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Evaluation of theoretical models of non electrolyte solutions in the prediction of Kováts retention indices of branched alkanes in alkane stationary phases

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Abstract

The models of Flory and of Elbro et al. were used for the prediction of Kováts retention indices of alkane solutes in squalane at three temperatures. The results were compared with experimental indices for sixty-two alkanes containing six to nine carbon atoms. Both models resulted in a better agreement with experimental indices than former prediction methods. A linear relationship was found between $(I_X - I_{*,X})$ and $(V_X - V_N)$, where I_X, $I_{*,X}$ and V_X represent the experimental index, the calculated index and the molar volume of solute X, and V_N is the molar volume of its isomeric normal alkane. The application of a correction formula based on this finding lowered the errors of the prediction to a half of its original value. Errors in the retention indices predicted by the model recently proposed by Kontogeorgis et al. [Fluid Phase Equilibria, 92 (1994) 35] were affected by temperature.

Keywords: Retention indices; Retention prediction; Alkanes, branched

1. Introduction

Since its introduction in 1958 [1], great efforts have been made to predict Kováts retention indices. Because of the abscense of important specific interactions, systems involving branched alkane solutes and paraffinic stationary phases have been the objective of numerous investigations. A successful approach to the treatment of these systems seems to be a prerequisite to tackle more complicated cases.

Methods employed to calculate the retention indices of branched alkanes in paraffinic stationary phases can be classified into two groups:

(a) Correlation methods, based on the fitting of experimental I_X to an equation of the type

$$I_X = a + bB_X + cC_X + ... \quad (1)$$

where B_X, C_X,... represent independent and complementary solute parameters (descriptors) and a, b, c,...are the coefficients obtained in the multiparameter regression analysis. Descriptors of many types have been used in these studies, and comprehensive reviews are available [2–4].

(b) Predictive methods, based upon a well-known expression inferable from the principles of formal thermodynamics:

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$$I_X = 100\left[N + \frac{\ln(\gamma_N^{\infty} p_N^{o} / \gamma_X^{\infty} p_X^{o})}{\ln(\gamma_N^{\infty} p_N^{o} / \gamma_{N+1}^{\infty} p_{N+1}^{o})}\right] \quad (2)$$

where p_i^o and γ_i^{∞} represent the vapour pressure and the infinite dilution activity coefficient of solute i in the stationary phase, respectively, and subscripts X, N and $N+1$ identify the solute of interest and the normal alkanes with N and $N+1$ carbon atoms whose retention volumes encompass that of solute X.

Only methods derived from Eq. (2) shall be treated in the present paper. From our point of view, since this is an exact relationship and since vapour pressures can be obtained from several reliable sources, efforts should be placed in the calculation of the quotients between activity coefficients. This objective can be pursued by resorting to models with sound theoretical basis; correlation methods should be reserved for those cases in which theoretical models fail or cannot be applied because of lack of basic information about the solutes or the stationary phase.

Deviations from the ideal behaviour are attributed to three contributions by present theories of non electrolytes mixtures [5]: combinatorial, free volume and interactional or chemical contributions. Accordingly, activity coefficients can be expressed as a product of three factors:

$$\gamma_i^{\infty} = \gamma_i^{\infty}(\text{comb}) \cdot \gamma_i^{\infty}(fv) \cdot \gamma_i^{\infty}(\text{int}) \quad (3)$$

Starting from these concepts, several calculation procedures have been suggested.

A first approach is to neglect differences between the alkane activity coefficients, i.e., assuming that $\gamma_X^{\infty} \simeq \gamma_N^{\infty} \simeq \gamma_{N+1}^{\infty}$. Under this assumption an estimator $I_{p,X}$ can be defined by

$$I_{p,X} = 100\left[N + \frac{\ln(p_N^{o} / p_X^{o})}{\ln(p_N^{o} / p_{N+1}^{o})}\right] \quad (4)$$

$I_{p,X}$ values were employed by Bonastre and Grenier [6] in their studies on the characterization of stationary phases.

Hammers and de Ligny [7] assumed that differences between the free volume and the interactional contributions to the alkane activity coefficient were negligible in comparison with differences between their combinatorial contributions, i.e., $\gamma_i^{\infty}/\gamma_j^{\infty} \simeq \gamma_i^{\infty}(\text{comb})/\gamma_j^{\infty}(\text{comb})$ for any pair of alkanes i and j. Flory–Huggins [8] equation was employed for the combinatorial activity coefficient

$$\ln\gamma_i^{\infty}(\text{comb}) = \ln(V_i/V) + 1 - (V_i/V) \quad (5)$$

where V_i and V represent the solute and the stationary phase molar volumes. Combination of Eq. (2) and Eq. (5) results in

$$I_{HL,X} = 100\left[N + \frac{\ln(p_N^{o}V_N / p_X^{o}V_X) - (V_n - V_X)/V}{\ln(p_N^{o}V_N / p_{N+1}^{o}V_{N+1}) - (V_N - V_{N+1})/V}\right] \quad (6)$$

Dimov and Shopov [9] considered that on account of the large differences between solute and stationary phase molar volumes the terms $(V_N - V_X)/V$ and $(V_N - V_{N+1})/V$ could be neglected in Eq. (6). The parameter thus obtained was called the physicochemical index (PCI) and postulated as an estimator of I_X:

$$PCI_X = 100\left[N + \frac{\ln(p_N^{o}V_N / p_X^{o}V_X)}{\ln(p_N^{o}V_N / p_{N+1}^{o}V_{N+1})}\right] \quad (7)$$

In subsequent papers Dimov and collaborators proposed several corrections to the PCI [10–12] that involved the addition of terms containing a series of structural parameters, as the number of methyl groups, the number of tertiary and quaternary carbon atoms, the number of Gosh conformations, etc. The resulting equations were fitted to experimental retention indices; the method was thus transformed into a correlation method.

Two new predictive methods that originate from Eq. (2) are proposed in the present paper. It is assumed in both methods that the interactional contributions to the activity coefficients in alkane mixtures are negligible. The general expression for the calculated retention indices, $I_{*,X}$, thus becomes

$$I_{*,X} = 100\left[N + \frac{\ln(\gamma_N^{*} p_N^{o} / \gamma_X^{*} p_X^{o})}{\ln(\gamma_N^{*} p_N^{o} / \gamma_{N+1}^{*} p_{N+1}^{o})}\right] \quad (8)$$

where

$$\gamma_i^{*} = \gamma_i^{\infty}(\text{comb}).\gamma_i^{\infty}(fv) \quad (9)$$

Values of γ_i^{*} are calculated by means of the original Flory state equation theory [13] in one of the proposed methods ($I_{*,X} = I_{F,X}$) or using the simplified

version of Elbro [14] in the other method ($I_{*,X} = I_{E,X}$).

1.1. Flory state equation theory

Application of this theory demands the previous knowledge of the solute and the stationary phase characteristic molar volumes (V_1^* and V^*, respectively), plus the solute characteristic temperature (T_1^*) and pressure (P_1^*). They are calculated by means of the equations [13]

$$\tilde{V}_i = V_i / V_i^* = \{1 + \alpha_i T/3(1 + \alpha_i T)\}^3 \quad (10a)$$

$$\tilde{T}_i = T/T_i^* = (\tilde{V}_i^{1/3} - 1)/\tilde{V}_i^{4/3} \quad (10b)$$

$$\tilde{p}_i = p/p_i^* = p/\gamma_i T\tilde{v}_i^2 \quad (10c)$$

where $\tilde{V}_i$, $\tilde{T}_i$ and $\tilde{p}_i$ are the reduced volume, temperature and pressure, respectively, using molar volumes (V_i), thermal expansion coefficients (α_i) and thermal pressure coefficient (γ_i) at a given temperature. Since the characteristic parameters are theoretically independent of temperature, experimental values of V_i, α_i and γ_i at 20°C are usually employed because of the availability of information. The Flory equation for the combinatorial and free volume contributions to the solute activity coefficient at infinite dilution in the stationary phase is

$$\begin{aligned}\ln\gamma_i^* &= \ln\gamma_i^\infty(\text{comb}) + \ln\gamma_i^\infty(\text{fv}) \\ &= \ln(V_i^*/V) + 1 - (V_i^*/V) \\ &\quad + (p_i^* V_i^*/RT)\{3\tilde{T}_i \ln[(\tilde{V}_i^{1/3} - 1)/\tilde{V}^{1/3} - 1)] \\ &\quad + \tilde{V}_i^{-1} - \tilde{V}^{-1}\} \end{aligned} \quad (11)$$

where $\tilde{V}$ represents the stationary phase reduced volume.

1.2. Elbro model

An important limitation in the application of the theory of Flory is the lack of reliable experimental values for the thermal pressure coefficients of branched alkanes. In 1990 Elbro et al. [14] proposed a pragmatic modification of Flory's model that permits to circumvent this difficulty. Their approach consists in assuming that the free volume for a pure component i can be expressed as the difference $V_i - V_i^W$, where V_i^W is the van der Waals molar volume computed from Bondi's group increments [15]. By using this assumption and a generalized van der Waals partition function, the following expression is deduced:

$$\begin{aligned}\ln\gamma_i^* &= \ln\gamma_i^\infty(\text{comb}) + \ln\gamma_i^\infty(\text{fv}) \\ &= \ln\frac{V_i - V_i^W}{V - V^W} + 1 - \frac{V_i - V_i^W}{V - V^W}\end{aligned} \quad (12)$$

Infinite dilution activity coefficients for alkane/alkane systems are underestimated by Eq. (12) and Kontogeorgis el al. [16] developed an equation of the following general form:

$$\ln\gamma_i^* = \ln\left(\frac{V_i - V_i^W}{V - V^W}\right)^A + 1 - \left(\frac{V_i - V_i^W}{V - V^W}\right)^A \quad (13)$$

A group of empirical equations are obtained by assigning different values to the exponent A. The equation of Elbro, obtained by making $A = 1$, has been designated E-FV. By making $A = p = 1 - V_i^W/V^W$, an equation identified as E-pfv is obtained. This equation produced better estimations than the Elbro equation for infinite dilution activity coefficients of some alkane–alkane mixtures [16].

2. Results and discussion

The accuracy of the two proposed methods (IE and IF) as well as those of the former models (IP, IHL and PCI) was tested by comparing their predictions against the experimental Kováts retention indices measured by Tourres [17] for alkanes having from six to nine carbon atoms in squalane at 30, 50 and 70°C. This comparison involved sixty-two branched alkanes: four hexanes, eight heptanes, sixteen octanes and thirty-four nonanes.

Vapor pressures were calculated by means of the equation of Antoine, using the coefficients listed in the compilation of Dreisbach [18], whose original source was the API Project 44 [19]. Densities of the hydrocarbon solutes were also taken from Dreisbach [18], and those of squalane at different temperatures (0.8004, 0.7900, 0.7834 and 0.7770 g cm^{-3} at 30, 50, 60 and 70°C, respectively) were from Cadogan and Purnell [20] and Ashworth and Everett [21].

Flory state equation characteristic parameters for hexanes, heptanes and octanes were calculated by

means of Eqs. (10a), (10b), (10c), using α_i and γ_i values at 20°C compiled by Allen et al. [22]. To calculate the characteristic pressures of the nonanes, the criteria suggested by Tancréde et al. [23] were followed. Characteristic parameters for squalane were taken from Croucher and Patterson [24]. van der Waals molar volumes were calculated by means of the group increments of Bondi [15].

The products $\gamma^*_N p^o_N$ for normal alkanes at 60°C, where γ^*_N were calculated by means of Flory (Eq. 11) or by Elbro (Eq. 12) models, have been gathered in Table 1. The specific retention volume of a solute i in a stationary phase whose molecular mass is M can be expressed by [25]

$$V_{g,i} = 273.15R/\gamma^{\infty}_i p^o_i M \quad (14)$$

Specific retention volumes of normal alkanes (with the exception of the first members) obey the equation [25]

$$\ln V_g(N) = a + bN \quad (15)$$

According to the proposed approach, a plot of $\ln(1/\gamma^*_N p^o_N)$ against N should result in a straight line whose slope shall be designated b^*. Similar values of the theoretically calculated slope b^* and of the experimentally measured slope b can be considered as an indication of the accuracy of the approach. The value of b at 60°C, as measured by Ettre and Billeb [26], is 0.402. The results obtained using Flory's and Elbro's models at the same temperature for $N \geq 7$ are 0.401 ± 0.004 and 0.401 ± 0.003, respectively, for a 95% confidence interval.

In Table 2 the performances of five predictive methods are compared. Standard deviations, s, and maximum discrepancies, Δ_{max}, were calculated from experimental and predicted indices at 50°C; results at 30 and 70°C reproduce the trends observed in the table. IE and IF behave clearly better than the former three predictors, as indicated by the values of s and Δ_{max}. Unexpectedly, IP values show the third smaller standard deviation, in spite of being based on the ideal solution model. If it is accepted that deviations of ± 1 i.u. are experimentally attained in interlaboratory reproducibility, it must be concluded that all the tested methods need to be improved.

In order to detect tendencies between experimental and calculated retention indices, differences $I_X - I_{F,X}$ and $I_X - I_{E,X}$ at 50°C have been plotted against molar volumes V_X in Fig. 1 and Fig. 2, respectively. A strong correlation was found between both pairs of variables. Almost parallel straight lines could be drawn through the points corresponding to solutes with the same number of carbon atoms. Fig. 3 and Fig. 4 show that $I_X - I_{F,X}$ and $I_X - I_{E,X}$ are linearly related with $V_X - V_N$, where V_N is the molar volume of the normal alkane with equal number of carbon atoms than the branched alkane X. It should be noted that the scatter of the points about these lines has been magnified by the ordinate scales and that, in order to preserve the individuality of the points, the diameter of the circles corresponds to only 0.3 i.u., a value quite smaller than the precision attainable in experimental measurements of retention indices.

The slopes, α, their standard deviations, $s(\alpha)$ and the correlation coefficients obtained on fitting $I_X - I_{F,X}$ and $I_X - I_{E,X}$ to $V_X - V_N$, r, have been gathered in Table 3. Although the slopes decrease slightly with temperature, their standard deviations indicate that

Table 1
Values of $\gamma^*_N p^o_N$ for n-alkanes at 60°C calculated by the Flory and the Elbro models

Solute	Flory	Elbro
n-Pentane	896.9	945.6
n-Hexane	339.9	354.7
n-Heptane	132.1	137.1
n-Octane	52.07	53.95
n-Nonane	20.81	21.33
n-Decane	8.280	8.464
n-Undecane	-	3.3602
n-Dodecane	-	1.364

Table 2
Standard deviations, s, and maximum discrepancies, Δ_{max}, for the Kováts retention indices calculated according to different approaches for sixty-two branched alkanes at 50°C

Estimator	s^a/i.u.	Δ^b_{max}/i.u.
I_P	6.0	16.1
PCI	7.4	14.2
I_{HI}	6.4	14.9
I_F	4.6	11.5
I_E	4.2	10.3

[a] $s = \left[\Sigma(I'_{exp} - I'_{calc})^2/(n-1)\right]^{1/2}$, where $n = 62$; i.u.: index units.
[b] Largest absolute value of I'_{exp}-I'_{calc}.

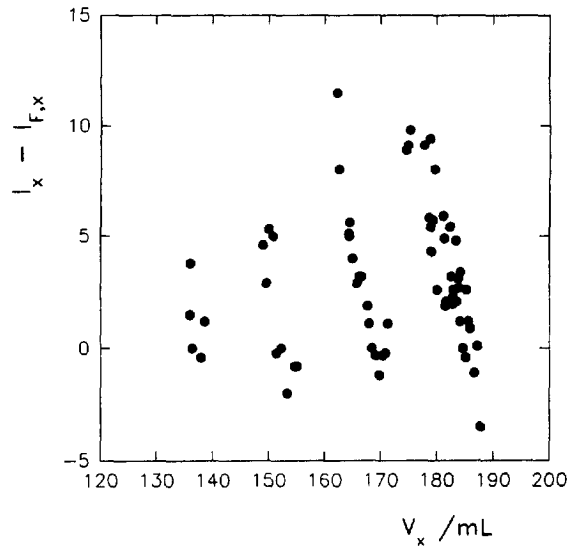

Fig. 1. Plot of differences between experimental and calculated (by means of Flory's model) retention indices $I_X - I_{F,X}$, against molar volumes, V_X, at 50°C.

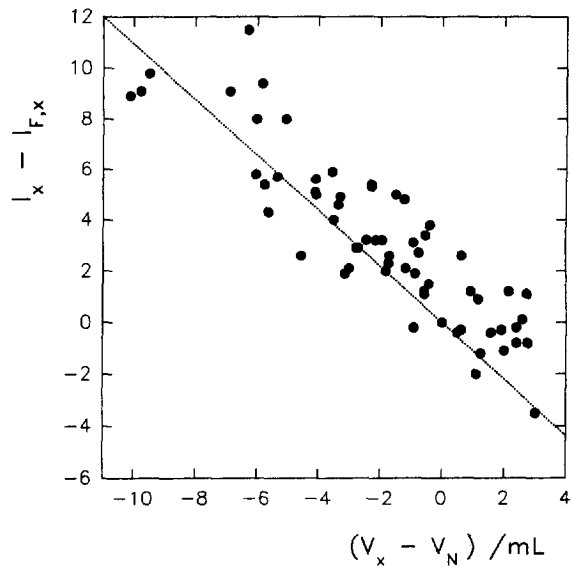

Fig. 3. Plot of $I_X - I_{F,X}$ differences vs. differences between molar volume of branched and of isomeric normal alkane, $V_X - V_N$, at 50°C.

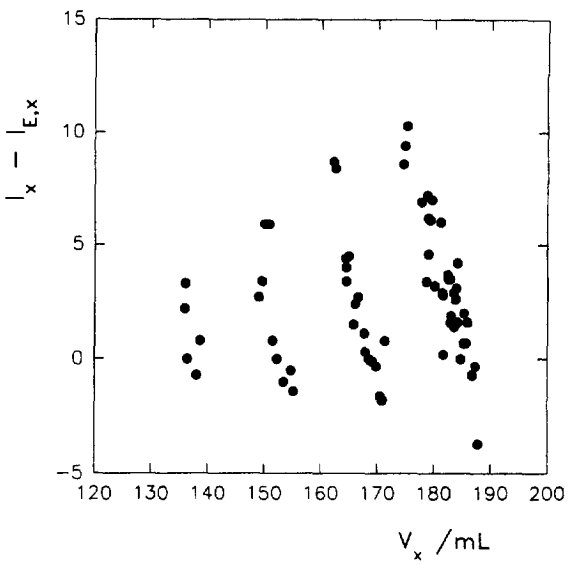

Fig. 2. Plot of differences between experimental and calculated (by means of Elbro's model) retention indices $I_X - I_{E,X}$, against molar volumes, V_X, at 50°C.

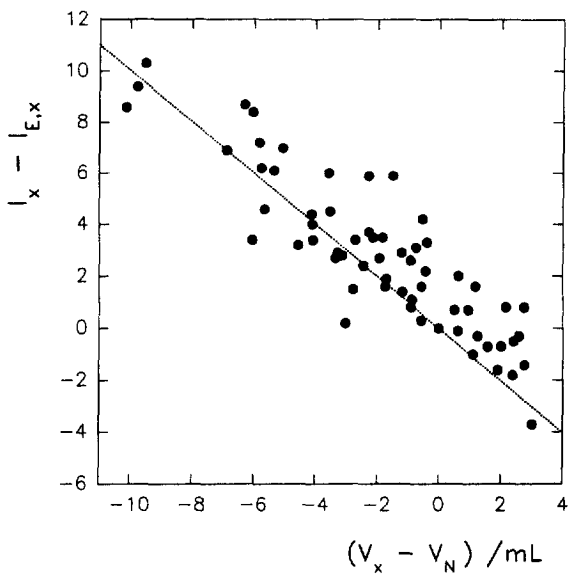

Fig. 4. Plot of $I_X - I_{E,X}$ differences vs. differences between molar volume of branched and of isomeric normal alkane, $V_X - V_N$ at 50°C.

Table 3
Slopes, α, standard deviations of the slopes, $s(\alpha)$ and correlation coefficients, r, obtained on fitting $I_X - I_{F,X}$ and $I_X - I_{E,X}$ to $V_X - V_N$ at 30, 50 and 70°C

	Flory model			Elbro model		
T/°C	30	50	70	30	50	70
α	−1.09	−1.09	−1.01	−1.04	−1.00	−0.90
s(α)	0.065	0.064	0.063	0.062	0.058	0.052
r	−0.874	−0.887	−0.875	−0.870	−0.888	−0.883

none of the results obtained differ significantly from −1. These findings suggest an empirical correction to the predicted indices; two new parameters, $I^C_{F,X}$ and $I^C_{E,X}$, defined by Eqs. (16a), (16b) were introduced:

$$I^C_{F,X} = I_{F,X} + V_N - V_X \quad (16a)$$

$$I^C_{E,X} = I_{E,X} = V_N - V_X \quad (16b)$$

In Table 4 the results of the direct application of the models of Flory and of Elbro (i.e., I_F and I_E) as well as those obtained after the corrections represented by Eqs. (16a) and (16b) are compared through their respective standard deviations s and maximum deviations Δ_{max}. It can be seen that neither s nor Δ_{max} were sensitive to temperature changes. However both s and Δ_{max} drop to less than a half of their original values when the corrections expressed in Eqs. (16a) and (16b) are applied.

Table 4
Standard deviations, s, and maximum discrepancies, Δ_{max}, for the Kováts retention indices calculated by means of Flory and Elbro models

	T/°C					
	30		50		70	
Estimator	s[a]	Δ^a_{max}	s	Δ_{max}	s	Δ_{max}
I_F	4.3	11.1	4.6	11.5	4.6	11.9
I_E	4.1	10.4	4.2	10.3	4.0	10.0
I^C_F	1.9	4.8	1.9	4.6	2.1	5.0
I^C_E	1.8	3.6	1.8	4.4	1.7	4.7

I_F and I_E: original values; I^C_F and I^C_E: values corrected with Eqs. (16a), (16b).
[a] Index unit.

Table 5
Summary of results obtained by means of the E-pfv equation (Eq. (13) with $A = p = 1 - V_i^W/V^W$ at three temperatures

T/°C	30	50	70
s/i.u.	3.2	5.3	5.6
Δ_{max}/i.u.	7.9	13.6	14.2
α	−0.79	−1.33	−1.31
$s(\alpha)$	0.051	0.057	0.054

s, Δ_{max}, α and s(α): same meaning as in Tables 1–4.
[a] Index units.

Finally, the results obtained when retention indices are calculated by means of the E-pfv equation are summarized in Table 5. It can be seen that the errors in the prediction depends on the temperature, as indicated by the corresponding values of s and Δ_{max}. Furthermore, the slope α of the plots $I_X - I_{pfv,X}$ against $V_X - V_N$ varies significantly and erratically with temperature. The application of corrections similar to those represented in Eqs. (16a) and (16b) would improve the prediction, but it demands the previous knowledge of the value of α at each temperature. This characteristic disqualify this approach as a predictive method.

Summarizing, the best results are obtained when the models of Flory or of Elbro are used to calculate retention indices. Although the results in Table 4 do not enable to decide which of both methods is better, we favour the choice of Elbro's approach because of its simplicity and because it demands very scarce previous information about solute and stationary phase.

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References

[1] E. sz. Kováts, Helv. Chim. Acta, 41 (1958) 1915.
[2] M. V. Budahegyi, E. R. Lombosi, T. S. Lombosi, S. Y. Mészáros, Sz. Nyiredy, G. Tarján, I. Timar and J. N. Takács, J. Chromatogr., 271 (1983) 213.
[3] G. Tarján, Sz. Nyiredy, M. Györ, E. R. Lombosi, T. S. Lombosi, M. V. Budahegyi, S. Y. Mészáros and J. N. Takács, J. Chromatogr., 472 (1989) 1.
[4] R. Kaliszan, Quantitative Structure – Chromatographic Retention Relationships, J. Wiley and Sons, New York, 1987.
[5] D. Patterson, J. Solution Chem., 23 (1994) 105.
[6] J. Bonastre and P. Grenier, Bull. Soc. Chim. Fr., (1967) 1395.
[7] W. E. Hammers and C. L. de Ligny, Recl. Trav. Chim. Pays-Bas 90, (1971) 175.
[8] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.
[9] N. Dimov and D. Shopov, J. Chromatogr., 44 (1969) 170.
[10] N. Dimov, J. Chromatogr., 119 (1976) 109.
[11] N. Dimov and D. Papazova, Chromatographia, 12 (1979) 720.
[12] N. Dimov, Anal. Chim. Acta, 201 (1987) 217.
[13] B. E. Eichinger and P. J. Flory, Trans. Faraday Soc., 64 (1965) 2035.
[14] H. S. Elbro, Aa. Fredenslund and P. Rasmussen, Macromolecules, 23 (1990) 4707.
[15] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968.
[16] G. M. Kontogeorgis, P. Coutsikos, D. Tassios and Aa. Fredenslund, Fluid Phase Equilibria, 92 (1994) 35.
[17] D. A. Tourres, J. Chromatogr., 30 (1967) 357.
[18] R. R. Dreisbach, Physical Properties of Chemical Compounds II, American Chemical Society, Washington, DC, 1959.
[19] F. D. Rossini et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, PA, 1953.
[20] D. F. Cadogan and J. H. Purnell, J. Chem. Soc., (1968A) 2133.
[21] A. J. Ashworth and D. H. Everett, Trans. Faraday Soc., 56 (1960) 1609.
[22] G. Allen, G. Gee and G. Wilson, Polymer 1 (1960) 456.
[23] P. Tancréde, P. Bothorel, P. de St. Romain and D. Patterson, J. Chem. Soc. Faraday Trans. II, 73 (1977) 15.
[24] M. D. Croucher and D. Patterson, J. Chem. Soc. Faraday Trans. II, 70 (1974) 1479.
[25] J.H. Purnell, Gas Chromatography, John Wiley, New York, 1962.
[26] L.S. Ettre and K. Billeb, J. Chromatogr., 30 (1967) 12.