CHROM. 25 659

Gas chromatographic study of solvation enthalpy by solvatochromically based linear solvation energy relationships

Jianjun Li[☆] and Peter W. Carr[*]

Department of Chemistry, University of Minnesota, 207 Pleasant Street Southeast, Minneapolis, MN 55455 (USA)

ABSTRACT

Solute retention in capillary GC columns can be correlated with a linear solvation energy relationship (LSER) equation using chromatographically determined solute parameters (log L^{16}, $\pi_2^{*,\mathrm{C}}$, α_2^{C} and β_2^{C}). The LSER coefficients obtained from correlation studies serve to quantitatively characterize the stationary phase. The effect of column temperature on retention was characterized by the temperature dependence of the LSER coefficients. Enthalpy and entropy of the retention process were also fitted quite well to the LSER equation. The main contributions to retention are from the solute–solvent interactions that give large favorable enthalpies and small unfavorable entropies. The LSER coefficients for the free energy and enthalpy regressions are linearly correlated.

INTRODUCTION

Temperature is the most important operating parameter in gas chromatography (GC) [1,2]. In general, because the enthalpies of solution of many compounds are similar, separations can often be improved by decreasing column temperature. At a fixed temperature, we [3–6] have shown that the retention of a wide variety of solutes can be modeled by a general linear solvation energy relationship (LSER) of the form of eqn. 1. In this work, we seek to examine the extension of eqn. 1 to the solvation enthalpy ΔH^0 as expressed in eqn. 2.

$$\log k' = SP_0 + l \log L^{16} + s\pi_2^{*,\mathrm{C}} + d\delta_2 + a\alpha_2^{\mathrm{C}} + b\beta_2^{\mathrm{C}} \tag{1}$$

$$\Delta H^0 = SP_0^{\mathrm{h}} + l^{\mathrm{h}} \log L^{16} + s^{\mathrm{h}}\pi_2^{*,\mathrm{C}} + d^{\mathrm{h}}\delta_2 + a^{\mathrm{h}}\alpha_2^{\mathrm{C}} + b^{\mathrm{h}}\beta_2^{\mathrm{C}} \tag{2}$$

In the above equations, k' is the capacity factor, ΔH^0 is the infinite dilution enthalpy of solution (see below). SP_0 is a solute-independent column-dependent constant, L^{16} is the partition coefficient for transfer of the solute from the gas phase to n-hexadecane at 298 K, $\pi_2^{*,\mathrm{C}}$ is a GC-based solute dipolarity/polarizability parameter, δ_2 is an empirical polarizability correction factor, defined as zero for aliphatics, 0.5 for polyhalogenated compounds and 1 for aromatics. α_2^{C} and β_2^{C} are solute hydrogen bond donor acidity and solute hydrogen acceptor basicity parameters also based on GC retention data [3–6].

In eqn. 1 the term $l \log L^{16}$ represents the

* Corresponding author.
☆ Present address: Procter and Gamble Company, Miami Valley Laboratories, P.O. Box 398707, Cincinnati, OH 45239, USA.

368

J. Li and P.W. Carr / J. Chromatogr. A 659 (1994) 367–380

combination of contributions to changes in retention due to solute-to-solute differences in cavity formation and dispersive (London) interactions. The term $s\pi_2^{*,C}$ is the contribution of the dipolarity/polarizability interaction to retention. For aromatic and polyhalogenated compounds, which have different polarizabilities relative to aliphatic solutes, a minor correction term $(d\delta_2)$ is often required. Finally, $a\alpha_2^C$ and $b\beta_2^C$ represent the contributions to retention resulting from solute-to-solvent and solvent-to-solute hydrogen-bond formation, respectively.

A very similar approach to correlating retention in GC, but which differs in some minor detail, was developed and used extensively by Abraham and co-workers [7–13]. In their work, they replaced the Kamlet–Taft δ_2 term with a new excess molar refraction parameter (R_2), defined as the molar refraction of the solute less the molar reflection of an alkane of the same Van der Waals volume. A comparison of our approach to that of Abraham and co-workers and Poole and co-workers' thermodynamic solvation model in predicting retention in GC and stationary phase characterization has appeared [14,15].

In general, we expect that solute–solvent interactions will decrease upon increasing temperature, due simply to increased thermal energy. That is, we expect that ΔH^0 will be negative. In the present case, any change in solute–solvent interactions (i.e. retention) with temperature could be due to temperature effects on the solute and on the solvent. We have no means (except for log L^{16} in a limited temperature range) of separating these, and hence adopt the convention that any change in a characteristic constant with temperature is due to a change in a solvent property only. This is consistent with Leffler and Grunwald's analysis of enthalpy effects in organic chemistry [16]. This has no effect in regard to inter-solvent comparisons, which is our present concern, but it would be important if absolute values of solvent properties were of interest.

In a study of characterization of some N-substituted amides as solvents by the LSER approach, Abraham et al. [8] found that the LSER coefficients for N-formylmorpholine (NFM) and N-methylpyrrolidinone (NMP) at lower temperatures (40–100°C and 50–70°C, respectively) were very nicely linearly correlated with $1/T$ (K). However, the temperature range studied was rather limited compared to that used in most GC analyses.

In this work, we investigated the temperature dependence of the characteristic constants in eqn. 1 on the eight most commonly used capillary columns. This was accomplished by regressing log k' data at different temperatures against eqn. 1. The characteristic constants were then studied as a function of temperature.

Based on the same log k' temperature data, *apparent* free energy $(\Delta G')$, enthalpy (ΔH^0) and *apparent* entropy $(\Delta S')$ (see below) for the retention process were obtained. The *apparent* free energy, enthalpy and entropy were examined by means of LSER equations. While there is a great body of work on application of LSERs of the type of eqn. 1 to free energy related studies there is relatively little information on its relationship to enthalpy and entropy.

EXPERIMENTAL

The retention data (log k') for 53 highly variegated compounds that span an extremely wide range in chemical characteristics on eight common capillary columns ranging from a methyl silicone oil to polyethylene glycol have been published [17]. The solute parameters used are taken from refs. 3–5 and are given in Table I.

RESULTS AND DISCUSSION

Regression results for log k' at all temperatures

The correlation results of using eqn. 1 with all the data are shown in Table II. We note that an average over all columns and temperatures gives a mean standard deviation of 0.047 and correlation coefficients of 0.998. Inspection of Table II suggests that the solute parameters can be applied to any column and temperature with an excellent goodness of good fit.

The LSER coefficients make good chemical sense and as expected they are much easier to interpret in comparison to the empirical approach described previously [17]. As shown in

TABLE I

SOLUTE SOLVATOCHROMIC PARAMETERS

Parameters from refs. 3–5.

No.	Compound	Log L^{16}	$\pi_2^{*,C}$	α_2^C	β_2^C
1	Cyclohexane	2.906	0.00	0.00	0.00
2	1-Hexene	2.571	−0.07	0.00	0.02
3	Pentane	2.163	−0.18	0.00	0.00
4	Hexane	2.668	−0.16	0.00	0.00
5	Octane	3.677	−0.12	0.00	0.00
6	Decane	4.685	−0.11	0.00	0.00
7	Undecane	5.191	−0.10	0.00	0.00
8	Tetradecane	6.705	−0.07	0.00	0.00
9	Pentadecane	7.209	−0.06	0.00	0.00
10	Ethyl acetate	2.359	0.30	0.00	0.49
11	Propyl acetate	2.861	0.31	0.00	0.48
12	Diethyl ether	2.066	0.03	0.00	0.40
13	Dipropyl ether	2.971	0.03	0.00	0.30
14	Dibutyl ether	3.954	0.04	0.00	0.29
15	Acetonitrile	1.537	0.62	0.05	0.37
16	Propionitrile	1.978	0.64	0.00	0.41
17	Acetone	1.766	0.38	0.01	0.52
18	2-Butanone	2.269	0.39	0.00	0.48
19	2-Pentanone	2.726	0.40	0.00	0.48
20	Dimethylformamide	2.922	0.81	0.00	0.97
21	Dimethylacetamide	3.357	0.80	0.00	1.06
22	Dimethylsulfoxide	3.110	1.00	0.00	1.54
23	Propionaldehyde	1.770	0.35	0.00	0.37
24	Tetrahydrofuran	2.521	0.27	0.00	0.61
25	Triethylamine	3.008	0.02	0.00	0.64
26	Nitromethane	1.839	0.67	0.06	0.16
27	Nitroethane	2.313	0.66	0.00	0.17
28	Nitropropane	2.773	0.65	0.00	0.18
29	Methanol	0.916	0.35	0.35	0.52
30	Ethanol	1.462	0.29	0.29	0.52
31	1-Propanol	1.975	0.30	0.32	0.52
32	2-Propanol	1.750	0.21	0.29	0.53
33	2-Methyl-2-propanol	1.994	0.19	0.25	0.53
34	Trifluoroethanol	1.315	0.37	0.66	0.15
35	Hexafluoroisopropanol	1.370	0.47	1.11	0.02
36	Acetic acid	1.750	0.50	0.72	0.50
37	Aniline	3.934	0.76	0.20	0.42
38	N-Methylaniline	4.492	0.70	0.14	0.31
39	Phenol	3.641	0.77	0.69	0.23
40	Benzyl alcohol	4.162	0.71	0.43	0.51
41	m-Cresol	4.187	0.78	0.66	0.24
42	Ethylamine	1.646	0.17	0.00	1.00
43	Propylamine	2.083	0.22	0.00	1.00
44	Butylamine	2.575	0.26	0.00	1.00
45	Benzene	2.792	0.29	0.00	0.10
46	Toluene	3.343	0.29	0.00	0.11
47	Ethylbenzene	3.785	0.30	0.00	0.11
48	Propylbenzene	4.239	0.30	0.00	0.11
49	p-Xylene	3.867	0.28	0.00	0.12
50	Benzaldehyde	3.935	0.75	0.00	0.42
51	Benzonitrile	3.913	0.85	0.00	0.40
52	N,N-Dimethylaniline	4.753	0.57	0.00	0.26
53	Carbon tetrachloride	2.822	0.16	0.00	0.04

TABLE II

REGRESSION RESULTS FOR LOG k' DATA AT ALL TEMPERATURES

Column	T (°C)	SP_0	l	s	d	a	b	S.D.[a]	r[b]	n[c]
DB-1	150	−2.120	0.438	0.217	0.070	−0.035	[d]	0.057	0.996	53
		0.026[e]	0.007	0.030	0.023	0.035				
	115	−2.013	0.513	0.281	0.026	0.058	[d]	0.044	0.998	53
		0.020	0.006	0.023	0.018	0.027				
	80	−1.957	0.627	0.323	−0.015	0.215	[d]	0.029	0.999	53
		0.013	0.004	0.015	0.012	0.018				
	45	−1.877	0.769	0.401	−0.104	0.372	[d]	0.038	0.999	52[f]
		0.017	0.005	0.020	0.016	0.023				
DB-5	150	−2.180	0.446	0.356	0.052	−0.046	[d]	0.050	0.997	53
		0.023	0.006	0.026	0.020	0.031				
	115	−2.095	0.517	0.414	0.019	−0.017	[d]	0.043	0.998	53
		0.019	0.005	0.022	0.017	0.026				
	80	−2.030	0.620	0.451	−0.023	0.146	[d]	0.034	0.999	53
		0.015	0.004	0.018	0.014	0.021				
	45	−1.961	0.760	0.523	−0.093	0.309	[d]	0.042	0.999	52[g]
		0.019	0.005	0.022	0.017	0.026				
DB-1301	115	−2.293	0.526	0.636	−0.031	0.360	[d]	0.056	0.997	52[h]
		0.026	0.007	0.030	0.023	0.035				
	80	−2.149	0.621	0.723	−0.073	0.557	[d]	0.048	0.998	52[h]
		0.022	0.006	0.025	0.019	0.029				
	60	−2.093	0.695	0.842	−0.139	0.698	[d]	0.051	0.998	51[i]
		0.024	0.007	0.027	0.021	0.031				
	45	−2.083	0.765	0.902	−0.156	0.884	[d]	0.056	0.998	50[j]
		0.027	0.007	0.029	0.023	0.035				
DB-1701	150	−2.294	0.427	0.824	−0.035	0.267	−0.133	0.033	0.998	53
		0.018	0.004	0.022	0.014	0.021	0.027			
	115	−2.233	0.507	0.931	−0.077	0.463	−0.085	0.024	0.999	53
		0.013	0.003	0.016	0.010	0.016	0.020			
	80	−2.156	0.616	1.071	−0.133	0.669	−0.086	0.032	0.999	53
		0.017	0.004	0.021	0.013	0.021	0.026			
	60	−2.102	0.687	1.157	−0.163	0.838	−0.069	0.038	0.999	53
		0.021	0.005	0.025	0.016	0.025	0.031			
	45	−2.016	0.744	1.239	−0.214	0.963	−0.111	0.044	0.999	53
		0.023	0.006	0.028	0.018	0.028	0.035			
DB-17	150	−2.420	0.427	0.827	0.081	−0.068	[d]	0.047	0.997	51[k]
		0.021	0.006	0.025	0.019	0.039				
	115	−2.354	0.506	0.960	0.058	−0.003	[d]	0.041	0.998	51[k]
		0.019	0.005	0.022	0.017	0.034				
	80	−2.266	0.600	1.121	0.031	0.034	[d]	0.043	0.999	51[k]
		0.020	0.006	0.023	0.018	0.036				
	45	−2.152	0.723	1.343	−0.017	0.171	[d]	0.049	0.999	51[k]
		0.022	0.006	0.026	0.020	0.040				
DB-210	115	−2.149	0.399	1.454	0.220	−0.319	[d]	0.049	0.997	53
		0.022	0.006	0.025	0.020	0.030				
	80	−2.052	0.489	1.667	0.285	−0.274	[d]	0.057	0.997	53
		0.026	0.007	0.030	0.023	0.035				

TABLE II (continued)

Column	T (°C)	SP_0	l	s	d	a	b	S.D.[a]	r[b]	n[c]
	60	−1.996	0.551	1.815	0.332	−0.224	[d]	0.063	0.997	53
		0.028	0.008	0.033	0.025	0.038				
	45	−1.938	0.606	1.930	−0.367	−0.181	[d]	0.054	0.998	50[l]
		0.025	0.007	0.029	0.022	0.034				
DB-225	150	−2.367	0.371	1.512	0.001	0.436	−0.096	0.053	0.997	53
		0.028	0.007	0.034	0.022	0.034	0.043			
	115	−2.287	0.445	1.618	−0.021	0.584	0.004	0.036	0.999	53
		0.019	0.005	0.023	0.015	0.023	0.029			
	80	−2.194	0.537	1.794	−0.044	0.837	0.073	0.036	0.999	53
		0.019	0.005	0.023	0.015	0.023	0.029			
	45	−2.060	0.654	2.006	−0.091	1.128	0.144	0.038	0.999	53
		0.020	0.005	0.025	0.016	0.025	0.031			
DB-WAX	115	−2.245	0.416	1.819	0.095	1.365	[d]	0.077	0.996	49[m]
		0.037	0.010	0.041	0.031	0.048				
	80	−2.195	0.505	2.127	0.058	1.953	[d]	0.052	0.998	45[n]
		0.027	0.007	0.028	0.022	0.051				
	60	−2.119	0.559	2.325	0.022	2.198	[d]	0.052	0.998	41[o]
		0.028	0.007	0.030	0.024	0.052				
	45	−2.062	0.606	2.501	0.004	2.414	[d]	0.059	0.998	41[o]
		0.033	0.008	0.034	0.027	0.060				

[a] Overall average standard deviation.
[b] Correlation coefficient.
[c] Number of data points.
[d] These coefficients were found to be not significantly different from zero and were omitted in the final fit.
[e] Standard deviation of the coefficients.
[f–o] The following are solutes excluded in the final regression due to their being not eluted from the column or being outliers: [f] benzaldehyde; [g] N,N-dimethylaniline; [h] propionaldehyde; [i] propionaldehyde, ethylamine; [j] propionaldehyde, ethylamine, propylamine; [k] hexafluoroisopropanol, acetic acid; [l] cyclohexane, acetone, carbon tetrachloride; [m] triethylamine, ethylamine, propylamine, butylamine; [n] triethylamine, ethylamine, propylamine, butylamine, hexafluoroisopropanol, phenol, benzyl alcohol, m-cresol; [o] triethylamine, ethylamine, propylamine, butylamine, hexafluoroisopropanol, phenol, benzyl alcohol, m-cresol, benzonitrile, aniline, N-methylaniline, N,N-dimethylaniline.

Fig. 1, the l coefficients are about the same for DB-1, DB-5, DB-1301 and DB-1701 since these phases are primarily methylsilicones, but, as the percentage of phenyl or cyanopropyl groups increases (i.e. as the phases become more polar) their l coefficients decrease as expected [3]. DB-210 has the lowest l coefficient due to fluorine substitution which decreases the dispersive interactions with the solutes.

The signs and magnitudes of s make chemical sense. In general, the s coefficient increases as the phase becomes more polar. This agrees with the idea that an increase in solute dipolarity should cause a greater increase in retention in a more dipolar phase. The a coefficients for the DB-1, DB-5, DB-17 and DB-210 columns are small since these phases are known to be very weak acceptors of hydrogen bonds based on their effect on the spectra of Kamlet–Taft indicators that are able to donate hydrogen bonds [18]. In contrast, the a coefficients for the three cyano phases (DB-1301, DB-1701 and DB-225) are significant and as expected increase as the percentage of the 3-cyanopropyl group increases. DB-WAX is the most basic phase so it has the largest a coefficient. No phase has a big b coefficient because none has any hydrogen bond donor group. Although one might expect DB-
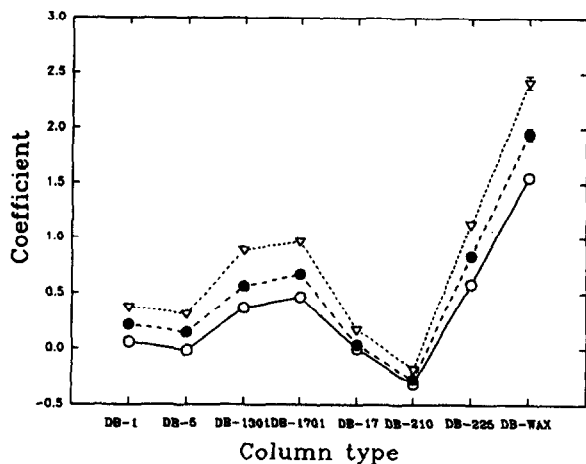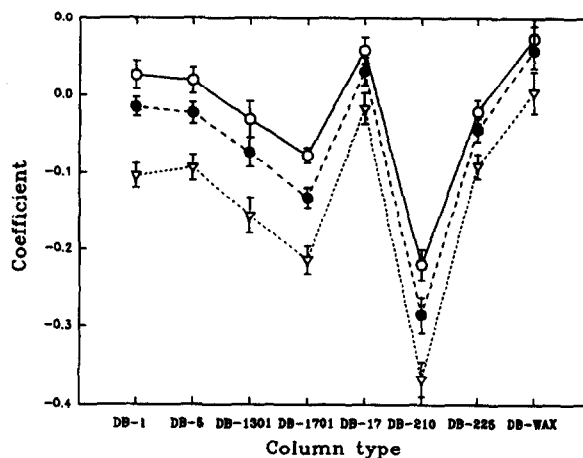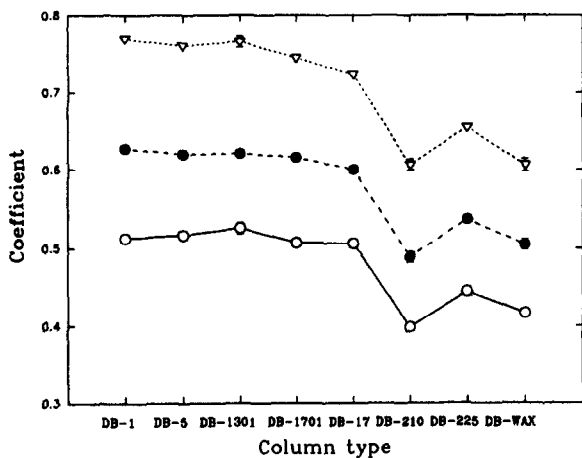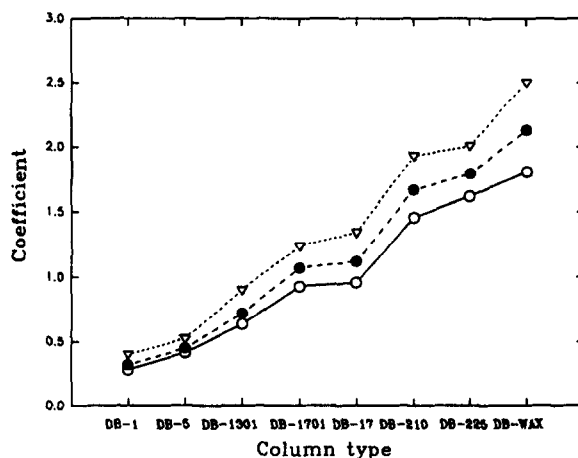
Fig. 1. Plots of LSER coefficients *vs.* column type at three temperatures: ∇ = 45°C; $\bullet$ = 80°C; $\circ$ = 115°C. (A) *a* coefficients; (B) *d* coefficients; (C) *l* coefficients; (D) *s* coefficients.

WAX to have some hydrogen bond donor ability, in fact, it does not have a significant *b* coefficient.

Temperature dependence of the LSER coefficients

We note that the LSER coefficients for all the phases change monotonically with temperature (Table III). Taking DB-1701 as an example, the LSER coefficients for this phase were plotted against $1/T$ (Fig. 2). We note that SP_0 and all

other coefficients (*l*, *s*, *d*, *a* and *b*) are approximately linear with $1/T$ (Fig. 2). Regression of the LSER coefficients against $1/T$ gives rise to the temperature dependence of the LSER coefficients (eqn. 3, Table III).

$$X = X_A + X_B/T \tag{3}$$

where $X = SP_0$, *l*, *s*, *d*, *a* or *b*. Subscript A and B represent the intercept and slope of the temperature dependence of the coefficient, respectively.

TABLE III

TEMPERATURE DEPENDENCE OF THE LSER COEFFICIENTS

Eqn. 3 was the regression equation employed.

Column	X	X_A [a]	X_B [b]	S.D. [c]	r^2 [d]	n [e]
DB-1	SP_0	−2.635	240.53	0.004	0.998	4
	l	−0.651	451.77	0.001	1.000	4
	s	−0.340	235.15	0.004	0.999	4
	d	0.602	−224.38	0.003	1.000	4
	a	−1.269	522.78	0.004	1.000	4
DB-5	SP_0	−2.701	235.86	0.004	0.998	4
	l	−0.590	428.71	0.005	0.999	4
	s	−0.149	213.22	0.004	0.999	4
	d	0.431	−160.5	0.001	1.000	4
	a	−1.487	572.94	0.013	0.997	4
DB-1301	SP_0	−3.517	477.65	0.019	0.982	4
	−	−0.558	418.93	0.008	0.996	4
	s	−0.581	472.75	0.005	0.999	4
	d	0.576	−234.09	0.014	0.963	4
	a	−1.684	792.85	0.005	1.000	4
DB-1701	SP_0	−3.006	300.58	0.002	1.000	5
	l	−0.546	410.24	0.003	1.000	5
	s	−0.436	531.82	0.004	1.000	5
	d	0.445	−203.24	0.003	0.999	5
	a	−1.832	888.05	0.009	0.999	5
	b	−0.367	99.30	0.000	1.000	5
DB-17	SP_0	−3.237	344.20	0.005	0.999	4
	l	−0.470	378.90	0.003	1.000	4
	s	−0.739	660.34	0.009	0.999	4
	d	0.333	−106.71	0.000	1.000	4
	a	−0.793	306.54	0.000	1.000	4
DB-210	SP_0	−3.097	368.23	0.004	0.999	4
	l	−0.540	364.09	0.002	1.000	4
	s	−0.717	842.37	0.020	1.000	4
	d	0.454	261.50	0.001	1.000	4
	a	−1.119	298.40	0.001	1.000	4
DB-225	SP_0	−3.296	391.91	0.007	0.998	4
	l	−0.489	363.13	0.003	1.000	4
	s	−0.143	683.62	0.001	1.000	4
	d	0.278	−116.02	0.006	0.985	4
	a	−1.660	885.17	0.012	0.999	4
	b	−0.628	246.29	0.005	0.998	4
DB-WAX	SP_0	−3.405	427.62	0.003	1.000	4
	l	−0.439	332.63	0.002	1.000	4
	s	−1.350	1225.48	0.006	1.000	4
	d	0.392	−123.26	0.000	1.000	4
	a	−2.350	1516.16	0.008	1.000	4

[a] Intercept of the plot LSER coefficient vs. $1/T$.
[b] Slope of the plot LSER coefficient vs. $1/T$.
[c] Standard deviation of the fit.
[d] Correlation coefficient squared.
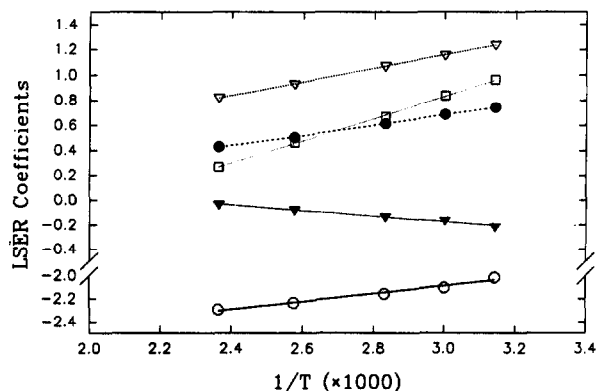[e] Number of data points (temperatures).

Fig. 2. Plots of (O) SP_0, (●) l, ($\triangledown$) s, ($\square$) a and (▼) d coefficients *vs.* $1/T$ for the DB-1701 column.

The temperature dependence of the LSER coefficients are very important when one compares the solute–solvent interaction strengths of solvents at different temperatures.

In addition the excellent linearity of these fits suggest that we can now predict retention of any solute whose parameters (log L^{16}, $\pi_2^{*,C}$, α_2^C and β_2^C) are known at any temperature for these eight columns. Since these eight columns are chemically the most commonly used stationary phases this suggests that the present results can be used as the basis for a broadly applicable optimization scheme for GC separations. For example, it should be possible to generate "window diagram" [19,20] as a function of temperature for each phase reported here for any set of

solutes whose LSER parameters are known. The optimum temperature and column could then be selected *a priori*.

We note from Tables II and III that the temperature dependences of the LSER coefficients depend on the magnitudes of the coefficients, *i.e.* the strength of the specific interaction that the stationary phase can have. For example, the temperature dependence of the s coefficient (s_B) increases as the phase s coefficient increases, that is, s_B becomes larger as the phase becomes more dipolar. The magnitude of the temperature coefficients (X_A, X_B) of the LSER coefficients are very close for chemically similar solvents. For example, the temperature dependence of the l coefficient for DB-1 is very close to that of chemically similar non-polar stationary phases such as OV-101 and SE-30. A comparison of predicted l coefficients based on the temperature dependence of the l coefficient of DB-1 (shown in Table III) with experimentally measured l coefficients for similar non-polar stationary phases is shown in Table IV. Excellent agreement is observed. All slopes shown in Table III are positive except for that of the d coefficient. This sign is expected since an increase of temperature should decrease solute–solvent interactions and thus decrease retention. The d coefficient has a small (the smallest among all the LSER coefficients) but negative temperature dependence.

TABLE IV

COMPARISON OF PREDICTED AND EXPERIMENTAL l COEFFICIENT FOR NON-POLAR STATIONARY PHASES

Phase	Temperature (°C)	$l_{pred.}$ [a]	$l_{expt.}$ [b]	Δl [c]	Ref. [d]
SE-30	120	0.499	0.522	0.023	3
SE-30	121.4	0.494	0.502	0.0075	3
OV-101	60	0.706	0.690	−0.016	19
OV-101	70	0.666	0.647	−0.019	19
OV-101	80	0.629	0.608	−0.021	19

[a] Predicted l coefficient was calculated using the temperature dependence of the l coefficient of DB-1 ($l = -0.651 + 451.773/T$).
[b] Experimental l coefficient was obtained by regressing the retention data (log k', log V_g) from the indicated references with eqn. 1; V_g is the specific retention volume.
[c] $\Delta l = l_{expt.} - l_{pred.}$.
[d] Source of experimental data.

Thermodynamics of the retention process

Since k' is proportional to the infinite dilution distribution coefficient, ΔH^0 is the enthalpy for the corresponding process. Thus ΔH^0 is the enthalpy corresponding to the transfer of solute from a 1 mol/l gas phase state to a 1 mol/l solution both acting as hypothetically infinitely dilute mixtures. Ben Naim [21] refers to this as a "solvation" parameter.

By regressing log k' against $1/T$ (Van 't Hoff plot), the enthalpy of the retention process (ΔH^0) can be calculated from eqn. 4.

$$\frac{d \log k'}{d(1/T)} = -\frac{\Delta H^0}{2.303R} \qquad (4)$$

where ΔH^0 is the enthalpy of the retention process and R is the gas constant. The relative standard deviation for the slope of log k' vs. $1/T$ is in general less than 2%. Therefore, the relative standard deviation for the enthalpy estimates is generally less than 2%.

The enthalpy estimates are given in Table V. We note that all enthalpies are negative as expected. Because some compounds did not elute at lower temperatures, we were not able to calculate the enthalpy for them.

From eqn. 4, we can also calculate the entropy ΔS^0 if we know the phase ratio ϕ. Because we do not know the phase ratio, we can only calculate an apparent entropy ($\Delta S'$). The apparent Gibbs free energy ($\Delta G'$) and entropy ($\Delta S'$) are defined as follows:

$$\Delta G' = -RT \ln k' = -RT \ln K\phi$$

$$= -RT \ln K - RT \ln \phi = \Delta G^0 - RT \ln \phi$$

$$(5)$$

$$\Delta S' = (\Delta H^0 - \Delta G')/T$$

$$= (\Delta H^0 - \Delta G^0 + RT \ln \phi)/T$$

$$= \Delta S^0 + R \ln \phi \qquad (6)$$

These equations are predicated on the assumption that the solute is retained by a pure partition process, that is, interfacial adsorption is assumed to be negligible. From the log k' and the enthalpy (ΔH^0) data, the apparent free energy and apparent entropy can be calculated from eqns. 5

and 6. We note that the apparent entropy ($\Delta S'$) is negative over the temperature range examined. The entropy of retention is expected to be negative due to the loss of some translational entropy when the solute interacts with the stationary phase.

Correlation of $\Delta G'$, ΔH^0 and $\Delta S'$ by linear solvation energy relationships

Log k' and $\Delta G'$ differ only by a factor of RT (eqn. 5). At a given temperature, the fitting coefficients for log k' and $\Delta G'$ using eqn. 1 will also differ only by a factor of RT. We show the regression results for $\Delta G'$ at only one temperature (80°C) for the purpose of comparison with the fitting coefficients for ΔH^0. The fitting results for both $\Delta G'$ and ΔH^0 are shown in Table VI. The fitting coefficients for $T\Delta S'$ can be calculated easily as $\Delta H^0 - \Delta G'$.

We must point out that all of the solute parameters (see Table I) used in eqn. 1 are free energy-based solute parameters. Whether free energy-based solute parameters can fit solution enthalpies and entropies is by no means guaranteed [22]. It is important to note that as pointed out by Hildebrand et al. [23] and by Leffler and Grunwald [16] that while many models of solution do an excellent job of correlating and predicting free energies they often fail quite badly in predicting enthalpies and entropies.

Fuchs et al. [24] correlated the ΔG^0, ΔH^0 and $T\Delta S^0$ of transfer of aliphatic and aromatic solutes from 2,2,4-trimethylpentane to aqueous solutions using free energy-based solute parameters. Their LSER fits of ΔH^0 and $T\Delta S^0$ are significantly poorer than are fits of ΔG^0. They concluded that this may be due to greater experimental errors in ΔH^0 and $T\Delta S^0$, since they are derived from differentiation of log k' with respect to $1/T$, rather than any intrinsic difficulty in handling "structural" contributions within the LSER framework.

We note that the standard deviation for the ΔH^0 regressions (see Table VI) are about three to seven times larger than those for the $\Delta G'$ regressions. Still the regression results for ΔH^0 are very acceptable. Although $\Delta G'$ differs from ΔG^0 by a constant $RT \ln \phi$ (eqn. 5), this constant only shows up in the SP_0 term. This will

TABLE V

ENTHALPY ($-\Delta H$) OF THE RETENTION PROCESS (kJ/mol)

No.	Compound	DB-1	DB-5	DB-1301	DB-1701	DB-17	DB-210	DB-225	DB-WAX
1	Cyclohexane	27.9	26.2	27.0	[a]	25.9	[a]	26.8	[a]
2	1-Hexene	25.0	23.3	25.2	24.7	23.2	23.9	25.9	22.7
3	Pentane	21.6	20.5	24.3	21.0	19.3	18.5	19.1	16.1
4	Hexane	29.3	24.5	28.1	25.6	24.1	22.6	23.0	18.9
5	Octane	34.1	33.0	36.4	32.9	31.2	29.8	30.2	26.0
6	Decane	43.3	40.8	43.6	42.1	39.3	38.5	39.8	34.8
7	Undecane	47.7	45.0	47.6	46.4	43.2	41.7	42.9	37.8
8	Tetradecane	61.3	58.5	61.0	59.4	56.5	52.1	53.3	48.0
9	Pentadecane	66.0	63.0	65.5	63.9	59.0	55.9	57.1	51.5
10	Ethyl acetate	27.2	25.5	29.7	29.2	28.5	29.9	30.9	29.6
11	Propyl acetate	31.1	28.8	33.4	33.0	33.4	33.5	35.0	32.7
12	Diethyl ether	23.7	21.2	23.4	24.3	22.3	22.6	25.4	19.6
13	Dipropyl ether	30.3	27.8	31.3	30.9	29.1	28.0	31.2	25.7
14	Dibutyl ether	38.4	35.3	38.8	39.2	36.8	35.0	37.3	34.1
15	Acetonitrile	[a]	20.3	24.8	26.2	24.9	27.6	28.5	32.3
16	Propionitrile	24.7	23.1	29.3	28.8	29.0	30.7	31.7	32.8
17	Acetone	20.1	19.3	28.1	24.4	24.9	26.8	27.1	26.2
18	2-Butanone	25.6	23.8	31.1	28.8	27.5	30.3	31.8	29.0
19	2-Pentanone	28.9	27.1	32.2	32.2	30.9	33.8	34.4	31.7
20	Dimethylformamide	32.3	31.4	37.4	38.9	37.5	41.2	41.4	42.4
21	Dimethylacetamide	35.6	33.3	40.9	42.0	41.2	45.3	44.8	45.2
22	Dimethylsulfoxide	34.6	32.3	40.9	41.1	41.3	44.6	45.2	49.6
23	Propionaldehyde	22.5	19.4	[a]	25.9	23.9	25.3	24.6	25.7
24	Tetrahydrofuran	26.3	24.1	32.5	27.8	28.0	27.9	29.4	30.3
25	Triethylamine	32.3	27.5	31.1	33.4	28.1	30.3	33.5	[a]
26	Nitromethane	25.7	25.8	27.9	29.7	28.4	30.6	32.1	[a]
27	Nitroethane	27.8	25.0	31.9	32.3	31.2	33.6	33.8	37.7
28	Nitropropane	30.5	30.2	35.7	35.3	34.4	36.5	36.5	39.5
29	Methanol	16.5	19.9	22.2	24.1	[a]	20.5	27.7	31.0
30	Ethanol	[a]	23.8	[a]	27.1	23.1	22.5	28.0	33.5
31	1-Propanol	24.0	27.5	29.3	29.9	25.4	28.0	[a]	37.2
32	2-Propanol	23.2	22.9	25.0	27.1	21.5	24.0	30.0	33.6
33	2-Methyl-2-propanol	23.6	22.1	26.6	27.2	24.5	25.7	29.8	32.8
34	Trifluoroethanol	27.8	23.7	35.1	34.6	23.9	25.2	33.1	44.1
35	Hexafluoroisopropanol	34.0	30.1	43.3	43.5	[a]	29.9	44.2	[a]
36	Acetic acid	[a]	30.0	40.8	[a]	[a]	[a]	[a]	[a]
37	Aniline	37.9	36.9	44.4	44.3	43.8	42.9	49.0	[a]
38	N-Methylaniline	41.4	38.5	47.0	46.6	47.3	45.4	50.6	[a]
39	Phenol	41.1	40.0	52.1	50.6	43.8	41.2	53.6	[a]
40	Benzyl alcohol	40.4	38.5	48.7	47.3	45.8	43.4	51.9	[a]
41	m-Cresol	44.1	[a]	55.6	54.8	47.3	45.1	56.9	[a]
42	Ethylamine	19.3	18.6	[a]	23.3	19.5	19.8	26.8	[a]
43	Propylamine	25.7	22.3	[a]	26.8	23.5	23.8	28.9	[a]
44	Butylamine	29.0	24.6	32.2	32.3	29.3	28.6	32.2	[a]
45	Benzene	27.1	25.4	28.5	28.4	28.1	26.4	29.4	29.2
46	Toluene	31.1	29.3	32.9	32.4	32.2	31.3	32.9	32.5
47	Ethylbenzene	34.7	32.8	36.4	36.1	35.8	34.6	36.8	35.4
48	Propylbenzene	38.5	36.1	40.1	40.3	39.3	37.8	40.2	38.2
49	p-Xylene	35.6	33.3	37.0	36.3	36.0	35.4	37.1	35.7
50	Benzaldehyde	37.3	36.1	41.4	41.3	42.5	41.7	43.3	47.6
51	Benzonitrile	39.0	37.0	43.3	42.4	44.6	43.9	45.2	[a]
52	N,N-Dimethylaniline	43.2	38.6	45.9	44.8	46.8	45.8	47.8	[a]
53	Carbon tetrachloride	27.1	26.9	27.8	27.1	27.3	[a]	26.5	27.8

[a] No data due to missing log k' data at various temperatures on the respective column.

not complicate any discussion of the solute–solvent interactions involved in the free energies and enthalpies.

We note that in both the $\Delta G'$ and ΔH^0 regressions, all LSER coefficients are negative except for the d coefficient which is positive (see Table VI, exceptions to this include DB-17 and DB-WAX which have negative d coefficients and

DB-210 which has a small positive a coefficient for the $\Delta G'$ regression). This means that an increase in any solute parameter causes both $\Delta G'$ and ΔH^0 to become more negative (favorable). The magnitude of any coefficient for $\Delta G'$ is smaller than that for ΔH^0. This indicates that interactions (cavity dispersion, dipolar interaction, hydrogen bonding interactions) between
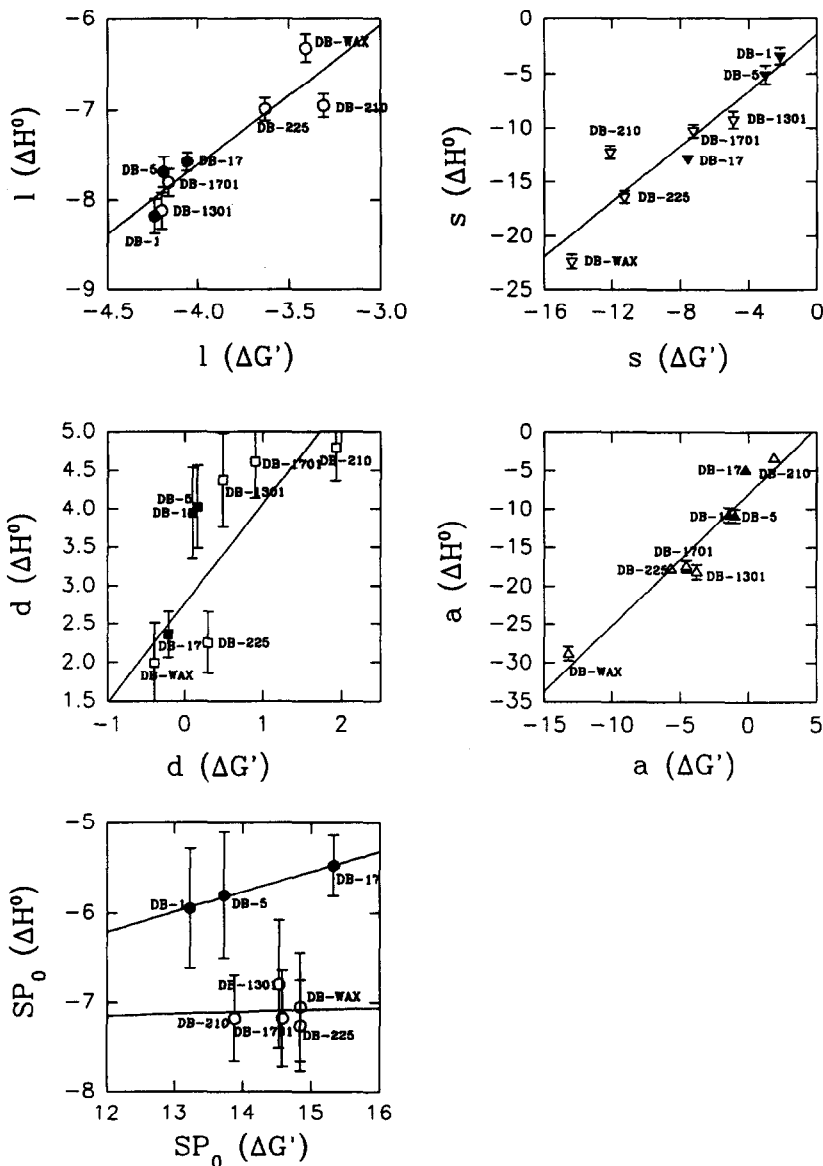

Fig. 3. Comparison of SP_0, l, s, a and d coefficients for the regressions of ΔH^0 and $\Delta G'$ against the LSER equations (eqns. 1 and 2). The solid lines represent the least squares regression lines. DB-1, DB-5 and DB-17 are represented by filled symbols. Other phases are represented by open symbols.

378

J. Li and P.W. Carr / J. Chromatogr. A 659 (1994) 367–380

TABLE VI

REGRESSION RESULTS OF APPARENT $\Delta G'$ AND ΔH^0 VS. LSER PARAMETERS

Eqn. 1 is the regression equation employed. Apparent $\Delta G'$ calculated at column temperature 80°C, both $\Delta G'$ and ΔH^0 are in kJ/mol.

Column	SP_0		l		s		d		b		a		S.D.[a]		r[b]		n[c]
	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	$\Delta G'$	ΔH^0	
DB-1	13.23 0.09	-5.95 0.67	-4.24 0.03	-8.18 0.19	-2.18 0.10	-3.39 0.77	0.10 0.08	3.94 0.59	-[d]	-	-1.45 0.12	-10.74 0.95	0.20	1.45	0.999	0.990	50[e]
DB-5	13.73 0.10	-5.80 0.70	-4.19 0.03	-7.69 0.17	-3.05 0.12	-5.07 0.84	0.16 0.09	4.02 0.54	-	2.20 1.04	-0.98 0.14	-10.88 0.87	0.23	1.29	0.999	0.991	52[f]
DB-1301	14.53 0.15	-6.80 0.72	-4.20 0.04	-8.12 0.20	-4.89 0.17	-9.23 0.79	0.49 0.13	4.37 0.61	-	-	-3.77 0.20	-18.11 0.93	0.32	1.50	0.998	0.989	49[g]
DB-1701	14.58 0.11	-7.18 0.54	-4.16 0.03	-7.81 0.15	-7.24 0.14	-10.29 0.61	0.90 0.09	4.61 0.47	0.58 0.18	-	-4.52 0.14	-17.37 0.76	0.22	1.17	0.999	0.993	51[h]
DB-17	15.32 0.14	-5.47 0.34	-4.06 0.04	-7.58 0.10	-7.58 0.16	-12.87 0.40	-0.21 0.12	2.36 0.30	-	-	-0.23 0.24	-4.96 0.50	0.29	0.75	0.999	0.997	51[i]
DB-210	13.88 0.18	-7.18 0.48	-3.31 0.05	-6.95 0.13	-11.27 0.20	-16.41 0.56	1.93 0.16	4.79 0.43	-	-	1.85 0.24	-3.39 0.69	0.39	1.05	0.997	0.993	51[j]
DB-225	14.84 0.13	-7.26 0.51	-3.63 0.03	-6.99 0.13	-12.13 0.16	-12.27 0.62	0.30 0.10	2.26 0.40	-0.49 0.20	-5.88 0.79	-5.66 0.16	-17.71 0.65	0.24	0.96	0.999	0.995	51[k]
DB-WAX	14.84 0.18	-7.05 0.61	-3.41 0.05	-6.32 0.15	-14.38 0.19	-22.40 0.65	-0.39 0.15	1.99 0.52	-	-	-13.21 0.34	-28.79 0.90	0.35	1.11	0.998	0.993	39[l]

[a] Standard deviation of the fits.
[b] Correlation coefficient of the fits.
[c] Number of solutes included in the regressions.
[d] These coefficients were found to be not significantly different from zero and were omitted from the final fit.
[e-l] The following lists the solutes excluded in the final regressions due to their missing $\Delta G'$ or ΔH^0 values or being outliers: [e] acetonitrile, ethanol, acetic acid; [f] m-cresol; [g] ethanol, propionaldehyde, ethylamine, propylamine; [h] cyclohexane, acetic acid; [i] methanol, acetic acid; [j] cyclohexane, triethylamine, nitromethane, acetic acid, aniline, N-methylaniline, phenol, benzyl alcohol, m-cresol, ethylamine, propylamine, butylamine, benzonitrile, N,N-dimethylaniline.

J. Li and P.W. Carr / J. Chromatogr. A 659 (1994) 367–380

379

the solute and the stationary phase produce large favorable negative enthalpies but unfavorable negative entropies.

In order to examine the relative contribution of the enthalpy and entropy to retention in terms of different kinds of interactions, we compare the LSER coefficients for $\Delta G'$ and ΔH^0. The most important contributions to retention are from the $l \log L^{16}$ term and the $s\pi_2^{*,C}$ term (keep in mind that the $\log L^{16}$ parameter has a much larger range than the solvatochromic parameters). Although these two terms also give unfavorable entropies, their contributions to enthalpies are much larger and outweigh the unfavorable entropy contributions. We note that for ΔH^0 the hydrogen bonding term $a\alpha_2^C$ gives very large and favorable enthalpies. However, this favorable enthalpy term must be largely compensated by the unfavorable corresponding $a\alpha_2^C$ term in the entropy term ($-T\Delta S'$) because the $a\alpha_2^C$ term in the $\Delta G'$ regression is relatively small except for DB-WAX and DB-225. No significant enthalpy contribution comes from the $b\beta_2^C$ term except for the DB-225 phase. This term does not produce any significant contribution to the free energy. In contrast to all other terms, the $d\delta_2$ term except for the DB-WAX and DB-17 phases gives unfavorable enthalpies and favorable entropies thus resulting in a small unfavorable contribution to the free energies.

We compare the LSER regression coefficients for both $\Delta G'$ and ΔH^0 in Fig. 3. In these plots the solid lines represent the least squares regression lines. We see that there are approximately linear relationships between the LSER coefficients, especially for the l, s and a coefficients. DB-1, DB-5 and DB-17 are methyl silicones of different percentages of phenyl substitution [8], we used filled symbols to identify these phases in the plots. We note that in all plots they fall on the regression lines for all phases except for the SP_0 plot in which these three phases form a separate line. DB-1301, DB-1701 and DB-225 are methylsilicones of different percentages of cyanopropylphenyl substitution. As shown in Fig. 3 there are systematic variations in SP_0 based on $\Delta G'$ and ΔH^0. While the SP_0 term does not influence the chromatographic selectivity, that is, the ratio of k' for two solutes, it clearly

must be encoding some information as to the net strength of the interaction between the solutes and the stationary phase. The relationship between $SP_0(\Delta H^0)$ and $SP_0(\Delta G')$ shown in Fig. 3 is also complicated by the fact that ΔH^0 is independent of the phase ratio (ϕ) while $\Delta G'$ depends on ϕ which varies from column to column. They also fall on the same regression lines for all phases.

The data presented in this paper regarding the enthalpy, entropy and free energy of the chromatographic retention process is very relevant to Trouton's rule for enthalpy–entropy relationships of vaporization of pure liquids at their normal boiling point [25], Barclay and Butler's [26] and Frank and Evans' [27,28] studies of enthalpy–entropy of vaporization of pure liquids at 25°C, and related studies [29,30]. The fact that the l, s and a coefficients for the $\Delta G'$ and ΔH^0 regressions correlate is very important. It means that contributions from the various stationary phase–solute interactions to the enthalpy and free energy are linearly related. It will have important implications as to the existence of enthalpy–entropy compensations in the chromatographic retention process which will be described in a subsequent study [31].

ACKNOWLEDGEMENT

REFERENCES

1 C.F. Poole and S.K. Poole, Chromatography Today, Elsevier, Amsterdam, New York, 1991.
2 T. Kuwana, Physical Methods in Modern Chemical Analysis, Academic Press, New York, 1978.
3 J. Li, Y. Zhang and P.W. Carr, Anal. Chem., 64 (1992) 210.
4 J. Li, Y. Zhang, A.J. Dallas and P.W. Carr, J. Chromatogr., 550 (1991) 101.
5 J. Li, Y. Zhang, H. Ouyang and P.W. Carr, J. Am. Chem. Soc., 114 (1992) 9813.
6 J. Li, Y. Zhang and P.W. Carr, Anal. Chem., 65 (1993) 1969.

380

J. Li and P.W. Carr / J. Chromatogr. A 659 (1994) 367–380

7 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chem. Soc., Perkin Trans. 2*, (1990) 1451.

8 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chem. Soc., Perkin Trans. 2*, (1990) 1851.

9 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 518 (1990) 329.

10 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 587 (1991) 213.

11 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 587 (1991) 229.

12 M.H. Abraham, I. Hamerton, J.B. Rose and J.W. Grate, *J. Chem. Soc., Perkin Trans. 2*, (1991) 1417.

13 M.H. Abraham and G.S. Whiting, *J. Chromatogr.* 594 (1992) 229.

14 C.F. Poole, T.O. Kollie and S.K. Poole, *Chromatographia*, 34 (1992) 281.

15 T.O. Kollie, C.F. Poole, M.H. Abraham and G.S. Whiting, *Anal. Chim. Acta*, 259 (1992) 1.

16 J.E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, Inc. New York, 1963.

17 J. Li, A.J. Dallas and P.W. Carr, *J. Chromatogr.*, 517 (1990) 103.

18 J.E. Brady, *Ph.D. Thesis*, University of Minnesota, Minneapolis, MN, 1984.

19 C.-F. Chien, R.J. Laub and M.M. Kopeecni, *Anal. Chem.*, 52 (1980) 1407.

20 R.J. Laub and J.H. Purnell, *Anal. Chem.*, 48 (1976) 799.

21 A. Ben-Naim, *Solvation Thermodynamics*, Plenum Press, New York, 1987.

22 M.J. Hait, C.L. Liotta, C.A. Eckert, J. Li and P.W. Carr, *J. Phys. Chem.*, submitted for publication.

23 J.H. Hildebrand, J.M. Prausnitz and R.L. Scott, *Regular and Related Solutions; The Solubility of Gases, Liquids and Solids*, Van Nostrand Reinhold, New York, 1970.

24 R. Fuchs, M.H. Abraham, M.J. Kamlet and R.W. Taft, *J. Phys. Org. Chem.*, 2 (1989) 559.

25 F. Trouton, *Phil. Mag.*, 18 (1884) 54.

26 I.M. Barclay and J.A.V. Butler, *Trans. Faraday Soc.*, 34 (1938) 1445.

27 H.S. Frank, *J. Chem. Phys.*, 13 (1945) 493.

28 H.S. Frank and M.W. Evans, *J. Chem. Phys.*, 13 (1945) 507.

29 D.H. Everett, *J. Chem. Soc.*, (1960) 2566.

30 L. Nash, *J. Chem. Educ.*, 61 (1984) 981.

31 J. Li and P.W. Carr, *J. Chromatogr.*, in press.