

Effect of temperature and organic modifier on the isocratic retention characteristics of nitrated polycyclic aromatic hydrocarbons on a reversed-phase octadecylsilane column

ALBERT ROBBAT, Jr.* and TYNG-YUN LIU

Chemistry Department, Trace Analytical Measurement Laboratory, Tufts University, Medford, MA 02155 (U.S.A.)

(First received January 30th, 1990; revised manuscript received April 3rd, 1990)

ABSTRACT

Nitrated polycyclic aromatic hydrocarbon (nitro-PAH) retention behavior was evaluated on a reversed-phase polymeric octadecylsilane column under isocratic conditions as a function of organic modifier and temperature. Several conclusions can be drawn from the retention and organic modifier study (*viz.*, methanol and acetonitrile-water). First, the logarithm of the capacity factor ($\log k'$) was linearly dependent on organic-water volume fraction (ϕ). Second, nitro-PAH k' values increased with decrease in organic modifier concentration. Third, the slopes of $\log k'$ vs. ϕ plots were solvent-dependent. Larger slope values were found for nitro-PAHs in methanol-water than in acetonitrile-water mixtures for a particular compound. Fourth, slope values were dependent on the molecular structure of individual nitro-PAHs.

Nitro-PAH retention times decreased with increase in column temperature. A linear dependence of $\log k'$ on the reciprocal of the absolute column temperature, the Van 't Hoff plot, was observed for both organic modifiers over the temperature range studied. The standard enthalpic change (ΔH^0) for nitro-PAH transfer from the mobile to the stationary phase was determined. ΔH^0 was dependent on organic modifier type and composition as well as solute structure. The enthalpy-entropy compensation effect was evaluated by plotting $\log k'$ vs. $-\Delta H^0$ and used to interpret nitro-PAH retention mechanisms. A compensation effect was found for some mononitrated PAHs for both organic modifiers. The compensation temperatures were within the accepted range described for reversed-phase high-performance liquid chromatography systems.

INTRODUCTION

Reversed-phase high-performance liquid chromatography (HPLC) retention and thus, solute selectivity, is influenced by several chemical (*e.g.*, type and concentration of organic modifier) and physical factors (*e.g.*, column temperature

and/or stationary phase chain length, density, surface area, pore volume, monomeric/polymeric coatings). The retention process in reversed-phase HPLC is thought to be primarily controlled by solute interactions within the mobile phase¹⁻³. Most research has focused on understanding the influence of mobile phase composition on retention. Studies have shown that variations in solvent composition (*i.e.*, water with one or more organic solvents) can produce dramatic retention differences⁴⁻⁷. Stationary phase studies are limited because details of the bonded-phase synthesis and silica substrates are not readily available. In addition to mobile-stationary phase effects on retention, changes in column temperature may alter retention characteristics as well⁸⁻¹¹.

In this investigation, the isocratic reversed-phase nitrated polycyclic aromatic hydrocarbon (nitro-PAH) retention behavior was studied as a function of mobile phase composition (acetonitrile-water and methanol-water) and column temperature (35-65°C) on a polymeric octadecylsilane column. For each organic modifier, the dependence of the logarithm of the capacity factor at a given volume fraction ($\log k'$) on the volume fraction of organic modifier in the organic solvent-water mixture (ϕ) was evaluated. The slope, S , for $\log k'$ vs. ϕ plots was discussed in terms of solute type and organic modifier. Van 't Hoff plots, $\log k'$ vs. $1/T$ (T = temperature), were used to determine the effect of column temperature on nitro-PAH retention. Based on these results, the standard enthalpic change (ΔH^0) for nitro-PAH transfer from the mobile to the stationary phases was evaluated. An extra-thermodynamic approach, based on enthalpy-entropy compensation¹², was used to further define the nitro-PAH retention process.

EXPERIMENTAL

Reversed-phase HPLC separations were achieved using a Hewlett-Packard 1090M liquid chromatography system (Hewlett-Packard, Palo Alto, CA, U.S.A.) equipped with a DR5 binary solvent system, diode-array detector (standard flow cell), and temperature-controlled autosampler and column compartments. A Hewlett-Packard HPLC ChemStation was used to control the HPLC experiments, record and evaluate chromatograms and spectra. Sample injections were made using the autosampler and autoinjector system. A 25 cm \times 2.1 mm, 5 μ m particle size reversed-phase C₁₈ column (Alltech, Deerfield, IL, U.S.A.) was used. A Rheodyne 3 mm \times 0.5 μ m column inlet filter was incorporated to protect the analytical column.

HPLC-grade acetonitrile and methanol (Fisher Scientific, Medford, MA, U.S.A.) were used as received. Water was purified by a Milli-Q water purification system (Millipore, Milford, MA, U.S.A.). All solvents were filtered through a 0.45- μ m nylon-66 filter (Rainin, Woburn, MA, U.S.A.), ultrasonicated and vacuum degassed prior to use. Helium sparging was performed throughout the HPLC experiment. The mobile phase consisted of 50, 60 and 70% (v/v) of acetonitrile or methanol in water at flow-rate of 0.5 ml/min. HPLC experiments were performed at column temperatures of 35, 45, 55 and 65°C for each mobile phase composition. 2% Sodium dichromate in water was used to determine the elution time for the unretained solute for each mobile phase and temperature.

Sources of nitro-PAHs have been identified elsewhere¹³. Nitro-PAHs were used without further purification. Standard solutions were prepared by dissolving ap-

proximately 1 mg of nitro-PAH in 1 ml of acetonitrile or methanol. Samples were stored in the dark and refrigerated. After the column was equilibrated with solvent and the column temperature stabilized, 1 μ l of a nitro-PAH solution mixture was injected. To reduce experimental time, multicomponent standard solutions were prepared. Identification of each compound peak was made by comparing HPLC retention times and UV absorption spectra with those of individual standards.

RESULTS AND DISCUSSION

Nitro-PAH retention as a function of mobile phase composition

The intent of this study was to evaluate nitro-PAH isocratic reversed-phase HPLC retention characteristics, on a polymeric octadecylsilane column (250 \times 2.1 mm, 5 μ m particle size), at various acetonitrile–water and methanol–water mobile phase compositions and temperatures. Shown in Table I are nitro-PAHs and their corresponding compound numbers. Tables II–V illustrate nitro-PAH retention behavior, measured by $\log k'$, as a function of ϕ (50:50, 60:40 and 70:30, v/v) and T (35–65°C). Cross-comparison of acetonitrile and methanol $\log k'$ values at the same volume fraction and temperature revealed two readily apparent observations. First, nitro-PAH elution order was markedly different between the two organic modifiers. Second, nitro-PAHs were retained in the column much longer by methanol–water than by acetonitrile–water mixtures. For instance, 1-nitropyrene eluted at 22 min with acetonitrile–water (50:50) (35°C). The same compound eluted after 1.5 h with methanol–water (50:50) (35°C). Data for compounds eluting after 1.5 h are not included in this study. Retention time reproducibility was monitored over a nine-month time period with data incorporated in relevant tables.

The dependence of nitro-PAH retention on mobile phase composition was evaluated by plotting $\log k'$ vs. ϕ at constant column temperature

TABLE I
IDENTIFICATION OF NITRO-PAHs

No.	Compound	No.	Compound
1	5-Nitroquinoline	18	3-Nitro-9-fluorenone
2	6-Nitroquinoline	19	1-Nitro-2-methylnaphthalene
3	5-Nitro-6-methylquinoline	20	2,7-Dinitrofluorene
4	8-Nitroquinoline	21	3-Nitrobiphenyl
5	1,8-Dinitronaphthalene	22	2,2'-Dinitrobibenzyl
6	1,3,6,8-Tetranitronaphthalene	23	4-Nitrobiphenyl
7	1,5-Dinitronaphthalene	24	9-Nitrophenanthrene
8	1,4-Dinitronaphthalene	25	2-Nitrofluorene
9	1,3-Dinitronaphthalene	26	9,10-Dinitroanthracene
10	3-Nitrodibenzofuran	27	3-Nitrophenanthrene
11	2,4,7-Trinitro-9-fluorenone	28	9-Nitroanthracene
12	1-Nitronaphthalene	29	3-Nitrofluoranthene
13	2-Nitro-9-fluorenone	30	1-Nitropyrene
14	2,7-Dinitro-9-fluorenone	31	1-Methyl-10-nitroanthracene
15	2-Nitronaphthalene	32	6-Nitrochrysene
16	2,6-Dinitro-9-fluorenone	33	3-Nitroperylene
17	2-Nitrobiphenyl	34	6-Nitrobenzo[a]pyrene

TABLE II
DEPENDENCE OF $\log k'$ ON ϕ AT 35°C

No.	Acetonitrile-water						Methanol-water						
	ϕ (%)			Intercept	S(error)	r	ϕ (%)			Intercept	S(error)	r	
	50	60	70				50	60	70				
1	0.294	0.151	-0.004	1.04	1.49(0.04)	-0.999	4	0.620	0.325	0.076	1.97	2.72(0.13)	-0.999
2	0.354	0.170	0.024	1.17	1.65(0.11)	-0.998	2	0.662	0.397	0.158	1.92	2.52(0.08)	-0.999
3	0.407	0.197	0.024	1.36	1.92(0.11)	-0.998	5	0.695	0.358	0.080	2.22	3.08(0.17)	-0.999
4	0.491	0.213	0.042	1.60	2.25(0.31)	-0.991	1	0.697	0.409	0.167	2.01	2.65(0.13)	-0.999
5	0.498	0.220	0.074	1.54	2.12(0.38)	-0.984	6	0.699	0.367	0.070	2.27	3.15(0.10)	-0.999
6	0.599	0.280	0.063	1.92	2.68(0.29)	-0.994	3	0.925	0.593	0.293	2.50	3.16(0.09)	-0.999
7	0.677	0.377	0.202	1.84	2.38(0.36)	-0.989	7	1.063	0.703	0.380	2.76	3.42(0.11)	-0.999
8	0.729	0.418	0.234	1.95	2.48(0.37)	-0.989	8	1.147	0.772	0.434	2.92	3.57(0.11)	-0.999
9	0.740	0.431	0.246	1.95	2.47(0.37)	-0.990	26	1.157	0.867	0.595	2.56	2.82(0.05)	-0.999
10	0.746	0.476	0.256	1.96	2.45(0.14)	-0.998	11	1.179	0.798	0.418	3.08	3.81(0.01)	-1.000
11	0.753	0.427	0.114	2.35	3.20(0.04)	-0.999	9	1.193	0.827	0.495	2.93	3.49(0.01)	-0.999
12	0.759	0.473	0.306	1.87	2.27(0.34)	-0.989	12	1.218	0.850	0.525	2.94	3.47(0.12)	-0.999
13	0.787	0.518	0.268	2.09	2.61(0.05)	-0.999	13	1.252	0.838	0.471	3.19	3.91(0.14)	-0.999
14	0.801	0.458	0.184	2.33	3.09(0.20)	-0.998	17	1.272	0.830	0.441	3.34	4.16(0.15)	-0.999
15	0.808	0.543	0.311	2.05	2.49(0.10)	-0.999	14	1.300	0.873	0.497	3.30	4.02(0.15)	-0.999
16	0.819	0.481	0.195	2.37	3.12(0.15)	-0.999	15	1.313	0.916	0.556	3.20	3.79(0.11)	-0.999

17	0.858	0.567	0.272	2.32	2.93(0.01)	-1.000	21	1.366	0.954	0.582	3.32	3.92(0.12)	-0.999
18	0.881	0.539	0.279	2.37	3.01(0.24)	-0.997	16	1.401	0.974	0.601	3.39	4.00(0.16)	-0.999
19	0.938	0.612	0.409	2.24	2.65(0.36)	-0.991	19	1.457	1.029	0.637	3.50	4.10(0.10)	-0.999
20	0.952	0.636	0.331	2.50	3.11(0.03)	-0.999	20	1.514	1.029	0.605	3.78	4.55(0.10)	-0.999
21	1.021	0.704	0.423	2.51	2.99(0.10)	-0.999	23	1.616	1.150	0.725	3.84	4.46(0.12)	-0.999
22	1.042	0.693	0.379	2.69	3.32(0.10)	-0.999	18	1.654	1.189	0.762	3.88	4.46(0.12)	-0.999
23	1.046	0.709	0.414	2.62	3.16(0.12)	-0.999	10	1.666	1.213	0.857	3.67	4.05(0.28)	-0.999
24	1.072	0.811	0.522	2.45	2.75(0.08)	-0.999	22	1.686	1.164	0.698	4.15	4.94(0.16)	-0.999
25	1.125	0.782	0.483	2.72	3.21(0.13)	-0.999	25	1.761	1.280	0.845	4.04	4.58(0.13)	-0.999
26	1.169	0.882	0.579	2.65	2.95(0.05)	-0.999	28	1.916	1.379	0.904	4.44	5.06(0.18)	-0.999
27	1.213	0.889	0.589	2.77	3.12(0.07)	-0.999	24	1.950	1.449	1.012	4.28	4.69(0.18)	-0.999
28	1.247	0.888	0.582	2.90	3.33(0.15)	-0.999	27	1.999	1.514	1.072	4.31	4.64(0.12)	-0.999
29	1.272	1.028	0.712	2.68	2.80(0.21)	-0.997	29		1.609	1.185			
30	1.430	1.058	0.739	3.15	3.56(0.15)	-0.999	30		1.749	1.267			
31	1.484	1.043	0.728	3.35	3.78(0.36)	-0.995	32		1.933	1.505			
32	1.503	1.194	0.847	3.15	3.28(0.11)	-0.999	34		1.62	1.62			
33	1.606	1.377	1.026	3.08	2.90(0.35)	-0.993	33		1.713	1.713			
34	1.788	1.419	1.056	3.62	3.66(0.02)	-1.000							

TABLE III
DEPENDENCE OF $\log k'$ ON ϕ AT 45°C

No.	Acetonitrile-water				No.	Methanol-water							
	ϕ (%)		Intercept	$S(\text{error})$		ϕ (%)		Intercept	$S(\text{error})$	r			
	50	60				70	50				60	70	
1	0.271	0.106	-0.035	1.03	1.53(0.07)	-0.999	4	0.536	0.259	0.047	1.75	2.45(0.19)	-0.999
2	0.333	0.121	0.003	1.14	1.67(0.27)	-0.988	6	0.568	0.284	0.012	1.96	2.78(0.03)	-0.999
3	0.361	0.164	-0.039	1.36	2.00(0.02)	-1.000	5	0.574	0.276	0.029	1.93	2.73(0.15)	-0.998
4	0.408	0.18	-0.009	1.44	2.09(0.11)	-0.999	2	0.579	0.314	0.096	1.78	2.42(0.14)	-0.998
5	0.410	0.188	0.041	1.32	1.85(0.22)	-0.993	1	0.599	0.333	0.120	1.79	2.40(0.15)	-0.998
6	0.500	0.210	0.021	1.68	2.39(0.29)	-0.993	3	0.836	0.504	0.238	2.32	2.99(0.19)	-0.999
7	0.595	0.334	0.162	1.66	2.17(0.26)	-0.995	7	0.939	0.613	0.312	2.50	3.14(0.07)	-0.999
8	0.640	0.381	0.193	1.75	2.23(0.20)	-0.996	8	1.020	0.684	0.363	2.66	3.29(0.04)	-0.999
9	0.641	0.391	0.201	1.73	2.20(0.17)	-0.997	9	1.065	0.729	0.415	2.69	3.25(0.06)	-0.999
11	0.684	0.357	0.057	2.25	3.14(0.08)	-0.999	11	1.069	0.682	0.347	2.87	3.61(0.15)	-0.999
12	0.684	0.446	0.264	1.72	2.10(0.16)	-0.997	13	1.075	0.688	0.356	2.86	3.60(0.16)	-0.999
10	0.697	0.421	0.244	1.83	2.27(0.29)	-0.992	26	1.086	0.805	0.544	2.44	2.71(0.06)	-0.999
14	0.710	0.389	0.131	2.15	2.90(0.18)	-0.998	14	1.101	0.705	0.369	2.92	3.66(0.17)	-0.998
16	0.745	0.415	0.149	2.22	2.98(0.18)	-0.998	12	1.102	0.771	0.499	2.60	3.02(0.17)	-0.999
18	0.749	0.484	0.239	2.02	2.55(0.06)	-0.998	17	1.156	0.745	0.391	3.06	3.83(0.16)	-0.998

13	0.761	0.463	0.221	2.10	2.70(0.17)	-0.998	15	1.169	0.793	0.497	2.84	3.36(0.23)	-0.999
15	0.785	0.493	0.260	2.09	2.63(0.17)	-0.998	21	1.198	0.819	0.518	2.89	3.40(0.23)	-0.999
17	0.816	0.507	0.229	2.28	2.94(0.09)	-0.999	16	1.230	0.832	0.492	3.07	3.69(0.17)	-0.999
19	0.859	0.568	0.362	2.09	2.49(0.25)	-0.995	20	1.313	0.859	0.477	3.39	4.18(0.21)	-0.999
20	0.920	0.563	0.267	2.54	3.27(0.17)	-0.999	19	1.313	0.927	0.558	3.20	3.78(0.05)	-0.999
23	0.986	0.662	0.361	2.54	3.13(0.07)	-0.999	23	1.469	1.031	0.639	3.54	4.15(0.13)	-0.999
24	0.997	0.641	0.396	2.48	3.01(0.32)	-0.994	18	1.499	1.065	0.706	3.47	3.96(0.22)	-0.997
21	1.002	0.658	0.366	2.58	3.19(0.01)	-0.999	22	1.502	1.008	0.629	3.67	4.37(0.35)	-0.999
22	1.021	0.636	0.320	2.76	3.15(0.20)	-0.998	10	1.512	1.112	0.762	3.37	3.75(0.14)	-0.999
25	1.056	0.735	0.419	2.65	3.19(0.01)	-1.000	25	1.597	1.144	0.746	3.72	4.26(0.16)	-0.999
26	1.089	0.781	0.461	2.66	3.14(0.03)	-0.999	28	1.746	1.245	0.810	4.08	4.68(0.19)	-0.999
28	1.176	0.827	0.519	2.81	3.29(0.12)	-0.999	24	1.790	1.325	0.914	3.97	4.38(0.16)	-0.999
29	1.177	0.929	0.625	2.57	2.76(0.16)	-0.998	27	1.847	1.384	0.949	4.09	4.49(0.08)	-0.999
27	1.192	0.811	0.519	2.86	3.37(0.27)	-0.997	29	1.974	1.485	1.065	4.25	4.55(0.20)	-0.999
32	1.306	1.094	0.735	2.76	2.85(0.42)	-0.989	30		1.589	1.149			
30	1.342	0.993	0.661	3.04	3.41(0.05)	-0.999	32		1.883	1.369			
31	1.379	0.979	0.647	3.20	3.66(0.20)	-0.999	34		1.977	1.472			
33	1.503	1.248	0.902	3.02	3.01(0.26)	-0.996	33			1.554			
34	1.671	1.298	0.943	3.49	3.64(0.05)	-0.999							

TABLE IV
DEPENDENCE OF $\log k'$ ON φ AT 55°C

No.	Acetonitrile-water				No.	Methanol-water					
	φ (%)		Intercept	$S(\text{error})$		r	φ (%)		Intercept	$S(\text{error})$	r
	50	60					70	50			
1	0.254	0.064	-0.060	1.03	4	0.467	0.200	-0.012	1.66	2.40(0.16)	-0.998
2	0.261	0.108	-0.047	1.03	6	0.469	0.205	-0.038	1.74	2.54(0.06)	-0.999
3	0.330	0.129	-0.054	1.29	5	0.481	0.200	-0.025	1.74	2.53(0.16)	-0.998
4	0.341	0.133	0.005	1.17	1	0.508	0.255	0.070	1.59	2.19(0.20)	-0.996
5	0.359	0.144	-0.040	1.35	2	0.536	0.243	0.052	1.73	2.42(0.29)	-0.993
6	0.413	0.156	-0.026	1.50	3	0.725	0.428	0.175	2.09	2.75(0.13)	-0.999
7	0.520	0.285	0.121	1.51	7	0.834	0.529	0.246	2.30	2.94(0.06)	-0.999
8	0.574	0.324	0.150	1.62	8	0.916	0.599	0.294	2.47	3.11(0.03)	-0.999
9	0.583	0.332	0.161	1.63	11	0.934	0.584	0.275	2.57	3.29(0.13)	-0.999
11	0.610	0.304	-0.016	2.18	14	0.944	0.585	0.282	2.59	3.31(0.16)	-0.999
12	0.615	0.386	0.224	1.58	9	0.951	0.644	0.338	2.48	3.06(0.01)	-1.000
14	0.622	0.324	0.077	1.98	13	0.993	0.575	0.279	2.76	3.57(0.35)	-0.999
10	0.638	0.389	0.215	1.68	12	1.001	0.718	0.382	2.56	3.10(0.15)	-0.999
16	0.656	0.347	0.092	2.06	26	1.014	0.734	0.500	2.29	2.57(0.13)	-0.999

13	0.683	0.402	0.166	1.97	2.59(0.13)	-0.999	15	1.043	0.699	0.397	2.65	3.23(0.12)	-0.999
15	0.718	0.441	0.218	1.96	2.50(0.16)	-0.998	17	1.047	0.657	0.335	2.82	3.56(0.20)	-0.999
18	0.721	0.428	0.186	2.05	2.68(0.15)	-0.999	21	1.063	0.696	0.392	2.73	3.36(0.18)	-0.999
17	0.759	0.455	0.190	2.18	2.85(0.11)	-0.999	16	1.093	0.724	0.417	2.77	3.38(0.18)	-0.999
19	0.786	0.514	0.321	1.94	2.33(0.23)	-0.995	20	1.151	0.739	0.392	3.04	3.80(0.19)	-0.999
20	0.831	0.490	0.208	2.38	3.12(0.17)	-0.999	19	1.216	0.831	0.483	3.04	3.67(0.11)	-0.999
24	0.915	0.599	0.355	2.30	2.80(0.21)	-0.997	10	1.327	1.011	0.655	3.01	3.36(0.12)	-0.999
23	0.917	0.594	0.316	2.41	3.01(0.13)	-0.999	23	1.337	0.921	0.562	3.27	3.88(0.16)	-0.999
21	0.925	0.596	0.320	2.43	3.03(0.15)	-0.999	22	1.345	0.888	0.503	3.44	4.21(0.21)	-0.999
22	0.941	0.575	0.262	2.63	3.40(0.15)	-0.999	18	1.364	0.950	0.590	3.29	3.87(0.16)	-0.999
25	0.980	0.652	0.368	2.50	3.06(0.13)	-0.999	25	1.446	1.025	0.657	3.41	3.95(0.15)	-0.999
26	1.013	0.679	0.413	2.50	3.00(0.20)	-0.998	28	1.589	1.122	0.722	3.75	4.34(0.19)	-0.999
29	1.086	0.862	0.556	2.42	2.65(0.24)	-0.996	24	1.651	1.214	0.830	3.69	4.11(0.15)	-0.999
28	1.101	0.748	0.463	2.68	3.19(0.20)	-0.998	27	1.704	1.269	0.881	3.75	4.12(0.14)	-0.999
27	1.103	0.750	0.458	2.71	3.23(0.18)	-0.999	30	1.941	1.467	1.044	4.18	4.49(0.15)	-0.999
32	1.221	1.014	0.690	2.57	2.66(0.34)	-0.992	29	1.827	1.345	0.934	4.05	4.47(0.20)	-0.999
30	1.254	0.890	0.594	2.89	3.30(0.20)	-0.998	32		1.736	1.252			
31	1.288	0.901	0.585	3.03	3.52(0.21)	-0.998	34		1.811	1.308			
33	1.414	1.152	0.820	2.91	2.97(0.20)	-0.998	33			1.414			
34	1.561	1.206	0.856	3.32	3.53(0.01)	-1.000							

TABLE V
DEPENDENCE OF $\log k'$ ON ϕ AT 65°C

No.	Acetonitrile-water				No.	Methanol-water							
	ϕ (%)		Intercept	$S(\text{error})$		r	ϕ (%)		Intercept	$S(\text{error})$	r		
	50	60					70	50				60	70
1	0.207	0.043	-0.090	0.94	1.49(0.09)	-0.998	6	0.376	0.135	-0.088	1.53	2.32(0.05)	-0.999
2	0.219	0.073	-0.108	1.04	1.64(0.10)	-0.998	5	0.391	0.137	-0.072	1.54	2.32(0.13)	-0.998
5	0.295	0.096	-0.036	1.11	1.66(0.19)	-0.993	2	0.397	0.176	0.009	1.36	1.94(0.16)	-0.997
3	0.311	0.082	-0.096	1.32	2.04(0.15)	-0.997	4	0.409	0.156	-0.043	1.53	2.26(0.16)	-0.998
4	0.315	0.104	-0.095	1.34	2.05(0.03)	-0.999	1	0.412	0.199	0.017	1.39	1.98(0.09)	-0.999
6	0.350	0.098	-0.062	1.36	2.06(0.27)	-0.992	3	0.639	0.357	0.117	1.94	2.61(0.12)	-0.999
7	0.470	0.237	0.084	1.42	1.93(0.23)	-0.993	7	0.738	0.448	0.188	2.11	2.75(0.09)	-0.999
8	0.522	0.283	0.110	1.54	2.06(0.27)	-0.996	8	0.812	0.507	0.233	2.25	2.90(0.09)	-0.999
9	0.530	0.286	0.124	1.53	2.03(0.24)	-0.993	13	0.818	0.483	0.205	2.34	3.07(0.16)	-0.999
11	0.540	0.243	-0.045	2.00	2.93(0.03)	-1.000	14	0.823	0.487	0.189	2.40	3.17(0.11)	-0.999
14	0.543	0.240	0.012	1.86	2.66(0.23)	-0.997	11	0.824	0.494	0.208	2.36	3.08(0.13)	-0.999
12	0.570	0.340	0.189	1.51	1.91(0.23)	-0.993	9	0.853	0.551	0.270	2.31	2.92(0.06)	-0.999
16	0.575	0.263	0.028	1.93	2.74(0.22)	-0.997	12	0.940	0.593	0.310	2.50	3.15(0.18)	-0.998
10	0.597	0.359	0.174	1.65	2.12(0.15)	-0.997	26	0.942	0.676	0.447	2.17	2.48(0.11)	-0.999
13	0.610	0.325	0.100	1.88	2.55(0.17)	-0.998	15	0.946	0.619	0.336	2.46	3.05(0.13)	-0.999

18	0.650	0.347	0.117	1.97	2.67(0.21)	-0.997	21	0.949	0.604	0.324	2.50	3.13(0.19)	-0.998
15	0.651	0.369	0.176	1.82	2.38(0.26)	-0.994	17	0.953	0.581	0.276	2.63	3.39(0.19)	-0.998
19	0.697	0.468	0.272	1.76	2.13(0.10)	-0.999	16	0.981	0.635	0.345	2.56	3.18(0.16)	-0.999
17	0.702	0.423	0.151	2.08	2.76(0.02)	-1.000	20	1.025	0.639	0.316	2.79	3.54(0.18)	-0.999
20	0.740	0.397	0.139	2.23	3.01(0.25)	-0.997	19	1.111	0.741	0.417	2.84	3.47(0.13)	-0.999
24	0.846	0.529	0.295	2.21	2.76(0.24)	-0.996	22	1.215	0.786	0.419	3.19	3.98(0.18)	-0.999
23	0.853	0.541	0.271	2.30	2.91(0.12)	-0.999	23	1.221	0.829	0.484	3.06	3.69(0.14)	-0.999
21	0.860	0.530	0.255	2.36	3.03(0.16)	-0.999	18	1.254	0.858	0.525	3.07	3.65(0.18)	-0.999
22	0.863	0.491	0.176	2.57	3.44(0.16)	-0.999	10	1.254	0.89	0.579	2.93	3.38(0.15)	-0.999
25	0.912	0.599	0.313	2.41	3.00(0.08)	-0.999	25	1.321	0.921	0.569	3.19	3.76(0.14)	-0.999
26	0.941	0.608	0.355	2.39	2.93(0.23)	-0.997	28	1.459	1.017	0.635	3.51	4.12(0.17)	-0.999
29	0.999	0.777	0.491	2.28	2.54(0.18)	-0.997	24	1.518	1.091	0.728	3.48	3.95(0.18)	-0.999
28	1.018	0.706	0.409	2.54	3.05(0.04)	-0.999	27	1.566	1.140	0.783	3.51	3.92(0.20)	-0.999
27	1.023	0.656	0.378	2.62	3.23(0.26)	-0.997	30	1.667	1.319	0.931	3.56	3.77(0.17)	-0.999
32	1.135	0.925	0.606	2.48	2.65(0.31)	-0.993	32	2.094	1.570	1.125	4.50	4.85(0.23)	-0.999
30	1.178	0.840	0.531	2.79	3.24(0.08)	-0.999	29	1.683	1.215	0.836	3.79	4.24(0.26)	-0.999
31	1.205	0.812	0.506	2.94	3.49(0.25)	-0.997	34		1.649	1.189			
33	1.321	1.053	0.732	2.80	2.95(0.15)	-0.998	33		1.732	1.269			
34	1.335	1.108	0.775	2.75	2.80(0.31)	-0.996							

$$\log k' = \log k_0 - S\varphi \quad (1)$$

where k_0 is the (extrapolated) value of k' for pure water as the mobile phase ($\varphi=0$). The slope, S , should be related to the solvent strength of the pure organic solvent¹⁴. Tables II–V also list the corresponding slopes (slope error), intercepts and correlation coefficients. Several conclusions were drawn from the data. First, $\log k'$ was linearly related to φ . Second, as might be expected¹⁵, the slope, S , for a particular nitro-PAH was significantly different between the two mobile phases. Nitro-PAHs had larger S values with methanol–water than with acetonitrile–water, *e.g.*, the slope for 9-nitroanthracene was 5.06 *vs.* 3.33, respectively, at 35°C. Third, at each temperature studied, a wide range of slope values were found for both mobile phases. For example, the S values ranged between 1.49 and 3.66 for nitro-PAHs in acetonitrile–water at 35°C. This resulted in nitro-PAH elution order sequence reversals for some compounds (see tables). Several researchers have observed this phenomena as well^{2,7,16–18}.

Eqn. 2 relates S with $\log k_0$

$$S = p \log k_0 + q \quad (2)$$

where p and q are assumed to be constants for a given experimental condition. Schoenmakers *et al.*² plotted S *vs.* $\log k_0$ for 32 benzene derivatives (having a wide range of functionality and molecular structure) in methanol–water ($p=0.79$, $r=0.98$) and acetonitrile–water ($r=-0.06$). The data revealed that the relationship between S and $\log k_0$ was solvent-dependent. Moreover, the slope value greatly differed from one suggesting that the same solute properties effected S and $\log k_0$ in much different ways. In contrast, Quarry *et al.*⁷ plotted S *vs.* $\log k_0$ for seven nitroaromatics in methanol–water. For these compounds, the same solute properties appeared to influence S and $\log k_0$ in a similar manner ($p=1.0$, $r=0.99$). Shown in Table VI are the results of S *vs.* $\log k_0$ plots for nitro-PAHs. Higher correlation coefficients were found for the compounds studied in methanol–water ($r=0.98$) than in acetonitrile–water ($r=0.94$). Nevertheless, the relatively small deviation in slope from one suggests that the same solute properties contribute to S and $\log k_0$ in the same way. The extent to which these properties contribute in each organic modifier however was greatly different as evidenced by the k' values.

TABLE VI
 S *vs.* $\log k_0$ PLOTS AT VARIOUS TEMPERATURES

Temperature (°C)	r	p	q	n
<i>Acetonitrile–water</i>				
35	0.94	0.83 ± 0.05	0.87 ± 0.19	34
45	0.95	0.88 ± 0.05	0.77 ± 0.18	34
55	0.95	0.91 ± 0.05	0.72 ± 0.18	34
65	0.94	0.91 ± 0.06	0.74 ± 0.19	34
<i>Methanol–water</i>				
35	0.98	0.94 ± 0.04	0.82 ± 0.15	28
45	0.98	0.91 ± 0.04	0.85 ± 0.14	29
55	0.98	0.90 ± 0.03	0.89 ± 0.13	30
65	0.98	0.90 ± 0.03	0.87 ± 0.13	31

Braumann and co-workers^{17,18} proposed the concept of using $\log k_0$ as a measure of the intrinsic property of the solute to partition itself between the mobile-stationary phases. For all common nitro-PAHs, the correlation coefficient for $\log k_{0(\text{CH}_3\text{OH})}$ vs. $\log k_{0(\text{CH}_3\text{CN})}$ averaged 0.84 ± 0.01 over the temperature range studied. The moderate correlation in retention data also suggested that the same molecular properties contribute to the separation process to much different degrees. These solute property differences result in greatly different retention behavior for nitro-PAHs in the two organic modifiers.

Nitro-PAH retention as a function of temperature

The extent to which individual nitro-PAH retention decreased was a function of column temperature. This resulted in elution order reversals for some nitro-PAHs (see Tables II-V). Eqn. 3 describes the relationship between solute retention and column temperature¹²

$$\log k' = -\Delta H^0/2.3RT + (\Delta S^0/2.3R) + \log \theta \quad (3)$$

where R is the gas constant, T is the absolute temperature, θ is the mobile-stationary phase ratio, ΔH^0 is the standard enthalpy change of solute transfer from the mobile phase to the stationary phase, and ΔS^0 is the associated change in the standard entropy.

Summarized in Tables VII and VIII are the results of $\log k'$ vs. $1/T$ plots at constant mobile phase composition. (Note: The data for these plots are given in Tables II-V). The standard enthalpy change, ΔH^0 , was constant and independent of temperature. The negative value indicated that nitro-PAH transfer from the mobile phase to the C_{18} stationary phase was enthalpically favored.

Nitro-PAH ΔH^0 values varied widely in a particular mobile phase composition. For example, at acetonitrile-water (50:50), ΔH^0 was between 1.32 and 6.96 kcal/mol (see Tables VII and VIII for other comparisons). In general, as the concentration of organic in the mobile phase increased, ΔH^0 decreased or remained constant (at the 95% confidence level). Further inspection revealed that nitro-PAHs were between 0.24 and 4.4 kcal/mol more favorable to transfer from methanol-water to the C_{18} stationary phase than were nitro-PAHs in acetonitrile-water. Nitro-PAH ΔH^0 values were dependent on solute structure as well as the type and concentration of organic modifier.

Eqn. 4 was used to examine the nitro-PAH transfer mechanism between the mobile and stationary phases¹². If a linear dependence is observed between $\log k'$ (determined at or close to the harmonic mean temperature, T_{eval}) and ΔH^0 , it implies that the retention mechanism is similar and that an enthalpy-entropy effect exists in the solute retention process. The compensation temperature, β , can be determined from the slope of $\log k'$ vs. $-\Delta H^0$ plot

$$\log k'_T = -\Delta H^0/2.3R (1/T - 1/\beta) - (\Delta G_\beta^0/2.3R\beta) + \log \theta \quad (4)$$

where, k'_T is the capacity factor at temperature T and ΔG_β^0 is the Gibbs free energy at the compensation temperature. If a family of compounds exhibit enthalpy-entropy compensation, the values of β and ΔG_β^0 will be invariant and the solute transfer process

TABLE VII
 ΔH° CALCULATED FROM $\log k' \text{ VS. } 1/T$ AT VARIOUS ACETONITRILE-WATER COMPOSITIONS

No.	Acetonitrile-water								
	50:50		60:40		70:30				
	Intercept	$-\Delta H^{\circ}$ (kcal/mol)	r	Intercept	$-\Delta H^{\circ}$ (kcal/mol)	r	Intercept	$-\Delta H^{\circ}$ (kcal/mol)	r
1	-0.63 ± 0.01	1.32 ± 0.25	0.967	-1.09 ± 0.01	1.76 ± 0.15	0.998	-0.96 ± 0.002	1.35 ± 0.04	0.999
2	-1.23 ± 0.02	2.26 ± 0.39	0.972	-0.87 ± 0.01	1.46 ± 0.18	0.985	-1.45 ± 0.02	2.11 ± 0.38	0.969
3	-0.68 ± 0.01	1.53 ± 0.15	0.992	-1.08 ± 0.01	1.81 ± 0.17	0.992	-1.26 ± 0.01	1.81 ± 0.25	0.982
4	-1.48 ± 0.01	2.77 ± 0.21	0.994	-1.01 ± 0.01	1.73 ± 0.11	0.996	-1.45 ± 0.01	2.11 ± 0.15	0.995
5	-1.82 ± 0.01	3.25 ± 0.22	0.996	-1.21 ± 0.01	2.03 ± 0.20	0.991	-1.16 ± 0.01	1.74 ± 0.12	0.995
6	-2.23 ± 0.01	3.99 ± 0.17	0.998	-1.75 ± 0.001	2.87 ± 0.03	0.999	-1.36 ± 0.004	2.01 ± 0.08	0.998
7	-1.69 ± 0.01	3.33 ± 0.17	0.997	-1.20 ± 0.01	2.23 ± 0.12	0.997	-1.13 ± 0.003	1.88 ± 0.07	0.999
8	-1.61 ± 0.01	3.30 ± 0.17	0.997	-1.13 ± 0.01	2.20 ± 0.19	0.993	-1.16 ± 0.003	1.98 ± 0.07	0.999
9	-1.61 ± 0.01	3.31 ± 0.25	0.994	-1.23 ± 0.01	2.35 ± 0.19	0.994	-1.13 ± 0.001	1.94 ± 0.02	0.999
10	-0.96 ± 0.01	2.41 ± 0.13	0.997	-0.83 ± 0.01	1.84 ± 0.14	0.995	-0.65 ± 0.01	1.30 ± 0.26	0.961
11	-1.65 ± 0.01	3.40 ± 0.14	0.998	-1.62 ± 0.002	2.89 ± 0.05	0.999	-1.75 ± 0.01	2.63 ± 0.27	0.990
12	-1.40 ± 0.01	3.05 ± 0.16	0.997	-1.06 ± 0.01	2.17 ± 0.29	0.983	-1.02 ± 0.002	1.87 ± 0.04	0.999
13	-1.23 ± 0.02	2.88 ± 0.51	0.973	-1.63 ± 0.01	3.04 ± 0.27	0.992	-1.61 ± 0.01	2.66 ± 0.23	0.992
14	-2.11 ± 0.004	4.12 ± 0.09	0.999	-1.96 ± 0.01	3.42 ± 0.23	0.996	-1.73 ± 0.01	2.71 ± 0.18	0.996
15	-0.97 ± 0.02	2.54 ± 0.46	0.969	-1.38 ± 0.01	2.73 ± 0.26	0.991	-1.20 ± 0.00	2.14 ± 0.003	1.000

16	-1.94 ± 0.01	3.91 ± 0.23	0.997	-1.94 ± 0.01	3.44 ± 0.25	0.995	-1.67 ± 0.01	2.65 ± 0.23	0.993
17	-0.90 ± 0.01	2.49 ± 0.21	0.993	-1.08 ± 0.01	2.32 ± 0.15	0.996	-1.09 ± 0.002	1.92 ± 0.04	0.999
18	-1.60 ± 0.03	3.48 ± 0.56	0.975	-1.58 ± 0.01	3.00 ± 0.29	0.990	-1.52 ± 0.01	2.56 ± 0.30	0.986
19	-1.74 ± 0.01	3.79 ± 0.20	0.997	-1.02 ± 0.01	2.31 ± 0.13	0.997	-1.12 ± 0.004	2.16 ± 0.09	0.998
20	-1.45 ± 0.03	3.42 ± 0.61	0.970	-2.02 ± 0.01	3.76 ± 0.26	0.995	-1.81 ± 0.01	3.03 ± 0.14	0.999
21	-0.83 ± 0.02	2.64 ± 0.51	0.964	-1.25 ± 0.01	2.77 ± 0.26	0.997	-1.43 ± 0.01	2.62 ± 0.16	0.996
22	-1.00 ± 0.03	2.91 ± 0.58	0.962	-1.54 ± 0.01	3.17 ± 0.31	0.991	-1.86 ± 0.01	3.17 ± 0.31	0.990
23	-1.13 ± 0.01	3.09 ± 0.16	0.997	-1.21 ± 0.01	2.72 ± 0.21	0.994	-1.19 ± 0.001	2.27 ± 0.02	0.990
24	-1.49 ± 0.01	3.63 ± 0.14	0.999	-2.26 ± 0.04	4.30 ± 0.77	0.969	-1.96 ± 0.02	3.49 ± 0.39	0.980
25	-1.28 ± 0.01	3.41 ± 0.15	0.998	-1.34 ± 0.01	3.00 ± 0.30	0.990	-1.42 ± 0.002	2.68 ± 0.03	0.999
26	-1.40 ± 0.003	3.63 ± 0.08	0.999	-2.25 ± 0.01	4.42 ± 0.19	0.998	-1.89 ± 0.02	3.48 ± 0.40	0.987
27	-0.96 ± 0.03	3.11 ± 0.63	0.961	-1.67 ± 0.01	3.62 ± 0.27	0.995	-1.75 ± 0.01	3.31 ± 0.19	0.997
28	-1.32 ± 0.01	3.63 ± 0.21	0.997	-1.22 ± 0.01	2.98 ± 0.23	0.994	-1.36 ± 0.002	2.75 ± 0.03	0.999
29	-1.80 ± 0.005	4.34 ± 0.10	0.999	-1.75 ± 0.01	3.92 ± 0.11	0.999	-1.77 ± 0.002	3.50 ± 0.05	0.999
30	-1.42 ± 0.01	4.03 ± 0.11	0.996	-1.49 ± 0.02	3.61 ± 0.36	0.990	-1.60 ± 0.001	3.30 ± 0.04	0.999
31	-1.66 ± 0.002	4.44 ± 0.05	0.999	-1.54 ± 0.01	3.66 ± 0.32	0.993	-1.73 ± 0.01	3.48 ± 0.12	0.999
32	-2.58 ± 0.003	5.74 ± 0.72	0.985	-1.81 ± 0.003	4.24 ± 0.07	0.999	-1.77 ± 0.01	3.69 ± 0.32	0.993
33	-1.58 ± 0.003	4.51 ± 0.07	0.999	-2.24 ± 0.002	5.11 ± 0.07	0.999	-2.25 ± 0.01	4.62 ± 0.15	0.999
34	-3.11 ± 0.05	6.96 ± 0.50	0.976	-2.05 ± 0.002	4.90 ± 0.05	0.999	-2.01 ± 0.04	4.45 ± 0.10	0.999

TABLE VIII
 ΔH° CALCULATED FROM $\log k' \text{ VS. } 1/T$ AT VARIOUS METHANOL-WATER COMPOSITIONS

No.	50:50				60:40				70:30			
	Intercept	$-\Delta H^\circ$ (kcal/mol)	r	$-\Delta H^\circ$ (kcal/mol)	Intercept	$-\Delta H^\circ$ (kcal/mol)	r	$-\Delta H^\circ$ (kcal/mol)	Intercept	$-\Delta H^\circ$ (kcal/mol)	r	
1	-2.49 ± 0.004	4.51 ± 0.14	0.999	3.38 ± 0.14	-1.99 ± 0.01	3.38 ± 0.14	0.998	2.38 ± 0.13	-1.51 ± 0.01	2.38 ± 0.13	0.997	
2	-2.15 ± 0.03	3.98 ± 0.68	0.997	3.51 ± 0.03	-2.09 ± 0.001	3.51 ± 0.03	0.999	2.35 ± 0.07	-1.51 ± 0.003	2.35 ± 0.07	0.999	
3	-2.34 ± 0.01	4.62 ± 0.26	0.997	3.75 ± 0.03	-2.06 ± 0.001	3.75 ± 0.03	0.999	2.82 ± 0.14	-1.70 ± 0.01	2.82 ± 0.14	0.997	
4	-1.76 ± 0.004	3.36 ± 0.09	0.999	2.71 ± 0.10	-1.59 ± 0.01	2.71 ± 0.10	0.999	1.98 ± 0.24	-1.32 ± 0.01	1.98 ± 0.24	0.986	
5	-2.71 ± 0.004	4.81 ± 0.08	0.999	3.53 ± 0.08	-2.14 ± 0.004	3.53 ± 0.08	0.999	2.43 ± 0.09	-1.64 ± 0.004	2.43 ± 0.09	0.999	
6	-2.93 ± 0.01	5.11 ± 0.12	0.999	3.70 ± 0.08	-2.25 ± 0.004	3.70 ± 0.08	0.999	2.50 ± 0.02	-1.70 ± 0.001	2.50 ± 0.02	0.999	
7	-2.60 ± 0.002	5.17 ± 0.06	0.999	4.05 ± 0.08	-2.16 ± 0.004	4.05 ± 0.08	0.999	3.07 ± 0.07	-1.78 ± 0.003	3.07 ± 0.07	0.999	
8	-2.61 ± 0.00	5.30 ± 0.01	1.000	4.20 ± 0.17	-2.19 ± 0.01	4.20 ± 0.17	0.998	3.21 ± 0.07	-1.84 ± 0.003	3.21 ± 0.07	0.999	
9	-2.65 ± 0.01	5.42 ± 0.10	0.999	4.36 ± 0.11	-2.26 ± 0.01	4.36 ± 0.11	0.999	3.59 ± 0.08	-2.05 ± 0.004	3.59 ± 0.08	0.999	
10	-3.78 ± 0.03	7.73 ± 0.86	0.994	4.62 ± 0.27	-2.05 ± 0.01	4.62 ± 0.27	0.999	4.61 ± 0.43	-2.40 ± 0.01	4.61 ± 0.43	0.996	
11	-2.86 ± 0.01	5.72 ± 0.32	0.997	4.83 ± 0.05	-2.62 ± 0.002	4.83 ± 0.05	0.999	3.35 ± 0.11	-1.95 ± 0.004	3.35 ± 0.11	0.999	
12	-1.96 ± 0.01	4.48 ± 0.31	0.995	3.92 ± 0.55	-1.91 ± 0.02	3.92 ± 0.55	0.981	3.60 ± 0.69	-2.00 ± 0.03	3.60 ± 0.69	0.965	
13	-3.44 ± 0.03	6.62 ± 0.57	0.993	5.65 ± 0.25	-3.16 ± 0.01	5.65 ± 0.25	0.998	4.20 ± 0.18	-2.51 ± 0.01	4.20 ± 0.18	0.998	
14	-4.10 ± 0.02	7.61 ± 0.35	0.998	6.13 ± 0.33	-3.48 ± 0.02	6.13 ± 0.33	0.997	4.84 ± 0.14	-2.94 ± 0.01	4.84 ± 0.14	0.999	
15	-2.85 ± 0.01	5.87 ± 0.20	0.999	4.72 ± 0.17	-2.43 ± 0.01	4.72 ± 0.17	0.999	3.62 ± 0.35	-2.00 ± 0.02	3.62 ± 0.35	0.991	

No. Methanol-water

16	-3.34 ± 0.01	6.69 ± 0.24	0.999	-2.85 ± 0.01	5.39 ± 0.22	0.998	-2.27 ± 0.01	4.04 ± 0.15	0.999
17	-2.33 ± 0.01	5.09 ± 0.10	0.999	-1.99 ± 0.01	3.98 ± 0.13	0.999	-1.41 ± 0.01	2.62 ± 0.16	0.996
18	-2.87 ± 0.01	6.39 ± 0.17	0.999	-2.56 ± 0.01	5.30 ± 0.14	0.999	-2.01 ± 0.02	3.93 ± 0.48	0.986
19	-2.40 ± 0.01	5.44 ± 0.16	0.999	-2.21 ± 0.004	4.58 ± 0.09	0.997	-1.85 ± 0.003	3.51 ± 0.07	0.989
20	-4.02 ± 0.02	7.81 ± 0.33	0.998	-3.36 ± 0.02	6.19 ± 0.33	0.999	-2.64 ± 0.01	4.57 ± 0.25	0.997
21	-3.33 ± 0.01	6.64 ± 0.20	0.999	-3.02 ± 0.01	5.61 ± 0.20	0.999	-2.44 ± 0.02	4.28 ± 0.50	0.987
22	-3.64 ± 0.01	7.51 ± 0.19	0.999	-3.10 ± 0.01	6.01 ± 0.21	0.999	-2.53 ± 0.02	4.58 ± 0.48	0.989
23	-2.84 ± 0.05	6.30 ± 0.10	0.999	-2.48 ± 0.01	5.13 ± 0.11	0.999	-1.98 ± 0.04	3.82 ± 0.07	0.999
24	-2.91 ± 0.003	6.86 ± 0.05	0.999	-2.55 ± 0.01	5.65 ± 0.18	0.999	-2.14 ± 0.01	4.46 ± 0.18	0.998
25	-3.22 ± 0.01	7.03 ± 0.16	0.999	-2.77 ± 0.004	5.72 ± 0.09	0.999	-2.25 ± 0.02	4.38 ± 0.07	0.999
26	-1.61 ± 0.01	3.42 ± 0.13	0.999	-1.30 ± 0.01	3.07 ± 0.14	0.998	-1.05 ± 0.004	2.33 ± 0.09	0.998
27	-2.87 ± 0.001	6.88 ± 0.15	0.999	-2.66 ± 0.01	5.90 ± 0.22	0.999	-2.10 ± 0.01	4.48 ± 0.23	0.998
28	-3.26 ± 0.01	7.31 ± 0.17	0.999	-2.71 ± 0.01	5.78 ± 0.11	0.999	-2.12 ± 0.004	4.27 ± 0.10	0.999
29				-2.65 ± 0.02	6.03 ± 0.56	0.996	-2.87 ± 0.01	5.73 ± 0.47	0.997
30				-3.03 ± 0.01	6.75 ± 0.18	0.999	-2.49 ± 0.01	5.31 ± 0.14	0.999
32				-2.16 ± 0.05	5.83 ± 0.11	0.965	-2.74 ± 0.01	6.00 ± 0.13	0.999
33							-3.26 ± 0.01	7.03 ± 0.13	0.999
34							-3.42 ± 0.02	7.12 ± 0.62	0.996

is assumed to be identical. On the other hand, differences in ΔG_{β}^0 and β suggest differing solute retention processes. Thus, the compensation temperature provides an indication of the retention process as a function of the nature and composition of organic modifier studied.

Plots of $\log k'_{45}$ vs. $-\Delta H^0$ yielded an average correlation coefficient of 0.80 ± 0.07 for both organic modifiers at the mobile phase compositions studied ($n=18$, 3 compositions \times 3 runs per composition \times 2 organic modifiers). The relatively moderate correlation suggested different retentive processes for the family of nitro-PAHs studied. However, much higher correlation, $r=0.96 \pm 0.03$ ($n=18$), was found for some mononitrated PAHs (*viz.* 1, 3, 10, 15, 17, 23, 25, 28, 30, 31 and 33). For these compounds an enthalpy-entropy compensation effect existed over a wide range of mobile phase conditions. The plots further suggested that changes in ΔH^0 were countered by changes in ΔS^0 at temperatures near β , 565 ± 54 K. Moreover, the compensation temperature fell within the accepted range (554–755 K) reported by other researchers^{10,12,19,20} and thus, the retention process for these compounds appeared to be same.

CONCLUSION

The data revealed that nitro-PAH $\log k_0$ values (defined as the solute capacity factor at 100% water) were dependent on organic modifier. Thus, the assumption that reversed-phase retention was primarily controlled by solute-mobile phase interactions was supported by the observed differences in $\log k_{0(\text{CH}_3\text{CN})}$ and $\log k_{0(\text{CH}_3\text{OH})}$. The extent to which the organic modifier influenced the retention process and therefore, $\log k'$ was significant. Nevertheless, the moderate correlation between $\log k_{0(\text{CH}_3\text{CN})}$ and $\log k_{0(\text{CH}_3\text{OH})}$ purported that the same solute properties contributed to the separation process to varying degrees. This was probably due to differences in nitro-PAH conformation in the two solvent systems. Why some mononitrated PAHs exhibit enthalpy-entropy compensation was unclear. The relationship cannot be explained by simple steric or electronic arguments.

ACKNOWLEDGEMENT

The authors thank Hewlett-Packard (Palo Alto, CA, U.S.A.) for providing the 1090M HPLC system through their university grants program.

REFERENCES

- 1 C. M. Riley, E. Tomlinson and T. M. Jefferies, *J. Chromatogr.*, 185 (1979) 197.
- 2 P. J. Schoemakers, H. A. H. Billiet and L. de Galan, *J. Chromatogr.*, 185 (1979) 179.
- 3 P. Jandera, H. Colin and G. Guiochon, *Anal. Chem.*, 54 (1982) 435.
- 4 X. Geng and F. E. Regnier, *J. Chromatogr.*, 296 (1984) 15.
- 5 X. Geng and F. E. Regnier, *J. Chromatogr.*, 332 (1985) 147.
- 6 L. R. Snyder, M. A. Quarry and J. L. Glajch, *Chromatographia*, 24 (1987) 33.
- 7 M. A. Quarry, R. L. Grob, L. R. Snyder, J. W. Dolan and M. P. Rigney, *J. Chromatogr.*, 384 (1987) 163.
- 8 J. A. Schmit, R. A. Henry, R. C. Williams and J. F. Dieckman, *J. Chromatogr. Sci.*, 9 (1971) 645.
- 9 J. Chmielowiec and H. Sawatzky, *J. Chromatogr. Sci.*, 17 (1979) 245.
- 10 G. Vigh and Z. Varga-Pauchony, *J. Chromatogr.*, 196 (1980) 1.
- 11 H. J. Issaq, S. D. Fox, K. Lindsey, J. H. McConnell and D. E. Weiss, *J. Liq. Chromatogr.*, 10 (1987) 49.
- 12 W. Melander, D. E. Campbell and Cs. Horváth, *J. Chromatogr.*, 158 (1978) 215.

- 13 P. J. Doherty, *Master thesis*, Tufts University, Medford, MA, 1985.
- 14 P. J. Schoenmakers, H. A. H. Billiet, R. Tijssen and L. de Galan, *J. Chromatogr.*, 149 (1978) 519.
- 15 L. R. Snyder, J. L. Glajch and J. J. Kirkland, *Practical HPLC Method Development*, Wiley-Interscience, New York, 1988.
- 16 A. Opperhuizen, T. L. Sinnige, J. M. D. van der Steen and O. Hutzinger, *J. Chromatogr.*, 338 (1987) 51.
- 17 T. Braumann, G. Weber and L. H. Grimme, *J. Chromatogr.*, 261 (1983) 329.
- 18 T. Braumann and L. H. Grimme, *J. Chromatogr.*, 206 (1981) 7.
- 19 J. H. Kruz and G. Vasvari, *J. Chromatogr.*, 83 (1973) 181.
- 20 K. Jinno and N. Ozaki, *J. Liq. Chromatogr.*, 7 (1984) 887.