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POLARITY OF PHTHALATE ESTERS IN GAS CHROMATOGRAPHY*

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SUMMARY

The importance of the concept of the "polarity" of stationary phases used in gas chromatography is discussed and a review of the principal methods proposed for the evaluation of gas chromatographic polarity is presented. These methods were employed for the gas chromatographic characterization of eight phthalate esters, and the discrepancies between the polarity scales obtained by different methods are considered.

INTRODUCTION

The concept of "polarity" is not wholly clear, because it has not yet been defined properly. It is connected with those molecular properties which give rise to intermolecular interaction forces of the non-dispersion type. As gas chromatography offers a valid aid in the determination of these forces, it seems convenient to introduce the concept of "gas chromatographic polarity". In fact, a knowledge of the properties of the solvents used in gas chromatography is essential for the selection of the appropriate liquid phase to be used in a given separation. It would therefore be necessary to classify the stationary phases according to a single parameter which allows the retentions of as many solutes as possible to be predicted *a priori*. A suitable classification could be that based on a "polarity scale". The principal criteria given in the literature for this type of classification are reported below; they were applied in the present study to a series of phthalate esters, *viz.*, diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), diisobutyl phthalate (DIBP), dicyclohexyl phthalate (DCyC₆P), di-2-ethylhexyl phthalate (D2EEP), diisodecyl phthalate (DIDP), *n*-butylbenzyl phthalate (BBP) and *n*-butyl-2-ethylhexyl phthalate (BEEP). The solubility parameters of these esters and the activity coefficients at infinite dilution of some homologous classes of organic solutes in them have been determined previously¹⁻⁴.

CRITERIA FOR THE CLASSIFICATION OF STATIONARY PHASES

In the last two decades, several criteria have been developed for evaluating

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the polarity of stationary phases. Pioneering work in this field was carried out by Keulemans *et al.*⁵. Later, Bayer⁶ suggested that the relative retention of two different solutes with identical boiling points could be taken as a measure of the selectivity of a liquid phase. Likewise, Rohrschneider⁷ and Maier and Karpathy⁸ proposed a polarity scale based on retention volumes of alkenes relative to those of the corresponding alkanes. In particular, Rohrschneider chose butadiene and *n*-butane as solutes and, taking the polarity of a polar reference phase (*e.g.*, β,β' -oxydipropionitrile) as 100 and that of a non-polar reference phase (*e.g.*, squalane) as 0, defined the polarity of any other liquid phase as follows:

$$P_R = 100 - 100 \cdot \frac{\ln \left(\frac{V_{g,\text{butadiene}}^0}{V_{g,n\text{-butane}}^0} \right)_p - \ln \left(\frac{V_{g,\text{butadiene}}^0}{V_{g,n\text{-butane}}^0} \right)_x}{\ln \left(\frac{V_{g,\text{butadiene}}^0}{V_{g,n\text{-butane}}^0} \right)_p - \ln \left(\frac{V_{g,\text{butadiene}}^0}{V_{g,n\text{-butane}}^0} \right)_{np}} \quad (1)$$

where the subscripts *x*, *p* and *np* refer to the stationary phase under study, β,β' -oxydipropionitrile and squalane, respectively.

Chovin and Lebbe⁹, with the aim of making Rohrschneider's method more generally applicable, proposed to take benzene-cyclohexane as the reference pair of solutes, so that polarity measurements can be extended to higher temperatures. They also suggested classifying the stationary phases on the basis of the relative retention (α) of two *n*-alkanes with *n*+1 and *n* carbon atoms, respectively; the parameter α does not depend on the number of carbon atoms in the two selected *n*-alkanes and varies inversely with the polarity of the liquid phase. In accordance with Rohrschneider, they constructed an empirical polarity scale in which 1 is the polarity of β,β' -oxydipropionitrile (polar reference phase) and 0 the polarity of squalane (non-polar reference phase). The polarity, P_{CL} , of any other liquid phase can be calculated as follows:

$$P_{CL} = \frac{\ln \alpha_{np} - \ln \alpha_x}{\ln \alpha_{np} - \ln \alpha_p} \quad (2)$$

Lazarre and Roumazeilles¹⁰ suggested the product of the relative retention, α , and the absolute temperature, *T*, of the column as a parameter for the characterization of stationary phases. They demonstrated that αT varies inversely with polarity and does not depend on temperature, and is therefore a characteristic property of the stationary phase examined.

Littlewood¹¹ classified stationary phases either (1) according to the specific retention volumes of alkanes or, if alkanes are less soluble in them, (2) according to the relative retention volumes of two successive homologous alkanes (in accordance with the criterion already proposed by Chovin and Lebbe⁹).

In 1963, Brown¹² suggested a suitable method for measuring the polarity of a stationary phase and its electron donor-acceptor properties. The method is based on the calculation of "retention fractions" defined as follows. If V_{np} , V_a and V_d are the retention volumes of a non-polar, an electron acceptor and an electron donor solute,

respectively, the retention fraction, F_{np} , relative to the non-polar solute (and similarly F_a and F_d) can be evaluated by the equation

$$F_{np} = \frac{V_{np}}{V_{np} + V_a + V_d} \quad (3)$$

For each stationary phase, the three values determined (F_{np} , F_a and F_d) can be reported in a triangular diagram from which it is easy to find out whether a phase is polar, an electron donor or an electron acceptor.

Interaction forces that develop between a solute and a stationary phase can be characterized and identified by means of empirical gas chromatographic indices¹³⁻¹⁶, as follows.

The Kováts retention index (I) is defined by the expression

$$I = 100 \cdot \frac{\ln V_{g,x}^0 - \ln V_{g,n}^0}{\ln V_{g,n+1}^0 - \ln V_{g,n}^0} + 100 n \quad (4)$$

where $V_{g,x}^0$ is the specific retention volume of solute x and $V_{g,n}^0$ and $V_{g,n+1}^0$ are the retention volumes of two n -alkanes with n and $n+1$ carbon atoms, respectively; hence $V_{g,n}^0 < V_{g,x}^0 < V_{g,n+1}^0$.

The retention index, $I_{x,np}$, of any solute in a non-polar stationary phase is a measure of the contribution of intermolecular forces of the dispersion type to solute-solvent interactions; on the other hand, the retention index, $I_{x,p}$, of the same solute in a polar stationary phase can be increased with respect to $I_{x,np}$ by a quantity ΔI_x ; so we have

$$\Delta I_x = I_{x,p} - I_{x,np} \quad (5)$$

ΔI_x is actually a measure of the contribution of intermolecular forces of the polar type (e.g., dipole-dipole forces or hydrogen bonds) to solute-solvent interactions. By comparing ΔI_x values determined using a non-polar reference stationary phase and polar solutes, stationary phases can be studied and arranged in order of polarity (the higher the ΔI_x value for any polar substance, the higher is the polarity of the stationary phase).

Rohrschneider¹⁷ proposed, as a measure of the polarity of a gas chromatographic column, the mean (\bar{x}_i) of the ΔI_x values calculated for different solutes in the column examined, and defined it as "mean polarity".

According to Schomburg¹⁸, the polarity of a stationary phase (P_S) can be defined by the expression

$$P_S = \Delta I_{\text{benzene}} - \Delta I_{\text{cyclohexane}} \quad (6)$$

while according to Rohrschneider¹⁹ a simpler and more accurate characterization of a partition column is obtained by using only the ΔI index relative to benzene. Rohrschneider²⁰ has recently characterized stationary phases by using the gas-liquid partition coefficients of some standard substances, each representative of one of the

most important classes of organic compounds (alkanes, aromatic hydrocarbons, alcohols, ketones, ethers and nitrocompounds). Partition coefficients, K (concentration of the solute in the solvent divided by the concentration of the solute in the gas phase) can be calculated by the relationship

$$K = \frac{RTd}{p^0 \gamma M} \quad (7)$$

where d and M are the density and molecular weight, respectively, of the liquid phase, R is the gas constant, p^0 is the vapour pressure of the pure solute at the column temperature, T , and γ is the activity coefficient of the solute in the stationary phase at temperature T .

Recently, Novak *et al.*²¹ presented a new criterion for evaluating the polarity of a stationary phase on the basis of the concept of the "reluctance" which a polar compound shows in accepting a non-polar compound. In particular, the polarity of a stationary phase can be defined by a simple parameter: the excess partial molar Gibbs free energy of a methylene group, $\Delta G^E(\text{CH}_2)$, which can be calculated by the relationship

$$\Delta G^E(\text{CH}_2) = -RT \cdot \frac{d \ln (V_g^0 p^0)}{dn} \quad (8)$$

where n is the number of methylene groups present in the molecule of the solute. Novak *et al.* demonstrated that $\Delta G^E(\text{CH}_2)$ is virtually independent of temperature and of the class of solutes selected as representative compounds.

According to Castello and D'Amato²², stationary phases can be classified simply on the basis of the activity coefficient of any n -alkane. This method can be visualized graphically by a Cartesian coordinate system in which the activity coefficients of an n -alkane given on the ordinate are arranged in a straight line; the stationary phases are then found on the abscissa in order of increasing polarity.

Finally, the interpretation of solute-solvent interactions, and hence the evaluation of the polarity of a liquid phase, can also be approached by utilizing the solubility parameter theory. In fact, the effects of solute-solvent interaction forces of the dispersion and polar types can be evaluated through the non-polar and polar components, λ and τ , of the vaporization energies of the pure compounds which form the mixture being examined^{23,24}. The gas chromatographic determination of λ and τ can be made on the basis of the activity coefficients at infinite dilution of the two compounds in the liquid binary mixture, as these parameters are related by the equation

$$\ln \gamma^\infty = \frac{V_2}{RT} \left[(\lambda_1 - \lambda_2)^2 + 2(\tau_1 - \tau_2)^2 - 2\psi_{12} \right] + \left[\ln \left(\frac{V_2}{V_1} \right) + \left(1 - \frac{V_2}{V_1} \right) \right] \quad (9)$$

where the subscripts 1 and 2 refer to the stationary phase and the solute, respectively, ψ_{12} is the induction energy and V_1 and V_2 are the molar volumes of the pure compounds.

POLARITY OF PHTHALATE ESTERS

Table I gives some polarity scales relative to the stationary phases studied. They were evaluated by the methods based on the relative retention of the benzene-

TABLE I

POLARITY SCALES ACCORDING TO ROHRSCHEIDER'S (P_R), CHOVIN AND LEBBE'S (P_{CL}) AND LITTLEWOOD'S ($V_g^0, n-C_8$) CRITERIA

Compound	P_R (at 120°)	P_{CL} (at 120°)	$V_g^0, n-C_8$ (at 125°)
DEP	45	0.37	32.40
DBP	37	0.30	44.02
DIBP	39	0.28	41.17
DC ₆ C ₆ P	38	0.25	29.98
D2EEP	26	0.11	41.65
DIDP	24	0.14	49.56
BBP	48	0.40	44.02
BEEP	31	0.29	40.03

cyclohexane pair, on the relative retention of two successive homologous n -alkanes and on the specific retention volumes of an n -alkane (n -octane).

The polarity scale P_R was determined according to eqn. 1 modified by Chovin and Lebbe⁹, using the retention volumes of the benzene-cyclohexane pair given by Petsev and Dimitrov²⁵. The polarity scale P_{CL} was determined according to eqn. 2, using literature data²⁶ for the relative retention of two successive homologous n -alkanes in squalane and β, β' -oxidipropionitrile.

There is good agreement between the P_R and P_{CL} scales as regards the extreme terms: the most polar phthalates are BBP ($P_R = 48$, $P_{CL} = 0.40$) and DEP ($P_R = 45$, $P_{CL} = 0.37$), while the least polar phthalates are D2EEP ($P_R = 26$, $P_{CL} = 0.11$) and DIDP ($P_R = 25$, $P_{CL} = 0.14$).

For the intermediate terms, some inversions in the order of polarity are observed on changing the scale. These inversions are explained by the similar polarities of some of the phthalate esters investigated. Good agreement was also found between the P_R values of DBP, DIBP, DCyC₆P, D2EEP and the corresponding values given by Petsev and Dimitrov²⁵.

In the polarity scale established according to the V_g^0 of n -octane, although the low polarity of DIDP was confirmed, some differences were noted with respect to the previous scales; this is in agreement with Littlewood's observation¹¹ on the impossibility of classifying stationary phases by using the specific retention volumes of compounds that have low solubilities in them.

TABLE II

POLARITY SCALE ACCORDING TO LAZARRE AND ROUMAZEILLES' CRITERION (αT)

Compound	αT			
	25°	75°	125°	Mean
DEP	830	766	735	777
DBP	870	789	746	802
DIBP	833	776	748	786
DCyC ₆ P	820	788	779	796
D2EEP	891	812	771	825
DIDP	938	827	766	844
BBP	839	767	746	784
BEEP	910	809	749	823

Table II gives the αT values calculated at three different temperatures. In accordance with the results of Chovin and Lebbe⁹, it is seen that the αT values decrease with increasing temperature; it is therefore necessary to take as the polarity index the mean of the αT values calculated at the three temperatures considered (see Table II). On the basis of the mean values of αT , the eight phthalates investigated can be classified in the following order of polarity: DEP > BBP > DIBP > DCyC₆P > DBP > BEEP > D2EEP > DIDP.

Table III reports the results obtained at 125° by the method proposed by Brown¹². The electron-acceptor, electron-donor and non-polar solutes selected were chloroform, carbon tetrachloride and *n*-hexane, respectively. For the extreme terms, this method gives the same order of polarity as found with the previous criteria. However, substantial differences are not observed for the polarities of the phthalate esters studied. It is also seen that D2EEP and DIBP are the stationary phases with the most marked electron-acceptor and electron-donor properties, respectively (see Table III).

TABLE III
RETENTION FRACTIONS AT 125° ACCORDING TO EQN. 3

Compound	F_a	F_d	F_{np}
DEP	0.490	0.381	0.129
DIBP	0.476	0.367	0.157
DCyC ₆ P	0.468	0.398	0.134
D2EEP	0.392	0.444	0.164
DIDP	0.408	0.389	0.203
BBP	0.466	0.401	0.133
BEEP	0.432	0.411	0.157

Table IV gives the polarity scales based on the determination of retention indices. ΔI indices were determined by means of eqns. 4 and 5 and the P_s index by means of eqn. 6. The non-polar reference phase selected was Apiezon L. The mean polarity, x_t , was calculated from the ΔI indices determined for 23 compounds belonging to the following classes: *n*-alkanes, cycloalkanes, olefins, aromatic hydrocarbons, alcohols, acetates, ketones and chloroalkanes. The three last polarity scales reported, in accordance with the previous ones, confirm that the highest polarities are shown by

TABLE IV
POLARITY SCALES ACCORDING TO ROHRSCHEIDER'S (x_t), SCHOMBURG'S (P_s) AND ROHRSCHEIDER'S ($\Delta I_{benzene}$) CRITERIA

Compound	x_t (at 125°)	P_s (at 125°)	$\Delta I_{benzene}$ (at 125°)
DEP	175	116	131
DBP	—	93	93
DIBP	142	70	87
DCyC ₆ P	144	93	107
D2EEP	106	62	58
DIDP	85	56	44
BBP	180	128	149
BEEP	117	77	69

BBP ($x_t = 180$, $P_S = 128$, $\Delta I_{\text{benzene}} = 149$) and DEP ($x_t = 175$, $P_S = 116$, $\Delta I_{\text{benzene}} = 131$), and the lowest by D2EEP ($x_t = 106$, $P_S = 62$, $\Delta I_{\text{benzene}} = 58$) and DIDP ($x_t = 85$, $P_S = 56$, $\Delta I_{\text{benzene}} = 44$).

Table V gives the gas-liquid partition coefficients, K , calculated at 25° by means of eqn. 7 for *n*-octane, benzene, ethanol, ethyl acetate, methyl ethyl ketone and chloroform. It clearly follows that this criterion does not allow a single order of polarity to be established; on the other hand, a knowledge of partition coefficients can be helpful in selecting the best solvent for any given separation.

TABLE V

GAS-LIQUID PARTITION COEFFICIENTS AT 25° ACCORDING TO EQN. 7

Compound	DEP	DIBP	DCyC ₆ P	D2EEP	DIDP	BBP	BEEP
<i>n</i> -Octane	786.5	1,165	1,248	1,787	2,064	779.0	2,569
Benzene	943.1	847.0	907.5	727.6	723.4	836.9	909.5
Ethanol	388.6	363.3	413.3	228.9	218.6	597.7	284.7
Ethyl acetate	761.9	677.5	532.4	435.5	437.3	770.0	539.0
Methyl ethyl ketone	986.2	3,030	731.7	598.5	507.1	768.4	670.2
Chloroform	1,012	895.3	1,034	780.7	681.6	765.2	807.0

Table VI reports the values of $\Delta G^E(\text{CH}_2)$ calculated at three temperatures by means of eqn. 8 using retention data of *n*-alkanes. As reported previously by Novak *et al.*²¹, the value of $\Delta G^E(\text{CH}_2)$ does not vary substantially with temperature. Slight variations, probably due to experimental errors, were noticed, however; therefore a mean value of $\Delta G^E(\text{CH}_2)$ was calculated (see Table VI). The results obtained by Novak *et al.*'s criterion show that the most polar phases are DEP [$\Delta G^E(\text{CH}_2)_{\text{mean}} = 109.5$] and BBP [$\Delta G^E(\text{CH}_2)_{\text{mean}} = 108.6$], and the least polar phase is DIDP [$\Delta G^E(\text{CH}_2)_{\text{mean}} = 57.3$].

TABLE VI

POLARITY SCALE ACCORDING TO NOVAK *et al.*'S CRITERION [$\Delta G^E(\text{CH}_2)$]

Compound	$\Delta G^E(\text{CH}_2)$ (cal/mole)			
	25°	75°	125°	Mean
DEP	104.9	103.7	119.9	109.5
DBP	75.9	83.2	108.1	89.1
DIBP	101.6	94.8	106.4	100.9
DCyC ₆ P	111.3	83.4	73.8	89.5
D2EEP	62.2	62.8	81.6	68.9
DIDP	34.6	50.2	87.1	57.3
BBP	98.1	102.5	125.1	108.6
BEEP	49.8	65.7	105.1	73.5

Fig. 1 shows the results obtained by the method suggested by Castello and D'Amato²². On the basis of the activity coefficients for *n*-octane at 75°, the following order of polarity was established: DEP > BBP > DCyC₆P > DIBP > D2EEP > BEEP > DIDP. If the above-mentioned method is applied to a solute other than an

n-alkane, the stationary phases will be arranged in a different order, which will reflect the specific selectivity of the solvent towards the functional group of the solute rather than its polarity.

Fig. 1 clearly illustrates the behaviour of each liquid phase studied towards each of the solutes; the minimum in the $\ln \gamma^\infty$ curve corresponds to the highest solute-solvent interaction. It should be noted that a very marked minimum is shown by methyl ethyl ketone (and likewise by acetone) for DIBP and that the behaviour of methanol differs from that of ethanol (and, likewise, of the other *n*-alkanols), which shows the strongest interactions with BBP. Ethyl acetate behaves in a similar manner to ethanol; cyclohexane, benzene and methylene chloride behave similarly to one another, their $\ln \gamma^\infty$ values increasing with the polarity order based on the $\ln \gamma^\infty$ of *n*-octane.

On the basis of the values of the polar component, τ , of the solubility parameters calculated previously³, the eight phthalates studied were arranged in an order of polarity that shows some differences with respect to all of the polarity scales discussed above: DEP ($\tau = 5.80$) > BBP ($\tau = 5.10$) > DIBP ($\tau = 4.95$) > DCyC₆P

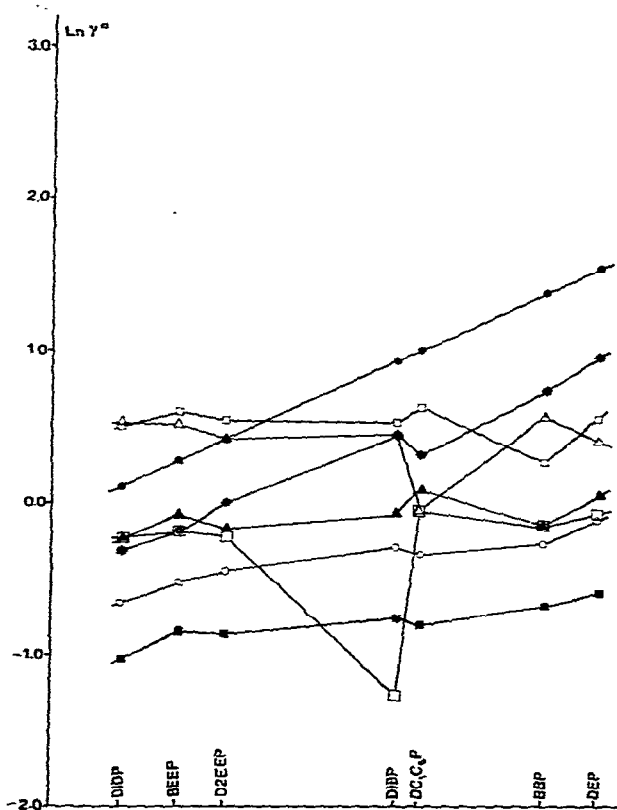


Fig. 1. Logarithm of activity coefficients at infinite dilution at 75° versus polarity of the stationary phases according to Castello and D'Amato's criterion ($\ln \gamma_{n-C_8}$). ●, *n*-Octane; *, cyclohexane; ○, benzene; △, methanol; □, ethanol; ▲, ethyl acetate; □, methyl ethyl ketone; ■, methylene chloride.

($\tau = 4.64$) > DIDP ($\tau = 4.18$) > DBP ($\tau = 4.11$) > D2EEP ($\tau = 4.10$) > BEEP ($\tau = 3.42$).

It should be noted that this scale agrees with the others presented here as far as the most polar terms (DEP and BBP) are concerned, but disagreement is observed especially for the least polar term. Such disagreement may be due to the fact that in the calculation of τ the contribution of entropy was not taken into account although it is relatively large with DIDP, BEEP and D2EEP.

CONCLUSIONS

The polarity scales obtained by the various methods considered here are compared in Fig. 2. The scales were modified by adopting a new criterion for the evaluation of polarity, according to which the value of the most polar phase is taken as 100 and that of the least polar one as 0; for the phases of intermediate polarity, their polarities can be calculated by means of the expression

$$P^* = 100 \cdot \frac{P' - P_x}{P' - P''} \quad (10)$$

where P' , P'' and P_x are the polarities of the least polar phase, the most polar phase and the phase being considered, respectively. A comparison of the results illustrated in Fig. 2 shows that, with the exception of the criterion based on the solubility parameter theory and of that based on the determination of the V_g^0 of *n*-octane, the eight phthalate esters studied can be divided into three general classes of polarity: a first class comprising the most polar esters (BBP and DEP), a second class comprising the esters with intermediate polarities (DBP, DIBP, DCyC₆P) and a third class comprising the least polar esters (D2EEP, BEEP and DIDP). It can be concluded that all of these methods give fairly consistent results. It seems opportune, therefore, to choose the criterion which provides an absolute value of the polarity with the least amount of experimental measurements.

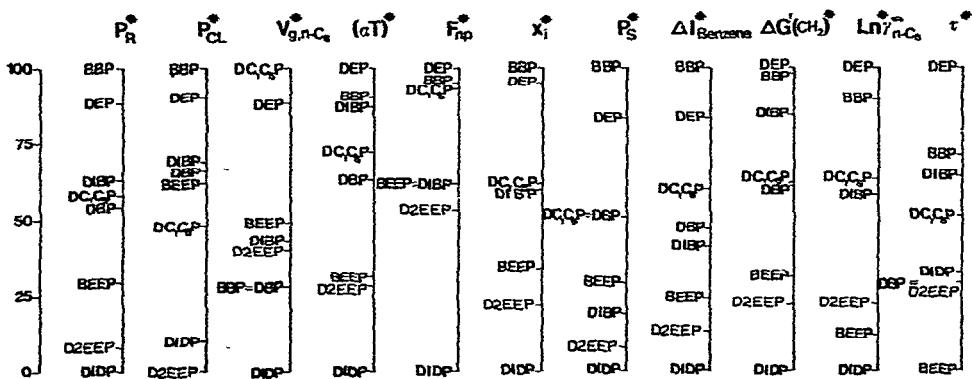


Fig. 2. Comparison of the different polarity scales reported in the text and modified according to eqn. 10.

Between the methods of Castello and D'Amato and that of Novak *et al.*, which are absolute criteria, the latter seems simpler because it does not require a knowledge of the data relative to *n*-alkanes. In fact, $\Delta G^E(\text{CH}_2)$ can be determined by using a pair of homologous alkyl-containing solutes and not necessarily *n*-alkanes; moreover, the determination of $\Delta G^E(\text{CH}_2)$ as the difference between two activity coefficients does not require a knowledge of the molecular weight of the stationary phase.

It still remains a problem (to be considered in future research) how to predict a polarity scale for stationary phases *a priori*.

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