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**Evolution of Investigations on Quantitative Retention — Phase Composition Relationships in Liquid Chromatography Carried out at the Department of Inorganic and Analytical Chemistry of the Lublin Medical Academy**

Ewolucja badań ilościowych zależności retencji od składu faz w chromatografii cieczowej, prowadzonych w Zakładzie Chemii Nieorganicznej Akademii Medycznej w Lublinie

Эволюция исследований количественных зависимостей задерживания от состава фаз в жидкостной хроматографии проведенных в Кафедре Неорганической и аналитической химии Медицинской академии в Люблине

The success of chromatographic separation, expressed in terms of the resolution  $R_s$ , is given by the well-known Fournell equation:

$$R_s = \frac{1}{4} \sqrt{n} \frac{a - 1}{a} \frac{k'}{1 + k'} \quad (1)$$

I    II    III

the three terms of which refer to the column efficiency (number of theoretical plates, n) (I), selectivity (II) and retention (III, fraction of the more retained solute in the stationary phase;  $k'$  — capacity factor). The optimal values of the third term are obtained for a narrow range of  $k'$  values. For low values ( $k' < 1$ ) the resolution is also lower. For  $k' > 10$  the third term is close to unity; however, too long retention times are obtained. Therefore, one of the goals of the system optimization in chromatography is to secure a sui-

table range of  $k'$  values of the solutes which are to be separated:  $1 \div 10$  in column chromatography (HPLC) and  $0.1 \div 10$  in thin-layer chromatography (TLC). This is most easily accomplished by the use of mixed solvents: variation of composition of one of the phases, especially for mixtures of strongly differing properties, permits to vary retention in a continuous manner; moreover, differentiated variations are often obtained for the individual components of the sample which are to be separated so that the control of the second term (selectivity) of eq. 1 can also be accomplished.

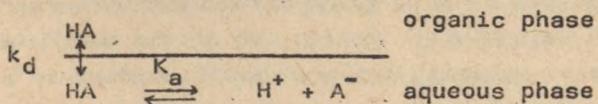
These principles have formed one of the main guidelines of the scientific investigations of the chromatographic group at the Department of Physical Chemistry of the University of Lublin. The origin of this direction of chromatographic research can be traced back to the early 1950's, when Prof. Waksmundzki formulated a question concerning optimal quantitative compositions of eluents for paper chromatography.

At that time (1953), the author of the present review joined the staff of the Department of Physical Chemistry, after the completion of MSc thesis on the Craig countercurrent distribution of pyridine bases. The main topic of the research was already the physical chemistry of surfaces and several teams of scientists were being formed. Jarosław Ościk gradually developed his investigations of adsorption from multicomponent solutions, Janusz Barcicki and Anna Barcicka specialized in flotation phenomena. An important event, which directed attention towards chromatographic analysis, was the preparation of a handbook of chromatography [1] co-edited by A. Waksmundzki, who wrote most of the chapters on the theory and technique of chromatography.

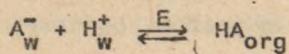
Under the influence of Craig's ideas of continuous liquid-liquid extraction as the model of partition chromatography [2] and Martin and Synge's work [3], a special paper chromatographic technique was adopted by the Physical Chemistry group: paper strips were impregnated with buffer solutions or water, dried to suitable impregnation degree (ca 50%) to secure unhampered flow of the mobile phase and eluted with water-immiscible solvents (hexane, benzene, chloroform, etc.). The chromatographic technique ("moist paper" method) was first intro-

duced in the course of two parallel investigations for the M.Sc. dissertations (1954) of Aksanowski [4] and Frelek [5], and had important consequences for the further research in the field of liquid-liquid partition chromatography. The type of phase systems used and predominating liquid-liquid partition mechanism, permitted to apply the simple paper chromatographic technique for investigation of ionization, solvation and ion-pairing equilibria in extraction processes and determination of selective extraction systems suitable for the separation of organic electrolytes by Craig counter-current distribution [6]. In some cases, strong contribution of adsorption phenomena was observed [7]; the analogies and differences of adsorption from solutions and liquid-liquid distribution in analogous systems have also been investigated using the "moist paper" technique [8].

It was very fortunate for the evolution of chromatographic investigations at the Department that Prof. Waksmundzki was interested not only in the successful separation of the analysed samples but also in the elucidation of the physico-chemical phenomena involved, and theoretical foundations of optimization principles. Thus, from the very beginning of chromatographic investigations at the Department the chromatographic method was employed mainly for the physico-chemical investigations of partition and adsorption equilibria, quantitative relationships between retention and composition of the eluent or stationary phase and molecular structure of the solute. As early examples of this approach, the investigations from the "moist buffered paper chromatography" series can be cited: the regular S-shaped  $R_F$  vs. pH curves [4] were interpreted in the following papers [9-11], assuming liquid-liquid partition mechanism combined with ionization equilibria in the aqueous phase according to the scheme:



and the overall equilibrium



The extraction constant is then

$$E = [\text{HA}]_{\text{org}} \frac{[\text{A}^-]_w^{-1} [\text{H}^+]_w^{-1}}{D} \quad (2)$$

and for  $[\text{A}^-]_w \gg [\text{HA}]_w \quad (k_d = [\text{HA}]_{\text{org}} [\text{HA}]_w^{-1} \gg 1)$

$$D = [\text{HA}]_{\text{org}} \frac{[\text{A}^-]_w^{-1}}{E} = [\text{H}^+]_w \quad (3)$$

For normal phase systems (organic mobile phase):

$$k' = D^{-1} \frac{V_w}{V_{\text{org}}} V_{\text{org}}^{-1}$$

$$R_M = \log k' = \text{const} - \log [\text{H}^+] = \text{const} + \text{pH} \quad (4a)$$

$$\left( \text{const} = \log \frac{K_a' V_w}{k_d V_{\text{org}}} \right)$$

For bases a symmetrical relationship is obtained

$$R_M = \text{const} + \log [\text{H}^+] = \text{const} - \text{pH} \quad (4b)$$

For conditions of strong ionization, linear  $R_M$  vs. pH plots are thus obtained [11], the vertical distance of the lines (selectivity) being determined by differences of ionization constants  $K_a'$  and partition coefficients  $k_d$  of the organic electrolytes. For  $R_F$  vs. pH relationships, S-shaped curves are obtained [6,9,10,13]. The theory of optimization of buffered paper chromatography was summarized in the D.Sc. thesis of the author [12]; the investigations were later published in a review [13] and their main conclusions were discussed in several monographs on chromatography [14-17] and other separation methods [18].

The advantages of the "moist buffered paper" technique (rapidity, high selectivity, analogy to static extraction equilibria) were also utilized for practical purposes in several investigations for Ph.D. degree at the Department of Inorganic and Analytical Chemistry, Pharmaceutical Faculty of the Medical Academy of Lublin [19-22] which also was directed by Prof. A. Waksmundzki in the years 1946-1964. Buffered paper chromatogra-

phy was used for the preliminary analysis of alkaloid extracts, choice of suitable, selective liquid-liquid systems for preparative counter-current distribution and analysis of the separated fractions [23].

In the D.Sc dissertation [12] it was already mentioned that ionization equilibria and variation of pH are but one of the possible methods of controlling retention. Another more general way is to use mixed solvents: for certain types of liquid-liquid systems (e.g. binary organic solvent - water), the relationship between the partition coefficient  $k_{1+2}$  and composition of the mixed phase (1+2) is expressed by the equation [24-26]:

$$\log k_{1+2} = \phi_1 \log k_1 + \phi_2 \log k_2 \quad (5)$$

where  $\phi$  is the volume fraction of the component solvent and  $k_1$ ,  $k_2$  and  $k_{1+2}$  denote, respectively, partition coefficients for the pure solvents 1 and 2 and the mixed solvent 1+2. The relationship, reported originally for ideal [24,25] or regular [26] mixtures of organic solvents (1+2), was found to apply as a semiempirical equation for chromatographic systems of the type water (1) + dimethyl sulfoxide (2) - di-n-butyl ether in the form [27]

$$R_M(1+2) = \phi_1 R_{M1} + \phi_2 R_{M2} \quad (6)$$

$$\text{or } \log k_{(1+2)} = \phi_1 \log k_1 + \phi_2 \log k_2 \quad (6a)$$

in spite of the strong non-ideality of the mixed phase.

Equation 6 was found to be valid for numerous liquid-liquid and liquid-solid systems [28-30]. It was employed by Biagi et al. [31], and other groups as a standard method of determination of high partition coefficients by extrapolation of  $R_M$  vs. composition plots for systems of the type paraffin oil - water + acetone (in studies on quantitative structure - activity relationships, QSAR). The equation also describes the retention - eluent composition relationships well, in frequently used systems of the type: nonpolar adsorbent (e.g. ODS-silica, graphitized carbon) - water + polar modifier (e.g. methanol) [30-32].

The selectivity of the system can be controlled by the choice of the modifier [33].

The validity of eq. 6 was also tested by the Physical Chemistry group for gas chromatography systems with binary stationary liquids [34,35] and for liquid-solid systems of the type diluent + polar solvent-silica [36]. While for the former systems the experimental results were frequently well described by eq. 6, for adsorption systems parabolic relationships were usually obtained. Systematic investigations of binary eluents in liquid-liquid partition chromatography also demonstrated frequent deviations from linearity of  $R_M$  vs. eluent composition plots [37], the direction of deviations appearing to be related to deviations of the binary eluent from the Raoult's law.

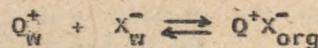
The investigations carried out at the Departments of Inorganic and Physical Chemistry under the direction of Prof. A. Waksmundzki were mainly concerned with chromatographic analysis of organic solutes, however, in the early 1960's, S. Przeszlakowski started experiments with extraction chromatography using cellulose impregnated with salts of high-molecular-weight amines (liquid anion exchangers), and eluted with aqueous electrolyte solutions [38-40]. His systematic investigations, including the effect of the type and concentration of ligand (halogenide and thiocyanate ions, organic acids), the type and concentration of the ion exchanger, the effect of diluent, owing to the partition mechanism of the chromatographic process, provide also extensive information about the extraction of metals by solutions of liquid ion exchangers. The results obtained by Przeszlakowski were discussed in several monographs and reviews [41-43].

The main trend of investigations at the Department of Inorganic and Analytical Chemistry was continued after the author was appointed to be chairman of the Department (1964). Several directions of the research, all concerned with quantitative retention - eluent composition relationships and physical chemistry of chromatographic, partition and adsorption processes, were gradually formed. Only a brief characterization of the results of investigations can be given in a short review; also the references are limited to representative papers.

The research group organized by S.Przeszlakowski continued the investigations of liquid-liquid partition of metals for various types of extractants - liquid ion exchangers [40,44], chelating extractants used in hydrometallurgy [45] and oxygen - containing solvents [46]. The partition of anions has also been systematically investigated [47]. The results were regularly presented as  $R_M$  ( $\lg D$ ) values plotted against the concentration of extractant, concentration of ligand, pH, so that the general characteristics of the partition systems were obtained.

Liquid ion exchangers, which belong to ion-pairing reagents, have also been applied to chromatography of organic electrolytes in one of the first investigations of the very popular, presently, system type [48]. As cation exchangers di(2-ethylhexyl) orthophosphoric acid [48] and oleic acid (49) were mostly used. The extraction with inorganic anions as counterions has also been investigated [50]. For practical purposes, the extraction of alkaloids as ion pairs has been systematically investigated by L.Jusiak's group [e.g. 51,52]; his investigations resulted in the elaboration of a simple and efficient technology of isolation of chelidonine, applied since 1978 on industrial scale by the "Herbapol" in Wrocław.

The molecular model of ion-pair partition applied in the interpretation of experimental results is, in the simplest case, described by the following equilibrium:



where  $Q^+$  represents the cationic form of a base and  $X^-$  is the counterion which forms the ion pair  $Q^+X^-$ . It follows from the law of mass action that:

$$E = \frac{[Q^+X^-]_{org}}{[Q^+]_w[X^-]_w} \quad (7)$$

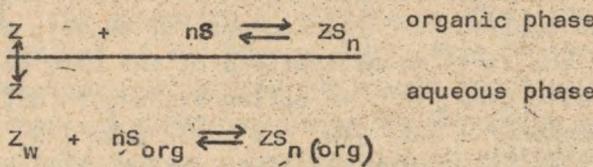
$$D = [Q^+X^-]_{org}[Q^+]_w^{-1} = E[X^-]_w \quad (8)$$

$$\log k' = R_M = \log D + \log V_w V_{org}^{-1} = \text{const} + \log [X^-]_w \quad (9)$$

(reversed - phase system)

The simple relationship has been confirmed for numerous solutes (inorganic and organic) and various partition systems [40, 42-52].

Extensive investigations have also been carried out on the effect of solvation equilibria on the liquid-liquid partition of organic compounds with polar groups capable of H-bonding. The molecular mechanism of partition was analysed on the basis of the law of mass action: a similar approach was applied by Purnell [53] for GC systems. In the simplified case of single predominating solvate  $ZS_n$ , the equilibrium can be represented as:



$$E = [ZS]_{\text{org}} [Z]^{-1} W [S]^{-n}_{\text{org}} \quad (10)$$

$$D = [zs]_{org}^n [z]_w^{-1} = E[s]_{org}^n \quad (11)$$

Therefore, as in the former case

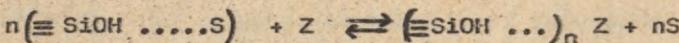
$$R_M = \log k' = \text{const} \pm n \log [S]_{\text{org}} \quad (12)$$

where the sign depends on the formation of solvates in the mobile or stationary phase. The slope of the  $R_M$  vs.  $\log[S]$  line (solvation number "n") thus depends on the composition of the predominant solvate. In broader  $R_M$  and  $\log [S]$  ranges, various slopes can be obtained owing to the shifting solvation equilibrium.

Partition of large groups of solutes was investigated using lipophilic polar solvents (ethers, ketones, alcohols, esters) diluted with cyclohexane as the eluent, and cellulose impregnated with aqueous buffer solutions [54,55] or formamide [56] as the stationary phase. The systematic investigations, occasionally confronted with static extraction experiments, permitted to characterize the effect of molecular structure of the solute (mostly derivatives of benzene, naphthalene and other

aromatic compounds with OH, NH<sub>2</sub>, COOH, heterocyclic nitrogen, CO and other H-bonding groups) on liquid-liquid partition and solvation effects in the organic phase. The solvation numbers "n" were also related to the molecular structure (number of H-bonding groups); it was found that formation of intramolecular hydrogen bonds decreases the slopes of  $R_M$  vs. log [S] plots [55,56]. A similar mechanism of partition was also demonstrated in a series of papers on systems of the type cyclohexane + + polar solvent - polyamide [58].

In the late 1960's the investigation of quantitative retention - eluent composition relationships were extended also for liquid-solid systems. The observation that the plots of  $R_M$  vs. concentration of polar solvent in the eluent [36], parabolic in shape, were similar to those obtained for liquid-liquid partition systems with one of the component solvents strongly interacting with the solute, lead to the conclusion that liquid-solid systems of the type diluent + polar solvent - silica can also be described by the law of mass action, assuming the formation of discrete complexes between the surface silanol groups and polar solute and solvent molecules in a competitive manner [58]. In fact, linear plots were obtained for the  $R_M$  vs. log concentration scale [58], as in case of liquid-liquid partition systems [54]. The concept of mechanistic model of competitive adsorption according to the equation



leading to a simple relationship

$$R_M = \log k' = \text{const} + n \log [S] \quad (13)$$

has been confirmed for numerous adsorbates and polar component solvents in the systematic investigations of Gołkiewicz [59], and applied as the basis of optimization of gradient programs. The approach can be considered a modification of Snyder's model and more realistic for polar solvents (also diluted with nonpolar diluents to control the eluent strength), and silica as adsorbent [60]. The equation has also been confirmed by experiments of a number of other authors (see ref. 61 for review).

including the more precise HPLC method. The approach is simplified and thus, easily acceptable to practical chromatographers; however, more general theories have recently been elaborated by several groups [62-65], which take into account solvation effects in the mobile phase, variation of activity coefficients in the two phases and surface heterogeneity [cf. also ref. 66].

Although the model was originally limited to silica as adsorbent, it was later demonstrated that the simple equation (13) frequently describes satisfactorily, as semiempirical formula, adsorption on other polar adsorbents such as alumina and Florisil [67]. The investigations of LSC systems have recently been extended to include silanized silica as adsorbent and aqueous solutions of methanol or acetonitrile as eluents, for which  $R_M \log k'$  value varies linearly with the concentration of the organic modifier [68] (in accordance with eq. 6) as in case of results obtained for cellulose impregnated with paraffin oil [33,69].

Owing to the marginal role of the Department of Inorganic and Analytical Chemistry in the Medical Academy and virtually nil purchases of modern chromatographic equipment since 1964, the experiments had to be limited to paper - and thin-layer chromatography which limited the scope of research. Only in recent years increasing contribution of HPLC could be introduced.

The review is restricted mainly to investigations concerned with the theory of liquid chromatography. Some related problems have also been investigated, for instance, solubility equilibria of dimethyl sulfoxide [70] and the adsorption layer capacity of homologous series of solvents (ethers, ketones) [71].

The investigations of various liquid-liquid and liquid-solid systems demonstrated that depending on the system type, the retention - eluent composition relationship are frequently described by either of the two equations [28,29,54],

$$\text{I} \quad \log k' = \text{const} + n \log C_M \quad (14)$$

$$\text{II} \quad \log k'' = \text{const} + a \cdot C_M \quad (15)$$

where  $C_M$  is the concentration of the modifier in the eluent and  $a$ ,  $n$ , are constants which depend on the system and structure of

Table 1. Types of chromatographic systems investigated and equations describing retention - eluent composition relationships

Stationary phase	Eluent	Modifier	Solutes	Equation
LLC Cellulose + aqueous buffer solution	water-immiscible solvents	H <sup>+</sup>	organic bases (quinolines, alkaloids etc.)	I
Cellulose + formamide + HCOOH	nonpolar and weakly polar solvents + polar diluent + polar solvent (alcohols, ketones, etc.)	HCOOH	organic bases	I
Polyamide	nonpolar diluent (alcohols, ethers, CHCl <sub>3</sub> )	polar solvent	phenols, phenolic acids, aminoacids	I
Cellulose + water, buffer solution or formamide	nonpolar diluent + polar solvent (alcohols, ethers, ketones, esters, CHCl <sub>3</sub> ) diluent + ion-pairing reagent (lipophilic amines or acids)	polar solvent	phenols, acids, quinolines and other aromatic compounds, complexes of metals	I
Cellulose + water or electrolyte solutions	water + polar solvent (CH <sub>3</sub> OH, CH <sub>3</sub> Cl, (CH <sub>3</sub> ) <sub>2</sub> CO, (CH <sub>3</sub> ) <sub>2</sub> SO, etc.)	polar solvent	salts of metals, acids, organic acids or bases	I
Cellulose + paraffin oil, oleyl alcohol, etc.			various aromatic compounds	II
LSC Silanized silica (RP-18, RP-8, RP-2)	water + polar solvent	polar solvent	various aromatic compounds	II
Silica, alumina, Florisil	diluent + polar solvent	polar solvent	various aromatic compounds	I

the solute. The LLC and LSC systems for which the relationships were observed (with occasional deviations from linearity) are summarized in Table 1.

It should be emphasized that description of a chromatographic system by graphical retention vs. eluent composition plots, is much more informative than mere recipes of optimal eluent compositions since the optimization can be easily tuned to changing conditions and the variations of selectivity for the various pairs of solutes can be taken into account. This fact is realized by an increasing number of chromatographers.

It is also worth pointing out that the advantages of liquid chromatography as a technique for physico-chemical investigations, is yet not fully recognized. It can be expected that following the example of gas chromatography, this direction of applications of LC will tend to develop in the near future.

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#### STRESZCZENIE

Przedstawiono przegląd badań zależności retencji od składu eluentu i molekularnej struktury substancji, przeprowadzonych w Zakładzie Chemii Nieorganicznej i Analitycznej Wydziału Farmaceutycznego Akademii Medycznej w Lublinie. Badania rozpoczęto pod koniec lat pięćdziesiątych pod kierownictwem prof. A. Waksundzkiego (kierownika Zakładu w latach 1946-1964); były one oparte na molekularnych modelach solwatacji, podziału ciecz - ciecz i adsorpcji z roztworów. Badano liczne związki i układy chromatograficzne, w tym także układy jonowo-asocjacyjne. Stwierdzono, że w licznych przypadkach logarytm współczynnika pojemnościowego ( $\log k' = R_M$ ) był liniową funkcją stężenia modyfikatora organicznego (eluenty wodne - układy z odwróconymi fazami). W innych przypadkach, gdy równowagi jonizacji, solwatacji, tworzenia par jonowych lub adsorpcji stosowały się do prawa działania mas,  $\log k'$  był liniową funkcją logarytmu stężenia rozpuszczalnika polarnego (układy niewodne), przy czym współczynnik kierunkowy prostej ( $n$ ) odzwierciedlał molekularny mechanizm podziału:

$$\log k' = \text{const.} + a \cdot C_M$$

$$\log k' = \text{const.} + n \log C_M$$

### Резюме

В данной работе описана эволюция исследований зависимости удерживания в жидкостной хроматографии от состава элюента и молекулярной структуры веществ. Исследования велись в Кафедре Неорганической и Аналитической химии Фармацевтического факультета Медицинской академии в Люблине от пятидесятых годов под руководством проф. А. Ваксмундзкого (заведующего кафедрой в 1946-1964 гг.) и основывались на молекулярных моделях сольватации, распределения жидкость-жидкость или конкуренционной адсорбции из растворов. Исследовалось большое количество веществ в различных хроматографических системах, включая системы ионных ассоциатов. Зависимости удерживания от состава элюента часто описывается удовлетворительно одним из двух уравнений:

$$\log k' = \text{const} + n \log C_M$$

$$\log k' = \text{const} + a \cdot C_M$$

В первом из них логарифм коэффициента ёмкости является линейной функцией логарифма объемной концентрации ( $C_M$ ) органического модификатора (неводные элюенты; к равновесиям ионизации, сольватации, образования ионных ассоциатов, конкуренционной адсорбции применяется закон действующих масс), а наклон линии ( $n$ ) определяется молекулярным механизмом распределения. В других случаях (водные элюенты - системы с обращенными фазами)  $\log k'(R_m)$  - линейная функция объемной концентрации органического модификатора ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$  и др.).

