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CORRELATION OF HAMMETT SUBSTITUENT CONSTANTS WITH REVERSED-PHASE "ION-PAIR" LIQUID CHROMATOGRAPHIC ADSORPTION PARAMETERS OF CHARGED ORGANIC COMPOUNDS

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SUMMARY

Capacity factors for 28 *trans*-cinnamic, hydrocinnamic, phenylalkylcarboxylic and benzoic acids were determined at nine combinations of pH (3.4, 4.7, 6.0) and ion-interaction reagent concentration (0, 2.0, 4.0 mM octylamine hydrochloride) in methanol-water (30:70) eluents at 25.0°C. An ion-interaction model was fit to capacity factor data for each of the solutes. Correlation coefficients were calculated among estimated model parameters, carbon number, $\sigma_{p,m}$ and π values. For the 28 aromatic monocarboxylic acids studied, the Hammett $\sigma_{p,m}$ values correlate with estimated pK_a values only. Other correlations suggest that the increased retention resulting from the addition of surface-active ion-interaction reagent to the eluent is caused by electrostatic effects at the stationary phase surface.

INTRODUCTION

Bidlingmeyer *et al.*¹ have suggested that neither the "ion-pair" model²⁻⁵ nor the "ion-exchange" model⁶⁻⁹ adequately describes chromatographic phenomena observed in reversed-phase high-performance liquid chromatographic (HPLC) systems containing surface-active ions intentionally added to the mobile phase. Rather, they have proposed an ion-interaction mechanism¹ which does not require classical ion-exchange "sites" or ion-pair formation in either phase. Important features of the ion-interaction model are that (a) adsorbed surface-active ions (ion-interaction reagent, IIR) are responsible for a charged primary ion layer at the surface of the stationary phase; (b) the charged primary ion layer electrostatically attracts or repels solute ions of opposite or similar charge, respectively; (c) the charged primary ion layer does not exert an effect upon neutral molecules; and (d) other differences in distribution behavior can be explained by forces that are eluophilic (having an affinity for the mobile phase), eluophobic (having an aversion for the mobile phase), adsorbophilic (having an affinity for the surface of the stationary phase) and adsorbophobic.

This ion-interaction model was expressed in quantitative form by Kong *et al.*¹⁰ as

$$k' = f_{HA} k'_{HA} + f_A (k'_A + f_{HS} \beta [IIR]^{1/n}) \quad (1)$$

where k' is the observed capacity factor; f_{HA} and f_A are the fractions of a weak organic

acid in its protonated and unprotonated forms, respectively; k'_{HA} and k'_A are the capacity factors of the weak organic acid in its protonated and unprotonated forms, respectively; f_{HS} is the fraction of IIR in its protonated, positively charged form; $[IIR]$ is the concentration of IIR in the eluent; and β and n are parameters of the Freundlich adsorption isotherm. The adequacy of the model was verified experimentally using a positively charged IIR (octylamine hydrochloride) and positively charged, negatively charged, uncharged and zwitterionic solutes.

A recent paper by Knox and Hartwick¹¹ further confirms the appropriateness of the ion-interaction model. They concluded that the degree of retention is directly related to the surface charge arising from the adsorbed IIR and is relatively independent of the hydrophobic part of the IIR.

This paper presents the results of an experimental study designed to investigate the effect of molecular structural parameters on the electrostatic interaction of charg-

TABLE I
SOLUTE STRUCTURES AND PROPERTIES

No.	Compound	Structure	$\sigma_{p,m}$	π	C No.
<i>TCA series</i>					
1	<i>trans</i> -Cinnamic acid (TCA)		0.00	0.00	9
2	<i>p</i> -Cl-TCA		0.23	0.73	9
3	<i>m</i> -Cl-TCA		0.37	0.77	9
4	<i>p</i> -F-TCA		0.06	0.15	9
5	<i>m</i> -F-TCA		0.34	0.22	9
6	<i>p</i> -CH ₃ -TCA		-0.17	0.60	10
7	<i>m</i> -CH ₃ -TCA		-0.07	0.52	10
8	<i>p</i> -CH ₃ O-TCA		-0.27	-0.03	10
9	<i>m</i> -CH ₃ O-TCA		0.12	0.12	10
10	<i>p</i> -NO ₂ -TCA		0.78	0.22	9
11	<i>m</i> -NO ₂ -TCA		0.71	0.11	9
<i>HCA series</i>					
12	Hydrocinnamic acid (HCA)	$\phi\text{CH}_2\text{CH}_2\text{COOH}$	0.00	0.00	9
13	<i>p</i> -Cl-HCA	0.23	0.73	9	
14	<i>m</i> -Cl-HCA	0.37	0.77	9	
15	<i>p</i> -F-HCA	0.06	0.15	9	
16	<i>m</i> -F-HCA	0.34	0.22	9	
17	<i>p</i> -CH ₃ -HCA	-0.17	0.60	10	
18	<i>m</i> -CH ₃ -HCA	-0.07	0.52	10	
19	<i>p</i> -CH ₃ O-HCA	-0.27	-0.03	10	
20	<i>m</i> -CH ₃ O-HCA	0.12	0.12	10	
<i>PAA series</i>					
21	5-Phenylvaleric acid	$\phi(\text{CH}_2)_4\text{COOH}$	-	-	11
22	4-Phenylbutyric acid	$\phi(\text{CH}_2)_3\text{COOH}$	-	-	10
12	3-Phenylpropionic acid	$\phi(\text{CH}_2)_2\text{COOH}$	-	-	9
23	2-Phenylacetic acid	$\phi\text{CH}_2\text{COOH}$	-	-	8
24	<i>m</i> -Cl-2-phenylacetic acid	<i>m</i> -Cl- $\phi\text{CH}_2\text{COOH}$	-	-	8
25	1-Phenylformic acid	ϕCOOH	-	-	7
<i>BA series</i>					
25	Benzoic acid (BA)	ϕCOOH	0.00	0.00	7
26	<i>p</i> -CH ₃ -BA	<i>p</i> -CH ₃ - ϕCOOH	-0.17	0.60	8
27	<i>p</i> -C ₂ H ₅ -BA	<i>p</i> -C ₂ H ₅ - ϕCOOH	-0.15	1.10	9
28	<i>m</i> -Cl-BA	<i>m</i> -Cl- ϕCOOH	0.37	0.77	7

ed solute molecules with the charged stationary phase surface. The study involved the 28 weak organic acids listed in Table I, subdivided into four groups: *trans*-cinnamic acids (TCA series), hydrocinnamic acids (HCA series), phenylalkylcarboxylic acids (PAA series) and benzoic acids (BA series). Molecular structural parameters are also listed in Table I: the Hammett substituent constant ($\sigma_{p,m}$)¹², the Hansch solubility parameter (π)¹³ and the number of carbon atoms in the molecule (C No.).

A recent, comprehensive, semi-empirical study by Riley *et al.*¹⁴ of functional group behavior in "ion-pair" reversed-phase systems was interpreted assuming ion-pair formation in the mobile phase followed by distribution to the stationary phase; their results are therefore not generally applicable to the present study.

EXPERIMENTAL

Chromatographic system

The chromatographic system consisted of a Model 6000 A solvent delivery system (Waters Assoc., Milford, MA, U.S.A.), 5 cm × 4 mm I.D. Bondapak C₁₈/Porasil pre-column (Waters), 30 cm × 4 mm I.D. μ Bondapak C₁₈ main column (Waters) and a Model SP8200 ultraviolet (UV) detector (Spectra-Physics, Santa Clara, CA, U.S.A.) operated at 254 nm. A Model U6K universal liquid chromatographic injector (Waters) was used to inject 2- to 5- μ l volumes of samples. Pre-column and column temperatures were held at 25.0 \pm 0.1°C by a Model FK constant temperature circulating bath (Haake, Saddle Brook, NJ, U.S.A.). Mobile phase flow-rate was maintained at 2.02 \pm 0.03 ml min⁻¹. The time equivalent of the void volume (t_0 = 1.728 min) was determined by injecting 20 μ l of water and measuring the time from injection to the first deviation from baseline.

Additional instrumentation

The analogue UV detector output was recorded by a Model 281 stripchart recorder (Soltex, Encino, CA, U.S.A.). Simultaneously, the signal from the detector was digitized by a Model ADC-12QZ analog-to-digital converter (Analog Devices, Norwood, MA, U.S.A.) interfaced to a Model 9830A digital computer (Hewlett-Packard, Calculator Products Division, Loveland, CO, U.S.A.). Chromatograms less than 60 min long were digitized at 1-sec intervals, longer chromatograms were digitized at 2-sec intervals. Retention times were determined by numerical treatment of the digitized chromatograms. Data analysis programs were written in BASIC language and used double-precision arithmetic throughout.

Experimental design

A three-level, two-factor (3²) factorial design^{15,16} was used to specify eluent compositions of nine different mobile phases corresponding to all combinations of three pH values (3.4, 4.7 and 6.0) and three concentrations of surface-active ion (0, 2.0 and 4.0 mM). The center combination (pH 4.7, 2.0 mM IIR) was replicated. Mean retention times were used to calculate the capacity factor for each solute. The experimental order of evaluating the eluents was randomized to minimize the possibility of confounding time trends with factor effects¹⁷.

Mobile phases and samples

Mobile phases were prepared by adding octylamine hydrochloride (Aldrich, Milwaukee, WI, U.S.A.) to 600 ml of HPLC grade methanol (Fisher Scientific, Chemical Manufacturing Division, Fair Lawn, NJ, U.S.A.) in a 2-l volumetric flask. A 20-ml volume of 1 *M* acetic acid (Fisher) and 1370 ml of distilled water were added; 1 *M* HClO₄ (Fisher) or 1 *M* NaOH (Fisher) was added dropwise until a glass electrode indicated the desired pH. The volumetric flask was then brought to volume with distilled water.

Solutions containing individual solutes were prepared in methanol-water (30:70) at a concentration of approximately 0.2 mg ml⁻¹.

Mobile phases and sample solutions were aspirated through 0.47- μ m cellulose acetate filters (HAW04700; Millipore, Bedford, MA, U.S.A.) and degassed in a Model ME4.6 ultrasonic bath (Mettler Electronics, Anaheim, CA, U.S.A.) before use.

Parameter estimation

A non-linear least squares simplex algorithm similar to that described by O'Neill¹⁸ was used to fit the model expressed by eqn. 1 to capacity factor data at each of the nine factor combinations of pH and [IIR] for each of the 28 solutes. Estimated parameters were the p*K*_a of the solute, *k*'_{HA}, *k*'_A, β , *n* and p*K*_{HS}. Conversion was verified by examination of the sum of squares of residuals divided by the average capacity factor¹⁰ and by inspection of plots showing both the capacity factors and the fitted model.

Coefficient of correlation

The first-order linear model

$$y_i = \beta_0 + \beta_1 x_i + r_i \quad (2)$$

was fit to sets of paired data, where *y*_{*i*} and *x*_{*i*} are the two numerical quantities being correlated, β_0 and β_1 are the intercept and slope, and *r*_{*i*} is a residual. The coefficient of correlation (*r*) was calculated as the square root of the ratio of the sum of squares due to the factor as it appears in the model (the sum of squares due to regression) divided by the sum of squares corrected for the mean¹⁹. For some sets of data, a different model was later used to express a first-order relationship constrained to pass through the origin.

$$y_i = \beta_1 x_i + r_i \quad (3)$$

The statistical significance of the coefficient of correlation may be obtained from the Fisher *F* ratio²⁰

$$F_{(1, n-2)} = \frac{r^2}{(1 - r^2)} \times \frac{(n - 2)}{1} \quad (4)$$

RESULTS AND DISCUSSION

Table II contains capacity factors for each of the 28 solutes at each of the nine combinations of pH and [IIR]. Table III contains the best non-linear least squares estimates¹⁸ of the parameters of the mathematical model of eqn. 1. In all cases, the standard deviation of residuals divided by the average capacity factor showed an excellent fit of the mathematical model to the experimental data¹⁰.

TABLE II
SOLUTE CAPACITY FACTORS

No.	pH								
	3.4			4.7			6.0		
	[IIR] (mM)								
	0	2	4	0	2	4	0	2	4
<i>TCA series</i>									
1	7.23	7.37	7.32	4.15	6.88	8.40	1.54	4.26	6.77
2	21.08	21.46	21.44	11.12	20.89	26.33	3.05	13.71	20.53
3	20.49	21.30	21.25	10.16	20.49	26.35	2.80	13.56	19.93
4	8.52	8.69	9.22	4.86	8.46	10.42	1.26	5.47	9.08
5	8.89	9.22	9.22	4.51	8.87	11.32	1.21	5.73	9.21
6	18.70	18.72	18.52	11.44	17.08	20.21	2.69	10.32	16.35
7	18.27	18.55	18.37	11.40	16.96	20.56	2.53	10.45	16.79
8	10.64	10.56	10.34	6.87	9.58	10.63	1.41	5.28	8.05
9	10.73	10.87	10.76	5.87	9.54	11.87	1.59	5.78	9.17
10	6.75	7.30	7.39	4.01	7.24	9.59	1.01	4.56	7.24
11	6.55	7.01	7.06	2.91	7.19	9.47	1.01	4.65	9.68
<i>HCA series</i>									
12	4.65	4.73	4.64	3.35	4.96	5.78	0.87	3.81	5.94
13	13.89	14.19	14.12	9.69	15.63	18.69	3.06	12.19	19.26
14	13.50	13.71	13.72	9.35	15.07	18.49	2.93	12.04	17.62
15	5.91	6.02	5.98	4.19	6.54	7.74	1.40	5.02	10.64
16	5.96	6.12	6.02	4.15	6.67	7.99	1.37	5.17	9.86
17	11.29	11.51	11.41	8.39	11.94	13.79	2.49	8.78	14.17
18	10.86	10.93	10.86	7.92	11.49	13.33	2.41	8.44	13.46
19	5.69	5.70	5.59	4.14	5.87	6.66	1.08	4.04	6.17
20	5.80	5.86	5.81	4.18	6.19	7.17	1.13	4.49	6.87
<i>PAA series</i>									
21	22.17	22.09	21.73	17.32	22.50	25.24	5.66	16.54	24.31
22	10.12	10.12	9.96	7.71	10.40	11.78	2.48	7.74	11.88
12	4.65	4.73	4.64	3.35	4.96	5.78	0.87	3.81	5.94
23	2.10	2.21	2.21	1.18	2.55	3.24	0.28	1.84	2.95
24	5.80	6.53	6.69	3.04	7.70	10.39	0.99	5.78	9.65
25	2.68	2.77	2.75	1.25	2.44	3.06	0.20	1.42	2.31
<i>BA series</i>									
25	2.68	2.77	2.75	1.25	2.44	3.06	0.20	1.42	2.31
26	6.52	6.55	6.48	3.66	5.59	6.67	0.69	3.06	5.55
27	15.19	15.21	15.08	8.55	12.85	15.45	1.78	7.16	11.44
28	7.73	8.92	9.25	2.60	7.24	10.09	0.69	4.61	7.78

TABLE III
ESTIMATED PARAMETERS

No.	pK_a	k'_{HA}	k'_A	β	n	pK_{HS}
<i>TCA series</i>						
1	4.68	7.40	1.23	2.51	1.14	6.26
2	4.64	21.56	2.19	10.76	1.41	6.25
3	4.58	21.28	2.07	11.12	1.48	6.24
4	4.72	8.92	0.84	3.58	1.18	6.39
5	4.61	9.22	0.86	4.23	1.28	6.30
6	4.85	18.88	1.51	6.73	1.22	6.37
7	4.86	18.61	1.33	6.95	1.19	6.35
8	4.95	10.65	0.56	3.45	1.34	6.48
9	4.69	10.98	1.11	3.71	1.19	6.32
10	4.74	7.17	0.66	3.80	1.22	6.12
11	4.44	6.93	0.82	3.53	1.27	6.26
<i>HCA series</i>						
12	5.08	4.68	0.39	2.81	1.29	6.37
13	4.98	14.04	1.98	8.76	1.25	6.31
14	4.96	13.61	1.92	9.63	1.42	6.25
15	5.06	5.97	0.84	2.02	0.79	6.84
16	5.00	6.03	0.87	2.62	0.92	6.58
17	5.10	11.42	1.32	5.73	1.15	6.36
18	5.08	10.90	1.36	5.67	1.18	6.32
19	5.11	5.68	0.46	3.11	1.31	6.26
20	5.07	5.83	0.55	3.52	1.32	6.26
<i>PAA series</i>						
21	5.22	22.04	2.90	11.28	1.29	6.30
22	5.16	10.09	1.33	4.99	1.21	6.36
12	5.08	4.68	0.39	2.81	1.29	6.37
23	4.75	2.16	0.17	1.60	1.36	6.25
24	4.56	6.26	0.78	4.36	1.26	6.33
25	4.60	2.80	0.09	1.15	1.33	6.33
<i>BA series</i>						
25	4.60	2.80	0.09	1.15	1.33	6.33
26	4.78	6.65	0.32	1.68	1.01	6.55
27	4.76	15.46	0.97	4.63	1.20	6.37
28	4.21	9.06	0.54	3.37	1.25	6.37

Correlation matrices

Tables IV–VII give correlation matrices for ten numerical quantities associated with the TCA, HCA, PAA and BA series of compounds, respectively. In addition to these ten quantities, 15 other quantities were also investigated, resulting in a total of 300 pairwise correlations for each series of compounds. The additional 15 quantities were n and pK_{HS} from eqn. 1, the sum of squares of residuals for the fitted model, the gram molecular weight of the solute, σ^+ and σ^- , and the capacity factors at each of the nine experimental factor combinations. Tables IV–VII show only the 45 most interesting or significant correlations.

Relationship between pK_a and $\sigma_{p,m}$

Tables IV, V, and VII show that in the TCA, HCA, and BA series, pK_a is highly correlated with $\sigma_{p,m}$ only, and that $\sigma_{p,m}$ is highly correlated with pK_a only.

TABLE VI
CORRELATION MATRIX FOR PAA SERIES

Coefficients of correlation (r) expressed as percent.

	pK_a	k'_{HA}	$\log k'_{HA}$	k'_A	$\log k'_A$	β	$\log \beta$	$\sigma_{p,m}$	π	C No.
pK_a	—	68	70	67	68	64	66	—	—	92
k'_{HA}	—	—	95	(100)	87	99	91	—	—	88
$\log k'_{HA}$	—	—	—	95	95	95	97	—	—	(100*)
k'_A	—	—	—	—	90	(99)	93	—	—	89
$\log k'_A$	—	—	—	—	—	90	99	—	—	(99**)
β	—	—	—	—	—	—	94	—	—	87
$\log \beta$	—	—	—	—	—	—	—	—	—	89
$\sigma_{p,m}$	—	—	—	—	—	—	—	—	—	—
π	—	—	—	—	—	—	—	—	—	—
C No.	—	—	—	—	—	—	—	—	—	—

* 1-Phenylformic acid (BA) and *m*-Cl-2-phenylacetic acid excluded; $r = 89$ when included.

** *m*-Cl-2-phenylacetic acid excluded; $r = 90$ when included.

Hansch hydrophobic parameter π . These relationships are shown in Fig. 2. The slopes of the two-parameter straight lines (eqn. 2) are 0.60, 0.59 and 0.67 for the TCA, HCA and BA series, indicating that the solubility parameter effect is approximately constant for each subset of compounds.

Relationships between $\log k'_{HA}$ or $\log k'_A$ and C No.

Linear free energy relationships predict a high degree of correlation between either $\log k'_{HA}$ or $\log k'_A$ and the number of carbon atoms in a homologous series. These correlations are evident in Tables VI and VII for the phenylalkylcarboxylic acid series and the benzoic acid series. In each series, methylene groups (CH_2) are added either between the phenyl ring and the COOH group (PAA series) or in the *p*-

TABLE VII
CORRELATION MATRIX FOR BA SERIES

Coefficients of correlation (r) expressed as percent.

	pK_a	k'_{HA}	$\log k'_{HA}$	k'_A	$\log k'_A$	β	$\log \beta$	$\sigma_{p,m}$	π	C No.
pK_a	—	13	3	8	3	11	19	(100)	3	70
k'_{HA}	—	—	96	(100)	94	97	95	13	95	79
$\log k'_{HA}$	—	—	—	96	100	93	95	3	(100)	(100*)
k'_A	—	—	—	—	94	(98)	96	9	94	76
$\log k'_A$	—	—	—	—	—	92	96	3	100	(100**)
β	—	—	—	—	—	—	99	11	91	62
$\log \beta$	—	—	—	—	—	—	—	19	94	56
$\sigma_{p,m}$	—	—	—	—	—	—	—	—	4	71
π	—	—	—	—	—	—	—	—	—	72
C No.	—	—	—	—	—	—	—	—	—	—

* *m*-Cl-BA excluded; $r = 72$ when included.

** *m*-Cl-BA excluded; $r = 67$ when included.

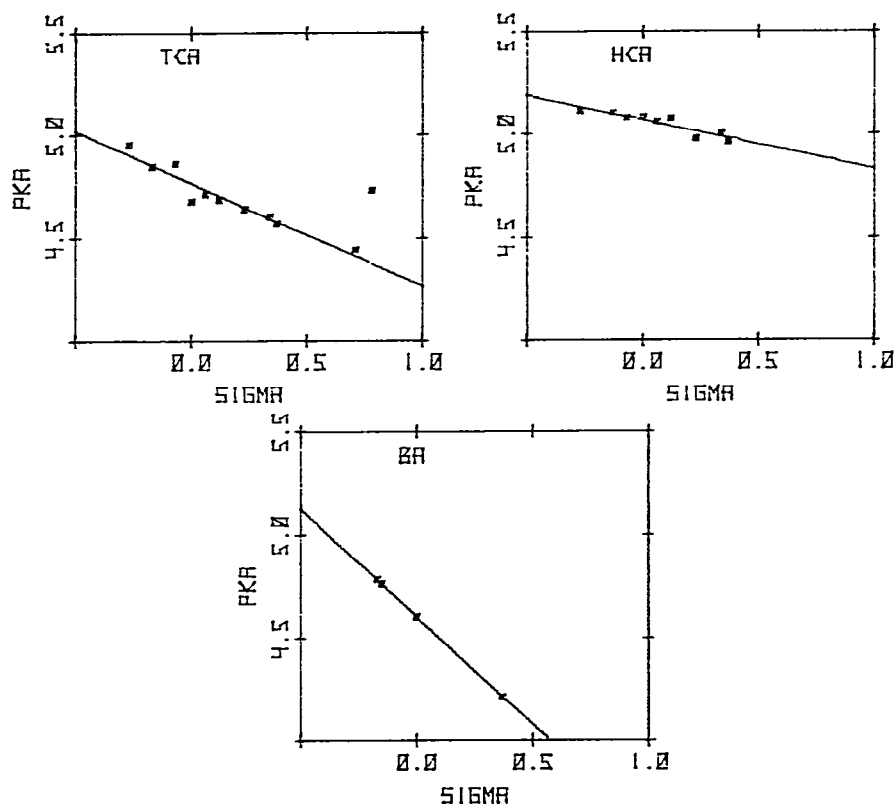


Fig. 1. Correlation plots of pK_a vs. $\sigma_{p,m}$ for TCA, HCA and BA series. $p\text{-NO}_2\text{-TCA}$ not included in regression. Regressions are significant at the following levels of confidence: TCA = 99.9991%, HCA = 99.95%, BA = 99.9995%.

position on the phenyl ring (BA series). These relationships are shown in Fig. 3; the two-parameter straight lines (eqn. 2) ignore $m\text{-Cl-BA}$ and $m\text{-Cl-2-phenylacetic acid}$ (and benzoic acid in the plot of $\log k'_{HA}$ for the PAA series).

The effects of adding methylene groups appear to be different for each conjugate acid–base species and for each series of compounds. Adding a methylene group between the phenyl ring and the COOH group (PAA series) causes an increase in capacity factor of 0.34 log units for the conjugate acid species and 0.40 log units for the conjugate base species. Adding methylene groups to the p -position (BA series) causes an increase in capacity factor of 0.37 log units for the conjugate acid species and 0.52 log units for the conjugate base species.

Relationship between k'_{HA} and k'_A

Tables IV–VII all reveal a high correlation between estimated values of k'_{HA} and k'_A . These correlations are shown in Fig. 4 where the single-parameter regression line of eqn. 3 is plotted.

The high degree of correlation between k'_{HA} and k'_A is expected from linear free

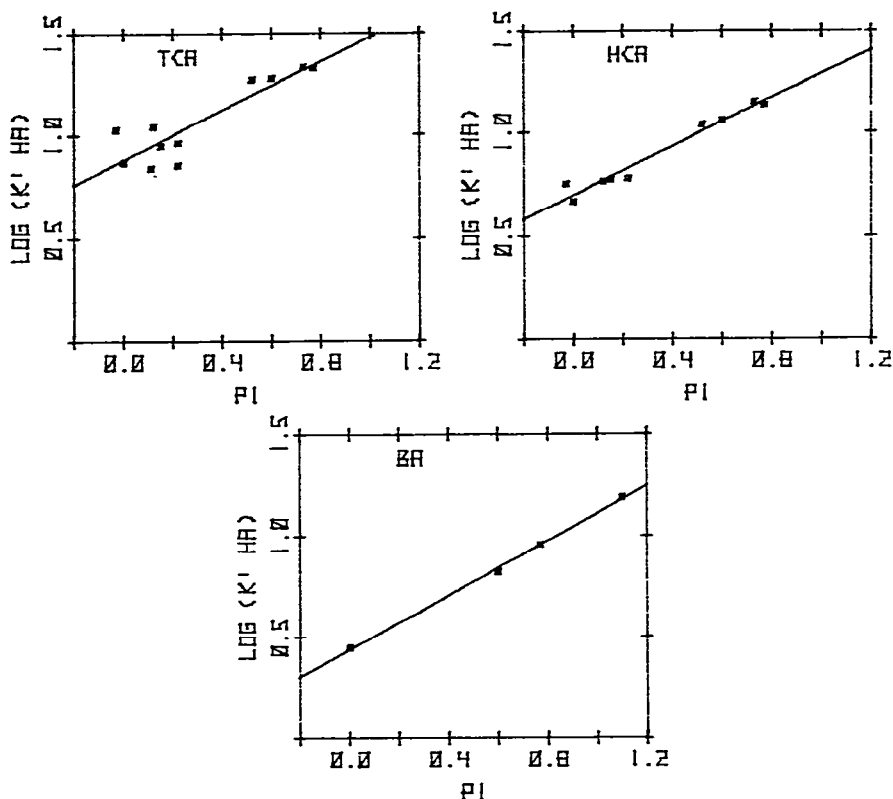


Fig. 2. Correlation plots of $\log k'_{HA}$ vs. π for TCA, HCA and BA series. Regressions are significant at the following levels of confidence: TCA = 99.97%, HCA = 99.9997%, BA = 99.90%.

energy relationships. For an unionized weak organic acid, $RCOOH$, Martin's equation²³ predicts

$$RT \ln K_{HA} = \Delta\mu_R + \Delta\mu_{COOH} \quad (5)$$

where R is the gas constant, T the temperature in $^{\circ}K$, K_{HA} the partition coefficient for the unionized solute and $\Delta\mu$ is the differential chemical potential—the free energy required to transport one mole of a given group (R or $COOH$) from the stationary phase to the mobile phase. Similarly, for an ionized weak organic acid, $RCOO^-$,

$$RT \ln K_A = \Delta\mu_R + \Delta\mu_{COO^-} \quad (6)$$

where K_A is the partition coefficient for the ionized solute. Subtraction of eqn. 6 from eqn. 5 gives

$$RT \ln \frac{K_{HA}}{K_A} = RT \ln \frac{k'_{HA}}{k'_A} = \Delta\mu_{COOH} - \Delta\mu_{COO^-} = \Delta\Delta\mu_{COO(H)} \quad (7)$$

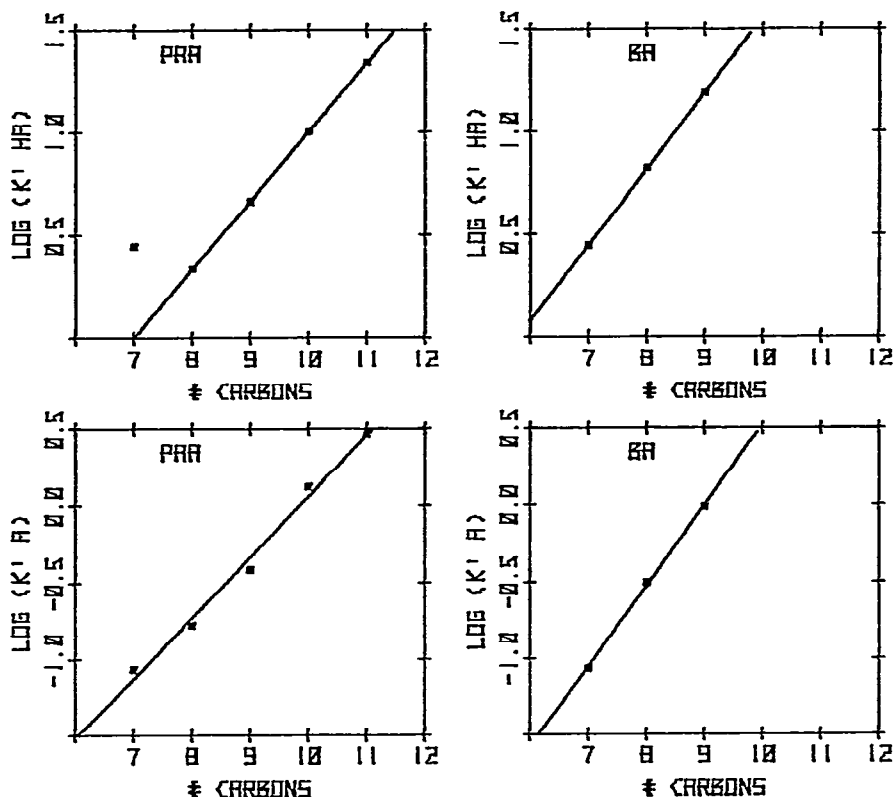


Fig. 3. Correlation plots of $\log k'_{HA}$ or $\log k'_A$ vs. C No. for PAA and BA series. *m*-Cl-BA and *m*-Cl-2-phenylacetic acid not included. BA not included in $\log k'_{HA}$ regression for PAA series. Regressions are significant at the following levels of confidence: PAA ($\log k'_{HA}$) = 99.9994%, PAA ($\log k'_A$) = 99.95%, BA ($\log k'_{HA}$) = 99.5%, BA ($\log k'_A$) = 97.5%.

where $\Delta\Delta\mu_{COO(H)}$ is the change in differential chemical potential associated with the ionization process. Thus,

$$\frac{k'_{HA}}{k'_A} = \exp(\Delta\Delta\mu_{COO(H)}/RT) \quad (8)$$

If it is assumed that $\Delta\mu_R$ is the same for both the unionized and ionized species, the relative slopes in Fig. 4 suggest that $\Delta\Delta\mu_{COO(H)}$ for a series decreases in the order BA > TCA > HCA \approx PAA. Alternatively, it could be assumed that $\Delta\Delta\mu_{COO(H)}$ is a constant in which case the relative slopes in Fig. 4 would suggest that

$$\Delta\Delta\mu_R = \Delta\mu_{R(\text{unionized})} - \Delta\mu_{R(\text{ionized})} \quad (9)$$

for a series decreases in the same order. It is possible that both of these assumptions are partially correct because of resonance interaction between the COOH and/or COO⁻ groups and the phenyl ring; the interaction would be greatest in the benzoic

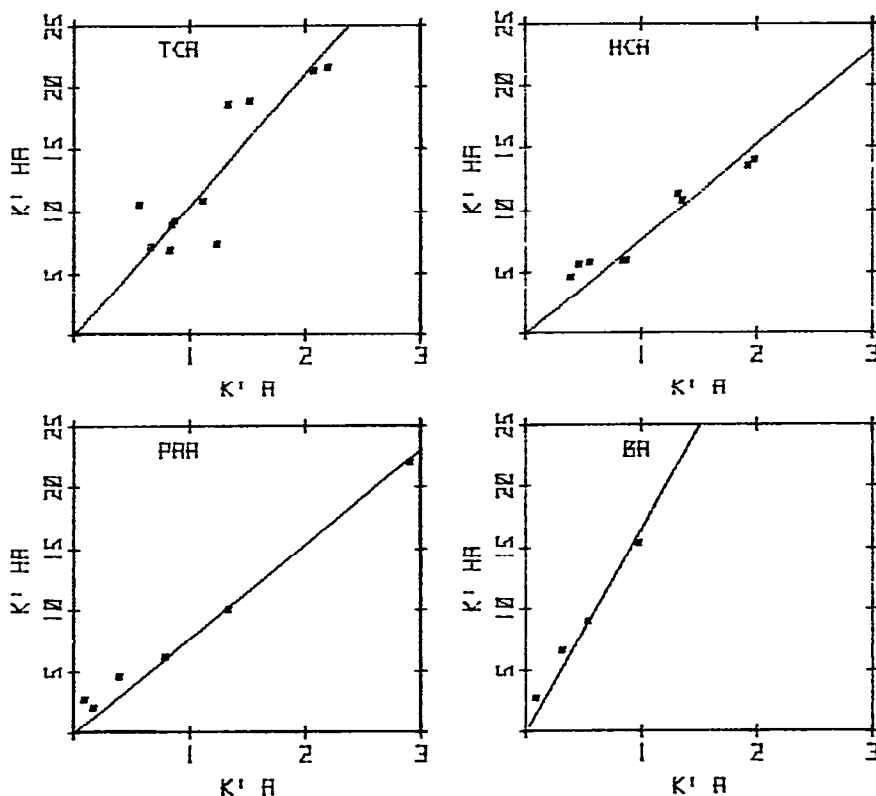


Fig. 4. Correlation plots of k'_{HA} vs. k'_A . Straight line relationships are constrained to pass through the origin (eqn. 3). Correlations are significant at the following levels of confidence: TCA = 99.95%, HCA = 99.9988%, PAA = 99.998%, BA = 99.8%.

acid series where the carboxylic acid group is attached directly to the phenyl ring; in the *trans*-cinnamic acid series, a more distant resonance interaction is possible through the conjugated methylene group; in the hydrocinnamic acid series and in the phenylalkylcarboxylic acid series, resonance interactions with the phenyl ring are not possible.

Relationship between k'_A and β

The correlations between k'_A and β (see Tables IV–VII) are all highly significant. These high correlations are seen in Fig. 5 which plots each of the four subsets of data as well as the composite 28-point set. The best least squares straight lines drawn in Fig. 5 are constrained to pass through the origin (eqn. 3).

The parameter β is a measure of the physicochemical interaction between a negatively charged solute ion and the adsorbed positively charged IIR (octylamine hydrochloride). It is evident from Fig. 5 that the interaction is approximately the same for each of the subsets and for the composite set—the slopes are TCA = 0.207, HCA = 0.216, PAA = 0.242, BA = 0.188 and ALL = 0.217. Thus, the proportional increase in the retention caused by the presence of surfactant in the system is approximately constant for each of the negatively charged solute ions.

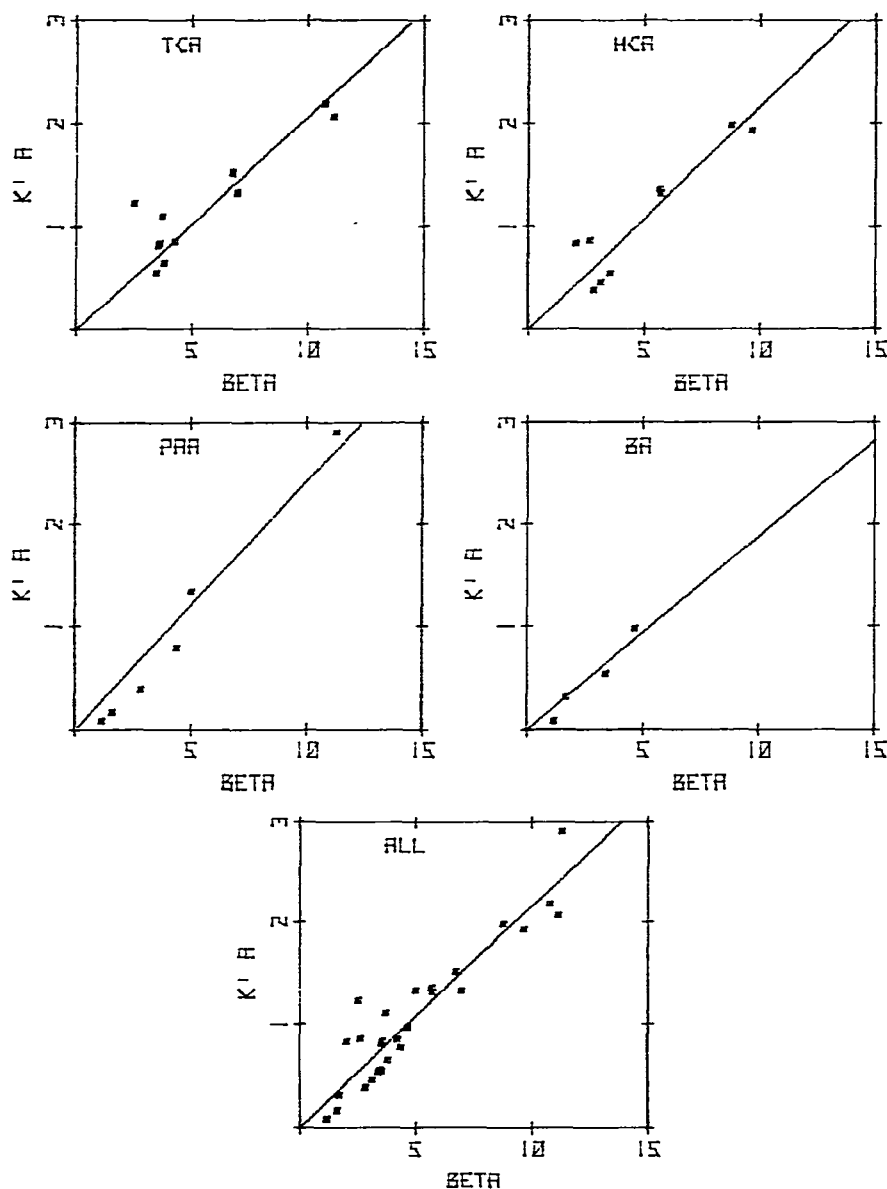


Fig. 5. Correlation plots of k'_A vs. β . Straight line relationships are constrained to pass through the origin (eqn. 3). Correlations are significant at the following levels of confidence: TCA = 99.987%, HCA = 99.96%, PAA = 99.991%, BA = 97.9%, ALL = 100.0000%.

CONCLUSIONS

In this study it has been demonstrated that Hammett $\sigma_{p,m}$ values correlate with estimated pK_a only, for the 28 aromatic monocarboxylic acids studied, and that the ion-interaction effect β correlates with k'_A with slope independent of the solute series.

These results suggest a purely electrostatic interaction between the adsorbed solute ions and the primary ion layer of adsorbed IIR on the surface. This conclusion is consistent with and lends support to the original ion-interaction model of Bidlingmeyer *et al.*¹ and its refinements^{10,11}.

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REFERENCES

- 1 B. A. Bidlingmeyer, S. N. Deming, W. P. Price, Jr., B. Sachok and M. Petrussek, *J. Chromatogr.*, 186 (1979) 419.
- 2 D. P. Wittmer, N. O. Nuessle and W. G. Haney, Jr., *Anal. Chem.*, 47 (1975) 1422.
- 3 J. H. Knox and G. R. Laird, *J. Chromatogr.*, 122 (1976) 17.
- 4 Cs. Horváth, W. Melander, I. Molnar and P. Molnar, *Anal. Chem.*, 49 (1977) 2295.
- 5 Cs. Horváth, W. Melander and I. Molnár, *J. Chromatogr.*, 125 (1976) 129.
- 6 J. C. Kraak, K. M. Jonker and J. F. K. Huber, *J. Chromatogr.*, 142 (1977) 671.
- 7 N. E. Hoffman and J. C. Liao, *Anal. Chem.*, 49 (1977) 2231.
- 8 P. T. Kissinger, *Anal. Chem.*, 49 (1977) 883.
- 9 J. L. M. van de Venne, J. L. H. M. Hendriks and R. S. Deelder, *J. Chromatogr.*, 167 (1978) 1.
- 10 R. C. Kong, B. Sachok and S. N. Deming, *J. Chromatogr.*, 199 (1980) 307.
- 11 J. H. Knox and R. A. Hartwick, *J. Chromatogr.*, 204 (1981) 3.
- 12 J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, New York, 1963.
- 13 C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley, New York, 1979.
- 14 C. M. Riley, E. Tomlinson and T. M. Jefferies, *J. Chromatogr.*, 185 (1979) 197.
- 15 G. E. P. Box, W. G. Hunter and J. S. Hunter, *Statistics for Experimenters—An Introduction to Design, Data Analysis, and Model Building*, Wiley, New York, 1978.
- 16 M. G. Natrella, *Experimental Statistics*, National Bureau of Standards Handbook 91, U.S. Government Printing Office, Washington, DC, 1963.
- 17 W. Mendenhall, *Introduction to Linear Models and the Design and Analysis of Experiments*, Duxbury, Belmont, CA, 1968.
- 18 R. O'Neill, *Appl. Statist.*, 20 (1971) 338.
- 19 S. N. Deming and S. L. Morgan, *Clin. Chem.*, 25 (1979) 840.
- 20 J. Neter and W. Wasserman, *Applied Linear Statistical Models—Regression, Analysis of Variance, and Experimental Designs*, Irwin, Homewood, IL, 1974.
- 21 L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 2nd ed., 1970.
- 22 R. Fuchs and E. S. Lewis, in E. S. Lewis (Editor), *Techniques of Chemistry, Vol. 6, Part I, Investigations of Rates and Mechanisms of Reactions*, Wiley, New York, 1974, p. 777.
- 23 A. J. P. Martin, *Biochem. Soc. Symp.*, 3 (1949) 4.