



ELSEVIER

Journal of Chromatography A, 969 (2002) 207–213

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Characterization of crude oils by inverse gas chromatography

F. Mutelet, G. Ekulu, M. Rogalski*

Laboratoire de Thermodynamique et d'Analyse Chimique (LTAC), Université de Metz, Ile du Saulcy, 57045 Metz Cedex 01, France

Abstract

It was shown that the flocculation onset of asphaltenes in crude oils could be predicted on the basis of the inverse gas chromatography characterization of the crude oil properties. Hildebrand's solubility parameters of four crude oils were calculated from inverse chromatography data and compared with values obtained from the onset of asphaltene flocculation measurements. A good agreement was observed with three crude oils of different origin. A relation between Hildebrand's solubility parameter and linear solvation energy relationship descriptors was established and it was demonstrated that the solubility parameter of a crude oil is determined mainly with dispersion interactions and the hydrogen bond basicity. A large basicity lowers the oil solubility parameter, and increases its stability in respect to flocculation.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Inverse gas chromatography; Oils; Molecular descriptors; Solubility parameter; Linear solvation energy relationship; Asphaltenes

1. Introduction

Asphaltenes are defined as the fraction of a crude oil that is soluble in toluene and not soluble in light *n*-alkanes [1]. Asphaltene deposition is a very well known problem that generates a large cost increase in the petroleum industry. It has been pointed out that the nature and content of the asphaltenes together with the nature and content of the remaining oil are the main factors that determine the relative stability of crude oils [2,3]. Flocculation of asphaltenes can be induced by changes in pressure, temperature and composition that reduce the stability in crude oils. However, because asphaltenes are the solubility class rather than a homogeneous compound family, they are difficult to characterize and

their solubility in crude oil is difficult to predict. Moreover, the flocculation onset is not directly related to the asphaltene content in the oil. Crude oils are colloidal systems whose dispersed phase is composed of asphaltene aggregates probably solvated by certain oil components [3]. The precipitation of asphaltenes depends on the colloidal stability of these systems. The stability is mainly governed by aggregation phenomena depending on the content and the polarity of asphaltenes and on the composition and properties of the dispersing medium [4,5].

With regard to asphaltene stability, the crude oil may be treated as a pseudo-binary system containing asphaltenes and the remainder of the oil.

Recently, Buckley et al. [6] observed that the onset of precipitation of asphaltenes occurs at characteristic refractive index for each oil/precipitant combination. They concluded that London dispersion forces dominate aggregation and precipitation of asphaltenes. While polar interactions such as dipole,

*Corresponding author. Tel.: +33-3-8731-5434; fax: +33-3-8731-5434.

E-mail address: rogalski@ipc.sciences.univ-metz.fr
(M. Rogalski).

ionic, hydrogen bonding are assumed to be of secondary importance, the London dispersion properties of a material can be characterized by the wavelength dependence of the refractive index. This approach is equivalent to Hildebrand's theory of regular solutions [7] that has been frequently used to elaborate thermodynamic models predicting asphaltene precipitation [8,9]. Hildebrand stated that the maximum of solubility is observed when the solute and solvent cohesive energy densities are identical. The cohesive energy density may be estimated using Hildebrand's solubility parameter calculated either from the vaporization energy or from the surface tension:

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} \quad (1)$$

where ΔE denotes cohesive energy and V is the molar volume of the solute. This simple method allows a satisfactory solubility prediction with a large range of solutes in non-polar solvents. Recent works [8,9] confirm its utility in determining the onset of asphaltene flocculation. It was shown in the literature that the onset of flocculation happens when the solvent solubility parameter overcomes a critical value [10]. Moreover, it was shown that the use of Hildebrand's solubility approach with the Flory–Huggins [11–13] theory allows prediction not only of the flocculation onset but also the amount of precipitated asphaltenes.

Apparently, the solubility parameter based approach is in contradiction with commonly used models considering asphaltene–resin interactions as a main factor of the crude oil stability. The latter models assume that polar interactions play a decisive role in asphaltene deposition. Indeed, the asphaltene polarity must intervene during the aggregate formation that leads to the colloidal stabilization of the oil. On the other hand, the flocculation onset corresponds to the destabilization of this system resulting from interactions between asphaltene aggregates and the remaining oil. The latter process is probably less dependent on the polarity of monomeric asphaltenes.

The objective of the present work is to determine the influence of the crude oil polarity on the flocculation onset and to validate the use of Hildebrand's theory to describe flocculation processes. Four crude oils supplied by the French petroleum company

TotalFinaElf were studied. Crudes C1, C2 and C3 contained, respectively, 21, 5 and 0.6% of asphaltenes. The crude C4 was the oil that flocculated in the pipe during the production process and was partly deasphalted. The flocculation onset induced by toluene/*n*-heptane mixtures with different ratio of both compounds was determined experimentally. The flocculation onset data were used to calculate the value of the crude oil solubility parameter using Hildebrand's solubility theory, while the oil solubility parameters were calculated from the retention data obtained by inverse chromatography using the current model based on the Flory–Huggins theory [11–13]. Retention volumes were obtained using chromatographic columns packed with the crude oil coated solid support. The polarity and the main contributions to molecular interactions characteristic for the four crude oils studied were determined using the linear solvation energy relationship (LSER) proposed by Abraham and co-workers [14–17].

Hildebrand's solubility parameter values obtained by two methods will be compared and discussed in terms of the fluids' polarity and basicity as determined by the LSER approach.

2. Experimental

Inverse chromatography experiments were carried out using a Shimadzu GC 14 gas chromatograph equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. Helium flow rate was adjusted to obtain adequate retention times. Exit gas flow rates were measured with a soap bubble meter. The temperature of the oven was measured with a Pt 100 probe and controlled to within 0.1 K. A PC directly recorded detector signals and corresponding chromatograms were obtained using Borwin 2.1 software. Stationary phases used with packed columns were prepared by soaking in 10% crude oil in cyclohexane solution. After evaporation of the cyclohexane under vacuum the support was equilibrated at 323 K during 6 h. The columns prepared in this way were coated with that part of crude oils which is less volatile than C9 fractions. The mass of the packing material was calculated from the mass of the packed and empty

column and was checked during experiments. The injected volumes of the sampled vapor were 0.1 μl . All other chemicals were obtained from commercial sources and used as received. All support materials used in the packed column studies were purchased from Supelco.

The molecular masses of crude oils were estimated by compositional analysis using gas chromatography and considering the molecular mass of asphaltene to be 1000 g/mol. Densities of C1, C2, C3 and C4 oils were measured at 298.15 K using the Anton Paar DMA 602 density meter and were 0.9617, 0.8596, 0.9147 and 0.8331 g/cm³, respectively.

3. Calculation

The retention data determined with inverse chromatography experiments were used to calculate the thermodynamic functions of the solute dissolution in the crude oil as well as Hildebrand's solubility and LSER parameters.

The probe specific retention volume, V_g^0 , was calculated with the usual relationship:

$$V_g^0 = \frac{t'_R F 273.15}{w T_R} \cdot \frac{3}{2} \cdot \frac{\left[\left(\frac{P_i}{P_o} \right)^2 - 1 \right]}{\left[\left(\frac{P_i}{P_o} \right)^3 - 1 \right]} \quad (2)$$

The reduced retention time t'_{R} was taken as the difference between the retention time of a probe and that of the air. F is the flow rate of the carrier gas measured at room temperature, T_R , while P_i and P_o are, respectively, the inlet and outlet pressures and w is the mass of the stationary phase.

The weight fraction activity coefficient, Ω_1^∞ , the partial molar free energy, ΔG_1^∞ and the average partial molar enthalpy, ΔH_1^∞ at infinite dilution of the solvents were calculated with the following expressions [18]:

$$\Omega_1^\infty = \frac{273.15R}{V_g^0 P_1^0 M_1} \cdot \exp\left(\frac{-P_1^0(B_{11} - V_1)}{RT}\right) \quad (3)$$

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \quad (4)$$

$$\Delta H_1^\infty = R \cdot \frac{\partial \ln(\Omega_1^\infty)}{\partial (1/T)} \quad (5)$$

where B_{11} is the second virial coefficient of the solute in the gaseous state, P_1^0 is the probe vapor pressure at temperature, T (K) and M_1 is the molecular mass of the probe. The values of P_1^0 and B_{11} have been taken from the literature [19]. The molar volume of the solute, V_1 was calculated using the liquid density taken from TRC tables [19].

According to the Flory–Huggins theory, the parameter χ_{12}^∞ characterizes interactions between the probe and the stationary phase and can be calculated using the following expression:

$$\chi_{12}^\infty = \ln\left(\frac{273.15Rv_2}{V_g^0 P_1^0 V_1}\right) - P_1 \cdot \frac{(B_{11} - V_1)}{RT} \quad (6)$$

In Eq. (6), R is the gas constant and v_2 is the specific volume of the stationary phase.

If it is assumed that the interaction parameter can be expressed in function of the solubility parameters of the probe and of the stationary phase:

$$\chi = \frac{v_0^1(\delta_1 - \delta_2)^2}{RT} \quad (7)$$

where v_0^1 is the molar volume of the solute and δ_1 and δ_2 are solubility parameters. Then, the solubility parameter of the stationary phase, δ_2 , can be calculated by fitting χ_{12}^∞ and δ_1 to the following equation:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right) \cdot \delta_1 - \frac{\delta_2^2}{RT} \quad (8)$$

If the left-hand side of Eq. (8) is plotted against δ_1 , a straight line having a slope of $2\delta_2/RT$ and an intercept of $-\delta_2^2/RT$ is obtained. The solubility parameter of the stationary phase, δ_2 , can be calculated from the slope or the intercept of the straight line.

The LSER approach [14–17] was used for characterizing the properties of the crude oils studied. The LSER model proposed by Abraham and co-workers is represented by the following expression:

$$\log t'_R = c + rR_2 + s\pi_2^H + a \sum \alpha_2^H + b \sum \beta_2^H + l \log L^{16} \quad (9)$$

The independent variables in Eq. (9) are the solute excess molar refraction (R_2), the effective solute

dipolarity/polarizability (π_2^H), the effective solute hydrogen bond acidity ($\Sigma \alpha_2^H$), the effective solute hydrogen bond basicity ($\Sigma \beta_2^H$) and the solute gas–liquid partition coefficient on *n*-hexadecane at 25 °C ($\log L^{16}$). The coefficients *c*, *r*, *s*, *a*, *b* and *l* are not simply fitting coefficients, because they reflect complementary properties of the solvent phase. The *r* coefficients reflect the tendency of the phase to interact with gaseous solutes through dispersive type interactions via electron pairs and π electrons. Coefficient *s* is a measure of the phase dipolarity/polarizability. Coefficient *a* represents the complementary property to solute hydrogen bond acidity and is a measure of the hydrogen bond basicity. Likewise, coefficient *b* is a measure of the phase hydrogen bond acidity. Finally, coefficient *l* is a combination of the work needed to create a cavity in the phase, and the general dispersion interaction energy between solute and solvent phase.

Table 2
LSER descriptors of four crude oils determined at 323 K

Crude oil	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>
C1	−2.79	0	0.517	1.08	0.188	0.801
C2	−3.02	0	0.528	1.2	0.302	0.854
C3	−2.17	0	0.374	0.732	0	0.805
C4	−2.35	0	0.396	0.911	0	0.822

4. Results and discussion

4.1. LSER characterization

Eq. (9) was used to characterize the four crude oils studied. Coefficients *c*, *r*, *s*, *a*, *b* and *l* of oils were obtained by multiple linear regression of retention data of 26 solutes. LSER parameters of probes are given in Table 1. Values of crude oil LSER parameters are reported in Table 2. It can be

Table 1
LSER descriptors of probes used to characterize crude oils

Sondes	R_2	π_2^H	$\Sigma \alpha_2^H$	$\Sigma \beta_2^H$	$\log L^{16}$
<i>n</i> -Hexane	0	0	0	0	2.668
<i>n</i> -Heptane	0	0	0	0	3.173
<i>n</i> -Octane	0	0	0	0	3.677
<i>n</i> -Nonane	0	0	0	0	4.182
Cyclohexane	0.305	0.1	0	0	2.964
1-Hexene	0.078	0.08	0	0.07	2.572
Benzene	0.61	0.52	0	0.14	2.768
Toluene	0.601	0.52	0	0.14	3.325
Ethylbenzene	0.613	0.51	0	0.15	3.778
CH ₂ Cl ₂	0.387	0.57	0.1	0.05	2.019
CHCl ₃	0.425	0.49	0.15	0.02	2.48
CCl ₄	0.458	0.38	0	0	2.833
1-Butanol	0.224	0.42	0.37	0.48	2.601
2-Methyl-1-propanol	0.217	0.39	0.37	0.48	2.413
2-Propanol	0.212	0.36	0.33	0.56	1.764
2-Pentanone	0.143	0.68	0	0.51	2.755
Methyl ethyl ketone	0.166	0.7	0	0.51	2.287
Triethylamine	0.101	0.15	0	0.79	3.04
Pyridine	0.631	0.84	0	0.52	3.022
Thiophene	0.687	0.57	0	0.15	2.819
Nitropropane	0.242	0.95	0	0.31	2.894
Trifluoroethanol	0.015	0.6	0.57	0.25	1.224
Diethylether	0.041	0.25	0	0.45	2.015
Hexafluoroisopropanol	−0.24	0.55	0.77	0.1	1.392
1,4 Dioxane	0.329	0.75	0	0.64	2.892

Table 3

Specific retention volume V_g^0 (cm³/g), mass fraction activity coefficient Ω_1^∞ , the partial molar free energies of mixing, ΔG_1^∞ (kcal/mol) and Flory–Huggins interaction coefficients χ_{12}^∞ of crude oils C1 and C2 determined at 323 K

Probe	C1				C2			
	V_g^0	Ω_1^∞	ΔG_1^∞	χ_{12}^∞	V_g^0	Ω_1^∞	ΔG_1^∞	χ_{12}^∞
Toluene	266.71	7.473	54.03	0.1957	236.07	8.442	57.31	0.2055
<i>n</i> -Heptane	109.93	10.805	63.94	0.3246	95.51	12.435	67.71	0.3530
<i>n</i> -Octane	281.12	9.317	59.96	0.1944	246.88	10.609	63.45	0.2121
<i>n</i> -Nonane	690.20	9.741	61.15	0.2638	627.12	10.721	63.73	0.2474
Butanol	194.62	34.587	95.20	1.6142	192.82	34.910	95.45	1.5113
Benzene	95.51	8.284	56.80	0.3181	82.90	9.545	60.61	0.3475
Triethylamine	122.54	16.308	75.00	0.8128	421.69	4.739	41.80	−0.5352
Pyridine	295.54	26.404	87.94	1.5969	299.14	26.086	87.62	1.4725

observed that crude oils C1 and C2 are strongly basic and slightly acid and that C3 and C4 are slightly basic only. The polar character of C1 and C2 is evidenced by the value of the polarizability parameter which is twice as large as that in the case of fluids C3 and C4. Dispersive interactions are described with parameters r and l . The value of the l term expressing general dispersion interactions is large with all fluids studied. This is not surprising in the case of a mixture of hydrocarbons. On the other hand, the r term is equal to zero as was previously observed by Selves et al. [20] and Burg et al. [21] with 47 crude oils of different origin. Nevertheless, it could be expected that the aromatic part of the crude oil characterized by a large R_2 value, induces dispersion interactions related to the presence of π electrons. The fact that r parameter is equal to zero in the case of petroleum fluids may be tentatively explained by aromatic compound stacking occurring in petroleum fluids.

4.2. Solubility parameter determination

The solubility parameter of crude oils was calculated from Eq. (8) using retention results obtained with eight probes of different polarity. Specific retention volume V_g^0 , mass fraction activity coefficient Ω_1^∞ , the partial molar free energies of mixing ΔG_1^∞ , and solute interaction coefficients χ_{12}^∞ obtained with different probes are given in Table 3. According to Klein and Jeberien [22] when χ_{12}^∞ is lower than 0.5, stationary phase–solute interactions are favorable for solute dissolution. As shown in Table 3 alkanes and aromatic compounds are good solvents but butanol and pyridine are bad solvents for C1 and C2.

The calculated values of the solubility parameter are given in Table 4. In the same table solubility parameters obtained with flocculation experiments with C1, C2 and C3 are reported. The flocculation onset was not determined in the case of C4 oil,

Table 4

Values of the crude oil solubility parameter δ_2 (cal/cm³)^{1/2}

Crude oil	Intercept	Slope	δ_2 from intercept	δ_2 from slope	δ_2^a	δ_2^b
C1	−0.02452	0.00579	8.12	7.78	7.95	8.12
C2	−0.02526	0.00590	8.24	7.93	8.085	8.19
C3	−0.03191	0.00804	9.26	10.80	10.03	10.37
C4	−0.03088	0.00788	9.11	10.58	9.845	

^a δ_2 , determined with Eq. (8) using retention data obtained with inverse chromatography 323 K.

^b δ_2 , calculated from the onset of asphaltene flocculation data measured at 298 K (1 cal=4.184 J).

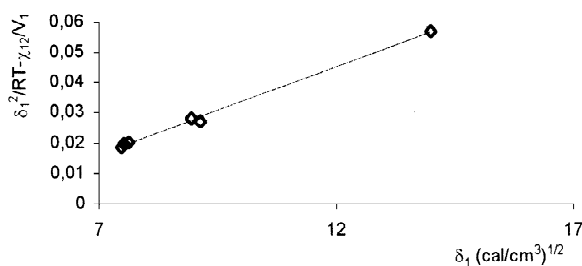


Fig. 1. Determination of the solubility parameter of the crude oil C1 from Eq. (8). The solubility parameter of the stationary phase, δ_2 , can be calculated from the slope or the intercept of the straight line. The agreement of both values proves that δ_2 does not depend on the probe polarity.

which spontaneously flocculated in pipes during transport. The solubility parameter of the oils C1 and C2 does not depend on the probe polarity, and results obtained with all probes can be used to fit Eq. (8) as shown in Fig. 1. In the case of oils C3 and C4 the solubility parameter depends on the probe polarity, as illustrated by Fig. 2. Consequently, the values of the solubility parameters of C3 and C4 reported in Table 4 were obtained with hydrocarbon probe data. The asphaltene content in C3 and C4 is much smaller than that observed with C1 and C2. Moreover, both the latter fluids have a lower polarity than fluids C1 and C2. We hypothesize that asphaltenes are less aggregated and more active with respect to polar probes in the fluids C3 and C4.

It should be pointed out that the solubility parameters calculated from retention data and from floccula-

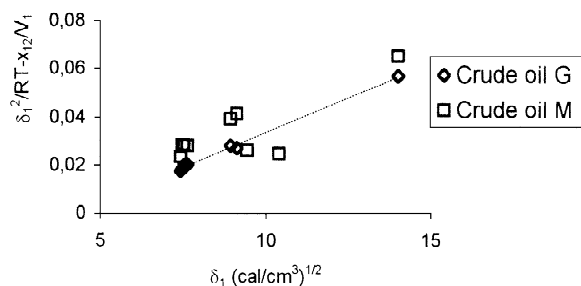


Fig. 2. Determination of the solubility parameter of the crude oil C3 and C4 from Eq. (8). The solubility parameter of the stationary phase, δ_2 , calculated from the slope is different from that calculated from the intercept of the straight line. In this case, δ_2 depends on the probe polarity and should be determined with non-polar probes only.

tion experiments are very close. This suggests that the crude oil solubility parameter determined by the method proposed in this work might be used to predict the onset of asphaltene flocculation. An example of the flocculation onset prediction is given in Fig. 3. It can be seen that the solubility parameter obtained with the inverse chromatography makes it possible to predict the onset of the asphaltene flocculation. The agreement between experimental and calculated data is satisfactory in a relatively large range of *n*-heptane/toluene ratio.

4.3. Relation between Hildebrand's solubility parameter and LSER descriptors

As already discussed, the four crude oils have a significant polarity as expressed by their LSER parameters. We established a relationship between the solubility parameter and corresponding LSER parameters (a , b , r , s , l). Eq. (10) shows that the solubility parameter is determined mainly with dispersion interactions and the hydrogen bond basicity:

$$\begin{aligned} \delta_2 &= 18.524l - 6.343a \\ r^2 &= 0.938; F = 1411 \end{aligned} \quad (10)$$

This confirms a hypothesis that the asphaltene flocculation is mainly dependent on dispersive force equilibrium in the oil. The aggregation of asphaltene is probably driven by polyaromatic π electron mobility that is characterized by the hydrogen bonding basicity parameter a . We hypothesize that the

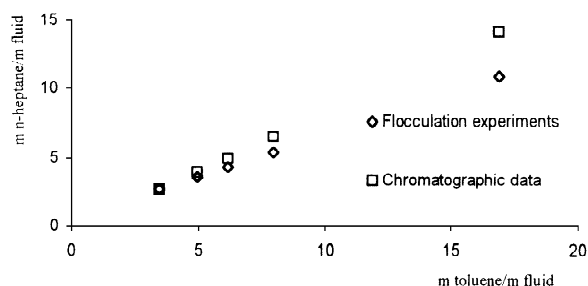


Fig. 3. Prediction of the onset of asphaltene flocculation using solubility parameters determined by inverse chromatography. The graph reports the masses of *n*-heptane necessary to flocculate asphaltenes from a solution formed by 1 g of the crude oil C1 and corresponding masses of toluene. Predicted data: \square ; experimental data: Δ .

fluid basicity influences the flocculation process and the solubility parameter value via its role in determining the aggregate size. A large basicity lowers the oil solubility parameter, and increases its stability with respect to the flocculation. This explains the fact that the C3 oil containing only 0.6% of asphaltenes has the largest solubility parameter value and is rather unstable.

Indeed, the flocculation mechanism is different in the case of fluids with low asphaltenes contents. The initial aggregation ratio is probably low and flocculation follows a different pathway strongly influenced by a large polarity of non-aggregated asphaltenes.

5. Conclusions

Hildebrand's solubility parameters of four crude oils were calculated from inverse chromatography data and compared with values obtained from the onset of asphaltene flocculation measurements. Results obtained with two methods are very close. Thus, the method proposed in this work might be used to predict the onset of asphaltene flocculation.

Relation between Hildebrand's solubility parameter and LSER descriptors was established and it was demonstrated that the solubility parameter is determined mainly with dispersion interactions and the hydrogen bond basicity. A large basicity lowers the oil solubility parameter, and increases its stability with respect to the flocculation. This statement explains the fact that the C3 oil containing only 0.6% of asphaltenes has the largest solubility parameter value and is rather unstable.

References

[1] D.L. Mitchell, J.G. Speight, *Fuel* 52 (1973) 149.

- [2] O. Leon, E. Rogel, J. Espidel, G. Torres, *Energy Fuels* 14 (2000) 6.
- [3] H. Laux, I. Rahimian, T. Butz, *Fuel Process. Technol.* 53 (1997) 69.
- [4] J.S. Buckley, *Fuel Sci. Technol. Int.* 14 (1996) 55.
- [5] L. Carbognani, J. Espidel, A. Izquierdo, in: T.F. Yen, G.V. Chilingarian (Eds.), *Asphaltenes and Asphalts: Developments in Petroleum Science*, Vol. 40, Elsevier, Amsterdam, 1999.
- [6] J.S. Buckley, G.J. Hirasaki, Y. Liu, S. Von Drasek, J.-X. Wang, B.S. Gill, *Petroleum Sci. Technol.* 16 (1998) 251.
- [7] H.J. Hildebrand, R.L. Scott, *The Solubility of Nonelectrolytes*, Van Nostrand, Princeton, NJ, 1950.
- [8] J.X. Wang, J.S. Buckley, *Energy Fuels* 15 (2001) 1004.
- [9] K.D. Mannistu, H.W. Yarranton, J.H. Masliyah, *Energy Fuels* 11 (1997) 615.
- [10] M.A.G. Teixeira, *Prepr. Am. Chem. Soc. Div. Petroleum Chem.* 46 (2001) 114.
- [11] A. Hirschberg, L.N. deJong, B.A. Schipper, J.G. Meijer, *Soc. Pet. Eng. J.* 24 (1984) 283.
- [12] H. Rassamdana, B. Dabir, M. Nematy, F. Farhani, M. Sahimi, *AIChE J.* 42 (1996) 10.
- [13] Z. Yang, C.F. Ma, X.S. Lin, J.T. Yang, T.M. Guo, *Fluid Phase Equilib.* 157 (1999) 143.
- [14] M.H. Abraham, P.L. Grellier, R.A. McGill, *J. Chem. Soc., Perkin Trans. 2* (1987) 797.
- [15] M.H. Abraham, *Chem. Soc. Rev.* 110 (1993) 73.
- [16] M.H. Abraham, G.S. Whiting, *J. Chem. Soc., Perkin Trans. 2* (1990) 1451.
- [17] M.H. Abraham, G.S. Whiting, *J. Chromatogr.* 587 (1991) 213.
- [18] J.R. Conder, C.L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, New York, 1979.
- [19] Thermodynamics Research Center (TRC), Texas Engineering Experiment Station, Texas A&M University System, College Station, TX, April 1987.
- [20] J.L. Selves, M.H. Abraham, P. Burg, *Fluid Phase Equilib.* 148 (1998) 69.
- [21] P. Burg, J.L. Selves, J.P. Colin, *Anal. Chim. Acta* 317 (1995) 107.
- [22] J. Klein, H.E. Jeberien, *Macromol. Chem.* 181 (1980) 1237.