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THE APPLICABILITY OF THE LINEAR FREE ENERGY RELATIONSHIPS FOR THE IDENTIFICATION OF SOME ALKYL AROMATIC HYDROCARBONS BY OPEN TUBULAR COLUMN GAS CHROMATOGRAPHY

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SUMMARY

The validity of some relationships existing between the structure of C_6 to C_{10} alkyl aromatics and their retention data, found on capillary polyethylene glycol and squalane columns, is discussed. A new substitution constant was determined for the correlation of the activity coefficient ratio. A relationship between the linear correlation of free energies for the alkyl aromatics and the differences of the Kováts' indices found on two liquid phases is proposed. An empirical relationship existing between the Kováts' indices and the new substitution constant was determined. The validity of the correlations found was proved experimentally and used in the identification of some C_{11} -alkyl aromatics.

INTRODUCTION

The analysis of complex hydrocarbon mixtures has been facilitated by progress in open tubular gas chromatography. The identification of the chromatographic peaks found may be difficult, because not only are the necessary standards, but also the retention data, often missing or inaccessible.

The identification of the components separated by gas chromatography can be carried out either by a combination of gas chromatography with IR or mass spectrophotometry, or by the application of the correlations existing between retention data and the structure of the separated molecules^{1,2}. KEULEMANS³ studied the identification of aromatic hydrocarbons, after hydrogenation, on the basis of relationships between retention time and the structure of the cycloparaffins so formed. GRANT AND VAUGHAN⁴ derived from the Clausius-Clapeyron equation and the Trouton law correlations for the boiling points and the logarithm of retention data. A linear relationship between the logarithm of retention time and saturation vapour pressure for alkyl aromatics was found by HOARE AND PURNELL⁴. The applicability of the Kováts' indices for the identification of C_6 to C_{10} hydrocarbons has been demonstrated in our preceding publications^{5,6}.

The scope of this work was the examination of the validity of relationships existing between the structure of C_6 to C_{10} dialkyl derivatives of aromatic hydrocarbons and their retention data, and if possible, to determine the possibility of using retention data calculations for some aromatics during the analysis of C_{11} alkyl aromatic hydrocarbons formed in *n*-undecane dehydrogenation.

THEORETICAL

The linear function of free energy was successfully applied in the investigation of relationships between the equilibrium or rate constants of similar chemical reactions and the structure of the reacting substances⁷.

KARGER *et al.*^{8,9,14} used gas chromatography to study the linear correlation of free energy with the structure of the substances separated. If the standard state for the vapour phase is an ideal gas and an infinitely dilute solution that for the liquid phase, then a relationship exists between the standard molar mixing free energy, during the change of structure from "s" into "x", and the separation factor α , *viz.*

$$\Delta(\Delta\bar{G}_s^0) = \Delta(\bar{G}_s^0)_x - \Delta(\bar{G}_s^0)_s = -RT \ln \alpha \quad (1)$$

The separation factor in gas chromatography can be expressed as:

$$\alpha = \frac{K_x}{K_s} = \frac{\gamma_s^\infty \cdot P_s^0}{\gamma_x^\infty \cdot P_x^0} = \frac{t'_{Rx}}{t'_{Rs}} \quad (2)$$

where K_s and K_x are the thermodynamic distribution coefficients, γ_s^∞ and γ_x^∞ the activity coefficients; P_s^0 and P_x^0 the saturation vapour pressures at the column temperature; and t'_{Rs} and t'_{Rx} are the retention times corrected for the retention time of the unabsorbed component^{8,9,14}. The variation of the standard molar free energy of mixing can be expressed as:

$$\Delta\bar{G}_s^0 = \Delta\bar{G}_i^0 + \Delta\bar{G}_e^0 = RT \ln P^0 + RT \ln \gamma^\infty \quad (3)$$

where $\Delta\bar{G}_i^0$ is the standard free energy of the ideal solution; $\Delta\bar{G}_e^0$ is the excess partial mixing free energy expressed as^{4,8,9,14}:

$$\Delta\bar{G}_e^0 = RT \ln \gamma^\infty \quad (4)$$

The variation of the standard excess molar energy of mixing can, for the change of structure of the substance from "s" to "x", be expressed by the equation⁸:

$$\Delta(\Delta\bar{G}_e^0) = (\Delta\bar{G}_e^0)_x - (\Delta\bar{G}_e^0)_s = -RT \ln \left(\frac{\gamma_s^\infty}{\gamma_x^\infty} \right) \quad (5)$$

Considering the mixing process in several phases (I, II ... N), the ratio of the variations of the standard excess molar energies for the transformation of the substance having structure "s" into structure "x" can be expressed as:

$$C_1 \ln \left(\frac{\gamma_s^\infty}{\gamma_x^\infty} \right)_I = C_2 \ln \left(\frac{\gamma_s^\infty}{\gamma_x^\infty} \right)_{II} = \dots = C_N \ln \left(\frac{\gamma_s^\infty}{\gamma_x^\infty} \right)_N \quad (6)$$

Using the same method as Hammett for the derivation of the equation^{7,10}, we found that the equation for the linear correlation of standard molar free energies in gas chromatography is:

$$\log \left(\frac{\gamma_s^\infty}{\gamma_x^\infty} \right)_N = \rho_N \cdot \sigma_C^* \quad (7)$$

where "s" belongs to the original substance and "x" to the derivative; ρ_N is the constant characterizing the liquid phase; σ_C^* is the chromatographic substitution constant.

By means of regression analysis KARGER *et al.*⁹ transformed the original σ values of Hammett into σ_C values. Correlating the logarithm of the ratio of activity coefficients of phenol derivatives and the substitution constants, he expressed eqn. 7 in the form:

$$\log \left(\frac{\gamma_s^\infty}{\gamma_x^\infty} \right)_N = \rho_N \cdot \sigma_C + b_1 \quad (8)$$

where the term b_1 is a constant independent of the electron shifts in the molecule⁹.

Eqn. 8 is only valid for the separation of phenols on polyester phases because the variation of the excess energy expresses, in the main, only the interactions between the liquid phase and the separated phenols (the formation of hydrogen bonds). On a non-polar phase (SE-30), which is only a weak proton acceptor, the values for σ_C are unsuitable and eqn. 8 is not valid. (The correlation coefficient in this case was $r = 0.61$ (ref. 9).) In the case where substituted anilines are separated by chromatography on polyester phases the correlation coefficient for eqn. 8 was also found to be insufficient (a value of $r = 0.89$ was found).

Since the experimental results showed that the correlation coefficient, according to eqn. 8, gives low values for the alkyl aromatics, a new suitable equation resulting from the variation of excess free energies was proposed.

EXPERIMENTAL

The open tubular columns (Chrom-3, Laboratorní přístroje N.E. Prague) were wetted by a dynamic method¹¹. The samples were injected with a $1 \mu\text{l}$ Hamilton microsyringe. A mixture of C_6 to C_{10} aromatic hydrocarbons, separated from reformates and made up with standards prepared in the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava, was used for the analysis. The retention times and the Kováts' retention indices were corrected for the retention time of air (Table I). The values of the vapour pressures were calculated by the Antoine equation (see

TABLE I

EXPERIMENTAL CONDITIONS

	Polyethylene glycol 400	Squalane ¹	Squalane ²
Instrument	Perkin-Elmer F 11	Perkin-Elmer F 11	Chrom-3
Detector	Flame ionization	Flame ionization	Flame ionization
Column dimensions	45 m/0.2 mm	45 m/0.2 mm	200 m/0.2 mm
Column temperatures	60, 72, 82 °C	86, 92 °C	86; 115 °C
Carrier gas;	Nitrogen;	Nitrogen;	Nitrogen;
inlet pressure	0.9-1.3 kp/cm ²	1.3 kp/cm ²	3-4 kp/cm ²
Sample size; split	0.1-0.3 μl ; 1/100	0.1-0.3 μl ; 1/100	0.5 μl ; 1/300
Column efficiency	$n = 118000$ TP; $N = 93000$ EP at $k = 7.8$ and $t = 72$ °C	$n = 105000$ TP; $N = 80000$ EP at $k = 7.0$ and $t = 92$ °C	$n = 250000$ TP; $N = 190000$ EP at $k = 6.6$ and $t = 115$ °C

TABLE II
 PEG = polyethylene glycol, SQ = squalane, t'_R = corrected retention time, I = Kováts' index.

Compound	PEG		SQ		$\log \gamma_i^m / \gamma_i^\infty$											
	60 °C		72 °C		82 °C		92 °C		60 °C		72 °C		82 °C		92 °C	
	t'_R	I	t'_R	I	t'_R	I	t'_R	I	t'_R	I	t'_R	I	t'_R	I	t'_R	I
Toluene	21.1	1061	19.9	1073	15	1079	35.0	758	—	—	—	—	—	—	—	—
1,2-Dimethylbenzene	55.0	1194	48.3	1208	35.2	1217	93.7	883	—	—	—	—	—	—	—	-0.04246
1,3-Dimethylbenzene	40.8	1153	36.1	1164	26.5	1172	80.0	863	-0.1629	-0.1664	-0.1966	-0.03808	-0.1664	-0.1966	-0.03808	-0.03808
1,4-Dimethylbenzene	39.0	1147	34.9	1158	25.9	1167	78.9	861	-0.1647	-0.1651	-0.1547	-0.03110	-0.1651	-0.1547	-0.03110	-0.03110
1-Methyl-2-ethylbenzene	89.8	1263	75.9	1267	54.8	1285	175.0	964	—	—	—	—	—	—	—	-0.06445
1-Methyl-3-ethylbenzene	70.9	1230	60.2	1240	43.4	1249	155.0	948	-0.2786	-0.2824	-0.2698	-0.06335	-0.2824	-0.2698	-0.06335	-0.06335
1-Methyl-4-ethylbenzene	69.8	1228	59.7	1229	43.2	1249	157.4	950	-0.2897	-0.2919	-0.2783	-0.06214	-0.2919	-0.2783	-0.06214	-0.06214
1-Methyl-2- <i>n</i> -propylbenzene	142.3	1329	118.1	1342	84.3	1353	324.8	1045	—	—	—	—	—	—	—	-0.09438
1-Methyl-3- <i>n</i> -propylbenzene	115.3	1299	95.6	1311	68.2	1320	296.0	1033	-0.4398	-0.4298	-0.4036	-0.09231	-0.4298	-0.4036	-0.09231	-0.09231
1-Methyl-4- <i>n</i> -propylbenzene	117.5	1300	97.0	1312	69.5	1323	309.0	1039	-0.4428	-0.4354	-0.4076	-0.08670	-0.4354	-0.4076	-0.08670	-0.08670
1-Methyl-2-isopropylbenzene	115.3	1299	95.6	1313	68.2	1320	260.8	1015	—	—	—	—	—	—	—	-0.07548
1-Methyl-3-isopropylbenzene	93.7	1268	78.0	1278	56.3	1289	234.0	1002	-0.3863	-0.3849	-0.3617	-0.07716	-0.3849	-0.3617	-0.07716	-0.07716
1-Methyl-4-isopropylbenzene	92.2	1270	76.8	1280	56.3	1290	248.0	1010	-0.4221	-0.4190	-0.3513	-0.07810	-0.4190	-0.3513	-0.07810	-0.07810

Table IV)¹². The calculations were done on a digital Celatron Serie 2c computer (G.D.R.).

RESULTS AND DISCUSSION

As, in our experiments, we have used small amounts of sample and relatively low pressures, we can presume that the experimental conditions coincide with the standard states.

Twelve derivatives of methyl monoalkyl benzenes were used in the investigation of the influence of the alkyl substituent upon the thermodynamic properties of the aromatic hydrocarbons. The effect of the alkyl substituent on the properties was compared with regard to toluene, which after preliminary experiments was shown to be a more suitable standard than benzene.

The squalane phase used for the separation of the alkyl aromatics is less selective than polyethylene glycol (Table III), but it permits the study of *ortho*-derivatives which when using a polyethyleneglycol phase exhibited decided *ortho*-effects.

Correlation of the activity coefficients ratio and substituent constants

The logarithms of the relative activity coefficients of toluene and its monoalkyl derivatives (Table II) were calculated from the corrected retention times and the

TABLE III

s = standard deviation; *r* = correlation coefficient, *n* = number of components.

Column	Temp. (°C)	Equation	<i>s</i>	<i>r</i>	<i>n</i>
Squalane	92	$\log \gamma_t^\infty / \gamma_x^\infty = 0.3650 \cdot \sigma_c - 0.03390$	$8.30 \cdot 10^{-3}$	0.560	5
Polyethylene glycol 400	60	$\log \gamma_t^\infty / \gamma_x^\infty = 2.0245 \cdot \sigma_c - 0.1504$	$3.08 \cdot 10^{-2}$	0.936	5
	72	$\log \gamma_t^\infty / \gamma_x^\infty = 1.9913 \cdot \sigma_c - 0.1533$	$3.05 \cdot 10^{-2}$	0.964	5
	82	$\log \gamma_t^\infty / \gamma_x^\infty = 1.6284 \cdot \sigma_c - 0.1561$	$3.12 \cdot 10^{-2}$	0.946	5

vapor pressures calculated from eqn. 2. Table III gives the straight line equations, the correlation coefficients and the standard deviations. The straight line equations were found by the method of least squares, from eqn. 8, using the σ_c values obtained by KARGER and co-workers⁹. Because of the different types of interaction the values of σ_c obtained were not suitable in the case of aromatics separated on a squalane phase. The correlation coefficients obtained on a polyethylene glycol phase are more suitable. This can be partially explained by the formation of a donor-acceptor hydrogen bond (the formation of π -complex) (Table III).

On the basis of the experimental results we found eqn. 9 for the correlation of C_6 to C_{10} alkyl aromatics

$$\log \frac{\gamma_t^\infty}{\gamma_x^\infty} = \rho_N \cdot \tau_T + b_2 \quad (9)$$

which expresses the relationship between the alkyl aromatic structures and their excess free energy. The original value of σ_c was substituted by $\tau_T = \log (T_t / T_x)$; τ_T expresses the variations in the electron configuration of methyl-alkyl aromatics (*x*) according to the reference standard toluene (*t*); *T* is the boiling point in °K.

TABLE IV

 σ_c = chromatographic substituent constant, $\tau_T = \log T_t/T_x$.

Compound	Boiling point (°K)	Vapor pressures (mm Hg)				σ_c	τ_T
		60 °C	72 °C	82 °C	92 °C		
Toluene	383.79	138.94	219.26	311.82	433.72	—	—
1,2-Dimethylbenzene	417.57	40.828	68.732	102.72	149.58	—	—0.0
1,3-Dimethylbenzene	412.26	49.380	82.372	112.25	176.46	+0.01	—0.0
1,4-Dimethylbenzene	411.51	51.445	85.472	126.458	182.395	—0.01	—0.0
1-Methyl-2-ethylbenzene	438.31	18.838	32.992	50.820	76.088	—	—0.0
1-Methyl-3-ethylbenzene	434.47	21.770	37.819	57.907	86.230	—0.05	—0.0
1-Methyl-4-ethylbenzene	435.15	21.522	37.309	57.046	84.854	—0.09	—0.0
1-Methyl-2- <i>n</i> -propylbenzene	457.96	8.264	15.266	24.470	37.985	—	—0.0
1-Methyl-3- <i>n</i> -propylbenzene	454.96	9.235	16.963	27.075	41.867	—	—0.0
1-Methyl-4- <i>n</i> -propylbenzene	456.46	9.000	16.503	26.308	40.635	—	—0.0
1-Methyl-2-isopropylbenzene	451.31	11.414	20.609	32.466	49.593	—	—0.0
1-Methyl-3-isopropylbenzene	448.30	12.854	23.051	36.125	54.922	—0.11	—0.0
1-Methyl-4-isopropylbenzene	450.26	12.031	21.642	33.995	51.786	—0.13	—0.0

The straight line equations, the standard deviations s and the correlation coefficients r , calculated using eqn. 9, are given in Table V. Comparison of Tables III and V shows that by using the values of τ_T instead of σ_c more exact correlations are obtained.

TABLE V

Column	Temperature (°C)	Equation	s	r	n
Squalane	92	$\log \gamma_t^\infty/\gamma_x^\infty = 0.9853 \cdot \tau_T + 0.002787$	$3.73 \cdot 10^{-3}$	0.9853	12
Polyethylene glycol 400	60	$\log \gamma_t^\infty/\gamma_x^\infty = 6.4180 \cdot \tau_T + 0.04230$	$1.63 \cdot 10^{-3}$	0.9917	8
	72	$\log \gamma_t^\infty/\gamma_x^\infty = 6.2090 \cdot \tau_T + 0.03191$	$1.39 \cdot 10^{-3}$	0.9940	8
	82	$\log \gamma_t^\infty/\gamma_x^\infty = 5.1326 \cdot \tau_T - 0.01055$	$1.75 \cdot 10^{-3}$	0.9854	8

The linear correlation of free energies and the structure of aromatic hydrocarbons, as given by eqns. 7–9, calls for very exact and reproducible retention times and correct values of vapor pressures at several temperatures^{9,14}.

Correlation of Kováts' indices on two phases

The following relationship¹³ exists between the logarithm of the ratio of retention times and the difference of the Kováts' indices:

$$\log \frac{t'_{Rx}}{t'_{Rs}} = \frac{(I_x - I_s)}{100} \log \frac{t'_{Rn+1}}{t'_{Rn}} \quad (10)$$

where "s" is the standard substance and "x" the substance having the structure x ; t'_{Rn+1}/t'_{Rn} is the separation factor of the n -alkanes on the phases considered.

From eqns. 1 and 2 for the variation of the standard free mixing energy caused by a structural change, it follows that:

$$\Delta(\Delta G_s^0) = RT \ln \frac{t'_{Rx}}{t'_{Rs}} \quad (11)$$

The comparison of eqns. 10 and 11 with respect to eqn. 6 results, for the chromatographic process on two different phases, in eqn. 12

$$C_1 \cdot \Delta I_1 \cdot \log a_1 = C_2 \cdot \Delta I_2 \cdot \log a_2 = \dots = C_N \cdot \Delta I_N \cdot \log a_N \quad (12)$$

where $C_1 \dots C_N$ are constants; the numbers 1 ... N define the liquid phases; $a_1 \dots a_N$ are the separation factors of the n -alkanes; and $\Delta I = I_x - I_s$.

In the case where one of the phases is the standard phase and the separation factor for the n -alkane is in a certain section of the homologous series constant for this phase then eqn. 13 will be valid:

$$\Delta I_N = \rho' \cdot \Delta I_1 \quad (13)$$

where ρ' is slope characterizing the phase. From eqn. 12 follows that:

$$\rho' = \frac{C_1 \cdot \log a_1}{C_N \cdot \log a_N} \quad (14)$$

After studying the differences of the Kováts' indices for toluene and mono-substituted alkyl toluenes on squalane and polyethylene glycol phases we found that eqn. 13 has to be corrected into the form:

$$(I_x - I_t)_{\text{PEG 400}} = \rho'(I_x - I_t)_{\text{SQ}} + b_3 \quad (15)$$

The values for the alkyl derivatives of toluene, calculated by the least squares method from eqn. 15, are given in Table VI.

TABLE VI

Column	Temp. (°C)	Equation	s	r	n
Squalane	92	—	—	—	—
Polyethylene glycol 400	60	$(\Delta I)_{\text{PEG}} = 0.8434 \cdot (\Delta I)_{\text{SQ}} + 2.77$	4.25	0.998	8
	72	$(\Delta I)_{\text{PEG}} = 0.8455 \cdot (\Delta I)_{\text{SQ}} + 1.21$	4.50	0.997	8
	82	$(\Delta I)_{\text{PEG}} = 0.8558 \cdot (\Delta I)_{\text{SQ}} + 2.72$	4.19	0.998	8

As the variations of the retention indices with temperature on a polyethylene glycol phase are substantially higher than on a squalane phase^{5,6} one can assume that a more exact control of thermostat temperature decreases the standard deviation s (Table VI). This problem will be the subject of our further work.

Correlation of the Kováts' indices and the substituent constants

The relationship existing between the Kováts' indices and the substituent constant τ_T was found by the least squares method to be given by

$$\log \frac{I_t}{I_x} = \rho \cdot \tau_T + b_4 \quad (16)$$

The equations, the correlation coefficients and the standard deviations for mono-alkyl substituted toluenes, calculated from eqn. 16 are given in Table VII.

The deviations of the Kováts' indices determined for aromatic hydrocarbons are given in Table VIII. They were calculated from three measurements on a 200 m

TABLE VII

Column	Temp. (°C)	Equation	s	r	n
Squalane	92	$\log I_T/I_x = 1.8071 \cdot \tau_T - 5.89 \cdot 10^{-5}$	$5.4 \cdot 10^{-4}$	0.995	12
Polyethylene glycol 400	60	$\log I_T/I_x = 1.1779 \cdot \tau_T + 9.69 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	0.997	8
	72	$\log I_T/I_x = 1.1702 \cdot \tau_T + 15.94 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	0.995	8
	82	$\log I_T/I_x = 1.1886 \cdot \tau_T + 4.10 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$	0.978	8

squalane column at 115°. The validity of the relationship in accordance with eqn. 16 was verified by recalculating the boiling points and by comparison of the values found with those tabulated (Table VIII).

TABLE VIII

Compound	$I_{115}^{SQ} \pm s$	$T_{b.p.} (°K)$	ΔT
Toluene	761.1 ± 0.4	383.79	—
1,2-Dimethylbenzene	888.4 ± 0.1	417.57	± 0.2
1,3-Dimethylbenzene	867.1 ± 0.5	412.26	± 0.1
1,4-Dimethylbenzene	865.5 ± 0.6	411.51	± 0.3
1-Methyl-2-ethylbenzene	969.3 ± 0.3	438.31	± 0.1
1-Methyl-3-ethylbenzene	952.7 ± 0.4	430.47	± 0.4
1-Methyl-4-ethylbenzene	955.6 ± 0.3	435.15	± 0.3
1-Methyl-2- <i>n</i> -propylbenzene	1051.0 ± 0.3	457.96	± 0.4
1-Methyl-3- <i>n</i> -propylbenzene	1037.0 ± 0.4	454.96	± 0.2
1-Methyl-4- <i>n</i> -propylbenzene	1044.0 ± 0.2	456.46	± 0.2
1-Methyl-2-isopropylbenzene	1024.7 ± 0.2	451.31	± 0.6
1-Methyl-3-isopropylbenzene	1006.4 ± 0.1	448.30	± 0.6
1-Methyl-4-isopropylbenzene	1015.0 ± 0.1	450.26	± 0.6

Eqn. 16 was applied practically for the identification of aromatic compounds formed in the dehydrogenation of *n*-undecane. The results found so far confirm the validity of the suggested relationship for C₁₁-alkyl aromatics as well.

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