

## Thin-Layer Chromatography of 2-Imino-3-(Substituted Aryl)-1-Thiazolidin-4-Ones and Their Intermediates, Chloroacetanilides

Minbale Aschale

Ethiopian Institute of Water Resources, Addis Ababa University, Ethiopia.

### ABSTRACT

Chloroacetanilides, prepared by the reaction of primary amines with chloroacetylchloride in benzene, were cyclocondensed with potassium thiocyanate in acetone to obtain 2-imino-3-(substituted aryl)-1-thiazolidin-4-ones. Intermediates and final products have been chromatographed on silica gel G. thin-layers using one- and two-component solvent systems and effects of various properties of developing solvents and migrating species on  $R_f$  values have been investigated beside the separation and identification.

### I. INTRODUCTION

Although thin-layer chromatographic (TLC), being superior to other techniques in providing rapid and better separation, is used in routine in the identification and qualitative separation of organic compounds as one of the classical methods but mechanistic aspects of analytes migration and diverse interactions of properties of solvents and analytes leading to various effects of analytes structures, viz. nature and position of substituted group(s), number and size of ring(s) etc., on  $R_f$  values of high academic importance are usually ignored. A large number of publications on inorganic and organic compounds have dealt with the impact of physico-chemical properties related to the molecular structure of analytes in conjugation with developing solvents properties on their migration rates besides synthesis and resolution. In our previous reports on organic compounds, azomethines [1-4] and thiazolidinones [5, 6], we have described correlations of  $R_f$  with solvents properties, viz. polarity, dielectric constant etc., structural features of analytes, viz. spectral parameters, nature and position of substituted groups etc. and qualitative and quantitative separations including determination of limits of separations by TLC method. In continuation of our previous work we have thought it worthwhile to conduct TLC studies on a few chloroacetanilides, obtained by the reaction of primary amines with chloroacetylchloride, and their cyclocondensation products with potassium thiocyanate, iminothiazolidinones, to look at the possibility of separations of their diverse multinary mixtures, and to investigate the effects of properties of developing solvents and structures of analytes on  $R_f$  values and

mechanism of differential migration of solutes in various solvents which have not been reported as yet on the mentioned new compounds.

### II. EXPERIMENTAL

#### Materials

Chloroacetanilides, obtained by the reaction of various primary amines with chloroacetylchloride in benzene, were cyclocondensed with potassium thiocyanate in acetone to synthesize 2-imino-3-(substituted aryl)-1-thiazolidin-4-ones [7]. Structures of all these compounds have been supported by their spectral studies and molecular weights [7]. In synthetic work reagent-grade chemicals were used as received whereas in TLC studies HPLC grade solvents were used.

#### Procedure

TLC plates of 20 x 20 cm size coated with silica gel G. (gypsum binder) were activated by heating in oven at 60 °C before loading. Activated plates were loaded with sample solutions in acetone by applying series of spots in a line 2 cm from the lower edge of the plates as small drops using glass capillaries.

Oven-dried loaded plates were developed in rectangular glass chambers with ground-in-lids by ascending technique. To obtain reproducible results the development chambers were presaturated with solvents before use. When development had proceeded for about 6-7 cm the plates were removed from the chamber(s). Owing to light colours of the analytes their spots were visualized in iodine vapours.

### III. RESULTS AND DISCUSSION

Perusal of  $R_f$  data (Table 1) reveals that irrespective to the nature and position of substituent in benzene ring of both series of compounds with substituents, chloroacetanilides and iminothiazolidinones, their  $R_f$  values are higher than respective non-substituted compound in all the pure solvents whether oxygen-containing or non-oxygen-containing. It is also interesting to observe that cyclization of acetanilide group that is introduction of thiazolidinone moiety adversely affects the  $R_f$  values irrespective to the nature of solvent almost in all cases.

Position of substitution seems to have contribution in establishing  $R_f$  values; in bromo substituted acetanilides and iminothiazolidinones  $R_f$  values are in para  $\geq$  meta order. The effect of nature of substituted group on  $R_f$  values has been studied in para-substituted – chloroacetanilides and – iminothiazolidinones, as in this position steric effects are almost negligible and nature of substituent predominates; the  $R_f$  order Br > N(CH<sub>3</sub>)<sub>2</sub> evidently show that increase of electronegativity adversely affects

the  $R_f$  values irrespective to nature of solvent or compound structure.

In binary solvent mixtures abnormally higher  $R_f$  values than those obtained in their pure solvents, most probably could be due to formation of hemiacetals or acetals owing to enhanced protonation of alcohol in presence of benzene inert solvent in mixtures.

Differential migration of analytes on gel layers is governed by different numbers and strengths of hydrogen bonds formed by silanol OH and Si-O-Si with analytes electronegative atoms and hydrogen atoms attached with them and their interaction with solvation energy or dielectric constant of developing solvents.

In order to test the application of TLC method in the analysis of these compounds, various binary and ternary mixtures of chloroacetanilides and iminothiazolidinones were spotted and qualitatively resolved (Table 2). The  $R_f$  values have been found to be almost same whether compounds migrated individually or in mixture under similar conditions of temperature, solvent and thin-layer thickness.

**Table 1: Spot colours and  $R_f$  values of chloroacetanilides and iminothiazolidinones**

Compound	Spot colour	$R_f \times 100$										$C_6H_6$ -EtOH (v/v)				
		MeOH	EtOH	n-PrOH	BuOH	Me <sub>2</sub> CO	Et <sub>2</sub> O	MeCN	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	CHCl <sub>3</sub>	8:2	6:4	5:5	4:6	2:6
		C <sub>8</sub> H <sub>8</sub> ClNO	Orange	91	90	82	98	92	00	97	00	00	00	91	98	98
C <sub>8</sub> H <sub>7</sub> BrClNO-m	Yellow	93	72	84	92	98	00	97	00	00	00	91	98	97	89	93
C <sub>8</sub> H <sub>7</sub> BrClNO-p	Yellow	86	84	84	94	97	00	97	00	00	00	96	98	95	87	93
C <sub>8</sub> H <sub>7</sub> Cl <sub>2</sub> NO-m	Yellow	94	74	86	94	98	00	97	00	00	00	95	98	98	89	94
C <sub>8</sub> H <sub>7</sub> IClNO-o	Golden red	89	88	92	96	95	00	98	00	00	00	98	98	97	93	93
C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O-p	Violet	74	86	82	86	92	00	92	00	00	00	89	98	95	86	91
C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> OS	Light red	87	88	88	92	92	00	97	00	00	00	95	98	95	86	93
C <sub>9</sub> H <sub>7</sub> BrN <sub>2</sub> OS-m	Orange	91	74	82	87	98	00	95	00	00	00	98	98	98	84	93
C <sub>9</sub> H <sub>7</sub> BrN <sub>2</sub> OS-p	Golden red	89	82	86	92	98	00	97	00	00	00	96	98	95	87	93
C <sub>9</sub> H <sub>7</sub> ClN <sub>2</sub> OS-m	Yellow	93	78	88	93	98	00	97	00	00	00	96	98	98	87	94
C <sub>9</sub> H <sub>7</sub> IN <sub>2</sub> OS-o	Yellow	87	88	80	92	95	00	95	00	00	00	96	98	95	89	94
C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> OS-p	Light gray	85	84	84	65	92	00	92	00	00	00	89	98	95	84	89

**Table 2: Qualitative resolution of multinary mixtures of compounds**

S. No.	Mixture resolved	Spot color	R <sub>f</sub>	Resolving solvent
1	C <sub>8</sub> H <sub>7</sub> BrClNO-p	Yellow	86	Methanol
	C <sub>8</sub> H <sub>7</sub> Cl <sub>2</sub> NO-m	Yellow	94	
	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O-p	Violet	74	
2	C <sub>8</sub> H <sub>8</sub> CINO	Orange	90	Ethanol
	C <sub>8</sub> H <sub>7</sub> BrClNO-m	Yellow	72	
3	C <sub>8</sub> H <sub>7</sub> ICINO-o	Golden red	92	n-Propanol
	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O-p	Violet	82	
4	C <sub>8</sub> H <sub>8</sub> CINO	Orange	98	Butanol
	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O-p	Violet	86	
5	C <sub>9</sub> H <sub>7</sub> ClN <sub>2</sub> OS-m	Yellow	93	Methanol
	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> OS-p	Light gray	85	
6	C <sub>9</sub> H <sub>7</sub> BrN <sub>2</sub> OS-m	Orange	74	Ethanol
	C <sub>9</sub> H <sub>7</sub> BrN <sub>2</sub> OS-p	Golden red	82	
	C <sub>9</sub> H <sub>7</sub> IN <sub>2</sub> OS-o	Yellow	88	
7	C <sub>9</sub> H <sub>7</sub> BrN <sub>2</sub> OS-m	Orange	87	Butanol
	C <sub>9</sub> H <sub>7</sub> ClN <sub>2</sub> OS-m	Yellow	93	
	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> OS-p	Light gray	65	

#### IV. ACKNOWLEDGEMENT

The author thanks the Ethiopian Institute of Water Resources, Addis Ababa University and Haramaya University for providing financial support and Prof. R.K.Upadhyay for his valuable comments.

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Author, Minbale Aschale, is studying his PhD in water and Health at Ethiopian Institute of Water Resources, Addis Ababa University and has M.Sc. in Chemistry and B.Sc. in Applied Chemistry. He published four original papers in the international journals.