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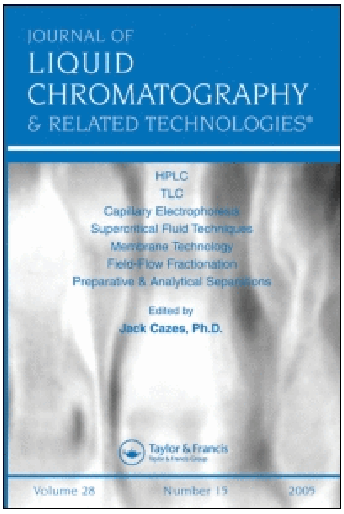

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LIQUID CHROMATOGRAPHIC H/D SEPARATION FACTORS FOR POLYCYCLIC AROMATIC HYDROCARBONS

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Introduction.

Kline, Wise and May(1) (KWM) recently reported liquid chromatographic separation factors for seven different polycyclic aromatic hydrocarbons (PAH's) dissolved in crude oil vs. aminosilane or polymeric octyldecylsilane substrates. The deuterolabelled materials were deliberately injected into the oil for use as internal standards. KWM advocate this method as a useful calibrating technique for complicated mixtures. The purpose of the present note is to show that the KWM results are consistent with predictions of the theory of isotope effects in condensed phases(2, 3) and are therefore of more general interest. Interpretation of chromatographic data in the context of the theory furnishes information about the interaction of PAH's with column substrate in the dilute Henry's law standard state. The analysis should stimulate a wider use of the technique advocated by KWM by placing it into a proper thermodynamic framework, thereby permitting useful theoretical rationalizations.

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Chromatographic Isotope Effects

The theory of isotope effects in condensed phases developed by Bigeleisen(2) and later reviewed by Jancso and Van Hook(3) was applied by Van Hook and coworkers(4-10) in interpreting gas-liquid chromatographic separation factors of protio-deutero isomers of hydrocarbons, including recent analysis of the use of deutero-labelled compounds as internal standards in GLC-MS analyses of halogenated hydrocarbons.(10) The present application to liquid/surface equilibria is an extension of this methodology.

In the Henry's law standard state appropriate for the treatment of chromatographic isotope effect data, the isotopic ratio of Henry's law constants K' or K is equal inversly to the ratio of corrected chromatographic retention volumes, V' or V, and is given in turn by the natural logarithmic reduced partition function ratio in the stationary (s) and mobile (m) phases, $\ln(f_s/f_m)$, with but minor correction

$$(1) \quad \ln(K'/K) = \ln(V/V') = \ln(f_s/f_m) + \mathrm{COR}$$

The last term in equation 1, COR, corrects for isotopic differences in the condensed phase PV terms in the mobile and stationary phases and is expected to be negligible.

Normally an harmonic cell model can be employed for the evaluation of the reduced partition function ratio.(2, 3) The rather complicated result of that theory can be usefully approximated as shown in equation 2.

$$(2) \quad \ln(f_s/f_m) = A/T^2 + B/T$$

In this equation the A term refers to those isotope dependent frequencies small enough to be treated in the high temperature approximation. For PAH's near room temperature these will include the six external or lattice modes, but because of the large masses and moments of inertia of the compunds of interest, as well as their relatively small isotope dependence, these will be found at very low frequencies and will only make a very small contribution to the isotope effects.

The B term in equation 2 refers to those frequencies of high enough energy to be treated in the low temperature or zero point energy approximation

$$(3)\quad B/T = (1/2)\sum((u'_{i,s} - u_{i,s}) - (u'_{i,m} - u_{i,m})$$

$$= (1/2)\sum(u'_{i,s} - u'_{i,m})(1 - u_i/u'_i)$$

because to a good approximation $(u/u')_m = (u/u')_s$. In equation 3 the u's are reduced frequencies, $u_i = h\nu_i/kT$, k is Boltzman's constant. The prime refers to the isotopic isomer of lighter mass. The most important contributors to the chromatographic isotope effect are those high lying frequencies which show the largest shift on isotopic substiutution. These are the carbon-hydrogen stetching modes where to a good approximation $(u_i/u_i')_{st} = ((1/12 + 1/2)/(1/12 + 1/1)) = 0.734$.

KWM report separation factors for seven PAH's from crude oil to aminosilane, or crude oil to octyldecylsilane columns. Base_e logarithmic K ratios (equation 1) extracted from their data(1,11) are summarized in table 1. The data show an inverse isotope effect for transfer of PAH's from oil to octyldecylsilane of $\ln(K'/K) = -0.003\pm0.001$ and a positve one, $\ln(K'/K) = 0.002\pm0.001$ for transfer from oil to the aminosilane column. The effects are normalized and reported per atom D/H substituted. At room temperature the positive effect corrosponds to a blue shift in the average CH stretch, $\nu_{CH}(\text{oil}) - \nu_{CH}(\text{amino column}) = -3$

Table 1.

Natural logarithims of thermodynamic activity ratios, H/D, as deduced from liquid chromatographic retention of polycyclic aromatic hydrocarbons (see reference 1), normalized to per H or D basis.

Compound	Number of		ln(V/V') = ln (K'/K)	
	C	H/D	NH_2 Column	C_{18} Column
Phenanthrene	14	10	0.001	-0.004
Flouranthene	16	10	0.002	-0.003
Pyrene	16	10	0.003	-0.004
Benz(a)anthracene	18	12	0.002	-0.003
Chrysene	18	12	0.002	-0.003
Perylene	20	12	0.002	-0.002
Benzo(a)pyrene	20	12	0.004	-0.003
Average	-	-	0.002 ±0.001	-0.003 ±0.001

cm^{-1}, while the isotope effect on the equilibrium between crude oil and octyldecylsilane column corrosponds to a red shift of 5 cm^{-1}. Thus the transfer of a protio PAH from the amino to the octadecyl surface is eqivalent to a red shift of 8 cm^{-1} in the average CH stretching frequency. These are upper limits, there must also be some changes in the CH/CD bending vibrations which also contribute to the isotope effects. The present calculation which lumps all of the effects into the stretching modes is an approximate one, but even so has come to an eminently reasonable conclusion. Carbon-hydrogen stretching frequencies for a wide variety of compounds are known to blue shift significantly on transfer from van der Waals solvents to ones of higher dielectric constant(12, 13), and the magnitude of the shifts calculated from the KWM chromatographic data falls nicely in the range of the spectroscopic observations.

Conclusions

Isotope effects in liquid chromatography as reported by KWM have been rationalized straightforwardly by the well established theory of isotope effects in condensed phases. The isotope effects are a consequence of shifts in the CH/CD zero point energies on transfer from the mobile phase solvent to the column substrate. Both normal and inverse effects were observed corrosponding to blue and red shifts respectively and these are in qualitative agreement with spectroscopic observation. It seems reasonable that rationalization of the separation factors of the PAH's themselves, from phenanthrene through flouranthrene to benzo(a)pyrene via consideration of molecular energetics analogous to that outlined above might be sucessful. At the moment the physical origin of the sucessful separation of these compounds is not well understood.(11) More importantly, the present analysis supports the suggestion of KWM that stable isotope tracing be more widely employed in chromatography. Modern LC technique allows resolution of molecules differing by only a few tenths of a percent in thermodynamic activity and the physical reason for isotopic effects in chromatography is well understood in terms of molecular properties.

Acknowledement

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