Separation of C_{60} and C_{70} fullerenes on silica modified with phthalocyanines

Leonid L. Gumanov,*[a] Boris L. Korsunsky,[a] Valentina M. Derkacheva,[b] Vladimir M. Negrimovsky[b] and Eugene A. Luk'yanets*[b]

[a] Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588
[b] Institute of Organic Intermediates and Dyes, 103787 Moscow, Russian Federation. Fax: +7 095 408 7872
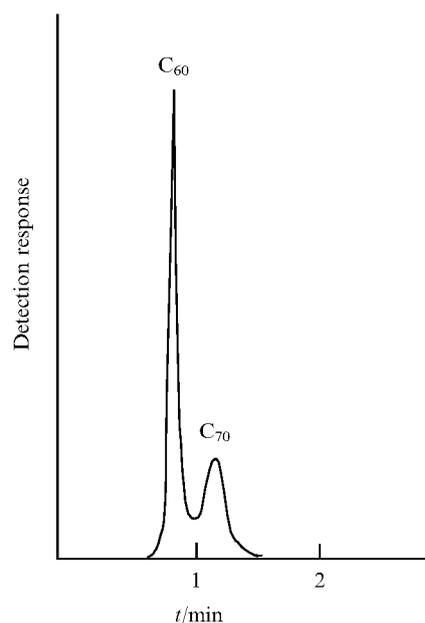
A series of stationary phases have been prepared by attachment of different phthalocyanines (PcM) to γ-aminopropyl silica and tested for HPLC separation of C_{60} and C_{70} fullerenes; strong dependence of chromatographic properties on the central metal ion and substituents of attached complexes was found, and for the phase containing 3-(β-naphthyloxy)-substituted PcCo good results were achieved.

The growing interest in the preparation of fullerenes has created the need for an effective means of separating them by HPLC.[1,2] To date, the best phase for the separation of C_{60} and C_{70} fullerenes with a 'good' solvent such as pure toluene is tetraphenylporphyrin–silica gel stationary phase (selectivity factors $\alpha = k'C_{70}/k'C_{60}$, $\alpha = 4.8$).[3]

In this article we report the preparation of new phases containing metal phthalocyanines (PcM) covalently attached to silica and the first results on the separation of C_{60} and C_{70} using these phases.

Our choice of PcM as a modifier of silica for fullerene separation arose from the following considerations: (a) the PcM molecular size corresponds well to the fullerene size; (b) the PcM π-system is larger than the porphyrin one; (c) PcMs are more readily synthetically available and allow a wide range of molecular design.

A series of phases 1–12 containing different PcMs attached to γ-aminopropyl silica via the sulfonamido group have been prepared. These phases can be divided into two groups — phases 1–5 prepared by the attachment of readily available PcM sulfochlorides,[4] and phases 6–12 prepared using recently synthesized by us 4-(chlorosulfonyl)phthalonitrile[5] via a well-

Table 1 Capacity (k') and selectivity factors (α) for C_{60} and C_{70} fullerenes on PcM modified stationary phases.

Stationary phase	Mobile phase	k' (C_{60})	k' (C_{70})	α (C_{70}/C_{60})
1	pentane–toluene (1:1)	0.47	0.82	1.8
2	pentane–toluene (1:1)	0.53	0.97	1.8
3	pentane–toluene (1:1)	0.75	1.4	1.9
4	pentane–toluene (1:1)	0.97	1.8	1.9
5	pentane–toluene (1:1)	1.4	2.9	2.1
6	heptane–toluene (1:1)	0.68	1.4	2.0
7	pentane–toluene (1:1)	1.6	4.1	2.6
8	pentane–toluene (1:1)	2.1	4.7	2.2
	toluene	0.46	0.9	2.0
9	toluene	0.42	0.75	1.8
10	pentane–toluene (1:1)	4.5	10.1	2.4
	toluene	0.68	1.4	2.1
11	toluene	0.46	0.75	1.6
12	toluene	2.2	17.1	7.8
	o-xylene	1.4	8.5	6.0
	heptane–1-methylnaphthalene (1:1)	1.2	4.5	3.8
	heptane–1-methylnaphthalene (1:19)	0.20	0.68	3.4

known procedure of solid-phase synthesis.[6†] Both procedures were simpler to prepare than the tetraphenylporphyrin phases.[3]
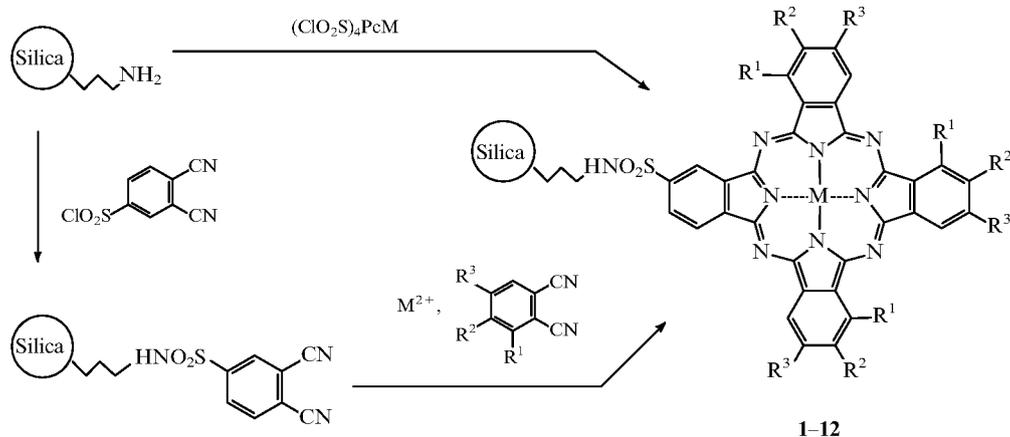
The examination of phases 1–5 demonstrated the remarkable influence of the PcM central metal ion on the retention (k') of C_{60} and C_{70}, accompanied by rather high

Figure 1 HPLC chromatogram of a mixture of C_{60} and C_{70} fullerenes: stationary phase **12**, mobile phase heptane–1-methylnaphthalene mixture (1:19), flow rate 0.2 ml min^{-1} in column 60 × 2 mm, detection 360 nm, injection 3 µl of 1.0 mg ml^{-1} fullerene solution in toluene.

$(ClO_2S)_4PcM$

Silica⟍NH₂

ClO₂S⟍⟍CN CN

Silica⟍HNO₂S⟍⟍CN CN

$M^{2+},$ R³⟍R²⟍R¹ CN CN

Silica⟍HNO₂S⟍...PcM macrocycle...R¹ R² R³

1–12

1–5 $R^1 = SO_2Cl$, $R^2 = R^3 = H$ **1** M = H₂, **2** M = Cu, **3** M = Zn, **4** M = VO, **5** M = Co
6 $R^1 = R^3 = NO_2$, $R^2 = H$, M = Co   7,8 $R^1 = R^3 = H$, $R^2 = Bu^t$ **7** M = Cu, **8** M = Zn
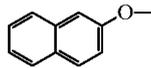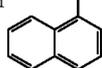
9 $R^1 =$ [1-naphthyloxy], $R^2 = R^3 = H$, M = Zn **10–12** $R^1 =$ [2-naphthyloxy],
$R^2 = R^3 = H$ **10** M = Cu. **11** M = Zn. **12** M = VO

selectivity (Table 1) unlike the porphyrin phases.[3] In this first series PcH₂ modified silica has the weakest fullerene retention while the PcCo modified silica has the strongest retention suggesting significant participation of d-π interaction between PcM and fullerenes.

In the second group of phases **6–12** the influence of substituents in the PcM macrocycle on the separation of C₆₀ and C₇₀ was investigated. It was found that strong electron-withdrawing nitro groups in the macrocycle decrease the chromatographic properties of PcM phases whereas electron-donating substituents (*tert*-butyl and naphthyloxy groups) enhance both retention and selectivity (Table 1). Phase **12**, possessing optimal structural factors — cobalt as central ion and β-naphthyloxy groups as substituents — provides high chromatographic properties using toluene as a mobile phase ($\alpha = 7.8$). Moreover, good results were also obtained for other solvents such as *o*-xylene and heptane–1-methylnaphthalene mixtures (Figure 1). These are very important for the preparative separation of fullerenes because their solubilities in these solvents are much higher than in toluene (according to our data, the solubility of a C₆₀, C₇₀ mixture in 1-methyl-naphthalene is ~ 10% and in toluene ~ 0.5%). However, it is necessary to increase sorbent capacity in order to use them for the separation of larger quantities of fullerene mixtures. These investigations are currently in progress.

6 (*a*) C. C. Leznoff and T. W. Hall, *Tetrahedron Lett.*, 1982, **23**, 3023; (*b*) T. W. Hall, S. Greenberg, C. R. McArthur, B. Khouw and C. C. Leznoff, *Nouv. J. Chim.*, 1982, **6**, 653; (*c*) D. Wohrle and G. Krawczyk, *Polym. Bull.*, 1986, **15**, 193.
7 V. M. Negrimovsky, V. M. Derkacheva, O. L. Kaliya and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1991, **61**, 460 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1991, **61**, 419].
8 S. A. Mikhalenko, S. V. Barkanova, O. L. Lebedev and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1971, **41**, 2735 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1991, **41**, 2770].
9 V. M. Derkacheva and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1980, **50**, 2313 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1980, **50**, 1874].

References

1 C. J. Welch and H. Pirkle, *J. Chromatogr.*, 1992, **609**, 89.
2 K. Kimata, K. Hosoya, T. Araki and N. Tanaka, *J. Org. Chem.*, 1993, **58**, 282.
3 C. E. Kibbey, M. R. Savina, B. K. Perseghian, A. H. Francis and M. E. Meyerhoff, *Anal. Chem.*, 1993, **65**, 3717.
4 Ye. G. Akopyants, S. V. Borisenkova, O. L. Kaliya, V. M. Derkacheva and E. A. Luk'yanets, *J. Mol. Catal.*, 1993, **83**, 1.
5 V. M. Negrimovsky, V. M. Derkacheva, E. A. Luk'yanets A. Weitemeyer, D. Wöhrle and G. Schneider, *Phosphorus, Sulfur, and Silicon*, 1995, **104**, 161.