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The Chromatographic Separation Model for Fullerenes

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Abstract: Based on the molecular thermodynamic theory the quantitative relationships between the separation factor and the column temperature, carbon number and mobile phase composition for fullerenes in high performance liquid chromatography are established. The corresponding models are testified by the experimental data of C_{70} and $C_{60} \sim C_{96}$ from different sources. The calculated results show good agreement with the experimental data.

Key words: Fullerenes; separation factor; quantitative relationship; molecular thermodynamics

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0 Introduction

For quite a long time, graphite and diamond were the only known forms of crystalline carbon. In diamond, each carbon atom is bound to four neighbors in a tetrahedral sp^3 arrangement. In graphite, each atom exhibits sp^2 hybridization and thus has three neighbors. Plane hexagonal networks consisting of individual layers are formed. Graphite or diamond crystals of finite size have dangling open carbon bonds at the outer boundaries, i.e. the atoms at these sites have no partners. In most practical applications these bonds do not present a problem since they soon become saturated by foreign atoms, e.g. by hydrogen. Under clean conditions, however, these dangling bonds drive the cluster to grow larger. In the case of graphitic carbon there is the possibility to saturate dangling bonds and to terminate extensive growth. The individual graphene layers may bend such that the outer edges contact, i.e. form closed cages. A perfect closure of a single graphene layer by maintaining the hexagonal (i.e. six-membered ring) network is impossible. The layer structure has to transform such that a limited number of lower membered rings are provided. In 1985, Kroto and co-workers^[1] discovered carbon molecules with closed cage structures, which, in honor of the American architect R.

Buckminster Fuller, were named fullerenes. In fullerenes, the carbon atoms show hybridization intermediate between sp^3 and sp^2 .

In fullerene family the least carbon number is 20 while the most is 540. Since 1990s fullerenes were prepared by vaporizing a pure graphite anode by the arc discharge method in bulk quantities^[2] so that fullerenes can be readily obtained. For fullerenes, all contain 12 pentagonal carbon rings. Furthermore, all fullerenes must also have an even number of carbon atoms. The most intriguing of the many possible fullerene cages consists of 20 hexagons and 12 pentagons, arranged as in the polyhedron known as the truncated icosahedron. This unique structure results in unusual physical and chemical properties with a large potential for applications such as superconductors, sensors, catalyst, optical and electronic devices, polymers, and biological and medical applications^[3-5]. At present, as the products of graphite vaporization with a laser or by resistive heating of graphite, approximately 85% of the fullerene material produced is C_{60} and 10% is C_{70} . Higher fullerenes are only 3%~5% by weight of the mixture. Since different fullerene molecules have very similar molecular structures they own very similar physical and chemical properties. Therefore, the separation and purification of fullerene products is the most challenging

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topics in this research field. Among these methods, high performance liquid chromatography (HPLC) is the most available. Based on former works from the molecular thermodynamics, we^[9] derived the quantitative relationship between the separation factor and the column temperature and carbon as well as the mobile phase composition. Meanwhile, this model was identified by the experimental data.

1 Theoretical Analysis

In HPLC, the separation factor α is the selective index^[7,8], which is usually used to express the separation extent of a chromatographic system, defined as:

$$\alpha = k' / k'_s \quad (1)$$

where k' , k'_s represent the capacity factor of solute and standard substance, respectively.

We^[9,10] have ever derived the intersection point relationship between the retention value and the column temperature of homologues in HPLC using the basic theory of mathematics:

$$\ln k' - \ln k'_0 = (g + bn)(T^{-1} - T_0^{-1}) \quad (2)$$

where k'_0 , T represent the intersection point constants of homologues; n represent the carbon number of solute molecules; g , b represent the homologous constants. From Eq. (1), applying Eq. (2) to fullerenes and using C_{60} as standard substance yields

$$\ln \alpha = b(n - 60)(T^{-1} - T_0^{-1}) \quad (3)$$

For given member of fullerenes, n is constant, then changing Eq. (3) obtains

$$\ln \alpha = [b(n - 60) / T] - [b(n - 60) / T_0] = H / T + G \quad (4)$$

For given chromatographic system, there exists the linear relationship between the logarithm of separation factor of fullerene members and the reciprocal of thermodynamic temperature. The ratio of the intercept and the slope for this line is constant.

Based on the molecular thermodynamics, we^[11] have ever theoretically derived and experimentally testified the linear relationship between the capacity factor and carbon number of polycyclic aromatic hydrocarbons in supercritical chromatography:

$$\ln k' = A + Bn \quad (5)$$

From Eq. (1), Expanding this relationship to the fullerenes in HPLC and using C_{60} as standard substance yields:

$$\ln k' = Bn - 60B \quad (6)$$

For a given chromatographic system, there exists the linear relationship between the logarithm of separation factor and carbon number, and the ratio of the intercept and the slope for this line equals -60 .

Based on the intersection point relationship between the retention value and the normal boiling point^[12], we^[13] derived the intersection point relationship between the retention value and the mobile phase composition C_B in reversed-phase liquid chromatography:

$$\ln k' - \ln k'_0 = B_2(C_B - C_B^0) \quad (7)$$

where k'_0 , C_B^0 represent the intersection point constant of homologues, which are independent of the properties of compound and the composition of mobile phase while dependent of the classification of homologues, stationary phases and mobile phases. As the constant independent of mobile phase composition, B_2 is dependent of the properties of compound.

From Eq. (1), using C_{60} as the standard substance, applying Eq. (7) to fullerenes yields:

$$\ln \alpha = [B_2 - (B_2)_{C_{60}}] C_B - [B_2 - (B_2)_{C_{60}}] C_B^0 = B_1 C_B + A_1 \quad (8)$$

For a chromatographic system, there exists the linear relationship between the logarithm of separation factor and mobile phase composition, and the ratio of the intercept and the slope for this line is constant.

2 Identification

In order to testify the relationship between the separation factor and the column temperature and carbon as well as the mobile phase composition, we used experimental data from different sources and the results are shown in Tab. 1~3.

In Tab. 1 it is shown that experimental values and calculated values according to Eq. (4) under different stationary phases and different column temperatures using n -hexane as mobile phase. Compared with the experimental values at 33 data sets, the average relative deviation (ARD) is 0.21%. The average relative deviation is calculated as follow:

$$ARD = [(\alpha - \alpha_c) / \alpha_c] / N \times 100\% \quad (9)$$

Tab.1 Comparison of the experimental values with the calculated values by Eq.(4)

Column	Temperature / $^{\circ}\text{C}$	α	α	RD/%
Triph ^[7] $H=3.717$ $G=0.4363$	20	1.57	1.57	0
	30	1.57	1.57	0
	40	1.57	1.57	0
	50	1.56	1.56	0
	60	1.56	1.56	0
C ₁₈ Hph ^[8] $H=82.83$ $G=0.2289$	0	1.72	1.70	-1.16
	20	1.66	1.66	0
	30	1.64	1.65	0.61
	40	1.63	1.64	0.60
	50	1.62	1.62	0
	60	1.62	1.61	-0.62
	70	1.60	1.60	0
BP ^[7] $H=38.63$ $G=0.5198$	20	1.92	1.92	0
	30	1.90	1.91	0.53
	40	1.90	1.90	0
	60	1.89	1.89	0
Develosil ^[7] ODS—5 $H=376.1$ $G=-0.6472$	80	1.88	1.88	0
	20	1.89	1.89	0
	30	1.84	1.84	0
	40	1.74	1.74	0
DMPP ^[7,20] $H=162.4$ $G=0.06716$	60	1.62	1.62	0
	80	1.52	1.52	0
	20	1.86	1.86	0
	30	1.83	1.83	0
Develosil ^[7,20] ODS—P—5 $H=157.9$ $G=-0.1568$	40	1.80	1.80	0
	60	1.74	1.74	0
	80	1.69	1.69	0
	0	1.54	1.53	-0.65
ODS—P—5 $H=157.9$ $G=-0.1568$	20	1.44	1.46	1.39
	40	1.42	1.42	0
	60	1.38	1.37	-0.72

Tab.2 Identification of Eq.(6) by experimental values

Stationary phase	Mobile phase	Fullerene number	Intercept	$B \times 10^2$	Relationship coefficient	Intercept /B
PYE	toluene	13	-3.3250	5.429	0.9978	-61.2
S ₂ O ₂	n-hexane	4	-0.8428	1.409	0.9992	-59.8
Hypersil ODS	Acetonitrile— dichloromethane	16	-0.6603	1.138	0.9898	-58.0
Cosmosil PYE	Acetonitrile— dichloromethane	18	-1.8360	2.974	0.9909	-61.1
Zorbax Rx—C ₁₈	Acetonitrile— dichloromethane	20	-0.8277	1.408	0.9895	-58.8

In Tab.2 and 3 it is shown that identification of the experimental values with the calculated values by Eq.(6) for fullerenes under different stationary phases and different mobile phases. At 71 experimental data sets compared with the experimental values^[14~19] the total average relative deviation is 2.92%. In the meantime the ratios of the interception and slope of the linear relationship Eq.(6) regressed by experimental values are also shown in tables. For five groups of experimental values all the ratios approach to -60, it further identifies the validity of Eq.(6).

In Tab.4 the identification of the calculated values by Eq.(8) with the experimental values of C₇₀ under different stationary phases and different mobile phases is shown. For 8 stationary phases and 7 binary mobile phases at 45 data sets compared with the experimental values^[17~19] the ARD is 2.34%.

3 Conclusions

Based on the thermodynamic theory, we derived the quantitative relationship between the separation factor and the column temperature and carbon as well as the mobile phase composition. Meanwhile, this model was identified by the experimental data of C₇₀ and C₆₀—C₉₆ from different sources. The results show that this model is widely valid and relatively reliable. It may offer some theoretical bases for the optimization of the separation and purification of fullerenes.

Tab.3 Comparison of the experimental values of fullerenes^[13] with the calculated values by Eq.(6) on Hypersil ODS column using acetonitrile-dichloromethane as mobile phase

fullerene	C ₆₀	C ₇₀	C ₇₆	C ₇₈	C ₈₀	C ₈₂	C ₈₄	C ₈₄
α	1.00	1.19	1.27	1.29	1.32	1.33	1.35	1.39
α	1.02	1.15	1.23	1.25	1.28	1.31	1.34	1.34
RD/%	2.00	-3.36	-3.15	-2.33	-3.03	-1.50	-0.74	-3.60
fullerene	C ₈₆	C ₈₈	C ₈₈	C ₉₀	C ₉₀	C ₉₂	C ₉₄	C ₉₆
α	1.38	1.41	1.43	1.43	1.51	1.46	1.48	1.49
α	1.37	1.41	1.41	1.44	1.44	1.47	1.50	1.54
RD/%	-0.72	0	-1.40	0.69	-4.64	0.68	1.35	3.36

Tab.4 Comparison of the experimental values with the calculated values by Eq.(8)

Stationary phase	Mobile phase	Data set	B ₁	A ₁	ARD/%	Ref.
Buckysep- ⁻ RP	Acetonitrile-toluene	6	1.886	-0.223 6	1.26	[17]
Astec C ₁₈	Acetonitrile-toluene	7	1.688	-0.271 3	3.35	[17]
Chromspher	Isopropanol-isooctane	4	0.072 62	1.093	1.23	[17]
Buckyducher	n-hexane-toluene	8	1.517	-0.186 6	5.80	[17]
Rosolve C ₁₈	n-hexane-ether	4	-0.144 1	0.690 9	0.28	[18]
Rosolve C ₁₈	n-hexane-isopropanol	6	-0.433 5	0.956 8	2.00	[18]
DNAP	n-hexane-benzene	3	-1.226	1.195	0.00	[19]
DNAP	n-hexane-dichloromethane	4	-2.947	1.209	1.69	[19]
DNAP	n-hexane-ether	3	-1.342	1.486	0.99	[19]

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富勒烯的色谱分离模型

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摘 要: 在分子热力学理论的基础上, 建立了高效液相色谱中富勒烯的分离因子与柱温、碳数、流动相组成之间的定量相关模型, 用不同来源的C₇₀和C₆₀~C₉₆实验数据对该模型进行了检验, 结果表明本模型具有广泛的适用性和相当令人满意的可靠性。

关键词: 富勒烯; 分离因子; 定量相关模型; 分子热力学