 90-170 | 15 | + 20.6 | -0.13$^{**}$ | + 4.1 | +0.87 | + 9.4 | +0.36 | 0.37 | 10 | + 6.4 | +0.05$^{**}$ | 0.44 |
| 12.10 | 1-Decyne | 90-170 | 15 | + 20.5 | -0.02$^{**}$ | + 3.6 | +0.85 | + 9.2 | +0.39 | 0.34 | 10 | + 6.4 | +0.17$^{*}$ | 0.48 |
| *Alkynes* | | | | | | | | | | | | | | |
| 13.01 | 2-Hexyne | 90-170 | 15 | + 13.5 | -0.48$^{**}$ | - 0.4$^{**}$ | -1.02$^{**}$ | + 4.9 | -0.53 | 1.20 | 10 | + 3.8 | -0.34 | 0.46 |
| 13.02 | 3-Hexyne | 90-170 | 15 | + 7.7 | -1.04$^{s}$ | + 1.1$^{**}$ | +1.30$^{s}$ | + 3.3 | +0.13 | 0.90 | 10 | + 2.8 | -0.08$^{**}$ | 0.37 |
| 13.03 | 4-Octyne | 90-170 | 15 | + 9.9 | -0.38$^{**}$ | - 0.3$^{**}$ | +0.36$^{**}$ | + 3.6 | +0.02 | 0.50 | 10 | + 2.5 | -0.23 | 0.10 |
| *Monocyclic hydrocarbons* | | | | | | | | | | | | | | |
| 14.05 | Cyclopentane | 90-170 | 15 | - 6.6 | -0.65$^{**}$ | - 5.8 | -1.38 | - 4.7 | -0.81 | 0.65 | 10 | - 2.0 | -0.51$^{s}$ | 1.06 |
| 14.06 | Cyclohexane | 90-170 | 15 | - 6.1 | -0.33$^{**}$ | - 3.4 | -0.54$^{**}$ | - 3.6 | -0.36 | 0.59 | 10 | - 1.6 | -0.12$^{**}$ | 0.78 |
| 14.07 | Cycloheptane | 90-170 | 15 | - 7.3 | -0.21$^{**}$ | - 3.3 | -0.18$^{**}$ | - 4.0 | -0.18 | 0.45 | 10 | - 1.9 | +0.01$^{**}$ | 0.58 |
| 14.08 | Cyclooctane | 90-170 | 15 | - 7.5 | -0.05$^{**}$ | - 3.2 | +0.06$^{**}$ | - 4.1 | -0.03 | 0.44 | 10 | - 3.3 | +0.73 | 0.74 |
| 14.10 | Cyclodecane | 130-210 | 15 | - 7.0 | -0.10$^{**}$ | + 0.9 | -0.23$^{**}$ | - 3.5 | -0.02 | 0.47 | 10 | - 3.7 | +0.70 | 0.49 |
| *Bicyclic hydrocarbons* | | | | | | | | | | | | | | |
| 15.01 | *cis*-Hydrindane | 130-210 | 15 | - 7.9 | -0.03$^{**}$ | - 3.5 | +0.20$^{**}$ | - 4.0 | -0.06 | 0.33 | 10 | - 1.8 | +0.12$^{**}$ | 0.29 |
| 15.02 | *trans*-Hydrindane | 130-210 | 15 | - 7.1 | +0.06$^{**}$ | - 3.3 | +0.20$^{**}$ | - 3.8 | +0.06 | 0.43 | 10 | - 0.9 | -0.23 | 0.20 |
| 15.03 | *cis*-Decalin | 130-210 | 15 | - 6.9 | -0.22$^{**}$ | - 3.3 | +0.08$^{**}$ | - 3.5 | -0.16 | 0.30 | 10 | + 1.1 | -0.69 | 0.39 |
| 15.04 | *trans*-Decalin | 130-210 | 15 | - 6.0 | -0.06$^{**}$ | - 2.5 | +0.09$^{**}$ | - 2.7 | -0.15 | 0.38 | 10 | - 0.1 | -0.56 | 0.37 |
| *Methylcyclohexanes (MCH)* | | | | | | | | | | | | | | |
| 16.01 | Methylcyclohexane | 90-170 | 15 | - 3.3 | -0.31$^{**}$ | + 0.2$^{**}$ | -0.38$^{**}$ | - 1.2 | -0.27 | 0.65 | 10 | - 0.5$^{*}$ | +0.17$^{**}$ | 0.53 |

| No. | Thermodynamic data : C78 / TTF | | | | | | | | | C78 / MTF | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TTF - C78 | | | Mixture | | id([CF$_3$]=1) - C78 | | | $\sigma$ | MTF - C78 | | | $\sigma$ |
| | $\Delta H$ | $\Delta S$ | $\Delta C_P$ | $\bar{h}$ | $s$ | $\Delta' H$ | $\Delta' S$ | $\Delta' C_P$ | | $\Delta H$ | $\Delta S$ | $\Delta C_P$ | |
| | (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$^{-1}$) | (cal mol$^{-1}$) | (cal mol$^{-1}$ K$^{-1}$) | | (cal mol$^{-1}$) |
| 10.12 | - 33 | -0.244 | + 1.7$^{s}$ | - 254 | -0.489 | -108 | -0.276 | +0.5 | 1.1 | - 59 | -0.108$^{s}$ | +1.8$^{*}$ | 2.3 |
| *1-Alkenes* | | | | | | | | | | | | | |
| 11.06 | - 12$^{**}$ | -0.137$^{s}$ | - 0.9$^{**}$ | - 108$^{**}$ | -0.118$^{**}$ | - 43 | -0.091 | -0.4 | 2.7 | - 98 | -0.183 | -0.5$^{**}$ | 2.4 |
| 11.07 | + 21$^{**}$ | -0.078$^{s}$ | - 1.3$^{**}$ | - 57$^{**}$ | +0.003$^{**}$ | - 13 | -0.027 | -0.5 | 1.8 | - 59 | -0.081$^{*}$ | -2.2$^{**}$ | 2.0 |
| 11.08 | + 25$^{*}$ | -0.097 | - 0.0$^{**}$ | - 93$^{*}$ | -0.097$^{**}$ | - 27 | -0.076 | -0.0 | 1.7 | - 55 | -0.092$^{s}$ | -0.6$^{**}$ | 1.7 |
| 11.09 | + 33$^{*}$ | -0.103 | + 0.5$^{**}$ | - 109$^{*}$ | -0.140$^{**}$ | - 31 | -0.097 | +0.1 | 1.9 | - 34$^{*}$ | -0.043$^{**}$ | -1.3$^{**}$ | 1.9 |
| 11.10 | + 59 | -0.069$^{s}$ | + 0.6$^{**}$ | - 152 | -0.255 | - 39 | -0.132 | +0.1 | 1.3 | - 2$^{**}$ | +0.022$^{**}$ | -1.4$^{**}$ | 1.7 |
| *1-Alkynes* | | | | | | | | | | | | | |
| 12.05 | - 111$^{s}$ | -0.169$^{**}$ | + 5.2$^{**}$ | + 52$^{**}$ | +0.370$^{**}$ | - 4 | +0.119 | +2.0 | 5.6 | - 99 | -0.089$^{**}$ | +1.6$^{**}$ | 2.6 |
| 12.06 | - 138 | -0.267 | + 2.6$^{**}$ | - 59$^{**}$ | +0.077$^{**}$ | - 59 | -0.034 | +0.9 | 2.5 | -167 | -0.269$^{s}$ | -2.5$^{**}$ | 4.5 |
| 12.07 | - 119 | -0.246 | + 1.5$^{**}$ | - 69$^{**}$ | +0.036$^{**}$ | - 58 | -0.047 | +0.5 | 1.8 | -130 | -0.194$^{s}$ | -1.4$^{**}$ | 3.3 |
| 12.08 | - 124 | -0.288 | + 1.9$^{*}$ | - 103$^{s}$ | -0.067$^{**}$ | - 75 | -0.107 | +0.6 | 1.7 | -107 | -0.156 | +0.3$^{**}$ | 2.4 |
| 12.09 | - 140 | -0.354 | + 2.0$^{**}$ | - 87$^{*}$ | -0.041$^{**}$ | - 76 | -0.127 | +0.7 | 1.9 | - 99 | -0.145$^{s}$ | +0.3$^{**}$ | 2.5 |
| 12.10 | - 105 | -0.296 | + 1.5$^{*}$ | - 79$^{s}$ | -0.044$^{**}$ | - 63 | -0.113 | +0.5 | 1.9 | - 68 | -0.077$^{**}$ | -1.5$^{**}$ | 2.9 |
| *Alkynes* | | | | | | | | | | | | | |
| 13.01 | - 166 | -0.435 | + 3.1$^{**}$ | - 461$^{s}$ | -0.987$^{*}$ | -228 | -0.515 | +0.8 | 7.0 | -170 | -0.327 | -1.3$^{**}$ | 2.3 |
| 13.02 | - 227 | -0.651 | + 2.3$^{**}$ | + 19$^{**}$ | +0.216$^{**}$ | - 74 | -0.152 | +0.8 | 5.7 | -104 | -0.180 | +1.8$^{**}$ | 1.9 |
| 13.03 | - 89$^{s}$ | -0.338 | + 2.3$^{**}$ | - 149$^{*}$ | -0.242$^{**}$ | - 88 | -0.215 | +0.7 | 2.8 | -119 | -0.240 | +1.0 | 0.4 |
| *Monocyclic hydrocarbons* | | | | | | | | | | | | | |
| 14.05 | - 33$^{**}$ | -0.339 | - 1.5$^{**}$ | - 487 | -1.125 | -203 | -0.569 | -0.9 | 4.1 | -164 | -0.378 | -2.9$^{**}$ | 5.9 |
| 14.06 | + 49$^{s}$ | -0.151 | - 2.5$^{**}$ | - 305 | -0.652 | -105 | -0.322 | -1.1 | 2.8 | - 72$^{*}$ | -0.153$^{*}$ | -2.8$^{**}$ | 3.9 |
| 14.07 | + 96 | -0.089$^{*}$ | - 2.1$^{**}$ | - 227 | -0.478 | - 61 | -0.242 | -0.9 | 2.3 | - 33$^{**}$ | -0.078$^{**}$ | -1.9$^{**}$ | 3.0 |
| 14.08 | + 144 | -0.011$^{**}$ | - 1.0$^{**}$ | - 179$^{s}$ | -0.376$^{*}$ | - 28 | -0.181 | -0.5 | 2.6 | +131 | +0.302 | -4.4$^{*}$ | 3.2 |
| 14.10 | + 145 | -0.060$^{**}$ | - 1.8$^{**}$ | - 245 | -0.541 | - 55 | -0.268 | -0.8 | 2.0 | +112$^{*}$ | +0.242$^{**}$ | -4.4$^{s}$ | 2.1 |
| *Bicyclic hydrocarbons* | | | | | | | | | | | | | |
| 15.01 | + 116$^{s}$ | -0.104$^{**}$ | + 0.8$^{**}$ | - 158 | -0.336 | - 32 | -0.205 | +0.2 | 1.8 | - 83$^{s}$ | -0.213 | +0.2 | 0.9 |
| 15.02 | + 167$^{s}$ | +0.040$^{**}$ | - 0.3$^{**}$ | - 155$^{*}$ | -0.323$^{*}$ | - 11 | -0.144 | -0.2 | 2.5 | - 12$^{**}$ | -0.037$^{**}$ | -1.0$^{**}$ | 1.6 |
| 15.03 | + 78$^{*}$ | -0.214$^{*}$ | + 1.0$^{**}$ | - 173 | -0.388 | - 53 | -0.269 | +0.2 | 1.6 | -123$^{*}$ | -0.317$^{s}$ | +0.7$^{**}$ | 1.8 |
| 15.04 | + 68$^{**}$ | -0.221$^{*}$ | + 1.7$^{**}$ | - 182 | -0.395 | - 59 | -0.270 | +0.5 | 1.7 | -175 | -0.438 | +2.1$^{*}$ | 1.6 |
| *Methylcyclohexanes (MCH)* | | | | | | | | | | | | | |
| 16.01 | + 36$^{**}$ | -0.179$^{s}$ | + 3.0$^{**}$ | - 319 | -0.649 | -112 | -0.324 | +0.9 | 3.6 | - 17$^{**}$ | -0.022$^{**}$ | +1.9$^{**}$ | 2.7 |

*(Continued on p. 194)*

Table 6 (*continued*)

| *No.* | *Compound* | *Temp. range* | *Retention index : C78 / TTF* | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *n* | *TTF - C78* | | *Mixture* | | *id([CF$_3$]=1) - C78* | | *σ* | *n* | *MTF - C78* | | *σ* |
| | | *(°C)* | | $\Delta I_{130}$ | *10 ×* $\Delta A_T$ *(K$^{-1}$)* | $A_L$ | *10 ×* $A_{LT}$ *(K$^{-1}$)* | $\Delta' I_{130}$ *(l mol$^{-1}$)* | *10 ×* $\Delta' A_T$ *(K$^{-1}$l mol$^{-1}$)* | | | $\Delta I_{130}$ | *10 ×* $\Delta A_T$ *(K$^{-1}$)* | |
| 16.02 | *cis*-1,2-Di MCH | 90-170 | 15 | - 2.4 | -0.16$^{**}$ | - 0.4$^{**}$ | +0.09$^{**}$ | - 1.1 | -0.03 | 0.52 | 10 | + 0.4$^{**}$ | +0.13$^{**}$ | 0.77 |
| 16.03 | *trans*-1,2-Di MCH | 90-170 | 15 | - 1.0$^{**}$ | -0.09$^{**}$ | - 0.1$^{**}$ | -0.10$^{**}$ | - 0.4 | -0.07 | 0.60 | 10 | + 0.0$^{**}$ | +0.22$^{**}$ | 0.85 |
| 16.04 | *cis*-1,4-Di MCH | 90-170 | 15 | - 1.6$^{*}$ | -0.19$^{**}$ | - 0.5$^{**}$ | +0.11$^{**}$ | - 0.8 | -0.04 | 0.62 | 10 | + 0.1$^{**}$ | +0.12$^{**}$ | 0.76 |
| 16.05 | *trans*-1,4-Di MCH | 90-170 | 15 | - 0.2$^{**}$ | -0.21$^{**}$ | - 0.7$^{**}$ | +0.05$^{**}$ | - 0.4 | -0.06 | 0.60 | 10 | + 0.8$^{*}$ | +0.27$^{*}$ | 0.71 |
| *Cyclohexenes* | | | | | | | | | | | | | | |
| 17.01 | Cyclohexene | 90-170 | 15 | - 1.5$^{*}$ | -0.53$^{*}$ | - 0.5$^{**}$ | -0.33$^{**}$ | - 0.8 | -0.33 | 0.67 | 10 | - 0.5$^{s}$ | -0.15$^{s}$ | 0.29 |
| 17.02 | 1,3-Cyclohexadiene | 90-170 | 15 | + 8.5 | -0.22$^{**}$ | + 0.6$^{**}$ | +0.78$^{*}$ | + 3.4 | +0.24 | 0.63 | 10 | + 3.2 | +0.39 | 0.47 |
| 17.03 | 1,4-Cyclohexadiene | 90-170 | 15 | + 6.3 | -0.49$^{*}$ | - 1.3$^{**}$ | +0.30$^{**}$ | + 1.9 | -0.06 | 0.57 | 10 | + 1.5$^{s}$ | -0.07$^{**}$ | 0.99 |
| *Alkylbenzenes* | | | | | | | | | | | | | | |
| 18.00 | Benzene | 90-170 | 15 | + 25.5 | +0.25$^{**}$ | + 4.1• | +1.25$^{*}$ | +11.2 | +0.66 | 1.10 | 10 | + 7.6 | +0.39$^{*}$ | 1.01 |
| 18.01 | Toluene | 90-170 | 15 | + 27.5 | +0.10$^{**}$ | + 3.1$^{*}$ | +0.89$^{**}$ | +11.6 | +0.47 | 0.96 | 10 | + 7.5 | +0.30$^{**}$ | 0.91 |
| 18.02 | Ethylbenzene | 90-170 | 15 | + 25.4 | -0.02$^{**}$ | + 2.8$^{*}$ | +0.71$^{**}$ | +10.7 | +0.35 | 0.84 | 10 | + 6.9 | +0.25 | 0.86 |
| *Miscellaneous* | | | | | | | | | | | | | | |
| 19.01 | Adamantane | 130-210 | 15 | - 10.8 | -0.48 | - 5.6 | -0.74$^{s}$ | - 6.0 | -0.56 | 0.45 | 10 | - 3.5 | -0.43 | 0.41 |
| 19.02 | Naphthalene | 130-210 | 15 | + 43.3 | -0.33$^{**}$ | + 3.9 | -0.31$^{**}$ | +17.2 | +0.06 | 0.79 | 10 | +10.7 | -0.09$^{**}$ | 0.84 |
| 19.03 | Azulene | 130-210 | 15 | + 39.5 | +0.92 | - 8.8 | +2.54 | +11.7 | +1.41 | 1.18 | 10 | + 8.6 | +0.28$^{**}$ | 1.61 |
| *ALKANE DERIVATIVES* | | | | | | | | | | | | | | |
| *1-Fluoroalkanes* | | | | | | | | | | | | | | |
| 20.05 | 1-Fluoropentane | 90-170 | 15 | + 36.1 | -0.38$^{**}$ | + 6.8 | -0.04$^{**}$ | +16.2 | -0.02 | 0.52 | 10 | +10.3 | -0.21$^{**}$ | 1.28 |
| 20.06 | 1-Fluorohexane | 90-170 | 15 | + 36.6 | -0.31$^{**}$ | + 5.9 | -0.33$^{**}$ | +16.1 | -0.11 | 0.39 | 10 | +10.3 | -0.10$^{**}$ | 0.91 |
| 20.07 | 1-Fluorooctane | 90-170 | 15 | + 36.1 | -0.27$^{**}$ | + 3.7 | -0.39$^{*}$ | +15.1 | -0.12 | 0.30 | 10 | +10.1 | -0.01$^{**}$ | 0.55 |
| *1,1,1-Trifluoroalkanes* | | | | | | | | | | | | | | |
| 21.08 | 1,1,1-Trifluorooctane | 90-170 | 15 | + 56.8 | -0.09$^{**}$ | +18.6 | -0.99 | +28.5 | -0.17 | 0.56 | 10 | +17.8 | +0.00$^{**}$ | 0.54 |
| 21.10 | 1,1,1-Trifluorodecane | 90-170 | 15 | + 57.3 | -0.07$^{**}$ | +19.3 | -1.11$^{s}$ | +29.0 | -0.20 | 0.73 | 10 | +18.2 | -0.02$^{**}$ | 0.57 |
| *1-Chloroalkanes* | | | | | | | | | | | | | | |
| 22.04 | 1-Chlorobutane | 90-170 | 15 | + 27.7 | +0.18$^{**}$ | + 4.8 | +1.03 | +12.4 | +0.56 | 0.57 | 10 | + 7.5 | -0.35$^{s}$ | 0.69 |
| 22.05 | 1-Chloropentane | 90-170 | 15 | + 28.6 | +0.58$^{*}$ | + 6.3 | +1.64 | +13.3 | +0.95 | 0.50 | 10 | + 8.0 | +0.12$^{**}$ | 0.72 |
| 22.06 | 1-Chlorohexane | 90-170 | 15 | + 29.1 | +0.36$^{*}$ | + 6.8 | +1.29 | +13.7 | +0.74 | 0.50 | 10 | + 8.3 | +0.02$^{**}$ | 0.70 |
| *1-Bromoalkanes* | | | | | | | | | | | | | | |

| No. | Thermodynamic data : C78 / TTF | | | | | | | | | C78 / MTF | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TTF - C78 | | | Mixture | | id([CF$_3$]=1) - C78 | | | $\sigma$ | MTF - C78 | | | $\sigma$ |
| | $\Delta H$ (cal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$K$^{-1}$) | $\Delta C_P$ | $\bar{h}$ (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$^{-1}$) | $\Delta H$ (cal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta C_P$ | (cal mol$^{-1}$) |
| 16.02 | + 70 | -0.121$^{s}$ | + 5.3 | - 211 | -0.405$^{s}$ | - 60 | -0.215 | +1.8 | 2.3 | - 25$^{**}$ | -0.045$^{**}$ | +3.8$^{**}$ | 3.6 |
| 16.03 | + 67$^{s}$ | -0.101$^{*}$ | + 4.6$^{s}$ | - 256 | -0.508$^{s}$ | - 77 | -0.243 | +1.6 | 3.1 | - 3$^{**}$ | +0.002$^{**}$ | +5.2$^{*}$ | 3.3 |
| 16.04 | + 52$^{**}$ | -0.139$^{*}$ | + 1.9$^{**}$ | - 203$^{*}$ | -0.384$^{**}$ | - 63 | -0.213 | +0.6 | 4.2 | - 29$^{**}$ | -0.048$^{**}$ | -0.1$^{**}$ | 4.4 |
| 16.05 | + 31$^{**}$ | -0.165$^{s}$ | + 1.4$^{**}$ | - 214$^{s}$ | -0.410$^{*}$ | - 74 | -0.229 | +0.4 | 3.6 | - 6$^{**}$ | +0.021$^{**}$ | -0.3$^{**}$ | 4.2 |
| *Cyclohexenes* | | | | | | | | | | | | | |
| 17.01 | - 31$^{**}$ | -0.309 | + 2.9$^{**}$ | - 307 | -0.622$^{s}$ | -131 | -0.358 | +0.9 | 3.7 | - 86 | -0.186 | +1.8$^{*}$ | 1.2 |
| 17.02 | - 73 | -0.285 | + 4.7 | - 86$^{**}$ | -0.058$^{**}$ | - 56 | -0.120 | +1.7 | 2.3 | - 15$^{**}$ | +0.046$^{**}$ | -1.6$^{**}$ | 2.8 |
| 17.03 | - 98 | -0.382 | + 2.8$^{**}$ | - 165$^{*}$ | -0.282$^{**}$ | - 99 | -0.249 | +0.9 | 3.5 | - 88$^{*}$ | -0.168$^{**}$ | +1.6$^{**}$ | 5.7 |
| *Alkylbenzenes* | | | | | | | | | | | | | |
| 18.00 | - 147 | -0.252 | + 6.2$^{s}$ | - 17$^{**}$ | +0.165$^{**}$ | - 45 | +0.009 | +2.3 | 4.2 | - 54$^{**}$ | +0.001$^{**}$ | +0.8$^{**}$ | 5.8 |
| 18.01 | - 189 | -0.365 | + 4.1$^{*}$ | - 82$^{**}$ | -0.025$^{**}$ | - 87 | -0.110 | +1.5 | 3.7 | - 69$^{**}$ | -0.049$^{**}$ | +0.9$^{**}$ | 5.2 |
| 18.02 | - 180 | -0.398 | + 5.0$^{s}$ | - 115$^{**}$ | -0.125$^{**}$ | - 99 | -0.168 | +1.8 | 3.0 | - 67$^{**}$ | -0.063$^{**}$ | +1.4$^{**}$ | 4.8 |
| *Miscellaneous* | | | | | | | | | | | | | |
| 19.01 | + 60$^{**}$ | -0.305$^{*}$ | + 1.1$^{**}$ | - 282 | -0.689 | -104 | -0.425 | +0.1 | 4.1 | - 91$^{**}$ | -0.272$^{*}$ | -0.3$^{**}$ | 2.0 |
| 19.02 | - 310$^{s}$ | -0.599$^{*}$ | - 1.3$^{**}$ | - 297$^{*}$ | -0.608$^{*}$ | -213 | -0.417 | -0.8 | 4.6 | -162$^{**}$ | -0.276$^{**}$ | -1.2$^{**}$ | 4.0 |
| 19.03 | - 127$^{s}$ | -0.199$^{*}$ | - 7.6$^{*}$ | + 298$^{*}$ | +0.699$^{*}$ | + 66 | +0.193 | -2.7 | 5.8 | - 53$^{**}$ | -0.051$^{**}$ | -0.7$^{**}$ | 7.3 |
| *ALKANE DERIVATIVES* | | | | | | | | | | | | | |
| *1-Fluoroalkanes* | | | | | | | | | | | | | |
| 20.05 | - 386 | -0.629 | - 0.5$^{**}$ | - 317 | -0.517 | -234 | -0.358 | -0.4 | 1.3 | -220 | -0.336$^{s}$ | -6.3$^{**}$ | 6.4 |
| 20.06 | - 363 | -0.627 | + 0.5$^{**}$ | - 362 | -0.661 | -247 | -0.421 | -2.4 | 1.4 | -186 | -0.277$^{s}$ | -3.4$^{**}$ | 4.5 |
| 20.07 | - 326 | -0.611 | + 0.7$^{**}$ | - 342 | -0.668 | -232 | -0.434 | -0.0 | 1.9 | -150 | -0.223 | -0.6$^{**}$ | 3.0 |
| *1,1,1-Trifluoroalkanes* | | | | | | | | | | | | | |
| 21.08 | - 491 | -0.726 | + 5.3 | - 617 | -1.138 | -371 | -0.590 | +1.6 | 1.8 | -225 | -0.302 | +2.8$^{**}$ | 2.6 |
| 21.10 | - 473 | -0.747 | + 6.2 | - 638 | -1.213 | -376 | -0.636 | +1.9 | 2.6 | -222 | -0.313 | +2.7$^{**}$ | 2.8 |
| *1-Chloroalkanes* | | | | | | | | | | | | | |
| 22.04 | - 181 | -0.290 | + 2.6$^{**}$ | - 69$^{**}$ | +0.050$^{**}$ | - 74 | -0.043 | +0.9 | 2.8 | -211 | -0.384 | +1.0$^{**}$ | 3.9 |
| 22.05 | - 92 | -0.091$^{*}$ | + 2.7$^{*}$ | + 47$^{**}$ | +0.339$^{s}$ | + 1 | +0.137 | +1.1 | 2.3 | -109 | -0.142$^{*}$ | +2.8$^{**}$ | 3.7 |
| 22.06 | - 138 | -0.234 | + 2.3$^{**}$ | - 31$^{**}$ | +0.139$^{**}$ | - 47 | +0.004 | +0.9 | 2.6 | -127 | -0.195$^{s}$ | +2.7$^{**}$ | 3.6 |
| *1-Bromoalkanes* | | | | | | | | | | | | | |

(Continued on p. 196)

Table 6 (*continued*)

| *No.* | *Compound* | *Temp. range* | *Retention index : C78 / TTF* | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *n* | *TTF - C78* | | *Mixture* | | *id([CF$_3$]=1) - C78* | | *σ* | *n* | *MTF - C78* | | *σ* |
| | | *(°C)* | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | $A_L$ | 10 × $A_{LT}$ ($K^{-1}$) | $\Delta' I_{130}$ ($l\ mol^{-1}$) | 10 × $\Delta' A_T$ ($K^{-1} l\ mol^{-1}$) | | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | |
| 23.03 | 1-Bromopropane | 90-170 | 15 | + 24.4 | $-0.25^{**}$ | + 3.4 | $+0.02^{**}$ | +10.5 | +0.00 | 0.44 | 10 | + 7.9 | $-0.01^{**}$ | 0.49 |
| 23.04 | 1-Bromobutane | 90-170 | 15 | + 24.9 | $-0.21^{**}$ | + 4.8 | $-0.21^{**}$ | +11.2 | -0.07 | 0.59 | 10 | + 8.2 | $-0.03^{**}$ | 0.80 |
| 23.05 | 1-Bromopentane | 90-170 | 15 | + 25.7 | $-0.05^{**}$ | + 6.2 | $-0.11^{**}$ | +12.1 | +0.04 | 0.56 | 10 | + 7.8 | $-0.10^{**}$ | 0.78 |
| *1-Cyanoalkanes* | | | | | | | | | | | | | | |
| 24.02 | Cyanoethane | 90-170 | 15 | +105.9 | $-0.35^{**}$ | +35.6 | $-0.05^{**}$ | +53.6 | +0.29 | 0.63 | 10 | +35.6 | $-0.60^{s}$ | 1.06 |
| 24.03 | 1-Cyanopropane | 90-170 | 15 | +102.6 | $-0.25^{**}$ | +28.9 | $-0.71^{**}$ | +49.8 | +0.05 | 0.80 | 10 | +31.8 | -0.54 | 0.61 |
| 24.04 | 1-Cyanobutane | 90-170 | 15 | +102.6 | $+0.06^{**}$ | +28.6 | $-0.44^{**}$ | +49.7 | +0.27 | 0.77 | 10 | +31.5 | -0.34 | 0.28 |
| 24.05 | 1-Cyanopentane | 90-170 | 15 | +102.8 | $+0.22^{**}$ | +28.2 | $-0.52^{**}$ | +49.6 | +0.30 | 0.83 | 10 | +31.5 | $-0.16^{*}$ | 0.44 |
| *1-Nitroalkanes* | | | | | | | | | | | | | | |
| 25.02 | Nitroethane | 90-170 | 15 | + 99.8 | $-0.31^{*}$ | +23.2 | -1.55 | +46.5 | -0.32 | 0.56 | 10 | +27.9 | $+0.06^{**}$ | 0.34 |
| 25.03 | 1-Nitropropane | 90-170 | 15 | + 96.8 | $-0.11^{**}$ | +21.3 | -1.27 | +44.7 | -0.15 | 0.41 | 10 | +27.1 | -0.43 | 0.51 |
| 25.04 | 1-Nitrobutane | 90-170 | 15 | + 95.6 | $-0.03^{**}$ | +20.4 | -1.50 | +43.9 | -0.21 | 0.34 | 10 | +27.4 | -0.49 | 0.34 |
| 25.05 | 1-Nitropentane | 90-170 | 15 | + 95.6 | $-0.04^{**}$ | +20.1 | -1.41 | +43.8 | -0.18 | 0.51 | 10 | +27.5 | -0.37 | 0.37 |
| 1-Acetoxyalkanes | | | | | | | | | | | | | | |
| 26.03 | 1-Acetoxypropane | 90-170 | 15 | + 59.9 | $-0.35^{*}$ | +12.4 | -1.00 | +27.3 | -0.28 | 0.59 | 10 | +18.1 | -0.27 | 0.30 |
| 26.04 | 1-Acetoxybutane | 90-170 | 15 | + 60.2 | $-0.27^{**}$ | +13.2 | $-0.72^{*}$ | +27.8 | -0.14 | 0.58 | 10 | +17.9 | -0.19 | 0.20 |
| 26.05 | 1-Acetoxypentane | 90-170 | 15 | + 59.9 | $-0.36^{*}$ | +13.5 | $-0.80^{s}$ | +28.1 | -0.20 | 0.57 | 10 | +17.8 | -0.28 | 0.19 |
| *1-Alkanols* | | | | | | | | | | | | | | |
| 27.04 | 1-Butanol | 90-170 | 15 | + 41.0 | $-0.53^{*}$ | +10.6 | -1.28 | +19.5 | -0.52 | 0.48 | 10 | +15.9 | -0.51 | 0.43 |
| 27.05 | 1-Pentanol | 90-170 | 15 | + 41.7 | $-0.30^{**}$ | + 9.9 | $-0.71^{**}$ | +19.5 | -0.22 | 0.79 | 10 | +15.3 | -0.22 | 0.30 |
| 27.06 | 1-Hexanol | 90-170 | 15 | + 41.8 | $-0.38^{**}$ | + 9.6 | $-0.81^{**}$ | +19.4 | -0.29 | 0.92 | 10 | +14.9 | -0.31 | 0.38 |
| 27.07 | 1-Heptanol | 90-170 | 15 | + 42.3 | $-0.33^{**}$ | +10.3 | $-0.79^{**}$ | +19.9 | -0.26 | 1.06 | 10 | +15.2 | -0.31 | 0.46 |
| *2-Alkanols* | | | | | | | | | | | | | | |
| 28.04 | 2-Butanol | 90-170 | 15 | + 40.2 | $-0.09^{**}$ | + 9.9 | $-0.36^{**}$ | +19.0 | -0.01 | 0.38 | 10 | +14.8 | $-0.04^{**}$ | 0.40 |
| 28.05 | 2-Pentanol | 90-170 | 15 | + 41.7 | $+0.09^{**}$ | +11.7 | $+0.15^{**}$ | +20.2 | +0.26 | 0.29 | 10 | +15.4 | $+0.08^{**}$ | 0.35 |
| 28.06 | 2-Hexanol | 90-170 | 15 | + 42.0 | $+0.01^{**}$ | +11.6 | $+0.07^{**}$ | +20.3 | +0.20 | 0.34 | 10 | +15.2 | $-0.04^{**}$ | 0.36 |
| 28.07 | 2-Heptanol | 90-170 | 15 | + 42.1 | $-0.07^{**}$ | +11.2 | $-0.08^{**}$ | +20.2 | +0.11 | 0.45 | 10 | +14.9 | $-0.12^{*}$ | 0.30 |
| *2-Methyl-2-alkanols* | | | | | | | | | | | | | | |
| 29.04 | 2-Methyl-2-propanol | 90-170 | 15 | + 42.2 | -0.91 | + 8.6 | $-0.36^{s}$ | +19.2 | -0.32 | 0.22 | 10 | +15.0 | -0.39 | 0.25 |
| 29.05 | 2-Methyl-2-butanol | 90-170 | 15 | + 39.9 | -0.67 | + 5.8 | -1.14 | +17.3 | -0.54 | 0.33 | 10 | +13.1 | -0.86 | 0.43 |
| 29.06 | 2-Methyl-2-pentanol | 90-170 | 15 | + 40.7 | -0.46 | + 6.6 | -0.89 | +17.9 | -0.36 | 0.33 | 10 | +13.1 | -0.57 | 0.23 |

| No. | Thermodynamic data : C78 / TTF | | | | | | | | | C78 / MTF | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TTF - C78 | | | Mixture | | id([CF$_3$]=1) - C78 | | | σ | MTF - C78 | | | σ |
| | ΔH (cal mol$^{-1}$) | ΔS (cal mol$^{-1}$K$^{-1}$) | ΔC$_P$ | 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 mol$^{-1}$) | ΔH (cal mol$^{-1}$) | ΔS (cal mol$^{-1}$ K$^{-1}$) | ΔC$_P$ | (cal mol$^{-1}$) |
| 23.03 | - 242 | -0.476 | + 1.8$^{**}$ | - 274 | -0.473$^{s}$ | -177 | -0.315 | +0.5 | 2.8 | -146 | -0.214 | -0.5$^{**}$ | 2.8 |
| 23.04 | - 226 | -0.455 | - 2.4$^{**}$ | - 324 | -0.594 | -191 | -0.356 | -1.1 | 3.0 | -149 | -0.221$^{s}$ | -3.8$^{**}$ | 3.7 |
| 23.05 | - 197 | -0.399 | - 4.9$^{s}$ | - 306 | -0.549 | -175 | -0.322 | -2.0 | 2.8 | -152 | -0.244 | -3.8$^{**}$ | 3.4 |
| *1-Cyanoalkanes* | | | | | | | | | | | | | |
| 24.02 | -1 076 | -1.374 | + 2.1$^{**}$ | - 628 | -0.867$^{s}$ | -542 | -0.601 | +0.4 | 4.7 | -550 | -0.832 | +8.4$^{s}$ | 4.5 |
| 24.03 | -1 038 | -1.431 | + 2.9$^{**}$ | - 729 | -1.231 | -578 | -0.789 | + 0.6 | 5.1 | -509 | -0.801 | +4.7$^{s}$ | 2.7 |
| 24.04 | - 944 | -1.254 | + 1.0$^{**}$ | - 639 | -1.049 | -514 | -0.668 | - 0.1 | 4.4 | -447 | -0.672 | +2.8 | 0.9 |
| 24.05 | - 911 | -1.228 | + 4.4$^{**}$ | - 647 | -1.092 | -508 | -0.682 | + 1.2 | 4.6 | -402 | -0.581 | +3.5 | 1.7 |
| *1-Nitroalkanes* | | | | | | | | | | | | | |
| 25.02 | -1 025 | -1.418 | + 4.7$^{s}$ | - 848 | -1.561 | -620 | -0.914 | +1.2 | 2.1 | -331 | -0.392 | +2.2$^{*}$ | 1.8 |
| 25.03 | - 931 | -1.282 | + 2.5$^{*}$ | - 746 | -1.388 | -555 | -0.821 | +0.4 | 2.0 | -427 | -0.661 | -1.6$^{**}$ | 2.1 |
| 25.04 | - 895 | -1.259 | + 3.0 | - 752 | -1.437 | -549 | -0.842 | +0.6 | 1.6 | -428 | -0.682 | +0.3$^{**}$ | 1.8 |
| 25.05 | - 881 | -1.266 | + 3.7 | - 733 | -1.418 | -540 | -0.846 | +0.8 | 1.8 | -401 | -0.631 | +1.8$^{**}$ | 2.0 |
| *1-Acetoxyalkanes* | | | | | | | | | | | | | |
| 26.03 | - 601 | -0.925 | + 5.7 | - 573 | -1.091 | -395 | -0.645 | +1.7 | 2.6 | -299 | -0.459 | -0.6$^{**}$ | 1.4 |
| 26.04 | - 569 | -0.879 | + 4.3$^{s}$ | - 513 | -0.950 | -363 | -0.581 | +1.2 | 2.5 | -270 | -0.407 | +0.2$^{**}$ | 1.1 |
| 26.05 | - 587 | -0.961 | + 5.4 | - 528 | -0.998 | -377 | -0.635 | +1.6 | 2.0 | -281 | -0.453 | +1.3$^{*}$ | 0.9 |
| *1-Alkanols* | | | | | | | | | | | | | |
| 27.04 | - 473 | -0.829 | + 4.2 | - 636 | -1.259 | -382 | -0.701 | +1.1 | 1.6 | -344 | -0.592 | -1.0$^{**}$ | 2.3 |
| 27.05 | - 404 | -0.690 | + 3.5$^{*}$ | - 487 | -0.924 | -304 | -0.532 | +1.0 | 2.9 | -256 | -0.402 | +0.3$^{**}$ | 1.7 |
| 27.06 | - 414 | -0.752 | + 4.3$^{*}$ | - 499 | -0.973 | -315 | -0.579 | +1.2 | 3.5 | -263 | -0.443 | +1.9$^{**}$ | 1.9 |
| 27.07 | - 395 | -0.726 | + 2.4$^{**}$ | - 494 | -0.967 | -308 | -0.572 | +0.5 | 3.5 | -259 | -0.435 | +0.2$^{**}$ | 2.6 |
| *2-Alkanols* | | | | | | | | | | | | | |
| 28.04 | - 363 | -0.519 | + 2.8$^{**}$ | - 412 | -0.708 | -256 | -0.375 | +0.8 | 2.7 | -221 | -0.292 | +0.4$^{**}$ | 2.4 |
| 28.05 | - 334 | -0.492 | + 3.3 | - 317 | -0.472 | -212 | -0.282 | +1.0 | 1.6 | -199 | -0.252 | +1.4$^{**}$ | 1.9 |
| 28.06 | - 337 | -0.534 | + 3.9 | - 330 | -0.525 | -220 | -0.324 | +1.2 | 1.5 | -210 | -0.300 | +2.8 | 1.2 |
| 28.07 | - 349 | -0.597 | + 3.6 | - 356 | -0.607 | -237 | -0.384 | +1.1 | 2.0 | -221 | -0.342 | +2.5 | 1.0 |
| *2-Methyl-2-alkanols* | | | | | | | | | | | | | |
| 29.04 | - 577 | -0.995 | + 0.2$^{**}$ | - 409 | -0.709 | -333 | -0.549 | -0.3 | 1.5 | -306 | -0.495 | +1.7$^{*}$ | 1.3 |
| 29.05 | - 495 | -0.889 | - 0.8$^{**}$ | - 551 | -1.118 | -364 | -0.682 | -0.7 | 1.4 | -385 | -0.738 | +1.4$^{**}$ | 2.5 |
| 29.06 | - 437 | -0.769 | - 0.2$^{**}$ | - 492 | -0.977 | -321 | -0.587 | -0.5 | 1.5 | -312 | -0.567 | +0.4$^{**}$ | 1.3 |

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Table 6 (*continued*)

| *No.* | *Compound* | *Temp. range* (°C) | *Retention index : C78 / TTF* | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *n* | *TTF - C78* | | *Mixture* | | *id([CF$_3$]=1) - C78* | | *σ* | *n* | *MTF - C78* | | *σ* |
| | | | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | $A_L$ | 10 × $A_{LT}$ ($K^{-1}$) | $\Delta' I_{130}$ ($l\ mol^{-1}$) | 10 × $\Delta' A_T$ ($K^{-1} l\ mol^{-1}$) | | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | |
| 29.07 | 2-Methyl-2-hexanol | 90-170 | 15 | + 41.4 | -0.50 | + 7.3 | -1.07 | +18.4 | -0.44 | 0.46 | 10 | +13.8 | -0.71 | 0.21 |
| *1-Alkanethiols* | | | | | | | | | | | | | | |
| 30.04 | 1-Butanethiol | 90-170 | 15 | + 12.8 | -1.28 | - 5.1 | -2.16 | + 3.1 | -1.28 | 0.39 | 10 | + 4.4 | $-0.30^{*}$ | 0.80 |
| 30.05 | 1-Pentanethiol | 90-170 | 15 | + 13.5 | -1.24 | - 5.4 | -2.24 | + 3.2 | -1.29 | 0.28 | 10 | + 3.9 | -0.56 | 0.68 |
| 30.06 | 1-Hexanethiol | 90-170 | 15 | + 14.9 | -1.21 | - 4.5 | -2.30 | + 3.9 | -1.30 | 0.22 | 10 | + 4.1 | -0.48 | 0.39 |
| *2-Alkanones* | | | | | | | | | | | | | | |
| 31.04 | 2-Butanone | 90-170 | 15 | + 72.7 | -0.90 | +14.1 | -1.58 | +32.9 | -0.67 | 0.35 | 10 | +22.9 | -0.81 | 0.44 |
| 31.05 | 2-Pentanone | 90-170 | 15 | + 72.2 | -0.66 | +14.2 | -1.19 | +32.7 | -0.43 | 0.26 | 10 | +21.7 | -0.73 | 0.29 |
| 31.06 | 2-Hexanone | 90-170 | 15 | + 73.2 | -0.51 | +14.3 | -1.22 | +33.1 | -0.38 | 0.23 | 10 | +21.4 | -0.52 | 0.37 |
| 31.07 | 2-Heptanone | 90-170 | 15 | + 73.9 | -0.55 | +15.1 | -1.06 | +33.7 | -0.33 | 0.24 | 10 | +21.5 | -0.32 | 0.34 |
| *Aldehydes* | | | | | | | | | | | | | | |
| 32.05 | Pentanal | 90-170 | 15 | + 63.9 | -0.48 | +12.6 | -1.13 | +28.9 | -0.37 | 0.30 | 10 | +18.8 | -0.79 | 0.64 |
| 32.06 | Hexanal | 90-170 | 15 | + 64.5 | -0.32 | +14.0 | -1.03 | +29.7 | -0.26 | 0.23 | 10 | +18.7 | -0.56 | 0.47 |
| 32.07 | Heptanal | 90-170 | 15 | + 64.5 | -0.30 | +14.1 | -0.68 | +29.7 | -0.12 | 0.40 | 10 | +17.0 | $-0.11^{**}$ | 0.33 |
| *Ethers* | | | | | | | | | | | | | | |
| 33.06 | Dipropylether | 90-170 | 15 | + 16.1 | -0.41 | $-0.5^{**}$ | -0.49 | + 5.9 | -0.29 | 0.19 | 10 | + 4.5 | $-0.21^{*}$ | 0.54 |
| 33.08 | Dibutylether | 90-170 | 15 | + 16.5 | -0.44 | + 1.0 | -0.61 | + 6.6 | -0.34 | 0.19 | 10 | + 4.5 | -0.24 | 0.27 |
| *Primary amines* | | | | | | | | | | | | | | |
| 34.04 | Butylamine | 90-170 | 15 | + 25.8 | $-0.54^{**}$ | +11.8 | $-1.98^{s}$ | +14.2 | -0.83 | 1.28 | 10 | +10.4 | $-0.60^{*}$ | 1.27 |
| 34.05 | Pentylamine | 90-170 | 15 | + 26.9 | $-0.31^{**}$ | +16.6 | -2.15 | +16.4 | -0.79 | 1.18 | 10 | +10.7 | $-0.60^{*}$ | 1.53 |
| 34.06 | Hexylamine | 90-170 | 15 | + 27.3 | $-0.20^{**}$ | +21.0 | -2.42 | +18.2 | -0.84 | 1.09 | 10 | + 9.9 | $-0.44^{*}$ | 0.95 |
| *Secondary amines* | | | | | | | | | | | | | | |
| 35.04 | Diethylamine | 90-170 | 15 | + 20.5 | $+0.80^{**}$ | + 8.4 | $+1.95^{s}$ | +11.0 | +1.13 | 1.36 | 10 | + 6.9 | $+0.24^{*}$ | 0.63 |
| 35.06 | Dipropylamine | 90-170 | 15 | + 13.5 | $-0.38^{**}$ | + 1.0 | $-0.35^{**}$ | + 5.5 | -0.23 | 1.13 | 10 | + 3.3 | $-0.41^{**}$ | 1.26 |
| *Tertiary amines* | | | | | | | | | | | | | | |
| 36.06 | Triethylamine | 90-170 | 15 | + 11.1 | -0.72 | + 4.0 | -0.83 | + 5.7 | -0.54 | 0.86 | 10 | + 3.4 | $-0.37^{*}$ | 0.59 |
| *Halomethanes* | | | | | | | | | | | | | | |
| 37.01 | Dichloromethane | 90-170 | 15 | + 27.8 | $+0.14^{**}$ | + 7.2 | $+0.01^{**}$ | +13.3 | +0.17 | 0.49 | 10 | +10.9 | $-0.03^{**}$ | 0.82 |
| 37.02 | Trichloromethane | 90-170 | 15 | + 17.1 | $-0.01^{**}$ | + 4.7 | $-0.28^{**}$ | + 8.2 | -0.04 | 0.49 | 10 | + 7.6 | $-0.32^{**}$ | 1.26 |

| *No.* | *Thermodynamic data : C78 / TTF* | | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *TTF - C78* | | | *Mixture* | | *id([CF$_3$]=1) - C78* | | | $\sigma$ | *MTF - C78* | | | $\sigma$ |
| | $\Delta H$ | $\Delta S$ | $\Delta C_P$ | $\hbar$ | $s$ | $\Delta' H$ | $\Delta' S$ | $\Delta' C_P$ | | $\Delta H$ | $\Delta S$ | $\Delta C_P$ | |
| | *(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$^{-1}$)* | *(cal mol$^{-1}$)* | *(cal mol$^{-1}$ K$^{-1}$)* | | *(cal mol$^{-1}$)* |
| 29.07 | - 442 | -0.806 | - 1.2$^{**}$ | - 520 | -1.049 | -335 | -0.632 | -0.9 | 1.4 | -337 | -0.631 | +0.5$^{**}$ | 1.3 |
| *1-Alkanethiols* | | | | | | | | | | | | | |
| 30.04 | - 332 | -0.873 | + 5.1 | - 638 | -1.495 | -360 | -0.879 | +1.3 | 2.8 | -165 | -0.318 | +0.6$^{**}$ | 4.7 |
| 30.05 | - 319 | -0.862 | + 4.0 | - 632 | -1.498 | -355 | -0.882 | +0.9 | 1.8 | -209 | -0.437 | -2.1$^{**}$ | 3.3 |
| 30.06 | - 309 | -0.851 | + 2.4 | - 643 | -1.526 | -357 | -0.891 | +0.3 | 1.2 | -187 | -0.394 | -1.5$^{**}$ | 1.7 |
| *2-Alkanones* | | | | | | | | | | | | | |
| 31.04 | - 869 | -1.337 | + 2.5$^{**}$ | - 740 | -1.435 | -543 | -0.891 | +0.4 | 2.4 | -476 | -0.809 | +0.4$^{**}$ | 2.7 |
| 31.05 | - 800 | -1.250 | + 2.3$^{*}$ | - 632 | -1.210 | -483 | -0.789 | +0.3 | 1.6 | -433 | -0.752 | +2.2$^{*}$ | 1.6 |
| 31.06 | - 760 | -1.179 | + 1.4$^{**}$ | - 628 | -1.215 | -469 | -0.771 | +0.0 | 1.6 | -374 | -0.626 | +2.3$^{*}$ | 1.8 |
| 31.07 | - 769 | -1.239 | + 2.4$^{s}$ | - 602 | -1.156 | -464 | -0.776 | +0.4 | 1.7 | -331 | -0.525 | -0.1$^{**}$ | 2.0 |
| *Aldehydes* | | | | | | | | | | | | | |
| 32.05 | - 683 | -1.067 | + 0.3$^{**}$ | - 594 | -1.137 | -432 | -0.710 | -0.3 | 1.8 | -417 | -0.752 | +2.6$^{**}$ | 3.5 |
| 32.06 | - 637 | -0.988 | - 0.6$^{**}$ | - 573 | -1.084 | -408 | -0.665 | -0.7 | 1.3 | -355 | -0.615 | +2.4$^{**}$ | 2.4 |
| 32.07 | - 627 | -1.001 | - 0.8$^{**}$ | - 505 | -0.934 | -382 | -0.621 | -0.7 | 2.1 | -243 | -0.362 | -1.1$^{**}$ | 1.7 |
| *Ethers* | | | | | | | | | | | | | |
| 33.06 | - 180 | -0.429 | - 0.6$^{**}$ | - 328 | -0.664 | -182 | -0.390 | -0.5 | 1.2 | -144 | -0.265 | +3.0$^{**}$ | 2.7 |
| 33.08 | - 164 | -0.450 | + 0.7$^{**}$ | - 357 | -0.743 | -190 | -0.435 | -0.0 | 1.2 | -141 | -0.267 | -1.3$^{*}$ | 1.0 |
| *Primary amines* | | | | | | | | | | | | | |
| 34.04 | - 301 | -0.630 | +13.8 | - 783 | -1.621 | -382 | -0.784 | +4.7 | 4.1 | -292 | -0.549 | +2.5$^{**}$ | 5.3 |
| 34.05 | - 249 | -0.516 | +11.8 | - 853 | -1.749 | -388 | -0.787 | +3.9 | 4.2 | -285 | -0.541 | +3.9$^{**}$ | 4.8 |
| 34.06 | - 229 | -0.482 | + 6.7 | - 941 | -1.929 | -413 | -0.841 | +2.0 | 4.5 | -241 | -0.441 | -2.5$^{**}$ | 5.6 |
| *Secondary amines* | | | | | | | | | | | | | |
| 35.04 | + 38$^{**}$ | +0.199$^{**}$ | + 4.0$^{**}$ | + 110$^{**}$ | +0.556$^{**}$ | + 75 | +0.331 | +1.7 | 8.2 | - 78 | -0.049$^{**}$ | +0.5$^{**}$ | 3.9 |
| 35.06 | - 137 | -0.381 | - 1.5$^{**}$ | - 311$^{s}$ | -0.614$^{*}$ | -162 | -0.359 | -0.9 | 4.9 | -174 | -0.349$^{s}$ | -2.4$^{**}$ | 6.4 |
| *Tertiary amines* | | | | | | | | | | | | | |
| 36.06 | - 194 | -0.539 | + 1.8$^{**}$ | - 456 | -0.924 | -236 | -0.529 | +0.3 | 3.5 | -172 | -0.339 | -0.8$^{**}$ | 4.1 |
| *Halomethanes* | | | | | | | | | | | | | |
| 37.01 | - 196 | -0.269 | + 5.6 | - 310 | -0.491$^{s}$ | -164 | -0.223 | +1.9 | 2.8 | -183 | -0.251$^{s}$ | +2.3$^{**}$ | 5.0 |
| 37.02 | - 123 | -0.266 | - 0.0$^{**}$ | - 342 | -0.623 | -161 | -0.301 | -0.2 | 2.5 | -213 | -0.373$^{s}$ | -3.3$^{**}$ | 7.3 |

*(Continued on p. 200)*

Table 6 (*continued*)

| *No.* | *Compound* | *Temp. range* | *Retention index : C78 / TTF* | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *n* | *TTF - C78* | | *Mixture* | | *id([CF$_3$]=1) - C78* | | σ | *n* | *MTF - C78* | | σ |
| | | (°C) | | $\Delta I_{130}$ | $10 \times \Delta A_T$ ($K^{-1}$) | $A_L$ | $10 \times A_{LT}$ ($K^{-1}$) | $\Delta' I_{130}$ ($l\ mol^{-1}$) | $10 \times \Delta' A_T$ ($K^{-1} l\ mol^{-1}$) | | | $\Delta I_{130}$ | $10 \times \Delta A_T$ ($K^{-1}$) | |
| 37.03 | Tetrachloromethane | 90-170 | 15 | + 1.6$^{s}$ | -0.48 | - 3.2 | -1.11 | - 0.7 | -0.61 | 0.36 | 10 | - 0.9$^{**}$ | -0.50$^{s}$ | 1.02 |
| 37.04 | CF$_2$Br$_2$ | 90-170 | 15 | + 7.8 | -1.06 | - 3.0$^{s}$ | +0.70$^{**}$ | + 1.8 | -0.12 | 0.70 | 10 | + 1.2s | -0.02$^{**}$ | 0.74 |
| *HALOBENZENES* | | | | | | | | | | | | | | |
| 38.01 | Fluorobenzene | 90-170 | 15 | + 35.9 | -0.15$^{**}$ | + 1.4$^{**}$ | +0.04$^{**}$ | +14.1 | +0.08 | 0.48 | 10 | + 9.8 | +0.03$^{**}$ | 0.87 |
| 38.02 | Hexafluorobenzene | 90-170 | 15 | + 61.1 | -0.40$^{*}$ | + 9.9 | +1.01 | +26.9 | +0.45 | 0.52 | 10 | +16.9 | +0.80 | 0.37 |
| 38.03 | Trifluoromethylbenzene | 90-170 | 15 | + 57.5 | -0.15$^{**}$ | + 9.1 | +0.17$^{**}$ | +25.2 | +0.22 | 0.62 | 10 | +15.7 | -0.30$^{**}$ | 1.04 |
| 38.04 | Chlorobenzene | 90-170 | 15 | + 29.3 | -0.22 | - 1.5$^{*}$ | -0.54$^{s}$ | +10.5 | -0.20 | 0.39 | 10 | + 7.5 | +0.08$^{**}$ | 0.55 |
| 38.05 | Bromobenzene | 90-170 | 15 | + 26.5 | -0.57$^{*}$ | - 1.6$^{*}$ | -0.70$^{s}$ | + 9.4 | -0.40 | 0.43 | 10 | + 6.0 | +0.33 | 0.52 |
| 38.06 | Iodobenzene | 130-210 | 15 | + 24.0 | -0.46$^{*}$ | - 7.2 | +0.74 | + 6.3 | +0.18 | 0.32 | 10 | + 3.9 | +0.78 | 0.28 |
| *ALKYLPYRIDINES* | | | | | | | | | | | | | | |
| 39.01 | Pyridine | 90-170 | 15 | + 56.0 | -0.66 | +11.8 | +0.29$^{**}$ | +25.7 | +0.07 | 0.32 | 10 | +17.7 | -0.57$^{s}$ | 0.76 |
| 39.02 | 2-Picoline | 90-170 | 15 | + 49.2 | -0.62 | + 8.7 | +0.61 | +21.9 | +0.18 | 0.24 | 10 | +15.0 | -0.42$^{s}$ | 0.65 |
| 39.03 | 3-Picoline | 90-170 | 15 | + 62.0 | -0.25$^{**}$ | +15.5 | +0.74$^{s}$ | +29.4 | +0.43 | 0.47 | 10 | +19.8 | -0.33$^{**}$ | 0.90 |
| 39.04 | 4-Picoline | 90-170 | 15 | + 63.7 | -0.31$^{**}$ | +15.2 | -0.66$^{s}$ | +29.9 | -0.12 | 0.42 | 10 | +19.6 | -0.60 | 0.52 |
| 39.05 | 2,3-Lutidine | 130-210 | 15 | + 54.9 | +0.10$^{**}$ | + 9.9 | +1.21 | +24.2 | +0.79 | 0.37 | 10 | +15.8 | +0.20$^{**}$ | 0.63 |
| 39.06 | 2,4-Lutidine | 130-210 | 15 | + 57.4 | +0.20$^{**}$ | + 8.4 | +1.66 | +24.9 | +0.89 | 0.35 | 10 | +15.1 | +0.34 | 0.09 |
| 39.07 | 2,5-Lutidine | 130-210 | 15 | + 53.8 | +0.36$^{*}$ | + 8.8 | +1.54 | +23.3 | +1.03 | 0.49 | 10 | +15.9 | +0.13$^{**}$ | 0.71 |
| 39.08 | 2,6-Lutidine | 130-210 | 15 | + 44.2 | -1.60 | + 7.2 | +0.66$^{*}$ | +17.9 | +0.18 | 0.56 | 10 | +15.5 | +0.22$^{**}$ | 0.69 |
| 39.09 | 3,4-Lutidine | 130-210 | 15 | + 72.9 | -0.33$^{**}$ | +18.7 | +0.54$^{**}$ | +33.3 | +0.69 | 0.58 | 10 | +20.5 | +0.26$^{*}$ | 0.65 |
| 39.10 | 3,5-Lutidine | 130-210 | 15 | + 68.1 | -0.17$^{**}$ | +19.4 | -0.15$^{**}$ | +33.7 | +0.29 | 0.49 | 10 | +19.9 | -0.14 | 0.17 |
| 39.11 | 2-Ethylpyridine | 130-210 | 15 | + 43.6 | -0.42$^{*}$ | + 5.8 | +0.66 | +18.4 | +0.34 | 0.36 | 10 | +13.7 | -0.79 | 0.10 |
| 39.12 | 3-Ethylpyridine | 130-210 | 15 | + 57.9 | -0.21$^{**}$ | + 6.9 | +0.74 | +24.5 | +0.43 | 0.31 | 10 | +15.8 | -0.35$^{s}$ | 0.51 |
| 39.13 | 4-Ethylpyridine | 130-210 | 15 | + 61.6 | +0.48$^{**}$ | +13.1 | +0.33$^{**}$ | +29.0 | +0.38 | 0.49 | 10 | +19.6 | -0.69 | 0.52 |
| 39.14 | 2-Propylpyridine | 130-210 | 15 | + 40.6 | -0.09$^{**}$ | + 5.1 | +1.13 | +18.2 | +0.35 | 0.40 | 10 | +16.6 | -1.64 | 0.67 |
| 39.15 | 4-Propylpyridine | 130-210 | 15 | + 60.7 | +0.96 | +12.1 | +2.30 | +26.9 | +1.64 | 0.24 | 10 | +18.9 | +0.32$^{*}$ | 0.81 |
| 39.16 | 2,3,6-Collidine | 130-210 | 15 | + 43.0 | -0.15$^{**}$ | + 6.9 | +0.78 | +19.2 | +0.35 | 0.34 | 10 | +13.9 | -0.49 | 0.39 |
| 39.17 | 2,4,6-Collidine | 130-210 | 15 | + 45.8 | -0.17$^{**}$ | + 7.7 | +0.74 | +19.9 | +0.49 | 0.34 | 10 | +14.6 | -0.52 | 0.84 |
| 39.18 | 4-*tert*-Butylpyridine | 130-210 | 15 | + 66.6 | +0.00$^{**}$ | +17.2 | -0.01$^{**}$ | +31.2 | +0.38 | 0.21 | 10 | +19.8 | -0.36$^{*}$ | 0.77 |
| 39.19 | 3-Chloropyridine | 90-170 | 15 | + 43.7 | -0.71 | + 3.0 | -0.23$^{**}$ | +17.6 | -0.21 | 0.29 | 10 | +12.4 | -0.31 | 0.36 |
| *ORGANOSILICON COMPOUNDS* | | | | | | | | | | | | | | |
| 40.01 | Tetramethylsilane | 90-170 | 15 | + 2.8 | -0.05$^{**}$ | - 0.2$^{**}$ | -0.53$^{*}$ | + 2.2 | -0.19 | 0.49 | 10 | + 4.9 | +0.82$^{*}$ | 1.89 |

| No. | Thermodynamic data : C78 / TTF | | | | | | | | | C78 / MTF | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TTF - C78 | | | Mixture | | id([$CF_3$]=1) - C78 | | | $\sigma$ | MTF - C78 | | | $\sigma$ |
| | $\Delta H$ | $\Delta S$ | $\Delta C_P$ | $\bar{h}$ | $s$ | $\Delta' H$ | $\Delta' S$ | $\Delta' C_P$ | | $\Delta H$ | $\Delta S$ | $\Delta C_P$ | |
| | (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$^{-1}$) | (cal mol$^{-1}$) | (cal mol$^{-1}$ K$^{-1}$) | | (cal mol$^{-1}$) |
| 37.03 | - 75 | -0.348 | + 3.0$^{s}$ | - 420 | -0.955 | -188 | -0.496 | +0.8 | 1.9 | -154 | -0.362 | +3.6$^{**}$ | 5.7 |
| 37.04 | - 266 | -0.706 | + 5.4 | - 66$^{**}$ | -0.029$^{**}$ | -119 | -0.262 | +1.8 | 2.8 | - 89$^{s}$ | -0.139$^{**}$ | -1.9$^{**}$ | 4.4 |
| HALOBENZENES | | | | | | | | | | | | | |
| 38.01 | - 339 | -0.574 | - 1.0$^{**}$ | - 230 | -0.394$^{s}$ | -192 | -0.310 | -0.6 | 2.4 | -159 | -0.215$^{s}$ | -4.0$^{**}$ | 4.3 |
| 38.02 | - 595 | -0.817 | + 1.5$^{**}$ | - 173 | -0.098$^{**}$ | -239 | -0.224 | +0.4 | 2.1 | - 51$^{s}$ | +0.162 | -1.8$^{**}$ | 2.2 |
| 38.03 | - 540 | -0.802 | + 1.9$^{**}$ | - 297$^{s}$ | -0.450$^{*}$ | -273 | -0.369 | +0.5 | 4.1 | -281 | -0.449 | -0.4$^{**}$ | 6.0 |
| 38.04 | - 268 | -0.556 | + 1.6$^{**}$ | - 324 | -0.690 | -211 | -0.439 | +0.3 | 1.6 | -113 | -0.159$^{s}$ | -2.3$^{**}$ | 2.9 |
| 38.05 | - 296 | -0.697 | + 4.7 | - 360 | -0.795 | -238 | -0.540 | +1.4 | 2.1 | - 44 | -0.021$^{**}$ | -0.8$^{**}$ | 2.9 |
| 38.06 | - 219 | -0.565 | + 0.6$^{**}$ | - 38$^{**}$ | -0.081$^{**}$ | - 97 | -0.243 | +0.1 | 1.7 | + 64$^{**}$ | +0.209$^{*}$ | -1.5$^{**}$ | 1.3 |
| ALKYLPYRIDINES | | | | | | | | | | | | | |
| 39.01 | - 626 | -1.067 | + 4.0 | - 302 | -0.446 | -309 | -0.465 | -0.5 | 1.6 | -350 | -0.618 | +5.6$^{s}$ | 2.8 |
| 39.02 | - 548 | -0.989 | + 3.5 | - 204 | -0.256$^{s}$ | -251 | -0.392 | +1.1 | 1.5 | -288 | -0.509 | +5.4 | 2.1 |
| 39.03 | - 598 | -0.974 | + 6.0 | - 240 | -0.261$^{*}$ | -272 | -0.359 | +2.0 | 2.3 | -313 | -0.521 | +7.4 | 2.5 |
| 39.04 | - 631 | -1.028 | + 2.8$^{**}$ | - 515 | -0.945 | -387 | -0.634 | +0.6 | 2.8 | -370 | -0.654 | +3.5$^{*}$ | 2.6 |
| 39.05 | - 402 | -0.596 | - 0.3$^{**}$ | - 116 | -0.039 | -163 | -0.160 | -0.2 | 2.5 | -168$^{**}$ | -0.206$^{**}$ | -0.0$^{**}$ | 3.3 |
| 39.06 | - 458 | -0.698 | + 0.9$^{**}$ | - 31$^{**}$ | +0.159$^{s}$ | -150 | -0.121 | +0.3 | 0.9 | -128 | -0.116 | -0.2$^{**}$ | 0.4 |
| 39.07 | - 316 | -0.393$^{*}$ | - 1.2$^{**}$ | - 39$^{**}$ | +0.139$^{**}$ | -103 | -0.021 | -0.5 | 3.2 | -181$^{*}$ | -0.240$^{**}$ | +1.0$^{**}$ | 3.3 |
| 39.08 | - 469 | -0.885 | - 3.3$^{*}$ | - 179$^{s}$ | -0.224$^{**}$ | -219 | -0.357 | -1.5 | 2.7 | -151$^{**}$ | -0.164$^{**}$ | +0.8$^{**}$ | 3.4 |
| 39.09 | - 547 | -0.762 | - 1.8$^{**}$ | - 305 | -0.403$^{s}$ | -274 | -0.324 | -0.9 | 2.3 | -228$^{s}$ | -0.289$^{**}$ | -1.4$^{**}$ | 3.0 |
| 39.10 | - 581 | -0.889 | + 0.6$^{**}$ | - 444 | -0.734 | -339 | -0.498 | -0.1 | 1.1 | -285 | -0.444 | +0.1$^{**}$ | 0.8 |
| 39.11 | - 389 | -0.688 | - 0.3$^{**}$ | - 179 | -0.240 | -190 | -0.290 | -0.3 | 1.1 | -333 | -0.649 | +3.1 | 0.5 |
| 39.12 | - 543 | -0.907 | + 1.3$^{**}$ | - 181 | -0.235$^{s}$ | -239 | -0.349 | +0.3 | 1.3 | -268 | -0.463$^{s}$ | +2.3$^{**}$ | 2.5 |
| 39.13 | - 545 | -0.859 | + 3.4$^{**}$ | - 298 | -0.452$^{s}$ | -277 | -0.396 | +1.0 | 3.0 | -366 | -0.669 | +4.7$^{s}$ | 2.4 |
| 39.14 | - 467 | -0.933 | + 4.5 | - 86$^{**}$ | -0.031$^{**}$ | -186 | -0.310 | +1.5 | 2.0 | -503 | -1.073 | +8.9 | 3.2 |
| 39.15 | - 227 | -0.125$^{*}$ | - 2.1 | + 102 | +0.513 | - 13 | +0.228 | -0.6 | 1.0 | -160$^{**}$ | -0.169$^{**}$ | +1.8$^{**}$ | 3.7 |
| 39.16 | - 400 | -0.753 | + 2.3$^{*}$ | - 145 | -0.162$^{**}$ | -183 | -0.289 | +0.7 | 1.8 | -265 | -0.493 | +3.5$^{s}$ | 1.8 |
| 39.17 | - 351 | -0.597 | + 0.2$^{**}$ | - 168 | -0.203$^{**}$ | -171 | -0.241 | -0.1 | 2.0 | -299$^{s}$ | -0.557$^{*}$ | +2.1$^{**}$ | 3.7 |
| 39.18 | - 514 | -0.777 | - 0.8$^{**}$ | - 392 | -0.650 | -300 | -0.437 | -0.6 | 1.1 | -309$^{s}$ | -0.525$^{*}$ | +1.3$^{**}$ | 3.6 |
| 39.19 | - 509 | -0.984 | + 2.1 | - 319 | -0.623 | -288 | -0.547 | +0.4 | 1.0 | -238 | -0.422 | +3.3 | 0.9 |
| ORGANOSILICON COMPOUNDS | | | | | | | | | | | | | |
| 40.01 | - 8$^{**}$ | -0.108$^{**}$ | +17.9 | - 361 | -0.713 | -130 | -0.287 | +6.5 | 3.6 | + 76$^{**}$ | +0.289$^{*}$ | +13.2$^{s}$ | 7.6 |

(Continued on p. 202)

Table 6 (*continued*)

| *No.* | *Compound* | *Temp. range* | *Retention index : C78 / TTF* | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | *n* | *TTF - C78* | | *Mixture* | | *id([CF₃]=1) - C78* | | *σ* | *n* | *MTF - C78* | | *σ* |
| | | *(°C)* | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | $A_L$ | 10 × $A_{LT}$ ($K^{-1}$) | $\Delta' I_{130}$ ($l\ mol^{-1}$) | 10 × $\Delta' A_T$ ($K^{-1} l\ mol^{-1}$) | | | $\Delta I_{130}$ | 10 × $\Delta A_T$ ($K^{-1}$) | |
| 40.02 | Hexamethyldisilane | 90-170 | 15 | + 11.5 | +0.06$^{**}$ | + 3.3 | -0.44 | + 5.7 | -0.10 | 0.16 | 10 | + 5.2 | +0.52 | 0.67 |
| 40.03 | Hexamethyldisiloxane | 90-170 | 15 | + 16.0 | -0.14$^{**}$ | + 4.9 | -0.59 | + 7.9 | -0.21 | 0.16 | 10 | + 7.2 | +0.44 | 0.33 |
| *MISCELLANEOUS* | | | | | | | | | | | | | | |
| 41.01 | Carbon disulphide | 90-170 | 15 | - 13.2 | -1.16 | - 8.8 | -2.63 | - 8.4 | -1.51 | 0.62 | 10 | - 2.9 | -0.15$^{**}$ | 0.58 |
| 41.02 | Tetramethyltin | 90-170 | 15 | + 6.1 | +0.32$^{**}$ | + 7.0 | +1.11$^{s}$ | + 5.0 | +0.59 | 0.72 | 10 | + 3.1 | +0.74 | 0.38 |
| 41.03 | Tetrahydrofuran | 90-170 | 15 | + 36.8 | -0.51 | + 7.4 | -0.66 | +16.7 | -0.30 | 0.34 | 10 | +12.0 | -0.12$^{**}$ | 0.56 |
| 41.04 | 1,4-Dioxane | 90-170 | 15 | + 48.5 | -0.55 | + 4.1 | -0.70 | +19.9 | -0.31 | 0.27 | 10 | +14.1 | -0.23$^{**}$ | 0.73 |
| 41.05 | Thiophene | 90-170 | 15 | + 23.4 | +0.21$^{**}$ | + 3.7 | +0.17$^{**}$ | +10.3 | +0.23 | 0.41 | 10 | + 8.1 | +0.63 | 0.69 |
| 41.06 | Cyclopentanone | 90-170 | 15 | + 77.5 | -0.11$^{**}$ | +19.7 | -0.24$^{**}$ | +36.8 | +0.18 | 0.61 | 10 | +23.3 | -0.28 | 0.37 |
| 41.07 | Cyclohexanone | 90-170 | 15 | + 78.5 | +0.48$^{**}$ | +19.6 | +0.20$^{**}$ | +37.2 | +0.57 | 0.69 | 10 | +23.6 | +0.29$^{*}$ | 0.70 |
| 41.08 | Cyclohexanol | 90-170 | 15 | + 36.3 | -0.15$^{**}$ | + 6.2 | -0.89$^{*}$ | +16.3 | -0.26 | 0.69 | 10 | +13.3 | -0.48 | 0.66 |
| 41.09 | Pyrrolidine | 90-170 | 15 | + 31.4 | +0.97$^{**}$ | - 6.3$^{*}$ | -2.58$^{*}$ | + 9.5 | -0.53 | 1.92 | 10 | + 8.3 | +0.27$^{*}$ | 0.80 |
| 41.10 | Piperidine | 90-170 | 15 | + 20.7 | +0.62$^{*}$ | +11.4 | +1.68 | +12.2 | +0.97 | 0.74 | 10 | + 6.0 | +0.31$^{**}$ | 0.94 |
| 41.11 | Nitrobenzene | 130-210 | 15 | + 91.0 | +0.33$^{**}$ | +26.0 | +0.01$^{**}$ | +44.8 | +0.38 | 0.85 | 10 | +32.5 | -0.96$^{*}$ | 1.42 |
| 41.12 | Benzyl alcohol | 130-210 | 15 | + 51.5 | +0.61 | + 5.9 | +1.14 | +21.3 | +0.96 | 0.37 | 10 | +19.4 | +0.20 | 0.18 |
| 41.13 | 2-Phenylethanol | 130-210 | 15 | + 60.6 | +0.44 | + 9.8 | +1.11 | +26.5 | +0.83 | 0.31 | 10 | +19.5 | -0.15$^{*}$ | 0.51 |
| 41.14 | Anisole | 130-210 | 15 | + 45.5 | -0.11$^{**}$ | + 4.7 | +0.39$^{*}$ | +19.8 | +0.08 | 0.34 | 10 | +12.8 | -0.37 | 0.12 |
| 41.15 | Phenetole | 130-210 | 15 | + 43.9 | +0.11$^{**}$ | + 5.2 | +0.80 | +19.1 | +0.38 | 0.31 | 10 | +13.1 | -0.38 | 0.34 |
| 41.16 | Aniline | 130-210 | 15 | + 67.4 | -2.29 | +19.9 | -3.64 | +32.6 | -1.87 | 0.59 | 10 | +14.4 | -0.42$^{*}$ | 1.17 |
| 41.17 | Cyclohexylamine | 130-210 | 15 | + 26.7 | +0.53 | +14.3 | +0.73$^{**}$ | +13.2 | +1.06 | 1.06 | 10 | +10.6 | -0.22$^{**}$ | 0.92 |
| *ERROR OF THE COEFFICIENTS (STANDARD DEVIATION)* | | | | | | | | | | | | | | |
| | *f (n-alkanes)* | *90-210* | | *def.* | | | | | | | | | | |
| | *f (n-alkanes)* | *150-210* | | *def.* | | | | | | | | | | |
| | *f (solutes)* | *90-170* | | *2.29* | *1.12* | *2.19* | *0.78* | *1.18* | *0.51* | | | *0.99* | *0.22* | |
| | *f (solutes)* | *130-210* | | *3.94* | *1.12* | *3.78* | *0.78* | *2.04* | *0.51* | | | *1.13* | *0.22* | |
| *CONVERSIONS* | | | | | | | | | | | | | | |
| *A* | *Data related to* $K_D$ | | | *0* | *0* | *0* | *0* | *0* | *0* | | | *0* | *0* | |
| *B* | *Data related to 1 bar* | | | *0* | *0* | *0* | *0* | *0* | *0* | | | *0* | *0* | |

| *No.* | *Thermodynamic data : C78 / TTF* | | | | | | | | | *C78 / MTF* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *TTF - C78* | | | *Mixture* | | *id([CF$_3$]=1) - C78* | | | *σ* | *MTF - C78* | | | *σ* |
| | *ΔH* | *ΔS* | *ΔC$_P$* | *$\bar{h}$* | *s* | *Δ'H* | *Δ'S* | *Δ'C$_P$* | | *ΔH* | *ΔS* | *ΔC$_P$* | |
| | *(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$^{-1}$)* | *(cal mol$^{-1}$)* | *(cal mol$^{-1}$ K$^{-1}$)* | | *(cal mol$^{-1}$)* |
| 40.02 | - 35 | -0.141 | + 1.7$^{s}$ | - 350 | -0.674 | -137 | -0.288 | +0.5 | 1.0 | + 2$^{**}$ | +0.107$^{**}$ | +1.6$^{**}$ | 3.7 |
| 40.03 | - 93 | -0.200 | + 1.9 | - 377 | -0.701 | -162 | -0.305 | +0.5 | 0.9 | - 22$^{**}$ | +0.092$^{s}$ | -0.9$^{**}$ | 1.7 |
| *MISCELLANEOUS* | | | | | | | | | | | | | |
| 41.01 | - 53 | -0.470 | - 4.1$^{*}$ | - 694 | -1.672 | -295 | -0.839 | -2.1 | 3.2 | - 71$^{s}$ | -0.169$^{s}$ | +3.8$^{*}$ | 3.1 |
| 41.02 | + 72$^{*}$ | +0.064$^{**}$ | + 5.7$^{*}$ | - 84$^{**}$ | +0.041$^{**}$ | + 3 | +0.058 | +2.2 | 4.3 | + 54 | +0.219 | +8.6 | 2.0 |
| 41.03 | - 423 | -0.757 | + 0.4$^{**}$ | - 461 | -0.879 | -304 | -0.546 | -0.2 | 1.8 | -374 | -0.700 | +0.1$^{**}$ | 0.7 |
| 41.04 | - 547 | -0.941 | + 2.8 | - 427 | -0.837 | -333 | -0.588 | +0.7 | 1.3 | -253 | -0.402 | -0.6$^{**}$ | 4.0 |
| 41.05 | - 144 | -0.255 | - 1.9$^{**}$ | - 233 | -0.375 | -127 | -0.200 | -0.8 | 2.0 | - 15$^{**}$ | +0.117$^{*}$ | -4.2$^{*}$ | 3.2 |
| 41.06 | - 731 | -1.069 | + 4.7 | - 466 | -0.743 | -391 | -0.538 | +1.4 | 2.3 | -346 | -0.532 | +1.7$^{**}$ | 1.9 |
| 41.07 | - 616 | -0.825 | + 7.4 | - 402 | -0.607 | -326 | -0.402 | +2.5 | 3.1 | -227 | -0.256 | +4.6$^{s}$ | 2.8 |
| 41.08 | - 327 | -0.612 | + 4.2 | - 479 | -0.975 | -281 | -0.543 | +1.2 | 2.2 | -280 | -0.514 | +4.1$^{*}$ | 3.3 |
| 41.09 | - 66$^{**}$ | +0.048$^{**}$ | - 5.4$^{**}$ | - 676$^{*}$ | -1.592$^{*}$ | -265 | -0.546 | -2.4 | 12.7 | - 90$^{s}$ | -0.068$^{**}$ | -3.5$^{**}$ | 4.1 |
| 41.10 | - 12$^{**}$ | +0.008$^{**}$ | - 0.4$^{**}$ | + 3$^{**}$ | +0.291$^{**}$ | + 12 | +0.150 | -0.1 | 4.7 | - 53$^{**}$ | -0.026$^{**}$ | +0.6$^{**}$ | 5.3 |
| 41.11 | - 838 | -1.268 | + 2.9$^{**}$ | - 471 | -0.728$^{*}$ | -429 | -0.597 | +0.7 | 5.7 | -541$^{*}$ | -0.951$^{*}$ | +2.9$^{**}$ | 7.6 |
| 41.12 | - 294 | -0.301$^{*}$ | - 0.4$^{**}$ | + 12$^{**}$ | +0.079$^{**}$ | - 74 | -0.036 | -0.2 | 2.1 | -209 | -0.187$^{s}$ | +0.5$^{**}$ | 0.9 |
| 41.13 | - 394 | -0.543 | - 0.2$^{**}$ | - 129$^{s}$ | -0.086$^{**}$ | -159 | -0.161 | -0.2 | 1.7 | -220$^{s}$ | -0.319$^{*}$ | +1.9$^{**}$ | 2.4 |
| 41.14 | - 495 | -0.927 | + 3.3 | - 205 | -0.322 | -238 | -0.408 | +1.0 | 1.0 | -243 | -0.433 | +1.3 | 0.3 |
| 41.15 | - 407 | -0.752 | + 3.2 | - 143 | -0.169$^{s}$ | -184 | -0.290 | +1.0 | 1.0 | -230 | -0.417 | +2.7 | 1.0 |
| 41.16 | -1 034 | -2.009 | + 2.7$^{**}$ | -1 033 | -2.194 | -729 | -1.463 | +0.1 | 3.3 | -312$^{*}$ | -0.546$^{**}$ | -3.3$^{**}$ | 5.2 |
| 41.17 | + 182$^{**}$ | +0.498$^{**}$ | - 6.7$^{**}$ | - 236$^{**}$ | -0.278$^{**}$ | - 4 | +0.121 | -2.4 | 6.2 | -134$^{s}$ | -0.233$^{*}$ | +6.3 | 1.7 |
| *ERROR OF THE COEFFICIENTS (STANDARD DEVIATION)* | | | | | | | | | | | | | |
| | *2.3* | *0.0039* | *0.30* | *7.2* | *0.0121* | *2.8* | *0.0047* | *0.11* | | *6.2* | *0.0134* | *0.29* | |
| | *2.3* | *0.0039* | *0.30* | *7.2* | *0.0121* | *2.8* | *0.0047* | *0.11* | | *6.2* | *0.0134* | *0.29* | |
| | *9.1* | *0.0223* | *0.76* | *31.3* | *0.0775* | *12.2* | *0.0302* | *0.28* | | *9.1* | *0.0224* | *0.76* | |
| | *33.7* | *0.0813* | *0.84* | *34.4* | *0.0775* | *18.0* | *0.0417* | *0.31* | | *34.4* | *0.0571* | *0.59* | |
| *CONVERSIONS* | | | | | | | | | | | | | |
| *A* | *+ 10* | *-0.229* | *+ 0.1* | *+ 1* | *-0.015* | *+ 4* | *-0.092* | *+0.1* | | *+ 4* | *-0.042* | *+0.03* | |
| *B* | *0* | *0* | *0* | *0* | *0* | *0* | *0* | *0* | | *0* | *0* | *0* | |

data for four additional solutes and corrected data for two solutes are given in Table 5. The method of analysis of these data is essentially the same as described previously [1].

*C78–TTF: pentane–tetradecane*

In addition to data used for the analysis of variance, measurements were completed with higher alkanes, hendecane–tetradecane, on the two stationary phases in the temperature range 150–210°C. Including data also on C78 gave a set of $3 \times 4 = 12$ data for each higher alkane. This data set was evaluated on the basis of the results of 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 $\Delta H_z^{\mathrm{P}}$, $h_z$ and $s_z$ are linear functions of $z$, whereas $\Delta S_z^{\mathrm{P}}$ and $\Delta C_{\mathrm{P},z}^{\mathrm{P}}$ are independent of the carbon number, $z$. Imposing these constraints, a multiple regression was performed on the set of 126 (lower alkanes) + 48 (higher alkanes) = 174 data points, where the values for C78, $\varphi_{\mathrm{TTF}} = 0$, have been included from ref. 1. The regression coefficients are listed in columns 17–21 of Table 6.

Data for the ideal solvent, idCF$_3$, were calculated as follows. Using the coefficients listed in Table 6 together with the molar volume of TTF (Eq. 16) the slope, $\Delta'\mu_z^{\mathrm{idX}}$, was calculated with the aid of Eq. 8, with $n = 4$, for 10 K intervals in the temperature range 90–210°C for a given alkane. An equation analogous to Eq. 4 was fitted to the points $\Delta'\mu_z^{\mathrm{idCF_3}}$ by multiple regression as a function of $T$ and $z$. The resulting regression coefficients, $\Delta' H_z$, $\Delta' S_z$ and $\Delta' C_{\mathrm{P},z}$, are given in columns 22–24 of Table 6.

*C78–MTF: pentane–tetradecane*

Standard chemical potential differences of $n$-alkanes (C$_5$–C$_{14}$) were determined on the stationary liquid MTF ($\varphi = 1$) in the temperature range 90–210°C at intervals of 20 K. Lower alkanes (C$_5$–C$_{10}$) were measured in the temperature range 90–210°C whereas higher alkanes (C$_{11}$–C$_{14}$) were measured between 150 and 210°C. Together with data from ref. 1, this gave a set of 116 data points. The results for $\Delta\mu_z^{\mathrm{A/P}}$ for all $n$-alkanes were fitted to Eq. 4 by multiple regression with first-degree dependence in $z$. The regression coefficients $\Delta H_z^{\mathrm{P}}$, $\Delta S_z^{\mathrm{P}}$ and $\Delta C_{\mathrm{P},z}^{\mathrm{P}}$ are given in columns 26–28 of Table 6.

### *3.5. Numerical value of the "methylene increment", $\delta\mu_z^{A/P}$*

*System C78–TTF*

Standard chemical potentials of $n$-alkanes (C$_5$–C$_{14}$) for the system C78–TTF can be represented as a function of $\Delta T$, $\varphi$ and a linear function of $z$ by

$$\begin{array}{llllll}
\Delta\mu_z^{\mathrm{A/P}} & = 3465.8 & -\,510.49z & +\,9.712\,\Delta T & +\,1.2379\,\Delta Tz & \\
\pm\sigma & = \quad 25.4 & \quad 2.60 & \quad 76 & \quad 77 & \\
 & +\,0.0043\,\Delta T^2 & -\,0.00244\,\Delta T^2 z & +\,3.5\varphi_{\mathrm{P}} & +\,11.26\varphi_{\mathrm{P}}z & \\
 & \quad 7 & \quad 7 & \quad 4 & \quad 4 & \\
 & +\,0.026\,\Delta T\varphi_{\mathrm{P}} & +\,0.0030\,\Delta T^2\varphi_{\mathrm{P}} & -\,0.00014\,\Delta T^2\varphi_{\mathrm{P}}z & & \\
 & \quad 19 & \quad 1 & \quad 1 & & \\
 & -\,98.6\varphi_{\mathrm{A}}\varphi_{\mathrm{P}} & +\,5.67\varphi_{\mathrm{A}}\varphi_{\mathrm{P}}z & +\,0.412\,\Delta T\varphi_{\mathrm{A}}\varphi_{\mathrm{P}} & & \\
 & \quad 3 & \quad 3 & \quad 57 & & (23)
\end{array}$$

The partial derivative of Eq. 23 with respect to the variable $z$ is the methylene increment; its value at $\varphi_{\mathrm{P}} = 0$ and $\varphi_{\mathrm{P}} = 1$ is given by the equations

$$\begin{array}{llllr}
\delta\mu_z^{\mathrm{A}} & = -510.5 & +\,1.2379\,\Delta T & -\,0.00244\,\Delta T^2 & (24) \\
\pm\sigma & = \quad 2.6 & \quad 77 & \quad 7 &
\end{array}$$

$$\begin{array}{llllr}
\delta\mu_z^{\mathrm{P}} & = -499.2 & +\,1.2379\,\Delta T & -\,0.00258\,\Delta T^2 & (25) \\
\pm\sigma & = \quad 2.6 & \quad 77 & \quad 7 &
\end{array}$$

Similarly, the data for $n$-alkanes on the ideal stationary phase idCF$_3$ at $[\mathrm{CF_3}] = 1$ mol l$^{-1}$ can be given as a function of $\Delta T$ and $z$ by Eq. 26 and the methylene increment by Eq. 27.

$$\begin{array}{lllll}
\Delta'\mu_z^{\mathrm{idCF_3}} & = 3430.4 & +\,9.849\,\Delta T & +\,0.0059\,\Delta T^2 & \\
\pm\sigma & = \quad 25.4 & \quad 76 & \quad 9 & \\
 & -\,504.21z & +\,1.2428\,\Delta Tz & -\,0.00251\,\Delta T^2 z & (26) \\
 & \quad 2.56 & \quad 76 & \quad 9 &
\end{array}$$

$$\begin{array}{llllr}
\delta'\mu_z^{\mathrm{idCF_3}} & = -504.2 & +\,1.2428\,\Delta T & -\,0.00251\,\Delta T^2 & (27) \\
\pm\sigma & = \quad 2.6 & \quad 76 & \quad 9 &
\end{array}$$

*System C78–MTF*

Standard chemical potentials of $n$-alkanes (C$_5$–C$_{14}$) for the system C78–MTF are represented as a function of $\Delta T$ and $z$ by Eq. 28. The partial derivative of Eq. 28 with respect to $z$ is given by Eq. 29, which is the methylene increment for pure MTF.

$$\begin{array}{lllll}
\Delta\mu_z^{\mathrm{A/P}} = 3465.8 & -\,510.49z & +\,9.712\,\Delta T & +\,1.2379\,\Delta Tz & \\
\pm\sigma \quad = \quad \mathit{25.4} & \mathit{2.60} & \mathit{76} & \mathit{77} & \\
\quad +\,0.0043\,\Delta T^2 & -\,0.00244\,\Delta T^2 z & -\,44.1\varphi_{\mathrm{P}} & +\,4.16\varphi_{\mathrm{P}}z & \\
\quad \mathit{7} & \mathit{7} & \mathit{3} & \mathit{3} & \\
\quad +\,0.143\,\Delta T\varphi_{\mathrm{P}} & -\,0.0060\,\Delta T\varphi_{\mathrm{P}}z & & & \\
\quad \mathit{1} & \mathit{1} & & & \\
\quad +\,0.0029\,\Delta T^2\varphi_{\mathrm{P}} & -\,0.00017\,\Delta T^2\varphi_{\mathrm{P}}z & & & \\
\quad \mathit{1} & \mathit{1} & & & (28)
\end{array}$$

$$\begin{array}{lllll}
\delta\mu_z^{\mathrm{P}} = & -506.3 & +\,1.2319\,\Delta T & -\,0.00261\,\Delta T^2 & (29) \\
\pm\sigma = & \mathit{2.6} & \mathit{77} & \mathit{7} &
\end{array}$$

### *3.6. Solution data for solutes other than n-alkanes*

*Retention indices*

Retention indices were determined at temperature intervals of 20 K in the temperature range indicated in Table 6. Two mixtures ($\varphi_{\mathrm{TTF}} = 0.5$ and 1) were used as stationary phases. Including data from ref. 1 for the stationary phase C78 ($\varphi_{\mathrm{TTF}} = 0$), we had a data set of fifteen points for C78–TTF for every solute. With the aid of this data set, coefficients of Eqs. 10, 11 and 12 were calculated by linear regression. The quadratic term $\bar{\Delta}A_{\mathrm{TT}}$ was never significant even at the 20% significance level. A second regression was performed by deleting the quadratic term. The results of the coefficients are presented in columns 5–8 of Table 6. With the data measured on the stationary phase MTF and using data from C78 (ten data for each solute), $\bar{\Delta}I$ values were calculated. Regression coefficients of $\bar{\Delta}I$ as a linear function of temperature are given in columns 13 and 14 of Table 6.

The regression coefficients of Eqs. 11 and 12 and the molar volume of TTF at 10 K intervals were used in Eq. 13 to calculate the slopes $\bar{\Delta}'I^{\mathrm{idX}}$ at every nominal temperature in the experimental domain. Linear regression of $\bar{\Delta}'I^{\mathrm{idCF_3}}$ ($n = 4$) with temperature resulted the coefficients $\bar{\Delta}'I_{130}$ and $\bar{\Delta}'A_{\mathrm{T}}$ given in Table 6. These slopes and the value of $\kappa$ (calculated using Eqs. 24 and 27) were used in Eq. 14 to obtain the retention index, $I^{\mathrm{idCF_3}}$, in the hypothetical solvent idCF$_3$.

*Thermodynamic data*

For a given solute, the experimental retention index data were converted one by one into standard chemical potentials by using Eq. 9 and thermodynamic data for *n*-alkanes calculated with coefficients listed in Table 6. The resulting standard chemical potentials, $\Delta\mu_j^{\mathrm{A/P}}$, were analysed by multiple regression using Eqs. 4–6. Coefficients of Eqs. 4 and 6 are given in columns 17–21 of Table 6. Finally, $\bar{\Delta}'\mu_j^{\mathrm{idCF_3}}$ values for the C78–TTF system were calculated for each solute by following the same procedure as described for *n*-alkanes. Regression of $\bar{\Delta}'\mu_j^{\mathrm{idCF_3}}$ as a function of $T$ gave the coefficients $\bar{\Delta}'H_j^{\mathrm{idCF_3}}$, $\bar{\Delta}'S_j^{\mathrm{idCF_3}}$ and $\bar{\Delta}'C_{\mathrm{P},j}^{\mathrm{idCF_3}}$ for each solute, which are presented in columns 22–24 of Table 6.

### *3.7. Conversion of thermodynamic data with respect to different reference states*

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

$$\Delta\mu_j^{\mathrm{L}} - \Delta\mu_j^{\mathrm{(D)L}} = RT\ln[\mathcal{R}T\rho_{\mathrm{L}}/(\mathrm{atm\,kg\,mol^{-1}})] \tag{30}$$

where $\rho_{\mathrm{L}}$ is the density of the stationary liquid. A data set, $\Delta\mu_j^{\mathrm{L}} - \Delta\mu_j^{\mathrm{(D)L}}$, was generated at 10 K intervals in the temperature range 90–120°C for the three solvents of C78–TTF ($\varphi_{\mathrm{TTF}} = 0$, 0.5 and 1) and for the two solvents of C78–MTF ($\varphi_{\mathrm{MTF}} = 0$ and 1). Densities at 10 K intervals were calculated using Eq. 16 for pure solvents. For mixed solvents the ideal mixing rule was applied. By fitting Eqs. 4–6 to the resulting data set, the necessary corrections were obtained. Information necessary for this conversion is listed in the next to the last line in Table 6.

### *3.8. Data listed in Table 6*

The principles involved in the evaluation of data presented in Table 6 are summarized as follows.

(i) Determinations of thermodynamic quantities of all substances were based on data collected for *n*-alkanes. Sets of standard chemical potentials of *n*-alkanes were first examined by variance analysis referring to the polynomial approximation given in Eqs. 20 and 22. Based on the results of the variance analysis, final data were calculated by fitting Kirchhoff's approximation to the original data (see Eq. 4) by non-linear regression techniques. For the regression it was assumed that $\Delta H$, $\Delta S$, $\Delta C_P$, $\hbar$ and $s$ are linear functions of the carbon number, $z$, of the *n*-alkanes and that the composition dependence in C78–TTF mixtures is described by Eqs. 5 and 6. Data on the standard alkane, C78, were always calculated with the coefficients given in Table 4 in ref. 1.

(ii) For all solutes other than *n*-alkanes, retention indices were determined. Temperature and composition dependences of the retention indices were analysed by linear regression where smoothed data on C78 were included from Table 4 in ref. 1. For the calculation of thermodynamic data, experimental retention indices were converted point by point into standard chemical potentials with the aid of the tabulated *n*-alkane data. Eq. 4 was then fitted to the resulting data as for *n*-alkanes. As a consequence of this procedure, retention indices calculated with Eq. 9 (*i.e.*, by using the "best" thermodynamic data) and the retention indices calculated with the coefficients of Eqs. 10–12 (*i.e.*, by using the "best" data fitted on the retention index scale) may be slightly different.

(iii) Thermodynamic data of *n*-alkanes in the ideal solvent idCF$_3$ ([CF$_3$] = 1 mol l$^{-1}$) were determined with the aid of the final regression described under (i). Using the resulting regression coefficients and the molar volume of TTF, the value of $\Delta'\mu^{\mathrm{idX}}$ was then calculated with Eq. 8 at 20 K intervals. Fitting Eq. 4 to the results, by assuming a linear dependence of $\Delta'H$, $\Delta'S$ and $\Delta'C_P$ on the carbon number $z$, gave the thermodynamic functions shown in Table 6.

(iv) Thermodynamic data for solutes other than *n*-alkanes in the ideal solvent idCF$_3$ were individually calculated following the procedure described under (iii).

(v) For retention indices on idCF$_3$, a combination of Eqs. 10, 11 and 12 was fitted to the retention index data set of a given solute to give the index as a function of temperature and composition on C78–TTF mixtures. The resulting regression coefficients were used in Eq. 13 to calculate the value of $\Delta'I^{\mathrm{idX}}$ at 20 K intervals in the experimental temperature range. The resulting data set was then used to determine the coefficients of the linear relationship listed in Table 6.

## 4. Results and discussion

Retention index and thermodynamic data for about 160 solutes are presented in Table 6 measured using C78–TTF mixtures and pure MTF. The solvent MTF contained one whereas TTF contained four trifluoromethyl (TF) groups in the molecule. The distance between TF groups can be increased at will in the melt of MTF by dilution with the standard alkane C78, contrary to the TTF melt. In fact, with C78–TTF mixtures ideally dilute TF solutions cannot be prepared as the four TF groups are in the same molecule. The study of the effect of this regroupment of the TF groups was the first objective of this project.

In future work, data on a stationary liquid containing TF groups will be determined at only one TF concentration in order to economize on experimental effort. Obviously, determination at only one concentration of the interacting group does not permit the calculation of the curvature of the relationship between chromatographic data and concentration of the interacting group and data at ideal dilution cannot be determined. Therefore, the question of the predictability of the curvature of the composition dependence was the second objective.

Concerning the correlation of data on the stationary phases MTF and TTF, based on experience with a primary alcohol-containing stationary phase (POH contains an OH group instead of CF$_3$), it was assumed that composition dependence of solution data in C78–TTF mixtures could be described by the simple quadratic Eqs. 5 and 10. Therefore, experimental data were determined at only two compositions ($\varphi_{TTF} = 0.50$ and 1). These data, together with data on pure C78 ($\varphi_{TTF} = 0$), permitted the determination of the constants $A_L$, $A_{LT}$ and $\hbar$, $s$ necessary to calculate the constants $i$ and $m$, respectively, at a given temperature (Eqs. 6 and 12). With these constants listed in Table 6, retention index differences $\Delta I$ were calculated for a mixture containing a 0.25 volume fraction of TTF. Certainly in this mixture the spatial distribution of the TF groups will be different from that in an MTF melt. However, if these interacting groups are distant enough in the TTF molecule, data in both liquids should be the same. As an example, in Fig. 4, retention index differences in the MTF melt determined at 130°C are plotted as a function of those found in the mixture. The correlation is excellent, the correlation coefficient being $r = 0.988$ with all data taken and without the four outliers (amines) $r = 0.990$. The data are represented by Eq. 31 (without outliers)

$$\Delta I_{130}^{MTF} = (0.82 \pm 0.17) + (0.994 \pm 0.013)\, \Delta I_{130}^{C78/TTF}(\varphi_{TTF} = 0.25) \quad (31)$$

The slope of the correlation line does not deviate from unity. The slight positive deviation of the intercept (less than 1 index unit) is the only difference between the two liquids.

In conclusion, mixtures of C78–TTF may be used to determine data representative of melts of the monosubstituted compound MTF. Consequently, it may be assumed that the initial slopes of the equation representing interaction energies as a function of the volume fraction of TTF are the same as those which would be found with data determined in C78–MTF mixtures. The latter system would give less precise data because of the weak interaction of the TF group with some solutes.

The curvature of the composition dependence of the retention data in terms of standard chemical potential is given by the constant $m$ in Eq. 5. In Part I [1] it was shown that this constant could be given as a function of the standard chemical potentials $\Delta\mu_j^{C78}$ and $\Delta\mu_j^{POH}$ with the exception

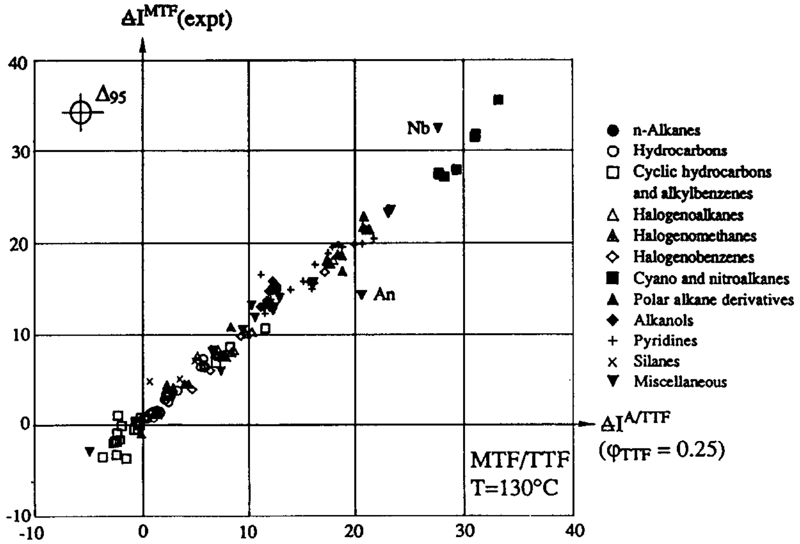

Fig. 4. Retention index differences on the MTF stationary liquid with reference of the standard alkane, C78, as a function retention index differences on a C78–TTF mixture with $\varphi_{TTF} = 0.25$. Both liquids contain the same molar concentration of TF groups. Outliers: Nb = nitrobenzene; An = aniline.

of the alcohols. The present data correlate without exception with the equation

$$m_j^{(e)} = a + b\,\Delta\mu_j^{A} + c\,\dot{\Delta}\mu_j^{TTF} \qquad (32)$$

where $a = -76 + 0.608\,\Delta T$, $b = -0.00895 + 0.000063\,\Delta T$, $c = 0.2757 - 0.00032\,\Delta T$, $\Delta T = T - T^{+}$ and $\sigma = \pm 25.1$ cal mol$^{-1}$. As an illustration, in Fig. 5 are plotted constants $m_j^{(e)}$, estimated with Eq. 32, as a function of the constants calculated with data listed in Table 6 ($\bar{h}$ and $s$ and use of Eq. 6).

Knowledge of the numerical values of the constants of Eq. 32 allows the estimation of the extent of curvature of the composition dependence. If working with a C78–TTF (or C78–MTF) mixture of known composition, $\varphi_{TTF}$, first the retention index of the compound in question is determined on this mixture and on the pure standard hydrocarbon. The index is now converted into standard chemical potentials by using data for $n$-alkanes listed in Table 6 to give $\Delta\mu_j^{C78}$ and $\dot{\Delta}\mu_j^{C78/TTF}(\varphi_{TTF})$. Rearrangement of Eq. 5 gives

$$\dot{\Delta}\mu_j^{TTF} = \frac{\dot{\Delta}\mu_j^{C78/TTF}}{\varphi_{TTF}} - \varphi_{C78} m_j \qquad (33)$$

Substitution of Eq. 33 in Eq. 32 gives after rearrangement

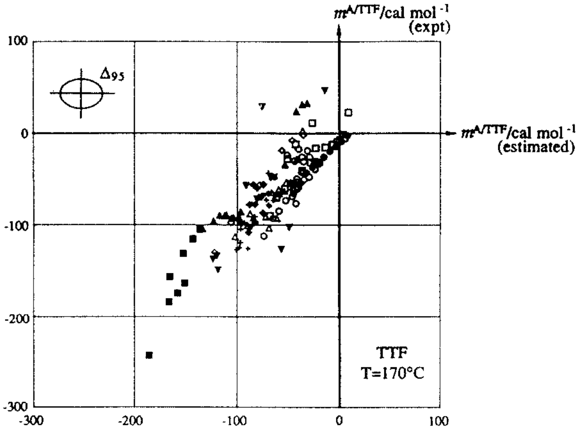

Fig. 5. Connection between experimental constants characterising the non-ideality of C78–TTF mixtures (constant $m$ in Eq. 5) and those estimated with Eq. 32 at 170°C.

$$m_j^{(e)} = \frac{\varphi_{TTF}(a + b\,\Delta\mu_j^{C78}) + c\,\dot{\Delta}\mu_j^{C78/TTF}}{\varphi_{TTF}(1 + c\varphi_{C78})} \qquad (34)$$

Use of the measured values in Eq. 34 allows the estimation of $m_j^{(e)}$ and by use of Eq. 33 the values of $\dot{\Delta}\mu_j^{TTF}$ can be calculated. The value of the derivative of $\dot{\Delta}\mu_j^{C78/TTF}$ with respect to the volume fraction can now be calculated as follows:

$$\left(\frac{\partial \dot{\Delta}\mu_j^{C78/TTF}}{\partial \varphi_{TTF}}\right)_{T,\varphi_{TTF}=0} = \dot{\Delta}\mu_j^{TTF} + m_j^{(e)} \qquad (35)$$

Finally, use of Eq. 8 permits the calculation of the standard chemical potential of the interaction at infinite dilution.

Fig. 6 illustrates the quality of the results when applying the proposed procedure. Data measured on MTF were considered as data measured on a C78–TTF mixture with $\varphi_{TTF} = 0.25$. With the aid of MTF data, the constant $m_j^{(e)}$ was estimated for each substance and the standard chemical potential of interaction was calculated with this estimated curvature. Estimated $\dot{\Delta}'\mu_j^{idCF_3}$ data are plotted as a function of data calculated with data measured on C78–TTF mixtures at 130°C.

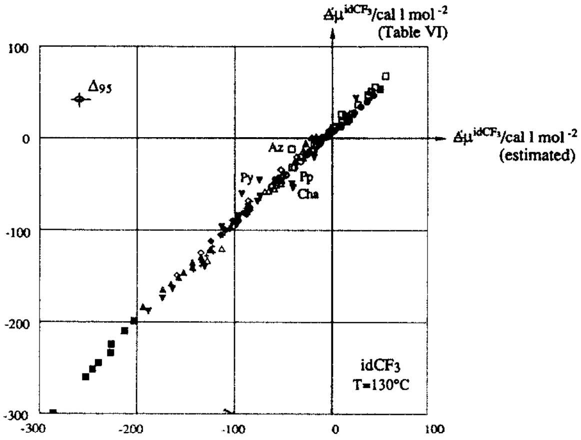

Fig. 6. Comparison of estimated and experimental standard chemical potential differences in an ideal TF solution ($[CF_3] = 1$). Estimated data were calculated from measurements on MTF with non-ideality given by Eq. 32. Outliers: Az = azulene; Py = pyrrolidine; Pp = piperidine; Cha = cyclohexylamine.

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