Deuterium Isotope Effects on Hydrophobic Interactions. The Importance of Dispersion Interactions in the Hydrophobic Phase

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Supporting Information

Table A. Retention Capacity Factors *k* for Isotopologues, and Methylene Unit Retention Factor $\alpha(CH_2)$, in Mobile Phases: 60%, 70%, and 80% Methanol/Water (Vol/Vol); (Italic) 60% Acetonitrile/Water (Vol/Vol), 30 °C

compound	C8	C18	PYE	POP	NPO	F_5POP	$F_{13}C_9$	CH_3SPOP	PBB
benzene	1.665	2.765	1.595	1.251	0.935	1.466	0.782	1.460	2.312
	0.872	1.507	0.850	0.695	0.514	0.801	0.420	0.980	1.393
	0.436	0.785	0.442	0.371	0.260	0.408	0.206	0.435	0.717
	1.241	*1.866*	*1.018*	*0.949*	–	*1.027*	*0.846*	*0.972*	*1.380*
benzene-d_6	1.610	2.650	1.537	1.217	0.914	1.443	0.775	1.413	2.221
	0.847	1.455	0.825	0.679	0.505	0.791	0.417	0.956	1.343
	0.425	0.759	0.431	0.364	0.256	0.403	0.206	0.426	0.695
	1.215	*1.812*	*0.996*	*0.932*	–	*1.018*	*0.840*	*0.954*	*1.342*
toluene	2.886	5.309	2.779	1.913	1.459	2.523	1.140	2.355	5.184
	1.358	2.609	1.342	0.977	0.733	1.250	0.564	1.387	2.426
	0.622	1.235	0.639	0.484	0.347	0.585	0.259	0.585	1.140
	1.707	*2.826*	*1.374*	*1.192*	–	*1.325*	*1.057*	*1.250*	*2.010*
toluene-d_8	2.769	5.041	2.649	1.851	1.418	2.478	1.132	2.259	4.917
	1.310	2.498	1.286	0.949	0.716	1.233	0.562	1.343	2.316
	0.604	1.185	0.616	0.472	0.340	0.581	0.260	0.569	1.095
	1.662	*2.722*	*1.334*	*1.167*	–	*1.311*	*1.052*	*1.218*	*1.938*

compound	C8	C18	PYE	POP	NPO	F_5POP	$F_{13}C_9$	CH_3SPOP	PBB
naphthalene	4.274	8.905	6.529	3.572	3.341	4.713	1.001	5.175	16.216
	1.768	3.847	2.745	1.624	1.470	2.045	0.451	2.581	7.299
	0.737	1.652	1.191	0.740	0.646	0.869	0.182	1.028	3.082
	2.133	*3.828*	*2.152*	*1.618*	–	*1.755*	*1.044*	*1.846*	*4.265*
naphthalene-d_8	4.075	8.376	6.191	3.447	3.253	4.595	0.988	4.954	15.232
	1.696	3.644	2.621	1.575	1.435	2.003	0.445	2.493	6.909
	0.712	1.573	1.145	0.721	0.634	0.856	0.181	0.997	2.938
	2.073	*3.642*	*2.082*	*1.584*	–	*1.729*	*1.037*	*1.795*	*4.075*
anthracene	11.356	34.072	35.859	10.781	14.274	14.956	1.343	21.145	–
	3.727	11.595	11.629	3.978	4.890	5.168	0.511	8.087	46.854
	1.287	4.053	4.072	1.520	1.783	1.808	0.172	2.713	15.628
	3.752	*8.743*	*5.271*	*2.818*	–	*3.093*	*1.290*	*3.763*	*16.479*
anthracene-d_{10}	10.681	31.363	33.311	10.269	13.717	14.451	1.315	20.012	–
	3.532	10.762	10.895	3.829	4.737	5.020	0.502	7.724	43.472
	1.228	3.795	3.849	1.472	1.739	1.771	0.171	2.609	14.640
	3.606	*8.211*	*5.023*	*2.739*	–	*3.027*	*1.277*	*3.622*	*15.420*
nitrobenzene	1.186	1.591	3.877	1.500	1.792	1.806	0.753	1.989	3.533
	0.629	0.887	2.016	0.835	0.950	0.952	0.379	1.292	1.897
	0.313	0.473	1.053	0.453	0.496	0.481	0.180	0.598	0.999
	1.004	*1.327*	*1.164*	*0.885*	–	*0.956*	*0.736*	*0.956*	*1.515*
nitrobenzene-d_5	1.173	1.570	3.724	1.468	1.766	1.791	0.751	1.934	3.418
	0.617	0.865	1.941	0.818	0.936	0.946	0.379	1.263	1.841
	0.308	0.462	1.017	0.444	0.490	0.480	0.180	0.584	0.972
	0.992	*1.303*	*1.137*	*0.875*	–	*0.950*	*0.734*	*0.940*	*1.482*
cyclohexane	–	–	–	–	–	–	–	–	–
	3.481	7.836	1.986	1.599	1.010	1.695	1.348	1.937	3.101
	1.382	3.123	0.816	0.641	0.383	0.823	0.562	0.726	1.251
	3.597	*8.259*	*2.054*	*1.760*	–	*1.826*	*1.785*	*1.864*	*2.885*

compound	C8	C18	PYE	POP	NPO	F_5POP	$F_{13}C_9$	CH_3SPOP	PBB
cyclohexane-d_{12}	–	–	–	–	–	–	–	–	–
	3.373	7.519	1.901	1.553	0.988	1.689	1.369	1.869	2.955
	1.346	3.013	0.786	0.623	0.375	0.824	0.573	0.703	1.196
	3.494	*7.915*	*1.986*	*1.719*	–	*1.815*	*1.796*	*1.807*	*2.767*
hexane	–	–	–	–	–	–	–	–	–
	5.055	12.136	2.608	1.856	1.166	2.510	2.226	2.224	3.840
	1.761	4.212	0.941	0.673	0.401	1.043	0.825	0.748	1.358
	5.022	*12.303*	*2.544*	*2.054*	–	*2.428*	*2.658*	*2.122*	*3.394*
hexane-d_{14}	–	–	–	–	–	–	–	–	–
	4.901	11.565	2.468	1.795	1.136	2.502	2.255	2.130	3.619
	1.710	4.036	0.897	0.652	0.391	1.044	0.845	0.718	1.287
	4.850	*11.694*	*2.438*	*1.996*	–	*2.413*	*2.678*	*2.052*	*3.228*
octane	–	–	–	–	–	–	–	–	–
	11.887	35.406	6.320	3.487	2.119	5.063	3.968	4.492	10.014
	3.298	9.700	1.836	1.093	0.638	1.630	1.203	1.273	2.821
	10.225	*31.851*	*4.798*	*3.329*	–	*3.935*	*4.295*	*3.566*	*6.940*
octane-d_{18}	–	–	–	–	–	–	–	–	–
	11.387	33.264	5.878	3.334	2.044	5.022	4.061	4.235	9.275
	3.180	9.183	1.721	1.051	0.619	1.632	1.241	1.210	2.634
	9.793	*29.781*	*4.530*	*3.218*	–	*3.905*	*4.344*	*3.412*	*6.502*
1-decanol	–	–	–	–	–	–	–	–	–
	5.278	10.292	4.307	2.166	1.349	2.508	1.843	2.680	5.580
	1.590	3.175	1.357	0.702	0.424	0.930	0.595	0.807	1.773
	3.303	*7.103*	*2.012*	*1.357*	–	*1.409*	*1.494*	*1.456*	*2.547*
1-decanol-d_{21}	–	–	–	–	–	–	–	–	–
	5.009	9.588	3.963	2.062	1.297	2.485	1.886	2.517	5.118
	1.523	2.990	1.262	0.671	0.409	0.930	0.614	0.762	1.644
	3.135	*6.582*	*1.877*	*1.300*	–	*1.384*	*1.495*	*1.377*	*2.361*

compound	C8	C18	PYE	POP	NPO	F_5POP	$F_{13}C_9$	CH_3SPOP	PBB
1-dodecanol	–	–	–	–	–	–	–	–	–
	12.036	29.850	9.573	3.991	2.390	4.907	3.248	5.266	13.930
	2.918	7.312	2.450	1.114	0.656	1.422	0.878	1.338	3.535
	6.640	*18.656*	*3.707*	*2.174*	–	*2.259*	*2.386*	*2.424*	*5.106*
1-dodecanol-d_{25}	–	–	–	–	–	–	–	–	–
	11.312	27.400	8.680	3.764	2.274	4.862	3.345	4.882	12.563
	2.778	6.797	2.251	1.059	0.631	1.423	0.908	1.253	3.234
	6.243	*16.976*	*3.415*	*2.071*	–	*2.220*	*2.395*	*2.273*	*4.664*
$\alpha(CH_2)$	1.711	1.888	1.750	1.508	1.501	1.548	1.492	1.609	1.811
	1.510	1.680	1.540	1.380	1.350	1.380	1.330	1.410	1.590
	1.357	1.492	1.379	1.262	1.233	1.250	1.220	1.287	1.407
	1.397	*1.555*	*1.363*	*1.265*	–	*1.251*	*1.258*	*1.286*	*1.405*

Table B. 33 Test Solutes and Their Physicochemical Descriptors Used in QSRR Analysis for Stationary Phase Characterization

solute	R_2	π_2^H	α_2^H	β_2^H	V_x
benzene	0.610	0.520	0	0.14	0.716
toluene	0.601	0.520	0	0.14	0.857
ethylbenzene	0.613	0.510	0	0.15	0.998
propylbenzene	0.604	0.500	0	0.15	1.139
butylbenzene	0.600	0.510	0	0.15	1.280
F-benzene	0.477	0.570	0	0.10	0.734
Cl-benzene	0.718	0.650	0	0.07	0.839
Br-benzene	0.882	0.730	0	0.09	0.891
CHO-benzene	0.820	1.000	0	0.39	0.873
NO_2-benzene	0.871	1.110	0	0.28	0.891
ethyl benzoate	0.689	0.850	0	0.46	1.214
CN-benzene	0.742	1.110	0	0.33	0.871
CH_3CO-benzene	0.818	1.010	0	0.48	1.014
CH_3O-benzene	0.708	0.750	0	0.29	0.916
o-di-Cl-benzene	0.872	0.780	0	0.04	0.961
m-di-Cl-benzene	0.847	0.730	0	0.02	0.961
p-di-Cl-benzene	0.825	0.750	0	0.02	0.961
o-di-Br-benzene	1.190	0.960	0	0.04	1.066
p-di-Br-benzene	1.150	0.860	0	0.04	1.066
o-di-CH_3-benzene	0.663	0.560	0	0.16	0.998
m-di-CH_3-benzene	0.623	0.520	0	0.16	0.998
p-di-CH_3-benzene	0.613	0.520	0	0.16	0.998
benzyl alcohol	0.803	0.870	0.33	0.56	0.916
o-nitrotoluene	0.866	1.110	0	0.27	1.032
m-nitrotoluene	0.874	1.100	0	0.25	1.032
p-nitrotoluene	0.870	1.110	0	0.28	1.032

solute	R_2	π_2^H	α_2^H	β_2^H	V_x
phenol	0.805	0.890	0.60	0.30	0.775
p-F-phenol	0.670	0.970	0.63	0.23	0.793
p-Cl-phenol	0.915	1.080	0.67	0.20	0.898
p-Br-phenol	1.080	1.170	0.67	0.20	0.950
p-I-phenol	1.380	1.220	0.68	0.20	1.033
p-CH_3-phenol	0.820	0.870	0.57	0.31	0.916
p-CH_3O-phenol	0.900	1.170	0.57	0.48	0.975

Table C. Results of QSRR Analysis for 33 Test Compounds, Mobile Phase 70% Methanol/Water (Vol/Vol) , 30 °C[a]

70% CH_3OH/H_2O	*m*	*ρ*	*S*	*a*	*b*	*v*	R^2 (*p*)
C8	–0.729	0.120	–0.445	–0.222	–1.225	1.348	0.986
SD	0.058	0.068	0.058	0.032	0.070	0.062	($\leq 10^{-4}$)
C18	–0.584	0.242	–0.679	–0.298	–1.509	1.632	0.989
SD	0.066	0.077	0.066	0.036	0.079	0.071	($\leq 10^{-4}$)
PYE	–1.218	–0.021	0.512	–0.845	–1.168	1.435	0.956
SD	0.109	0.127	0.109	0.060	0.131	0.117	($\leq 10^{-4}$)
POP	–0.858	0.063	–0.012	–0.390	–1.002	1.095	0.984
SD	0.048	0.056	0.048	0.026	0.058	0.052	($\leq 10^{-4}$)
NPO	–1.071	–0.058	0.366	–0.323	–1.205	1.075	0.952
SD	0.077	0.090	0.077	0.042	0.093	0.083	($\leq 10^{-4}$)
F_5POP	–0.756	–0.219	0.086	–0.278	–1.201	1.244	0.948
SD	0.090	0.105	0.090	0.049	0.108	0.097	($\leq 10^{-4}$)
$F_{13}C_9$	–0.692	–0.503	0.075	–0.439	–1.095	1.003	0.958
SD	0.086	0.100	0.086	0.047	0.103	0.093	($\leq 10^{-4}$)
CH_3SPOP	–0.910	0.137	0.032	–0.420	–1.110	1.184	0.979
SD	0.059	0.069	0.059	0.033	0.071	0.064	($\leq 10^{-4}$)
PBB	–0.893	0.345	–0.117	–0.473	–1.255	1.486	0.978
SD	0.075	0.088	0.075	0.041	0.090	0.081	($\leq 10^{-4}$)
MMA	–0.715	0.133	0.168	–0.161	–1.435	0.819	0.950
SD	0.076	0.097	0.084	0.045	0.096	0.076	($\leq 10^{-4}$)

[a] R^2 = determination coefficient of the multiple regression analysis; *p* = significance level of the equation. Variable coefficients as in eq 6. SD = standard deviation of the coefficient.

Adjustments to van der Waals Radii

For hydrogen and deuterium we introduced corrections to adjust the van der Waals radii appropriately. Details are explained here. Pauling's van der Waals radius for hydrogen was reported to be 1.10 Å[1]. Numerous papers discuss the distinction between van der Waals radii of hydrogen in inorganic and organic compounds; for our calculations, we need values for organic compounds. Bondi proposed values of 1.20 Å and 1.00 Å for hydrogen bound to sp^3 and sp^2 (aromatic) hybridized carbon, respectively.[2] However, Gavezzotti[3] proposed an equalized value of 1.17 Å, and Baur suggested 1.0 Å for all hydrogen van der Waals radii.[4] Very interesting work of Nyburg et al. using a set of CSD (Cambridge Structural Database) neutron diffraction data confirmed distinct values for van der Waals radii of hydrogen bound to sp^2 and sp^3 carbon.[5] Since so-called "polar flattening" of the radius sphere was observed in case of sp^3 carbon-bound H, two values characterize the van der Waals spheroid: major axis (side-on) and minor axis (head-on), 1.26 Å and 1.00 Å, respectively. For sp^2 carbon-bound H, polar flattening was much smaller (1.38 Å for the major and 1.35 Å for the minor axis), but also a displacement of the center of the van der Waals sphere toward the carbon nucleus by 0.42 Å. The van der Waals radius should be corrected for this displacement.

In our work we used the van der Waals radii from the paper of Nyburg et al. with a modification to obtain the radius of a hypothetical sphere. For an anisotropic van der Waals shape correction, we assumed an elliptical shape. The same area of contact was assumed to be present regardless of whether the electron cloud is spherical or elliptical. Therefore, we calculated the circumference (c) of the ellipse given by two (major and minor) axes and then used this value as the circumference of a hypothetical sphere. If a sphere's circumference is c, its radius is $r = c/2\pi$. One must note that for sp^2 carbon-bound H, the calculated van der Waals radius is decreased by 0.42 Å. The value of the van der Waals radius for hydrogen bound to oxygen, taken from a different paper, was 1.025 Å.[6] The values for hydrogen (thus corrected) and other elements are in Table D and the resulting molecular surface areas and volumes are in Table E.

Calculation of Atomic and Molecular Polarizabilities

Expressing atomic size in terms of van der Waals radii of the atoms r, polarizabilities a_A are given by the Slater–Kirkwood formula. The total polarizability of the molecular system is $a_{total} = Sa_A$, with $a_A = (4/a_0)(r^4/9)$, where a_0 is the Bohr radius (0.529177 Å).[7]

The Slater–Kirkwood approximation has been modified to the following form to provide an estimate of the experimental polarizability from experimentally measured van der Waals radii:[8] $(a_A)_{exp} = [r_{exp}/(1.05\sqrt{3})]^4/a_0$. All of the data utilized are included in Table I of Miller's paper. The atomic polarizabilities used are in Table D and the calculated molecular polarizabilities are in Table E.

Table D. Atomic van der Waals Radii and Polarizabilities[a]

atom	van der Waals radius *r*, [Å]	atomic polarizability α, [Å^3]
H bound to sp^3 carbon (aliphatic)	1.113	0.265
D bound to sp^3 carbon (aliphatic)	1.098	0.251
H bound to sp^2 carbon (aromatic)	0.942	0.136
D bound to sp^2 carbon (aromatic)	0.928	0.128
H bound to sp^3 oxygen (hydroxyl)	1.025	0.191
C	1.700	1.443
O	1.520	0.922
N	1.550	0.997

[a]Values for hydrogen and deuterium bound to carbon were calculated according to the method described above. Values for carbon, oxygen, nitrogen and hydrogen bound to O are taken from the original papers.

Table E. Calculated van der Waals Surface Areas, Volumes and Molecular Polarizabilities for H/D Pairs of Compounds Studied

solute	S_{vdW}, [Å^2]	V_{VdW}, [Å^3]	α, [Å^3]
benzene	97.071	75.507	9.474
benzene-d_6	96.719	75.227	9.426
toluene	123.372	93.414	11.576
toluene-d_8	122.451	92.748	11.494
naphthalene	139.835	116.833	15.518
naphthalene-d_8	139.201	116.456	15.454
anthracene	182.301	158.146	21.562
anthracene-d_{10}	181.666	157.676	21.482
nitrobenzene	128.033	100.092	12.179
nitrobenzene-d_5	127.694	99.85	12.139
cyclohexane	124.388	94.397	11.838
cyclohexane-d_{12}	122.691	93.241	11.670
hexane	145.386	104.541	12.368
hexane-d_{14}	143.648	103.187	12.172
octane	185.295	135.851	16.314
octane-d_{18}	183.276	134.108	16.062
1-decanol[a]	229.699	186.720	21.108
1-decanol-d_{21}[a]	227.106	184.683	20.814
1-dodecanol[a]	268.701	217.980	25.054
1-dodecanol-d_{25}[a]	265.336	215.556	24.704

[a]van der Waals surface areas and volumes for aliphatic chain only.

Table F. Correlation Matrix for Total Isotope Effects *TIE* vs. Differences in van der Waals Surface Areas ΔS, Volumes ΔV, and Molecular Polarizabilities $\Delta\alpha$ of Isotopologues, for Entire Group of 10 Solutes and Separated Into Groups *A, B*, and *C*. Regression Coefficients Followed by Significance Level (*In Parentheses*), 70% Methanol/Water (Vol/Vol), 30 °C

	all compounds			group *A* (aliphatic)			group *B* (aromatic)		
sample size	10			5			5		
correlated property	ΔS	ΔV	$\Delta\alpha$	ΔS	ΔV	$\Delta\alpha$	ΔS	ΔV	$\Delta\alpha$
C8	0.646	0.631	0.648	0.972	0.986	0.986	0.529	0.503	0.805
	(0.04)	*(0.05)*	(*0.04*)	*(0.006)*	*(0.002)*	(*0.002*)	*(0.36)*	*(0.39)*	(*0.10*)
C18	0.685	0.678	0.697	0.963	0.999	0.999	0.478	0.447	0.768
	(0.03)	*(0.03)*	(*0.02*)	*(0.008)*	*($\leq 10^{-4}$)*	($\leq 10^{-4}$)	*(0.42)*	*(0.45)*	(*0.13*)
PYE	0.871	0.877	0.889	0.944	0.998	0.998	0.435	0.421	0.702
	(0.001)	*(9×10^{-4})*	(6×10^{-4})	*(0.02)*	*(10^{-4})*	(10^{-4})	*(0.46)*	*(0.48)*	(*0.19*)
POP	0.880	0.886	0.898	0.939	0.995	0.995	0.556	0.536	0.828
	(8×10^{-4})	*(6×10^{-4})*	(4×10^{-4})	*(0.02)*	*(4×10^{-4})*	(4×10^{-4})	*(0.33)*	*(0.35)*	(*0.08*)
NPO	0.881	0.880	0.891	0.954	0.994	0.994	0.606	0.589	0.862
	(8×10^{-4})	*(8×10^{-4})*	(5×10^{-4})	*(0.01)*	*(6×10^{-4})*	(6×10^{-4})	*(0.28)*	*(0.30)*	(*0.06*)
F_5POP	–0.0431	–0.0441	–0.0419	0.800	0.914	0.914	0.360	0.321	0.672
	(0.21)	*(0.20)*	(*0.23*)	*(0.10)*	*(0.03)*	(*0.03*)	*(0.55)*	*(0.60)*	(*0.21*)
$F_{13}C_9$	–0.0914	–0.0929	–0.0922	–0.0904	–0.0947	–0.947	0.236	0.199	0.573
	(2×10^{-4})	*(10^{-4})*	(10^{-4})	*(0.04)*	*(0.02)*	(*0.01*)	*(0.70)*	*(0.75)*	(*0.31*)
CH_3SPOP	0.908	0.918	0.927	0.926	0.991	0.991	0.556	0.539	0.825
	(3×10^{-4})	*(2×10^{-4})*	(10^{-4})	*(0.02)*	*(0.001)*	(*0.001*)	*(0.33)*	*(0.35)*	(*0.08*)
PBB	0.831	0.834	0.848	0.947	0.998	0.998	0.492	0.468	0.780
	(0.003)	*(0.003)*	(*0.02*)	*(0.02)*	*(10^{-4})*	(2×10^{-4})	*(0.40)*	*(0.43)*	(*0.12*)

	group *C* (*aromatic with nitrobenzene except toluene*)			group *D* (*aromatic except toluene and nitrobenzene*)		
sample size	4			3		
correlated property	ΔS	ΔV	$\Delta\alpha$	ΔS	ΔV	$\Delta\alpha$
C8	0.903	0.990	0.994	0.856	0.999	0.999
	(0.10)	*(0.01)*	(*0.006*)	*(0.35)*	*(0.02)*	(*0.02*)
C18	0.914	0.999	0.999	0.860	0.999	0.999
	(0.09)	*(5×10^{-4})*	(*10^{-4}*)	*(0.34)*	*(0.02)*	(*0.01*)
PYE	0.816	0.917	0.905	0.834	0.997	0.998
	(0.18)	*(0.08)*	(*0.095*)	*(0.37)*	*(0.05)*	(*0.04*)
POP	0.906	0.999	0.999	0.848	0.999	0.999
	(0.09)	*(8×10^{-4})*	(*0.001*)	*(0.36)*	*(0.03)*	(*0.02*)
NPO	0.906	0.999	0.999	0.848	0.999	0.999
	(0.09)	*(8×10^{-4})*	(*0.001*)	*(0.36)*	*(0.03)*	(*0.02*)
F_5POP	0.909	0.990	0.994	0.868	0.999	1.000
	(0.09)	*(0.01)*	(*0.006*)	*(0.33)*	*(0.01)*	(*0.00*)
$F_{13}C_9$	0.895	0.989	0.993	0.840	0.998	0.999
	(0.11)	*(0.01)*	(*0.007*)	*(0.36)*	*(0.04)*	(*0.03*)
CH_3SPOP	0.895	0.994	0.991	0.840	0.998	0.999
	(0.11)	*(0.006)*	(*0.009*)	*(0.36)*	*(0.04)*	(*0.03*)
PBB	0.903	0.998	0.996	0.846	0.998	0.999
	(0.10)	*(0.002)*	(*0.004*)	*(0.36)*	*(0.04)*	(*0.03*)

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[8] In the original paper this formula has an error in the expression $[r_{exp}/(1.05\sqrt{3})]^4$ where the exponent is 3. It should be 4 to obtain polarizabilities from the given van der Waals radii.