

# The Solvent Eluotropic Strength on Carbon Adsorbents

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## Key Words

Carbon adsorbent  
Eluotropic strength  
Interfacial tension  
Solubility parameter

## Summary

Two theoretical approaches are discussed to calculate the solvent strength ( $\epsilon^\circ$ ) on carbon materials. One is based on the adsorbate-adsorbent interfacial tension and the other uses the theory of solubility parameters. It is shown that there is good agreement between these approaches. Experimental values are compared with theoretical ones and there is again a good agreement. Solvents having small and highly polar molecules have small  $\epsilon^\circ$  values. Solvents having large and aromatic molecules have high  $\epsilon^\circ$  values. Binary solvent mixtures can be classified in two groups depending on the rate of change of  $\epsilon^\circ$  with the mole fraction of the strongest solvent in the mixture.

## Introduction

It has been previously reported that the most important difference between carbon materials and nonpolar chemically bonded phases (CBP) is the large contribution of adsorbate-adsorbent interactions in the case of the carbon supports [1]. These interactions can be neglected as a first approximation with CBP and this assumption has permitted the development of a simple model for the prediction of retention in reversed phase chromatography using such phases which gives results in good agreement with experimental data [2]. However, it has been also shown that this model completely fails in the case of carbon adsorbents which can give elution orders completely different from those obtained with CBP. This is illustrated by the data in Table I for instance.

The retention mechanism with carbon materials is very similar to that observed in "classical" adsorption chromatography (with silica gel or alumina). The basic principle of

adsorption chromatography, as described by Snyder [3], is the exchange process between solute and solvent molecules at the surface of the adsorbent. The adsorption criteria are of course the same for solute and solvent molecules. With carbon adsorbents for instance, the higher the relative molecular mass, the flatter and the more aromatic the molecule, the stronger its adsorption. There is, however, a fundamental difference between the solute and the solvent. Under analytical conditions (low injected mass) the solute is infinitely diluted in both phases (mobile and stationary) whereas the solvent is almost pure. Consequently, if solute-solute interactions may be neglected, this is not true for the solvent.

If the free energies of adsorption from an infinitely diluted gas phase ( $i_{\text{gas}} \rightleftharpoons i_{\text{ads}}$ ) of the molecules of two different liquids A and B are the same, the retention times of compounds A and B will be close provided the mobile phase is such that it interacts more or less similarly with A and B. However, if the molecules of liquid A are more associated with each others than those of liquid B, then the eluotropic strength of A will be larger than that of B. It is even possible to have A less retained than B as solutes, but A stronger than B as solvents. This can be illustrated with benzene and *n*-hexane for instance. Taken as solutes, *n*-hexane is more strongly adsorbed than benzene (longer retention); taken as solvents, benzene has a larger eluotropic strength than *n*-hexane.

The purpose of this work is to give a more complete treatment of the eluotropic strength ( $\epsilon^\circ$ ) on carbon adsorbents than has been previously published [4]. It deals with both pure solvents and mixed ones. Different approaches will be examined to evaluate  $\epsilon^\circ$  and theoretical values will be compared with experimental ones.

Table I. Comparison of retention pattern ( $k'$ ) on three reversed phase materials

Support Solute	LiChrosorb RP 18	LiChrosorb RP 8	Carbon
Toluene	3.11	1.76	1.11
Benzene	1.97	1.10	0.71
Anisole	1.82	1.04	1.26
Nitrobenzene	1.17	0.63	2.95
Acetophenone	0.95	0.51	2.16

Dedicated to Professor Dr. István Halász for his 60th birthday.

## Theory

The eluotropic strength,  $\epsilon^\circ$ , of the mobile phase is a very important chromatographic parameter. It allows the calculation of the change of the capacity ratio ( $k'_i \rightarrow k'_j$ ) of a solute of molecular area  $A$  when the solvent  $i$  is replaced by the solvent  $j$  [3]:

$$\log(k'_j/k'_i) = \alpha A (\epsilon_j^\circ - \epsilon_i^\circ) + \log R_{j,i} \quad (1)$$

$\alpha$  is the activity of the adsorbent and  $R_{j,i}$  is the ratio  $V_j A_i / A_j V_i$  in which  $V_j$  and  $A_j$  are the molecular volume and molecular surface area of species  $j$  respectively.

The determination of an eluotropic scale is thus particularly useful to discover the most convenient solvent for a separation problem. Eq. (1) does not consider solute-solvent interactions. Thus it cannot account for specific solvation effects. This equation can only give rough estimates of  $k'$ . The contribution of solvent-solute interactions has been recently thoroughly investigated by Snyder et al. [5] with silica gels. We have not yet enough data to evaluate this effect in the case of carbon materials. The use of eq. (1) to calculate  $\epsilon^\circ$  seems, however, justified by the fact that rather similar values of solvent strength are obtained with different solutes. Nevertheless, it must be kept in mind that eq. (1) is only an approximation.

The solvent strength is a relative quantity. Two different approaches have been described to calculate  $\epsilon^\circ$  from physico-chemical parameters.

Eon [6] has shown that the strength of the solvent  $X$  relative to the reference solvent  $R$  can be obtained by writing the equality of the solute chemical potentials in the mobile and the stationary phases.  $\epsilon_{X/R}^\circ$  is given by the following equation:

$$\epsilon_{X/R}^\circ = (\sigma_R^A - \sigma_X^A) / 0.367 T \quad (2)$$

where  $T$  is the temperature (K) and  $\sigma_i^A$  is the interfacial tension between the liquid  $i$  and the adsorbent  $A$ .  $\sigma_i^A$  can be calculated using the model of Fowkes [7] or that of Girifalco and Good [8]:

$$\sigma_i^j = \sigma_i + \sigma_j - 2 \sqrt{\sigma_i^d \sigma_j^d} \quad \text{Fowkes} \quad (3)$$

$$\sigma_i^j = \sigma_i + \sigma_j - \phi \sqrt{\sigma_i \sigma_j} \quad \text{Girifalco and Good} \quad (4)$$

$\sigma_i^d$  is the dispersive contribution of the surface tension  $\sigma_i$  of compound  $i$  and  $\phi$  is an interaction parameter which can be estimated from the molecular volume of species  $i$  and  $j$  according to [9]:

$$\phi = 4 \sqrt{V_i V_j} / (V_i^{1/3} + V_j^{1/3})^2 \quad (5)$$

Because the Fowkes' model is more general than that of Girifalco and Good, only eq. (3) has been used in the following to estimate  $\sigma_i^j$ .

The combination of eqs. (2) and (3) yields:

$$\epsilon_{X/R}^{\circ, \sigma} = [(\sigma_R - \sigma_X) + 2 \sqrt{\sigma_A^d} (\sqrt{\sigma_X^d} - \sqrt{\sigma_R^d})] / 0.367 T \quad (6)$$

Superscript  $\sigma$  in  $\epsilon^{\circ, \sigma}$  indicates that the value of  $\epsilon^\circ$  is calculated using interfacial tension (to differentiate from  $\epsilon^\circ$  calculated with eq. (7)).

The surface tension of solids is mainly measured using some reference liquids (most often the  $n$ -alkanes for which  $\sigma^d = \sigma$ ). The  $\sigma^d$  values of some solids (including mercury)

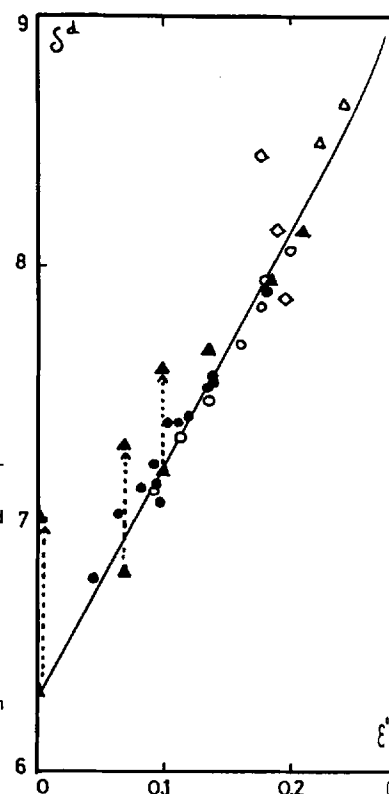


Fig. 1  
Correlation between dispersive solubility parameter ( $\delta^d$ ) and solvent strength ( $\epsilon^{\circ, \sigma}$ ) calculated from interfacial tension (eq. (6)).

○: linear alkanes;  
●: branched alkanes;  
△: aromatics;  
▲: linear alcohols  
▲---▲: correction for inductive forces;  
◇: polychloromethanes.

Table II

Material	$\sigma^d$ (dyne $\text{cm}^{-1}$ )
Graphite	123
Silica	78
Titania	91
Copper	60
Iron	107
Mercury	200

(data from ref. [7])

are given in Table II. The data indicate that graphite is the adsorbent which develops the highest dispersive forces.

Another approach to calculate  $\epsilon^\circ$  uses the solubility parameters. Karger et al. [10] have shown that in the case of carbon adsorbents with which only dispersive interactions can take place,  $\epsilon_{X/R}^\circ$  is given by:

$$\epsilon_{X/R}^{\circ, \delta} = C (\delta_X^d - \delta_R^d) \delta_A^d \quad (7)$$

where  $\delta_i^d$  is the dispersive solubility parameter contribution of species  $i$  and  $C$  is a constant. Keller et al. [11] have derived a good correlation between the heat of vaporisation of hydrocarbons and the Lorentz-Lorenz refractive index function, from which they have derived the value of  $\delta^d$ :

$$\delta^d = -2.24 + 53\chi - 58\chi^2 + 22\chi^3 \quad (8)$$

$\chi$  is the Lorentz-Lorenz function:

$$\chi = (n^2 - 1) / (n^2 + 2) \quad (9)$$

where  $n$  is the refractive index.

The correlation between  $(\delta_X^d - \delta_R^d)$  and  $\epsilon_{X/R}^{\circ, \sigma}$  (calculated using eq. (6)) is shown in Fig. 1 for more than 30 solvents. The values of  $\sigma$  and  $\sigma^d$  have been obtained or calculated from refs. [7, 12, 13]. The correlation is rather good, the regression coefficient of the line being 0.982. The solvents include alkanes (linear and branched) some alcohols and some chloro compounds.

It has not been possible to use more polar solvents in Fig. 1 because of the lack of data (mainly  $\sigma$  and  $\sigma^d$ ), although this would have been interesting. Indeed eq. (7) does not take into account the possibility of inductive interactions between polar solvents and the nonpolar but polarisable surface of graphite. Eq. (7) can be modified to include this possibility:

$$\epsilon_{X/R}^{\circ,\delta} = C [(\delta_X^d - \delta_R^d)\delta_A^d + (\delta_X^{in} - \delta_R^{in})\delta_A^{in}] \quad (10)$$

The inductive solubility parameter,  $\delta^{in}$ , could be derived from the dipole moment,  $\mu$ , and the molecular volume,  $V$ , according to:

$$\delta^{in} = C^{in} \mu^2/V \quad (11)$$

$C^{in}$  is a constant for the solvents having only one polar substituent.

The inductive forces can exist only if the dipole of the solvent is not parallel to the surface of the graphite because its polarizability parallel to the 001 plane is very small. Although it is likely that the alcohols (except methanol and perhaps ethanol) adsorb flat on the surface, little is known regarding the average orientation of the OH group over the surface, so an estimate of the contribution of the inductive forces from eq. (10) is questionable. This appears in Fig. 1 where the positions of the alcohols after correction for the inductive effect are given. It is clear that the correlation ( $\delta_X^d - \delta_R^d$ ) versus  $\epsilon_{X/R}^{\circ,\sigma}$  has deteriorated. The possibility of inductive interactions must not be ignored, however, this result suggests that the theory of solubility parameters must be used with caution in the case of adsorption phenomena as it does not account for orientation effects.

The good correlation between  $\delta^d$  and  $\epsilon^{\circ,\sigma}$  suggests that both eqs. (6) and (7) can be used to predict  $\epsilon^{\circ}$ . However, from a practical point of view, eq. (7) is more useful as it requires only the knowledge of the refractive index of the solvent to predict its strength, whereas eq. (6) requires the values of  $\sigma$  and  $\sigma^d$  (which are available for only a limited number of solvents).

Accordingly the theoretical estimates of the eluotropic strength of pure solvents was carried out using eq. (7). Whenever possible we have also used eq. (6).

The eluotropic strength of binary solvent mixtures can be calculated knowing the strength of both solvents. The problem is rather complex, however, as the composition of the adsorbed liquid is different from that of the bulk mobile phase because of the selective extraction of one of the components of the eluent. Snyder [3] has derived an equation taking into account this effect:

$$\epsilon_{A,B/R}^{\circ} = \epsilon_{A/R}^{\circ} + [\log(N_B 10^{n_b} (\epsilon_{B/R}^{\circ} - \epsilon_{A/R}^{\circ}) + 1 - N_B)]/n_b \quad (12)$$

$N_i$  and  $n_i$  are respectively the molar fraction of liquid  $i$  in the bulk mobile phase and its molecular area.  $B$  is the strongest solvent.

Eq. (12) has been evaluated for 4 solvent combinations. The results will be discussed below.

## Experimental

The carbon materials were prepared by pyrolysis of benzene on carbon black or silica particles [14]. The specific surface areas of the adsorbents were in the range 20 to 150 m<sup>2</sup>/g.

Various pumping systems were used: model 6000A (Waters, Milford, MA, USA), model 995 (Tracor, Austin, TX, USA) and model DMP 1515 (Orlita, Gießen, FRG). The solutes were monitored with a refractive index detector (Waters R 401) or a UV photometer (Tracor 960).

The columns were made from  $\frac{1}{8}$ " stainless steel tubings of various lengths. They were packed using slurries of the particles (15–30  $\mu$ m) in dibromomethane-acetonitrile mixtures. Experiments were carried out at room temperature (20–22 °C).

The solvents were Pro-analysis grade from Merck (Darmstadt, FRG) and used without further purification. Water was twice distilled. The binary mobile phases were prepared by use of a pipette. The solutes were obtained from various sources.

## Results and Discussion

### 1 Pure Solvents

More than 20 different solvents have been tested; their  $\epsilon^{\circ}$  values have been calculated using eq. (6) and derived from experimental data using eq. (1). Different types of solutes have been used: alkyl and methyl benzenes, methylphenols and polyaromatic hydrocarbons. These compounds are eluted over a large range of capacity ratios. The calculation of molecular area was made using Snyder's data [3]. Because of the impossibility of taking into account solute-solvent interactions, different values of  $\epsilon^{\circ}$  were obtained from experimental data for a given solvent, depending on the solute. As mentioned above, however, the scattering of these values was generally low (relative standard deviation smaller than 10%). The reference solvent (R) is methanol. The activity of the adsorbent is 1. The results are reported in Table III and in Fig. 2. The values of  $\epsilon^{\circ}$  given in Table III for each series of solutes are the arithmetic means of the values obtained with the different members of the series that have been injected.

The results suggest that there is good agreement between the experimental ( $\epsilon_{exp}^{\circ}$ ) and the theoretical ( $\epsilon^{\circ,\sigma}$  or  $\delta^d$ ) values, taking into account the basic simplification made in eq. (1) and the simple model chosen to estimate  $\sigma_j^i$ . It can be observed in Fig. 2 that the strength of the alcohols is lower than predicted (except for hexanol) whereas those of the alkanes are slightly larger. The difference between theoretical and experimental values is most probably due to the fact that solute-solvent interactions have been neglected in the determination of  $\epsilon_{exp}^{\circ}$ . Study of the data obtained with the  $n$ -alcohols, the  $n$ -alkanes and the  $n$ -alkylacetates reveals an unexpected fact which is illustrated in Fig. 3 where the measured values of  $\epsilon^{\circ}$  against the number of carbon atoms ( $n_C$ ) in the alkyl chain are plotted. On the basis of the well-known linear variation of  $\log k'$  vs carbon number for homologous compounds (when used as solutes)

Table III

Solvent	N°	$\epsilon_{AB}^{\circ}$ (1)	$\epsilon_{MB}^{\circ}$ (2)	$\epsilon_{MP}^{\circ}$ (3)	$\epsilon_{PAH}^{\circ}$ (4)	$\delta^d$ (5)	$\sigma$ (6)	$\sigma^d$ (6)	$\epsilon^{\circ, \sigma}$ (7)
Methanol	1	0.00	0.00	0.00	0.00	6.32	22.0	16.0	0.00
Ethanol	2	0.05	0.05	0.06	0.05	6.89	22.3	19.0	0.07
Propanol	3	0.08	0.07	0.06	0.06	7.28	23.7	20.8	0.095
Butanol	4	—	0.10	0.09	0.09	7.50	24.6	22.3	0.12
Pentanol	5	—	—	0.11	0.11	7.67	25.3	23.3	0.13
Hexanol	6	—	—	—	0.15	7.78	26.3 (8)	24.5 (8)	0.15
Methyl acetate	7	—	0.07	0.08	0.09	6.90	—	—	—
Ethyl acetate	8	0.09	0.11	0.08	0.09	7.07	23.9	—	—
Propyl acetate	9	—	0.12	0.11	0.11	7.27	—	—	—
Butyl acetate	10	—	0.13	0.11	0.115	7.47	25.2	—	—
Pentyl acetate	11	—	0.15	0.12	0.13	7.56	—	—	—
Hexyl acetate	12	—	0.17	0.14	0.15	—	—	—	—
Hexane	13	0.12	0.13	—	—	7.12	18.00	18.00	0.09
Heptane	14	0.14	0.14	—	—	7.33	19.70	19.70	0.11
Octane	15	0.15	0.15	—	—	7.45	21.40	21.40	0.135
Nonane	16	0.16	0.16	—	—	7.59	22.45 (8)	22.45 (8)	0.14
Acetonitrile	17	0.04	0.05	0.025	0.04	6.59	—	—	—
Butyl chloride	18	0.13	0.14	—	0.115	7.54	—	—	—
Tetrahydrofuran	19	0.13	0.14	—	0.14	7.67	—	—	—
Dichloromethane	20	0.13	0.14	—	0.13	7.87	—	—	—
Chloroform	21	0.20	0.20	—	0.19	8.15	—	—	—
Benzene	22	—	—	—	0.20	8.90	28.88	28.88	0.215
<i>m</i> -Xylene	23	—	—	—	0.24	8.85	28.88	28.88	0.215
Water	24	-0.34	-0.36	—	—	6.40	21.8	21.8	-0.38

(1), (2), (3) and (4): experimental solvent strength (eq. (1)) calculated from the retention data of alkylbenzenes (AB), methylbenzenes (MB), methylphenols (MP) and polyaromatic hydrocarbons (PAH) respectively  
 (5) calculated with eq. (8). (6) values from refs. [7, 12, 13]. (7) calculated with eq. (6). (8) values calculated from data in ref. [13].

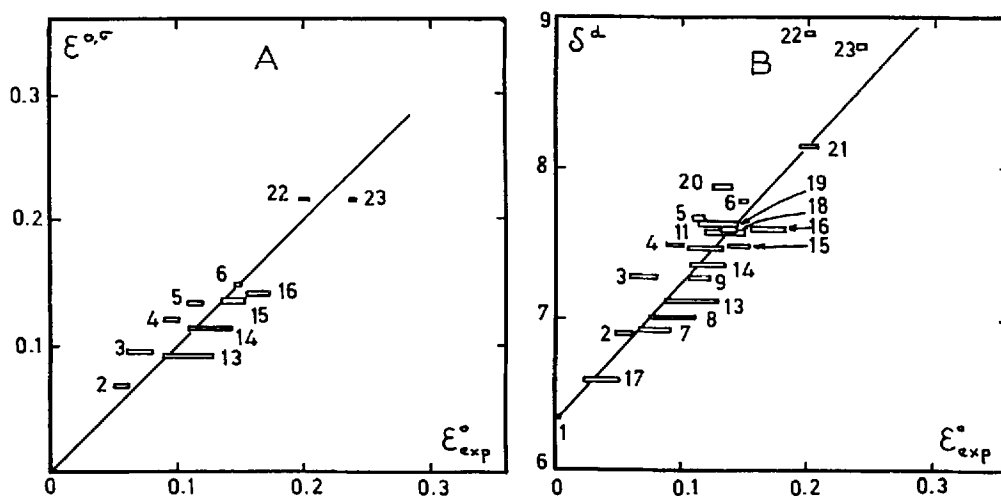


Fig. 2  
 A: Correlation between theoretical ( $\epsilon^{\circ, \sigma}$ ) and experimental ( $\epsilon_{exp}^{\circ}$ ) values of solvent strength. For solvent identification, see Table III.  
 B: Correlation between dispersive solubility parameter ( $\delta^d$ ) and experimental solvent strength ( $\epsilon_{exp}^{\circ}$ ).  
 The straight line is the linear regression derived from data in Fig. 1

one might have expected a linear increase of  $\epsilon^{\circ}$  with  $n_C$  for these compounds (when used as solvents) and the same incremental contribution of a  $-CH_2$ -group independently of the homologous series. The results in Fig. 3 show that this does not happen: if  $\epsilon^{\circ}$  seems to increase more or less linearly with  $n_C$ , the lines obtained with different series are not parallel. It must be noted that the two theoretical approaches to calculate  $\epsilon^{\circ}$  for homologous solvents do not yield linear and parallel plots of  $\epsilon^{\circ}$  vs  $n_C$ . This can be seen in Fig. 4 where the variations of  $\delta^d$  and  $\epsilon^{\circ, \sigma}$  with  $n_C$  for the *n*-alcohols, the *n*-alkanes and the *n*-alkyl-acetates are plotted.

This unexpected behaviour suggests that it is difficult to justify by qualitative reasoning from its molecular structure the position of a given solvent in the eluotropic scale. It is clear, however, that the chromatographic behaviour of a compound taken as a solute must be used with care to predict its eluotropic strength. We have already mentioned this point with benzene and *n*-hexane: with the solvent mixture 65 water-35 acetonitrile (v/v), the capacity ratios of benzene and *n*-hexane are 1.8 and 3.1 respectively, whereas the solvent strength of benzene is about twice that of *n*-hexane. Similarly, *n*-hexane which is more retained than *n*-hexanol has a smaller eluting power.

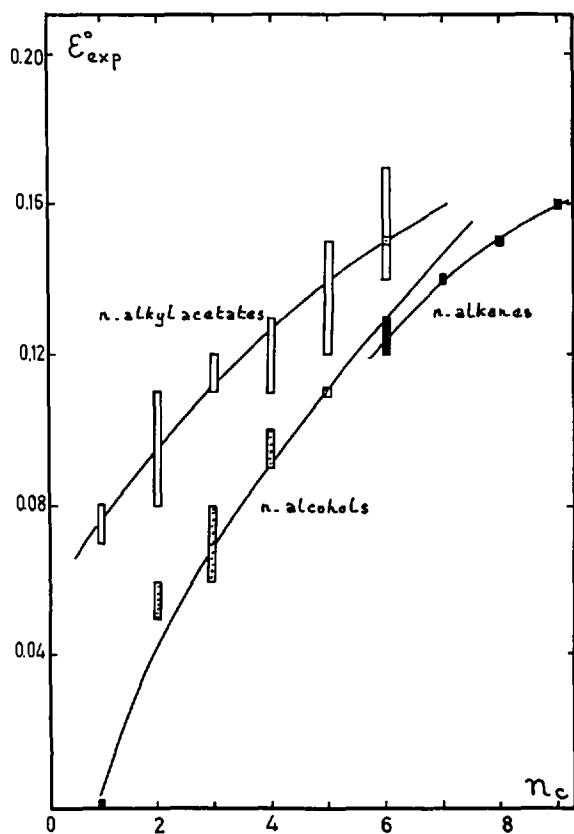


Fig. 3  
Variation of experimental solvent strength ( $\epsilon^{\circ}_{\text{exp}}$ ) with number of methylene groups ( $n_c$ ) in homologous series of solvents.

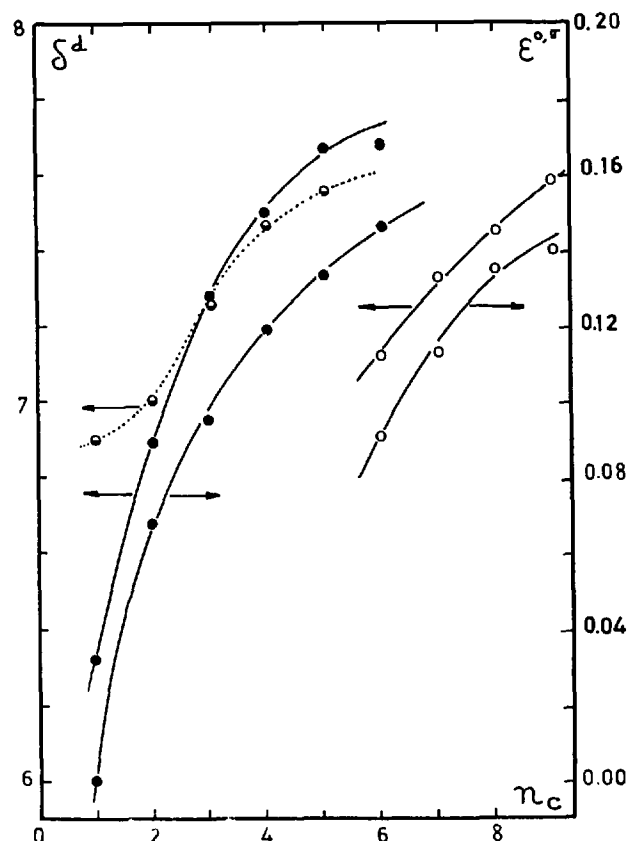


Fig. 4  
Variation of theoretical solvent strength ( $\epsilon^{\circ,\sigma}$ ) and dispersive solubility parameter ( $\delta^d$ ) with number of methylene groups ( $n_c$ ) in homologous series of solvents.  
○: *n*-alkanes; ●: *n*-alcohols; ◻: *n*-alkyl-acetates

The solvent strength of water is negative. This is not surprising as the reference solvent is methanol. The value of  $\epsilon^{\circ}_{\text{H}_2\text{O}}$  is difficult to determine accurately as this requires the injection of solutes in pure water, a solvent in which they have very large capacity ratios. It is remarkable, nevertheless, that the experimental value (about  $-0.35$ ) is very close to the calculated one using the interfacial tensions ( $-0.38$ ). It must also be noted that these results are in excellent agreement with those of Frei et al. [15] who have used breakthrough curves to determine  $\epsilon^{\circ}_{\text{H}_2\text{O}}$ . They have found  $\epsilon^{\circ}_{\text{H}_2\text{O}} = -0.36$ . Surprisingly, the dispersive solubility parameters predict  $\epsilon^{\circ}_{\text{H}_2\text{O}} > \epsilon^{\circ}_{\text{MeOH}}$  ( $\delta^d_{\text{H}_2\text{O}} = 6.4$ ;  $\delta^d_{\text{MeOH}} = 6.3$ ).

As it can be seen in Table III, aromatic compounds are very strong solvents. This can perhaps be explained first by the particular affinity of graphite for the aromatic compounds (especially the polyaromatic hydrocarbons) and second by the possible build-up of several adsorbed layers interacting strongly one with the others. This will be further investigated. It must be noted also that  $\epsilon^{\circ,\delta}_{\text{Benz}}$  and  $\epsilon^{\circ,\sigma}_{\text{Benz}}$  are slightly larger than the corresponding quantities for *m*-xylene. This is not what is observed experimentally, a result which is not too surprising as the data obtained with the other solvents indicate that  $\epsilon^{\circ}$  increases when  $-\text{CH}_2-$  (or  $-\text{CH}_3$ ) groups are introduced in the molecules.

## 2 Binary Mixture of Solvents

Four mixtures have been investigated: acetonitrile-*m*-xylene, methanol-chloroform, methanol-water and acetonitrile-water. The results are given in Fig. 5 where the experimental and the calculated values of  $\epsilon^{\circ}$  (using eq. (12)) vs the mole fraction of the strongest solvent in the mixture are shown. Eq. (12) requires knowledge of  $\epsilon^{\circ}$  for the pure solvents. The values we have chosen were the experimental ones and not the theoretical ones ( $\epsilon^{\circ,\delta}$  or  $\epsilon^{\circ,\sigma}$ ).

The results in Fig. 5 indicate that the agreement between experimental and predicted values is fairly good with methanol-water (C) and acetonitrile-water (D) mixtures but rather poor with nonaqueous mixtures (A and B). This can probably be explained by the approximate nature of the assumptions made in the derivation of eq. (12).

The basic equation of adsorption chromatography is:

$$A_{\text{ads.}} + mB_{\text{liq.}} \rightleftharpoons A_{\text{liq.}} + mB_{\text{ads.}} \quad (13)$$

where subscripts ads. and liq. denote that the corresponding species are either in the adsorbed or the mobile phase. The coefficient *m* is the ratio of the area occupied by one molecule of A at the surface of the adsorbent to the area occupied by one molecule of B. If  $\gamma$  and *N* are the activity coefficient and the mole fraction of the compounds in the

mobile phase and  $\theta$  the surface coverage of the adsorbent, then the thermodynamic constant ( $K_{th}$ ) of eq. (13) is:

$$K_{th} = \frac{(1 - N_B)(\theta_B)^m \gamma_A}{(1 - \theta_B)(N_B \gamma_B)^m} \quad (14)$$

In the derivation of eq. (12), the following simplified form of eq. (14) is used:

$$K_{th} = \frac{(1 - N_B)\theta_B}{(1 - \theta_B)N_B} \quad (15)$$

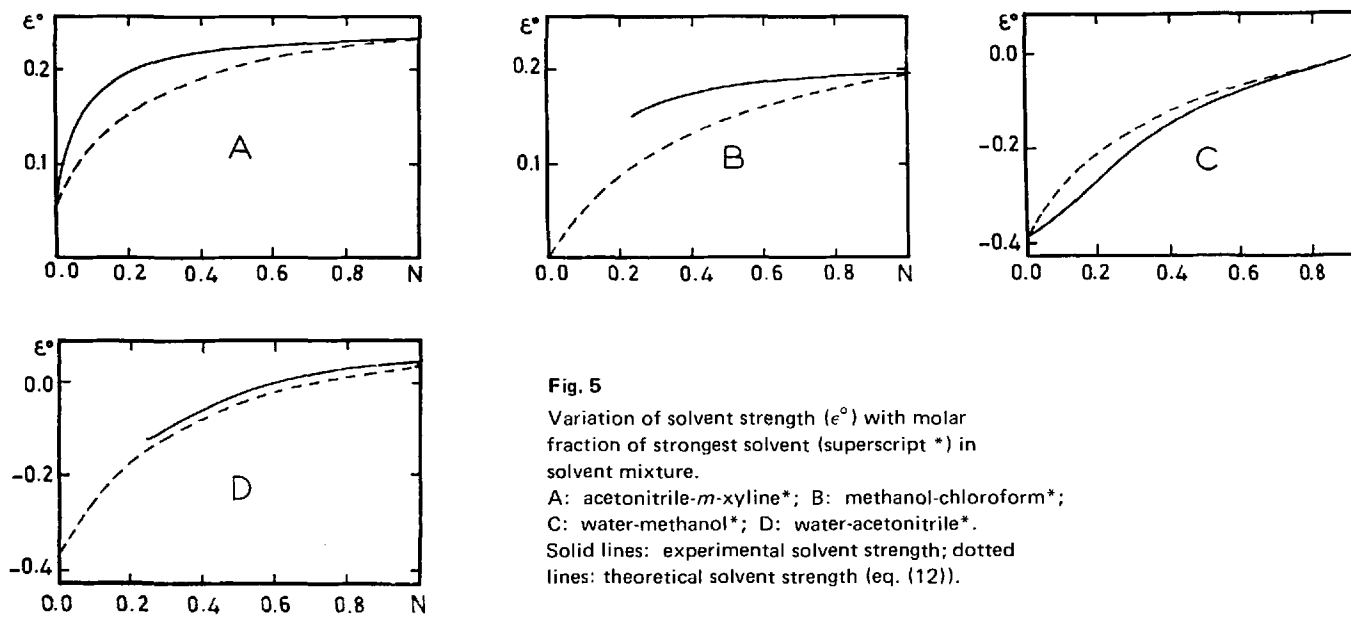
This simplification is necessary to calculate  $\theta_B$  (B being in this case the strongest solvent in the mixture A-B) from which  $\epsilon_{A,B}^\circ$  can be evaluated. Eq. (15) assumes that the mixture A-B is ideal and that the molecular areas of A and B are similar.

Although water-methanol and water-acetonitrile mixtures are known to be non-ideal, eq. (12) can apparently be used to describe the eluotropic strength of such systems as both of the components do not have a particularly strong affinity for graphite (although  $\epsilon_{H_2O}^\circ$  is considerably smaller than  $\epsilon_{MeOH}^\circ$  and  $\epsilon_{MeCN}^\circ$ ). With the systems acetonitrile-*m*-xylene and methanol-chloroform the situation is likely to be very different because of the strong affinity of graphite for *m*-xylene and chloroform.

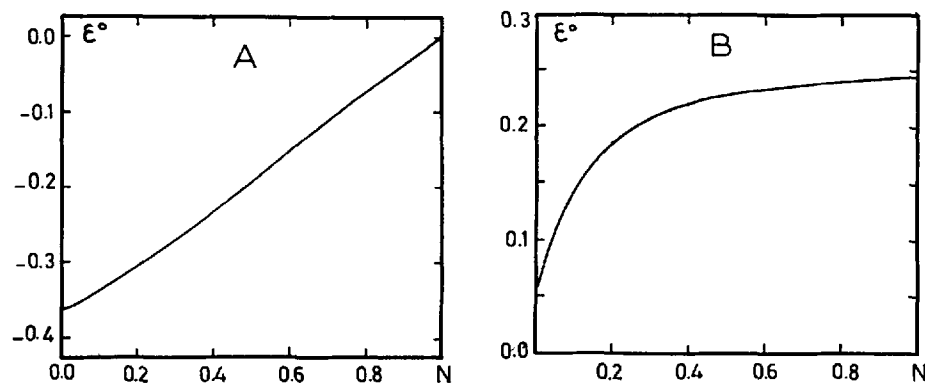
This suggests the classification of solvent mixtures of carbon adsorbents in (at least) two types. In type I mixtures both solvents have little affinity for the adsorbent whereas in type II mixtures, one of the solvents has a strong affinity for the adsorbent. The difference between types I and II is clear when  $\epsilon_{A,B}^\circ$  is plotted against the volume composition of the mixture rather than its molar composition. This is shown in Fig. 6. For type I mixtures,  $\epsilon^\circ$  varies almost linearly with the composition whereas for type II mixtures,  $\epsilon^\circ$  increases rapidly when the strong solvent is added to the weak one, until it almost reaches the value of  $\epsilon^\circ$  of the strong solvent (for a rather moderate volume composition) and then remains approximately constant. This is very similar to what happens with normal phase systems when mixing a strong and a weak solvent.

## Conclusion

The investigation of the behaviour of several solvents (pure or in mixture) shows that it is possible to adjust  $\epsilon^\circ$  between -0.36 and 0.22. The range of variation is quite large (0.58). This represents the same interval as that existing between *n*-pentane and a solvent intermediate between methanol



**Fig. 5**  
Variation of solvent strength ( $\epsilon^\circ$ ) with molar fraction of strongest solvent (superscript \*) in solvent mixture.  
A: acetonitrile-*m*-xylene\*; B: methanol-chloroform\*;  
C: water-methanol\*; D: water-acetonitrile\*.  
Solid lines: experimental solvent strength; dotted lines: theoretical solvent strength (eq. (12)).



**Fig. 6**  
Variation of experimental solvent strength ( $\epsilon_{exp}^\circ$ ) with volume composition of strongest solvent (superscript \*) in mixtures: A: water-methanol\*;  
B: acetonitrile-*m*-xylene\*.

and acetonitrile using silica gel. In term of change of capacity ratio for a solute such as naphthalene,  $\Delta\epsilon^\circ = 0.58$  means that  $k'$  is divided by 630,000. If the scale of solvent strength is limited at one extremity by water, there are many solvents that can yield  $\epsilon^\circ$  larger than 0.22. Although this has probably no experimental usefulness, it is likely that a mixture of benzene with a polyaromatic hydrocarbon like phenanthrene or pyrene could give an  $\epsilon^\circ$  value larger than 0.5 or 1.0. On the other hand, one can expect that a mixture of *n*-hexane with a small amount of a high relative molecular mass alkane such as squalane would give a high  $\epsilon^\circ$  value because the mixture is undoubtedly of type II (see above). Such mixtures of low viscosity, low toxicity and low UV absorbance should be of great interest for the analysis of heavy compounds. For these analyses, carbon adsorbents should probably give higher selectivities than the NARP technique. This is presently being investigated.

## References

- [1] *H. Colin, G. Guiochon*, *J. Chromatogr.* **158**, 183 (1978).
- [2] *P. Jandera, H. Colin, G. Guiochon*, *Anal. Chem.*, to be published, 1981.
- [3] *L. R. Snyder*, in "Principles of Adsorption Chromatography", M. Dekker, New York, 1968.
- [4] *H. Colin, C. Eon, G. Guiochon*, *J. Chromatogr.* **122**, 223 (1976).
- [5] *L. R. Snyder*, Vth. International Symposium on Column Liquid Chromatography, Avignon, France, 1981.
- [6] *C. Eon*, *Anal. Chem.* **47**, 1871 (1975).
- [7] *F. M. Fowkes*, in "Chemistry and Physics of Interfaces, I", ACS, Washington D.C, 1965.
- [8] *L. A. Girifalco, R. J. Good*, *J. Phys. Chem.* **61**, 904 (1957).
- [9] *L. A. Girifalco, R. J. Good*, *J. Phys. Chem.* **64**, 561 (1960).
- [10] *B. L. Karger, L. R. Snyder, C. Eon*, *Anal. Chem.* **50**, 2126 (1978).
- [11] *R. A. Keller, B. L. Karger, L. R. Snyder*, in "Gas Chromatography, 1970" *R. Stock* (Ed.), Institut of Petroleum, London, 1971.
- [12] *R. J. Good, E. Elbings*, in "Chemistry and Physics of Interfaces, II", ACS, Washington DC, 1971.
- [13] *W. R. Good*, *J. Colloid, Interf. Sci.* **44**, 63 (1973).
- [14] *H. Colin, G. Guiochon*, *Carbon* **16**, 145 (1978).
- [15] *W. Golkiewicz, C. E. Verkhoven-Goewie, U. A. Th. Brinkman, R. W. Frei, H. Colin*, Submitted for publication.

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