The Hammett equation and Snyder theory as a criterion for adsorption of a functional group under liquid–solid chromatography

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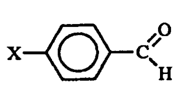
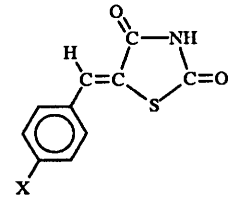
The application of the Hammett equation in a suitable form to TLC separations on silica of aromatic aldehydes, 4-X–C_6H_4–Y, and related 5-arylidene thiazolidine-2,4-diones has shown some substantial deviations to higher values from the correlation lines which are considered on the basis of Snyder theory as a proof for adsorption of the corresponding group X (from a substituent, it becomes a new adsorption centre Y′). Based on this criterion, the data of this paper and previous papers support the adsorption of group X when it is 3-OH, 4-OH, 3-NO_2, 4-NO_2 and 3-OCH_3. The adsorption of X seems to occur when its adsorptivity is similar to that of Y and the electronic interaction between X and Y is of limited importance.

Elucidation of adsorption pattern, *i.e.*, which group of a solute is adsorbed under liquid–solid chromatography such as TLC, HPLC, *etc.*, is important because of the possibility to govern the separation process and to use this type of chromatography as a method for configurational determinations.[1,2] So far, indications for adsorption pattern have been received on the basis of the Soczewiński method[2,3] and the critical value of solvent strength,[4–8] $\varepsilon_i^{\text{crit.}}$ (see below) from Snyder theory. The reaction constant, ρ, of the Hammett equation[9] is important for investigation of reaction mechanisms. Trying to use this equation for elucidation of adsorption pattern, our previous TLC study[10] has shown three substantial and puzzling deviations from the Hammett plots.

The present study reports the application of the Hammett equation in a combination with $\varepsilon_i^{\text{crit.}}$ to TLC on silica of aromatic aldehydes **1–6** as simple model compounds and the related 5-arylidenethiazolidine-2,4-diones **7–12** with a more complex structure.



1–6



7–12

X = H, CH_3, OH, OCH_3, $N(CH_3)_2$, NO_2

Theory

The Hammett equation[9] expresses the influence of a substituent X in *meta*- or *para*-position on reactivity of a reaction site Y. For TLC, it is given by eqn. (1)[10] where $R_{M(X)}$

$$R_{M(X)} = R_{M(0)} + \rho\sigma \qquad (1)$$

$$R_M \equiv \log k' = \log(1/R_F - 1) \qquad (2)$$

and $R_{M(0)}$ are the retention R_M of compounds having X ≠ H and X = H, respectively, σ is the Hammett constant of X depending on its electronic effects, ρ is a measure for the susceptibility of the adsorption centre to the electronic influence of X, k' is the retention factor in HPLC and R_F is the directly measured parameter in TLC. If there is enhanced resonance[9] between Y and electron-donating X, σ in eqn. (1) is replaced by the modified constant σ^+.

An idea about Snyder theory[4–7] can be obtained from its model, the so-called displacement model. According to this model, retention is considered as a displacement process where a sample (solute) molecule S displaces n molecules of mobile

$$S_n + nM_a \rightleftharpoons S_a + nM_n \qquad (3)$$

phase M from the adsorbent surface. The subscripts n and a denote non-adsorbed and adsorbed state, respectively.

Then the mobile phases are characterized by the following dimensionless parameters: strength, ε, measuring the dimensionless Gibbs energy ($\Delta G°/RT \ln 10$) of adsorption of the mobile phase per unit area of the adsorbent surface (having in mind eqn. (1), the greater the ε value, the weaker is the sample retention); localization, m, measuring the capability of the mobile phase for interaction *via* the available functional group(s) of the composing solvent(s) with specific adsorbent sites; polarity, P', measuring the total interaction of the mobile phase with the sample; it tunes the mobile-phase strength. The calculation of these parameters and especially of ε for mobile phases composed of two or more solvents requires a computer program.[11]

Another important point is that a solute group i is adsorbed if this process compensates the energy loss for desorption of mobile phase molecule(s) from the adsorbent surface (see the contribution of Snyder in ref. 12) [eqn. (4)], where Q_i° is the

$$Q_i^\circ - \varepsilon a_i > 0 \qquad (4)$$

dimensionless Gibbs energy of adsorption of solute group i, a_i is its relative effective area under adsorption and ε is the strength of the mobile phase used. If the mobile phase has ε greater than the following [eqn. (5)] critical for group i value then this

$$\varepsilon_i^{\text{crit.}} = Q_i^\circ / a_i \qquad (5)$$

group is not adsorbed any more (no energy of adsorption is gained).

Experimental

Compounds **1–6** were commercial products and compounds **7–12** were prepared.[13] TLC was done as in ref. 14 with adsorbent 1 = silica GF_{254}, Merck, Germany and adsorbent 2 = silufol, $UV_{254+366}$, Kavalier, Czech Republic. The solvents used were of analytical-reagent grade. The R_F values were arithmetic means of four to six measurements showing a reproducibility of ±0.02 R_F units. The mobile phases used were selected by

Table 1 Mobile phases used in TLC and their computer calculated[11] values of the dimensionless parameters strength, ε, localization, *m*, and polarity, *P′*

No.	Mobile phase	Ratio (vol. %)	ε	*m*	*P′*
1	Hexane–diethyl ether	73.6:26.4	0.300	0.64	0.81
2	Hexane–diisopropyl ether	30.1:69.9	0.300	0.10	1.71
3	Hexane–acetone	94.0:6.0	0.300	0.90	0.40
4	Hexane–ethyl acetate	84.7:15.3	0.300	0.59	0.76
5	Hexane–methylenechloride–diethyl ether	83.4:10.0:6.6	0.300	0.56	0.58
6	Chloroform–diisopropyl ether	48.7:51.3	0.300	0.05	3.23
7	Chloroform–ethyl acetate	92.4:7.6	0.300	0.11	4.12
8	Toluene–diethyl ether	90.4:9.6	0.300	0.25	2.44
9	Toluene–methyl *tert*-butyl ether	96.5:3.5	0.300	0.23	—
10	Toluene–tetrahydrofuran	87.9:12.1	0.300	0.48	2.59
11	Hexane–diethyl ether	48.0:52.0	0.350	0.65	1.50
12	Hexane–acetone	84.4:15.6	0.350	0.92	0.88
13	Tetrachloromethane-methyl *tert*-butyl ether	86.8:13.2	0.350	0.73	—
14	Toluene–methy *tert*-butyl ether	92.8:7.2	0.350	0.45	—
15	Hexane–diethyl ether	34.0:66.0	0.380	0.66	1.88
16	Hexane–methyl *tert*-butyl ether	50.4:49.6	0.380	0.81	—
17	Hexane–tetrahydrofuran	62.4:37.6	0.380	0.99	1.57

Table 2 Values of the dimensionless TLC retention, R_M,[a] of aromatic aldehydes **1–6**, values of ρ for the 'true Hammett plots'[b] and the corresponding correlation coefficient, *r*

Solute		R_M with adsorbent 1 and indicated mobile phase									
No.	X	1	2	3	4	5	6	7	8	9	10
1	H	−0.21	−0.63	0.03	−0.14	0.16	−0.95	−0.87	−0.31	−0.07	−0.66
2	CH_3	−0.21	−0.66	0.05	−0.14	0.18	−1.06	−0.79	−0.29	−0.02	−0.66
3	OH	0.79	−0.21	0.95	0.69	1.38	−0.16	0.41	0.75	1.00	0.03
4	OCH_3	0.23	−0.09	0.39	0.21	0.52	−0.72	−0.58	0.00	0.16	−0.41
5	$N(CH_3)_2$	0.50	0.21	0.55	0.39	0.91	−0.63	−0.27	0.33	0.48	−0.23
6	NO_2	0.31	0.00	0.52	0.25	0.58	−0.79	−0.69	−0.21	−0.02	−0.55
	ρ	−0.45	−0.53	−0.32	−0.33	−0.47	−0.23	−0.36	−0.40	−0.33	−0.27
	r	0.97	0.96	0.98	0.97	0.98	0.84	0.99	0.98	0.99	0.97

[a] The values of R_M are derived from the corresponding experimental R_F values by eqn. (2). [b] The 'true Hammet plots', R_M *vs.* σ^+, are constructed on the basis of compounds **1**, **2** and **5** having non-adsorbing group X. The values of σ^+ are from Table 4.

Table 3 Values of the dimensionless TLC retention, R_M,[a] of thiazolidinediones **7–12**, values of *ρ* for the 'true Hammett plots'[b] and the corresponding correlation coefficient, *r*

Solute		R_M with adsorbent 2 and indicated mobile phase							
No.	X	1	11	12	13	14	15	16	17
7	H	0.60	−0.27	1.00	0.14	0.45	−0.45	−1.06	−0.55
8	CH_3	0.58	−0.27	0.95	0.16	0.48	−0.50	−1.06	−0.55
9	OH	1.38	0.45	2.00	1.12	1.28	0.19	0.10	0.07
10	OCH_3	0.91	0.09	1.19	0.45	0.63	−0.16	−0.31	−0.31
11	$N(CH_3)_2$	1.19	0.27	1.38	0.63	0.75	0.00	−0.10	−0.10
12	NO_2	0.95	0.10	1.28	0.52	0.58	−0.16	−0.31	−0.33
	ρ	−0.37	−0.34	−0.25	−0.30	−0.18	−0.29	−0.60	−0.28
	r	0.96	0.97	0.93	0.98	0.99	0.94	0.97	0.97

[a] The values of R_M are derived from the corresponding experimental R_F values by eqn. (2). [b] The 'true Hammett plots', R_M *vs.* σ^+, are constructed on the basis of compounds **7**, **8** and **11** having non-adsorbing group X. The values of σ^+ are from Table 4.

the computer program[11] LSChrom Ver. 2, 1994. Details about such a computer choice are given in ref. 15.

Results and discussion

The mobile phases 1–17 used are given in Table 1 together with their computer calculated[11] values of strength, ε, localization, *m*, and polarity, *P′*. Mobile phases 1–10 used for TLC of compounds **1–6** are with a constant ε value (0.300) but they differ significantly in their values of *m* and *P′*. Therefore these mobile phases are similar but not equivalent. The same is valid for mobile phases 11–14 with ε = 0.350 and mobile phases 15–17 with ε = 0.380 all of them used for TLC of compounds **7–12**. The overall variation of *m* and *P′* was $0.05 \leqslant m \leqslant 0.99$ and $0.40 \leqslant P' \leqslant 4.12$. The expected tuning effect of *P′* on ε is seen as a greater value of *P′* means a stronger interaction of the mobile phase with the sample, *i.e.*, a weaker retention and *vice versa*. From mobile phases 1–10 with the same ε, mobile phase 3 has the lowest *P′* (0.40) and mobile phase 7 has the greatest *P′* (4.12) which accounts for the weaker retention and smaller R_M of any compound with mobile phase 7.

The values of the TLC retention R_M of aromatic aldehydes **1–6** and related thiazolidinediones **7–12** are given in Table 2 and Table 3, respectively. The values of *ρ* of the 'true Hammett

Table 4 Data[4,9] for the dimensionless parameters Q_i°, a_i, $\varepsilon_i^{crit.}$ on silica and σ_i^+ for the groups i^a participating in the compounds studied

	Group i	Q_i°	a_i	$\varepsilon_i^{crit.}$	σ_i^+
X	**C_6H_5-H**	1.50	6.00	0.25	0.00
	Ar-CH_3	0.11	0.80	0.14	−0.30
	Ar-OH	4.20	7.60	0.55	−0.92
	Ar-OCH_3	1.83	4.60	0.40	−0.78
	Ar-$N(CH_3)_2$	2.52	9.20	0.27	−1.70
	Ar-NO_2	2.77	7.50	0.37	0.81
Y	**Ar-CHO**	3.48	8.30	0.42	
	R-$CONH_2$	9.60	10.30	0.93	
	R-S-R	2.94	7.40	0.40	
	Ar-CH=CR_2	0.50	2.00	0.25	

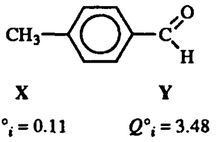
[a] In bold.

plots' (see below) and the corresponding correlation coefficient, r, are also included. Compounds **7**–**12** were studied with adsorbent 2 because of some tailing on adsorbent 1.

Table 4 summarizes the adsorption properties (Q_i°, a_i and $\varepsilon_i^{crit.}$) of the groups i participating in the compounds studied and their values of σ^+ used.

Let us discuss in detail the agreement of the data for R_M obtained with the Hammett eqn. (1). Passing from a reaction to a case where adsorption takes place, the Hammett equation could have the following particularity: except the usual cases when X is a non-adsorbing substituent modifying the electron density of the adsorption centre Y, there will be cases when X transforms from a substituent to a new adsorption centre Y′. The latter is possible if Gibbs energy of adsorption Q_X° is similar to Q_Y° (from compounds **1**–**12**, see compounds **2** and **3**, respectively) and the interaction between Y and Y′ is small because the values of Q_i° refer to such a case.

2



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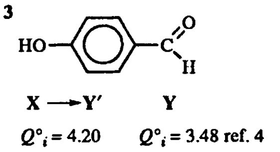

The presence of a second adsorption centre Y′ will lead to a better adsorption of the solute and its R_M will deviate only to higher values from the Hammett correlation line. Group X in the compounds studied is in *para*-position enabling its enhanced resonance[9] with Y. Thus, the hydroxy group X in compound **3** could either increase the adsorption of Y by its positive resonance effect or become an adsorbing group Y′ leaving Y unaffected to a significant extent.

This discussion shows that the experimental study of the Hammett eqn. (1) is important. The construction of the corresponding plots should exclude the compounds where both X and Y are adsorption centres. We will call such plots 'true Hammett plots'. To this end, we combined the Hammett equation with Snyder theory using the following procedure. The values of ε given in Table 1 were compared with the values of $\varepsilon_i^{crit.}$ of the groups participating in the compounds studied (Table 4) on the basis of the following relationships arising from eqn. (5).

$$\varepsilon \begin{cases} > \varepsilon_i^{crit.}, & \text{the group X or Y is non-adsorbing} \\ \approx \varepsilon_i^{crit.}, & \text{the conclusion is uncertain} \\ < \varepsilon_i^{crit.}, & \text{the group X or Y is adsorbing} \end{cases}$$

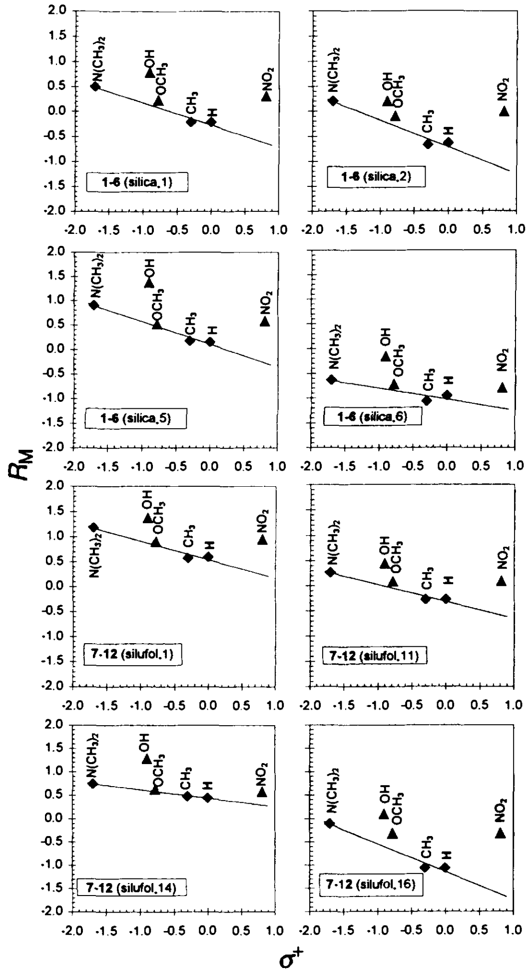

Fig. 1 Illustrations of the 'true Hammett plots' and the deviations from them in the TLC cases studied. The adsorbent and the mobile phase used are given in parentheses.

This comparison showed that the phenyl group (benzene ring) is non-adsorbing in all cases studied because $\varepsilon_{C_6H_6}^{crit.} = 0.250$ is less than ε of the mobile phases used (0.300–0.380). This comparison also showed that the compounds with X = H, CH_3 and $N(CH_3)_2$ in the *para*-position should satisfy the Hammett equation because X is non-adsorbing and Y (CHO for **1**–**6** and the heterocyclic ring for **7**–**12**) is adsorbing. Thus, ε used varies in the range 0.300–0.380 being greater than $\varepsilon_i^{crit.}$ for these three groups X, namely 0.25, 0.14 and 0.27, respectively. The corresponding 'true Hammett plots' were constructed and the points for the remaining compounds with X = OH, OCH_3 and NO_2 were incorporated to these plots as illustrated in Fig. 1. In all cases studied, the Hammett equation was really obeyed by the compounds with X = H, CH_3 and $N(CH_3)_2$ in the *para*-position as best agreement (r in the range 0.84–0.99) was obtained with the modified substituent constants σ^+ showing the presence of the expected enhanced resonance from X to Y. The 'true Hammett plots' have the expected[4] negative ρ values which are in the range from −0.60 to −0.18. These values correspond to an increase in the electron density and adsorption energy of Y by an electron-donating group X, *i.e.*, the group Y in these cases has possibility for a stronger hydrogen bonding to the silanol hydroxy groups of the adsorbent. Such a bonding is the most important with mobile phase 16 when ρ has the greatest absolute value of 0.60.

Substantial deviations from the 'true Hammett plots' were established for all compounds with X = OH and NO_2 in the *para*-position. Having in mind the above discussion, these deviations support the adsorption of the two groups and indicate that their electronic influence on Y is of limited importance. Except in the case of TLC with mobile phase 16, the compounds with X = 4-OCH_3 did not show considerable deviations and therefore 4-OCH_3 should not be adsorbed in these cases. In comparison with OH for instance, the methoxy group has smaller Q_i°, value (Table 4) and weaker adsorption

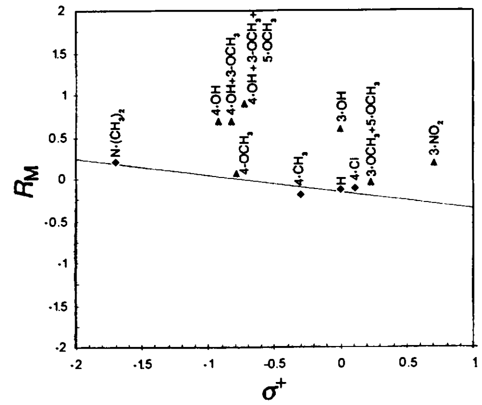

Fig. 2 'True Hammett plot' ($\rho = -0.20, r = 0.88$) and the deviations from it obtained on the basis of the R_F on silica reported in ref. 16. The values of σ^+ are from ref. 9. In the cases when more than one substituent is available on the benzene ring, the additivity rule is used for calculation of σ^+.

which enables its enhanced resonance with Y to become a dominant factor in the majority of the cases with X = 4-OCH_3.

The procedure used was applied also to the R_F values of a series of aromatic aldehydes X–C_6H_4–CHO from ref. 16. The corresponding Hammett plot (see Fig. 2) shows apparent deviations to a greater adsorption for the compounds with X = 3-OH, 4-OH and 3-NO_2, *i.e.*, adsorption of these groups.

On the basis of this criterion, the deviations in ref. 10 denote adsorption of 3-NO_2 and 3-OCH_3. On the contrary, 4-OCH_3 is not adsorbing which supports the above mentioned idea about the dominant role of the enhanced resonance in a similar case.

Conclusions

The present application of the Hammett equation to TLC has shown substantial deviations to higher R_M values from the corresponding plots which are more important for deriving conclusions about the adsorption pattern than the values of ρ.

Acknowledgements

This study was supported by the National Research Fund, Bulgaria.

References

1 M. Palamareva, M. Haimova, J. Stefanovsky, L. Viteva and B. Kurtev, *J. Chromatogr.*, 1971, **54**, 383.
2 M. D. Palamareva and I. D. Kozekov, *J. Chromatogr.*, 1992, **606**, 113.
3 E. Soczewiński, *J. Chromatogr.*, 1987, **388**, 91, and the refs. cited therein.
4 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
5 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley, New York, 2nd ed., 1979.
6 L. R. Snyder, in *High-performance Liquid Chromatography*, ed. Cs. Horváth, Academic Press, New York, 1983, vol. 3, p. 157.
7 L. R. Snyder, J. L. Glajch and J. J. Kirkland, *Practical HPLC Method Development*, Wiley, New York, 1988.
8 M. Palamareva, I. Kozekov and I. Jurova, *J. Chromatogr. A*, 1994, **670**, 181.
9 N. S. Isaacs, *Physical Organic Chemistry*, Longman, Harlow, 1987.
10 M. D. Palamareva, B. J. Kurtev and I. Kavrakova, *J. Chromatogr.*, 1991, **545**, 161.
11 M. D. Palamareva and H. E. Palamarev, *J. Chromatogr.*, 1989, **477**, 235.
12 E. Soczewiński, *Anal. Chem.*, 1969, **41**, 179.
13 S. N. Baranov, *Zh. Obshch. Khim.*, 1962, **32**, 1230.
14 L. R. Snyder, M. D. Palamareva, B. J. Kurtev, L. Z. Viteva and J. N. Stefanovsky, *J. Chromatogr.*, 1986, **354**, 107.
15 M. D. Palamareva, *J. Chromatogr.*, 1988, **438**, 219.
16 Y. C. Young, *J. Chromatogr.*, 1977, **130**, 392.

Paper 5/05605E
Received 23*rd August* 1995
Accepted 21*st November* 1995