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GAS–LIQUID CHROMATOGRAPHY AND LIPOPHILICITY OF ESTERS OF BENZOIC ACIDS

ENTHALPY–ENTROPY COMPENSATION

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SUMMARY

The use of gas–liquid chromatographic (GLC) retention indices for the determination of lipophilicity was studied for a series of alkyl and arylalkyl esters of substituted benzoic acids. The regression relationships between the logarithms of the partition coefficients and the retention characteristics measured on two capillary columns, SE-30 and OV-351, were evaluated. The behaviour of arylalkyl esters and of alkyl esters cannot be expressed in terms of a single regression equation. This is probably a consequence of the effect of the intramolecular hydrophobic interaction upon the retention of arylalkyl esters under GLC conditions. An analysis of the isokinetic relationships revealed differences in the mechanisms of separation of these groups of esters.

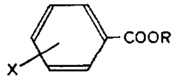
INTRODUCTION

Lipophilicity is usually evaluated by thin-layer chromatography (TLC) or high-performance liquid chromatography[1–4]. Recently, gas chromatography (GC) has been applied[5–9] using two stationary phases of different polarities. Capillary columns moistened with the polar phases SE-30 and OV-351 have been found[10] especially suitable in this text.

We have used retention indices to express logarithms of the partition coefficients (log P) in the system octanol–water for various series of esters of organic acids:

$$\log P = k_1 I_1 - k_2 I_2 + k_3 \quad (1)$$

where I_1 and I_2 were the Kováts indices of the compounds measured on the two stationary phases. The results stimulated us to extend the method to another series of compounds, namely different types of esters of substituted benzoic acids, I.



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CALCULATIONS

The gas–liquid chromatographic (GLC) characteristics of the compounds studied were determined by Korhonen[11–14]. The columns used were a vitreous silica, SE-30, and a fused silica, OV-351. The symbols used for the compounds are as in the original papers cited. Relationships between log P and the retention indices were determined by regression analysis. From the temperature dependencies of the retention indices, the enthalpic changes, $-\Delta H^0$, were calculated according to

$$\log k' = -\frac{\Delta H^0}{2.3R}\cdot\frac{1}{T}+\frac{\Delta S^0}{2.3R}+\log\varphi \qquad (2)$$

where k' is the capacity factor of a solute, ΔH^0 and ΔS^0 are the changes in standard enthalpy and standard entropy, respectively, and φ is the phase ratio of the column.

Differences in the mechanism of separation were estimated from the isokinetic relationships for the individual groups of esters using an equation derived by Melander *et al.*[15]

$$\log k'_T = -\frac{\Delta H^0}{2.3R}\left(\frac{1}{T}-\frac{1}{\beta}\right)-\frac{\Delta G^0_\beta}{2.3R\beta}+\log\varphi \qquad (3)$$

where k'_T is the capacity factor of a solute at a temperature, T, close to the harmonic mean temperature, T_{harm}, and ΔG^0_β is the Gibbs energy of the process at a compensation temperature, β.

The calculation of the log P values of alkyl esters of substituted benzoic acids (*cf.*, Table I) was based on the experimental[16] log P value of methyl benzoate (2.12). For aromatic substituents, parameters π derived for substituted benzoic acids[17] were used. Increments used for the log P calculations for unbranched alkyl esters were estimated as the differences between the log P values of the respective alcohol and methanol[16]. When log P of the alcohol was unknown, the increment for the methylene group, $\Delta f = 0.54$, was used. The differences among ethyl, 1-chloroethyl, 1,1-dichloroethyl and 1,1,1-trichloroethyl were considered to be equal to those among ethane (log P = 1.81), chloroethane (log P = 1.43), 1,1-dichloroethane (log P = 1.79) and 1,1,1-trichloroethane (log P = 2.49)[16]. A similar method was used for calculation of the log P values of arylalkyl esters of benzoic acids, based on log P of benzyl benzoate (3.97), to which the differences between the log P values of 1-phenylethanol (1.51) or 2-phenylethanol (1.36) and benzyl alcohol (1.10)[16] were added.

For the branched-chain alkyl esters of benzoic acids, the calculations were based on the log P value (2.12) for methyl benzoate. The increments for other esters were calculated from Σf for the corresponding alkyls, taking into account the difference between Σf and $f(\mathrm{CH_3})$. For example, for 1-methylpropyl benzoate (the branching factor, F_{cBr}, and the bonding factor, F_b, were taken from ref. 16):

$$\begin{aligned}\Sigma f &= 2f(CH_3) + f(CH_2) + f(CH) - F_{cBr} - 2F_b \\ &= 1.78 + 0.66 + 0.43 - 0.13 - 0.24 = 2.50\end{aligned}$$

$$\log P = 2.12 + \Sigma f - f(CH_3) = 2.12 + 2.50 - 0.89 = 3.73$$

TABLE I

LIPOPHILICITIES AND GLC CHARACTERISTICS OF ALKYL ESTERS OF SUBSTITUTED BENZOIC ACIDS

Values of Kováts indices, *I*(SE-30) and *I*(OV-351), measured at 180°C were taken from refs. 11–13.

Compound			*log P*	*I(SE-30)*	*I(OV-351)*
No.	*Acid*	*Alcohol*			
5	Benzoic	*n*-Pentyl	4.45	1454	1971
6		*n*-Hexyl	4.92	1555	2069
7		*n*-Heptyl	5.46	1657	2169
8		*n*-Octyl	6.04	1758	2270
9		*n*-Nonyl	6.58	1859	2372
12		*n*-Dodecyl	8.02	2159	2681
m1	4-Nitrobenzoic	Methyl	2.14	1427	2273
m2		Ethyl	2.66	1760	2739
m3		*n*-Propyl	3.16	1602	2376
m4		*n*-Butyl	3.79	1704	2472
m5		*n*-Pentyl	4.47	1805	2572
m10		*n*-Decyl	7.00	2308	3082
d1	3,5-Dinitrobenzoic	Methyl	2.04	1701	2729
d2		Ethyl	2.56	1760	2739
d3		*n*-Propyl	3.06	1853	2784
d4		*n*-Butyl	3.69	1950	2873
d5		*n*-Pentyl	4.37	2047	2969
d10		*n*-Decyl	6.90	2541	3469
15	Benzoic	Ethyl	2.64	1169	1693
16		2-Chloroethyl	2.26	1394	2137
17		2,2-Dichloroethyl	2.62	1482	2226
18		2,2,2-Trichloroethyl	3.32	1551	2199
4/1	4-Nitrobenzoic	Methylethyl	3.21	1551	2287
4/2		1-Methylpropyl	3.75	1652	2368
4/3		2-Methylpropyl	3.75	1671	2409
4/7		2-Propenyl	2.82	1601	2446
4/8		2-Propynyl	1.99	1603	2644
4/9		3-Butenyl	3.45	1698	2529
4/10		1-Methylbutenyl	3.86	1728	2498
4/15		Ethyl	2.66	1521	2307
4/16		2-Chloroethyl	2.28	1753	2808
4/17		2,2-Dichloroethyl	2.64	1841	2913
4/18		2,2,2-Trichloroethyl	3.34	1897	2847
35/1	3,5-Dinitrobenzoic	Methylethyl	3.11	1800	2738
35/2		1-Methylpropoyl	3.65	1891	2748
35/3		2-Methylpropyl	3.65	1910	2788
35/9		3-Butenyl	3.35	1942	2935
35/10		1-Methylbutenyl	3.76	1961	2866

For the unsaturated esters of benzoic acids, methyl benzoate was used as a starting compound. The increments for the other esters were taken as the differences between the value for methane and those for the corresponding unsaturated hydrocarbons. For example, for 2-propenyl benzoate:

$$\log P = \log P(\text{methyl benzoate}) + \log P\ (\text{2-propene}) - \log P(\text{methane}) = 2.12 + 1.77 - 1.09 = 2.80$$

RESULTS AND DISCUSSION

For a series of selected unbranched alkyl esters of benzoic acid and its 4-nitro and 3.5-dinitro derivatives, regression equations were calculated

	n	r	s	F	
$\log P = 0.0040\ I(\text{SE-30}) - 2.672$	18	0.652	1.419	11.8	(4)
$\log P = 0.0010\ I(\text{OV-351}) + 1.897$	18	0.218	1.826	0.8	(5)
$\log P = 0.0125\ I(\text{SE-30}) - 0.0075\ I(\text{OV-351}) + 1.026$	18	0.997	0.148	1265.1	(6)

where n = number of compounds, r = regression coefficient, s = standard deviation and F = Fischer–Snedecor criterion. The difference in statistical significance between the one- and two-term equations is evident.

Similar results were obtained by extending this series to other esters of benzoic

TABLE II

LIPOPHILICITIES AND GLC CHARACTERISTICS OF ARYLALKYL ESTERS OF SUBSTITUTED BENZOIC ACIDS

Values of Kováts indices, I(SE-30) and I(OV-351), measured at 180°C were taken from ref. 14.

Compound			*log P*		*I(SE-30)*	*I(OV-351)*
No.	*Acid*	*Alcohol*	*Est.**	*Calc.***		
B1	Benzoic	Benzyl	3.97	3.44	1741	2576
B2		1-Phenylethyl	4.38	3.99	1760	2530
B3		2-Phenylethyl	4.23	3.92	1825	2652
2ClB1	2-Chlorobenzoic	Benzyl	4.56	3.55	1900	2833
2ClB2		1-Phenylethyl	4.97	4.03	1912	2786
2ClB3		2-Phenylethyl	4.82	3.96	1989	2927
3ClB1	3-Chlorobenzoic	Benzyl	4.80	3.97	1897	2768
3ClB2		1-Phenylethyl	5.21	4.49	1910	2717
3ClB3		2-Phenylethyl	5.06	4.43	1978	2841
4ClB1	4-Chlorobenzoic	Benzyl	4.84	3.97	1899	2772
4ClB2		1-Phenylethyl	5.25	4.46	1911	2723
4ClB3		2-Phenylethyl	5.10	4.50	1985	2844
F5B1	2,3,4,5,6-Pentafluorobenzoic	Benzyl	5.12	4.32	1583	2180
F5B2		1-Phenylethyl	5.53	4.75	1601	2149
F5B3		2-Phenylethyl	5.38	4.82	1674	2265

* Estimated from log P (3.97) of benzyl benzoate (see Calculations).

** Calculated from eqn. 9 using the experimental I values.

TABLE III

LOGARITHMS OF CAPACITY FACTORS, log k', OF ALKYL ESTERS OF BENZOIC ACIDS AT VARIOUS TEMPERATURES

Compound No.	*SE-30, Temperature (°C)*						*OV-351, Temperature (°C)*		
	140	*160*	*180*	*200*	*220*	*240*	*180*	*200*	*220*
	1/T ($K^{-1} \cdot 10^3$)						*1/T ($K^{-1} \cdot 10^3$)*		
	2.4213	*2.3095*	*2.2075*	*2.1142*	*2.0284*	*1.9493*	*2.2075*	*2.1142*	*2.0284*
5		0.269	−0.006	−0.272	−0.488	−0.736	0.254	0.006	−0.216
6		0.454	0.172	−0.094	−0.306	−0.538	0.398	0.134	−0.113
7		0.643	0.338	0.051	−0.167	−0.429	0.551	0.282	0.017
8		0.826	0.504	0.203	−0.031	−0.278	0.704	0.419	0.152
9		1.013	0.669	0.357	0.103	−0.160	0.860	0.559	0.271
12		1.566	1.163	0.807	0.507	0.221	1.318	0.970	0.656
m1		0.219	−0.034	−0.252	−0.497	−0.737	0.709	0.440	0.168
m2		0.355	0.083	−0.160	−0.365	−0.605	0.746	0.469	0.203
m3		0.536	0.248	−0.014	−0.236	−0.472	0.867	0.578	0.271
m4		0.722	0.416	0.139	−0.094	−0.330	1.009	0.709	0.407
m5		0.906	0.581	0.290	0.041	−0.203	1.157	0.841	0.539
m10		1.822	1.405	1.034	0.715	0.418	1.905	1.524	1.160
d1		0.711	0.412	0.137	−0.097	−0.325	1.391	1.054	0.737
d2		0.829	0.513	0.217	−0.022	−0.241	1.406	1.057	0.737
d3		0.993	0.659	0.355	0.103	−0.131	1.473	1.116	0.792
d4		1.171	0.820	0.502	0.238	−0.016	1.602	1.234	0.899
d5		1.348	0.979	0.647	0.364	0.100	1.740	1.359	1.010
d10			1.779	1.372	1.021	0.700	2.458	2.010	1.600
15	−0.070	−0.322	−0.503	−0.716	−0.889		−0.222	−0.442	−0.574
16	0.395	0.101	−0.128	−0.374	−0.583		0.473	0.184	−0.049
17	0.576	0.265	0.014	−0.215	−0.442		0.611	0.319	0.089
18	0.715	0.395	0.133	−0.103	−0.338		0.570	0.283	0.054
4/1	0.737	0.402	0.163	−0.089	−0.321		0.704	0.412	0.178
4/2	0.935	0.584	0.304	0.067	−0.190		0.826	0.525	0.271
4/3	0.977	0.626	0.335	0.092	−0.169		0.887	0.580	0.321
4/7	0.824	0.494	0.220	−0.011	−0.256		0.942	0.626	0.360
4/8	0.838	0.507	0.224	−0.011	−0.260		1.239	0.897	0.596
4/9	1.023	0.671	0.380	0.131	−0.130		1.067	0.744	0.471
4/10	1.088	0.736	0.431	0.157	−0.108		1.019	0.697	0.428
4/15	0.651	0.337	0.080	−0.156	−0.387		0.734	0.448	0.193
4/16	1.129	0.768	0.474	0.208	−0.057		1.482	1.129	0.823
4/17	1.304	0.934	0.623	0.340	0.065		1.635	1.268	0.949
4/18	1.425	1.033	0.717	0.432	0.145		1.539	1.183	0.876
35/1	1.249	0.873	0.556	0.285	0.004		1.378	1.032	0.729
35/2	1.434	1.038	0.706	0.416	0.121		1.393	1.039	0.733
35/3	1.469	1.075	0.739	0.446	0.151		1.453	1.095	0.782
35/9	1.534	1.143	0.791	0.494	0.193		1.667	1.191	0.871
35/10	1.575	1.175	0.823	0.525	0.220		1.899	1.491	1.141

acid and their nitro derivatives (Table I):

	n	r	s	F	
$\log P = 0.0036\, I(\text{SE-30}) - 2.505$	38	0.629	1.168	23.5	(7)
$\log P = 0.0009\, I(\text{OV-351}) + 1.530$	38	0.209	1.469	1.6	(8)
$\log P = 0.0120\, I(\text{SE-30}) - 0.0070\, I(\text{OV-351}) + 0.585$	38	0.987	0.242	673.4	(9)

Another series of arylalkyl esters of substituted benzoic acids is summarized in Table II. Where two aromatic rings are separated by a flexible chain, an intramolecular interaction may influence the lipophilicity or retention behaviour. For example, such an interaction decreases the lipophilicity of benzyloxyarylalkanoic acids[18–20]. The decrease in lipophilicity can be described by retention indices obtained from partition chromatography[18,20]. In contrast, the effect of the intramolecular hydrophobic interaction on the retention behaviour of the esters of benzyloxyarylalkanoic acids in GLC made it impossible to estimate[21] their lipophilicity by this method.

The log P values of arylalkyl esters were calculated from the experimental values of the retention indices by use of eqn. 9. The values obtained (*cf.*, Table II) are markedly lower than those of the reference system octanol–water. The intramolecular hydrophobic interaction is probably stronger under GLC conditions. Breakdown of the additivity of log P is usually accompanied by ambiguity of the

TABLE IV

LOGARITHMS OF CAPACITY FACTORS, log k', OF ARYLALKYL ESTERS OF BENZOIC ACIDS AT VARIOUS TEMPERATURES

Compound No.	*SE-30, Temperature (°C)*					*OV-351, Temperature (°C)*		
	160	*180*	*200*	*220*	*240*	*180*	*200*	*220*
	1/T ($K^{-1} \cdot 10^3$)					*1/T* ($K^{-1} \cdot 10^3$)		
	2.3095	*2.2075*	*2.1142*	*2.0284*	*1.9493*	*2.2075*	*2.1142*	*2.0284*
B1	0.753	0.444	0.175	−0.075	−0.270	1.148	0.838	0.558
B2	0.790	0.478	0.207	−0.053	−0.260	1.079	0.771	0.493
B3	0.911	0.586	0.308	0.042	−0.176	1.261	0.938	0.649
2ClB1	1.046	0.716	0.422	0.150	−0.076	1.530	1.190	0.878
2ClB2	1.073	0.736	0.441	0.160	−0.070	1.460	1.116	0.806
2ClB3	1.207	0.864	0.560	0.287	0.041	1.669	1.310	0.992
3ClB1	1.047	0.711	0.388	0.150	−0.076	1.433	1.094	0.796
3ClB2	1.068	0.733	0.407	0.160	−0.090	1.358	1.023	0.724
3ClB3	1.193	0.847	0.518	0.266	0.021	1.542	1.196	0.884
4ClB1	1.044	0.715	0.390	0.150	−0.076	1.440	1.099	0.798
4ClB2	1.069	0.735	0.398	0.160	−0.070	1.366	1.028	0.727
4ClB3	1.201	0.858	0.524	0.275	0.031	1.547	1.198	0.886
F5B1	0.465	0.173	−0.076			0.867	0.547	0.256
F5B2	0.515	0.206	−0.056			0.796	0.500	0.246
F5B3	0.644	0.330	0.062			0.681	0.382	0.123

TABLE V

THE LINEAR RELATIONSHIPS $\log k' = a(1/T) + b$ AND THE ENTHALPY CHANGES, $-\Delta H^0$, FOR ALKYL ESTERS OF BENZOIC ACIDS

Compound	*SE-30*				*OV-351*			
	a	*b*	*r*	$-\Delta H^0$ (*kJ mol*$^{-1}$)	*a*	*b*	*r*	$-\Delta H^0$ (*kJ mol*$^{-1}$)
5	2630.1	−6.171	0.999	50.65	2624.6	−5.541	1.000	50.55
6	2763.9	−5.921	0.999	53.23	2852.7	−5.899	1.000	54.94
7	2973.5	−6.216	0.999	57.27	2980.0	−6.024	1.000	57.39
8	3081.7	−6.288	0.999	59.35	3081.5	−6.098	1.000	59.35
9	3271.4	−6.539	1.000	63.01	3287.6	−6.396	1.000	63.32
12	3761.1	−7.120	1.000	72.44	3696.6	−6.843	1.000	71.20
m1	2659.0	−5.897	0.998	51.21	3018.5	−5.950	1.000	58.14
m2	2656.7	−5.770	0.999	51.17	3030.8	−5.943	1.000	58.37
m3	2806.3	−5.936	1.000	54.04	3324.2	−6.464	0.999	64.02
m4	2935.9	−6.053	1.000	56.55	3358.9	−6.402	1.000	64.69
m5	30(98.2	−6.245	1.000	59.67	3449.5	−6.456	1.000	66.44
m10	3931.2	−7.255	1.000	75.71	4158.4	−7.272	1.000	80.09
d1	2871.1	−5.924	1.000	55.30	3650.8	−6.667	1.000	70.31
d2	2978.5	−6.061	1.000	57.37	3735.2	−6.840	1.000	71.94
d3	3121.6	−6.228	1.000	60.12	3802.5	−6.922	1.000	73.24
d4	3290.1	−6.438	1.000	63.37	3925.3	−7.064	1.000	75.60
d5	3462.5	−6.659	1.000	66.69	4075.8	−7.258	1.000	78.50
d10	4173.1	−7.441	1.000	80.37	4790.5	−8.117	1.000	92.27
15	2070.8	−5.089	0.999	39.88	1971.1	−4.585	0.993	37.96
16	2478.3	−5.610	0.999	47.73	2917.1	−5.972	0.999	56.18
17	2567.1	−5.650	1.000	49.44	2917.6	−5.836	0.999	56.19
18	2657.0	−5.728	1.000	51.17	2883.8	−5.802	0.999	55.54
4/1	2658.1	−5.712	0.998	51.19	2939.6	−5.791	0.999	56.62
4/2	2823.6	−5.918	0.999	54.34	3111.9	−6.046	1.000	59.93
4/3	2883.5	−6.018	0.999	55.54	3162.0	−6.097	1.000	60.90
4/7	2719.8	−5.773	0.999	52.38	3251.4	−6.240	1.000	62.62
4/8	2769.3	−5.878	0.999	53.34	3591.1	−6.691	1.000	69.16
4/9	2903.6	−6.020	0.999	55.92	3329.6	−6.287	1.000	64.13
4/10	3029.2	−6.252	1.000	58.34	3301.9	−6.274	1.000	63.59
4/15	2619.4	−5.700	1.000	50.45	3021.2	−5.937	1.000	58.19
4/16	2990.7	−6.124	1.000	57.60	3680.9	−6.647	1.000	70.89
4/17	3132.4	−6.289	1.000	60.33	3831.6	−6.826	1.000	73.80
4/18	3223.9	−6.394	0.999	62.09	3703.3	−6.640	1.000	71.33
35/1	3139.8	−6.365	0.999	60.48	3624.7	−6.626	1.000	69.81
35/2	3312.6	−6.598	1.000	63.80	3686.5	−6.748	1.000	71.00
35/3	3330.7	−6.605	1.000	64.15	3747.7	−6.893	1.000	72.18
35/9	3395.4	−6.694	1.000	65.39	4453.9	−8.185	0.996	85.78
35/10	3425.4	−6.728	1.000	65.97	4234.1	−7.452	1.000	81.55

isokinetic relationship. Thus, the relationships between the retention indices and corresponding enthalpy changes were evaluated for both series of esters. The capacity factors at different temperatures are summarized in Tables III and IV, and the slopes of the relationships $\log k'$ *vs.* $1/T$ and calculated $-\Delta H^0$ values are in Tables V and VI.

The separation process in GLC is divided into two steps, *i.e.*, the transfer from

TABLE VI

THE LINEAR RELATIONSHIPS $\log k' = a(1/T) + b$ AND THE ENTHALPY CHANGES, $-\Delta H^0$, FOR ARYLALKYL ESTERS OF BENZOIC ACIDS

Compound	*SE-30*				*OV-351*			
	a	*b*	*r*	$-\Delta H^0$ (*kJ mol*$^{-1}$)	*a*	*b*	*r*	$-\Delta H^0$ (*kJ mol*$^{-1}$)
B1	2856.3	−5.855	0.999	55.01	3336.9	−6.214	1.000	64.27
B2	2928.3	−5.981	1.000	56.40	3318.9	−6.243	1.000	63.92
B3	3025.0	−6.084	1.000	58.26	3449.9	−6.532	1.000	66.45
2ClB1	3127.2	−6.184	1.000	60.23	3640.3	−6.506	0.995	70.11
2ClB2	3184.8	−6.289	1.000	61.34	3651.9	−6.603	0.998	70.34
2ClB3	3236.8	−6.276	1.000	62.34	3780.8	−6.679	0.998	72.82
3ClB1	3113.5	−6.163	0.999	59.97	3557.6	−6.423	0.997	68.52
3ClB2	3173.2	−6.273	0.999	61.12	3540.5	−6.459	0.998	68.19
3ClB3	3257.1	−6.342	0.999	62.73	3674.3	−6.570	0.996	70.77
4ClB1	3124.5	−6.185	0.999	60.18	3585.4	−6.477	0.997	69.06
4ClB2	3178.5	−6.286	0.999	61.22	3568.5	−6.513	0.998	68.73
4ClB3	3255.1	−6.329	0.999	62.69	3691.2	−6.603	0.996	71.09
F5B1	2771.5	−5.939	1.000	53.38	3128.6	−6.359	0.997	60.26
F5B2	2925.3	−6.244	1.000	56.34	2817.5	−5.714	0.997	54.28
F5B3	2981.5	−6.245	1.000	57.42	3172.1	−6.318	1.000	61.10

the gaseous to the polar phase and that from the gaseous to the non-polar phase. Thus, the analysis of the isokinetic relationship makes it possible to examine separately the influence of the intramolecular hydrophobic interaction upon the solubility of the compounds studied in a polar and a non-polar phase. Regression analysis of the isokinetic relationship yields the equations:

	n	*r*	*s*	*F*	
$\log k'_{473} = 0.0489\,(-\Delta H^0) - 2.6472$	38	0.990	0.056	1754.2	(10)
$\log k'_{473} = 0.0687\,(-\Delta H^0) - 3.7656$	15	0.941	0.072	100.9	(11)
$\log k'_{473} = 0.0454\,(-\Delta H^0) - 2.2197$	38	0.975	0.109	700.0	(12)
$\log k'_{473} = 0.0670\,(-\Delta H^0) - 3.5525$	15	0.963	0.097	167.6	(13)

Eqns. 10 and 11 were calculated for the non-polar stationary phase SE-30, for alkyl esters without intramolecular hydrophobic interactions and for arylalkyl esters, respectively. Differences in the slopes, intercepts and in the values of the compensation temperature, β (848 and 1249 K respectively) are evident. Analogous results were obtained from an analysis of the isokinetic relationship for the polar stationary phase OV-351. The compensation temperatures for alkyl esters and arylalkyl esters were calculated from eqn. 12 and 13 to be 803 and 1200 K respectively.

It may be concluded that the analysis of the isokinetic relationship shows differences in the mechanism of separation between arylalkyl esters and other esters, which accounts for the additivity breakdown of log *P* for these compounds. The effect of the intramolecular hydrophobic interaction upon the solubility of arylalkyl esters is nearly the same in polar and non-polar phases. It is manifested by the similar differences of the dependencies of log *k'* on the enthalpic changes for alkyl and arylalkyl esters in both phases.

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