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Effect of Ionic Surfactants on the Resolution of Amines of Hydrated Stannic Oxide Impregnated Thin Layer Chromatography

SHAIL KULSHRESTHA†, ALOK AWASTHI and S.K. DABRAL*
Department of Chemistry, Pt. L.M.S. Government Post Graduate College, Rishikesh-249 201, India
E-mail: dabral.sk@gmail.com

The effect of ionic surfactants on the behaviour of various amines on hydrated stannic oxide impregnated silica gel thin layer chromatography was observed by employing various developing systems of different nature, with or without surfactant solutions of different concentrations. The behaviour of amines was also observed on unimpregnated thin layer chromatography for comparison purpose. Some of the important binary separations are reported.

Key Words: Ionic surfactants, Amines, Stannic oxide layers.

INTRODUCTION

Because of the excellent resolving power, rapidity, simplicity and low cost, silica gel thin layer chromatography has become an indispensable technique in almost all scientific and practical fields connected with identification and separation of organic compounds. A useful improvement in the separations can be achieved by introducing the electrostatic interaction between charged solutes and ionic micelles. The unusual properties of aqueous surfactant micelles have been shown to be a novel, highly effective mobile phase in liquid chromatography for the separation of various organic compounds[1]. The effect of miceller systems on solublization processes and chromatographic behaviour of wide variety of organic compounds have been described[2]. Many hydrophobic, amphiphilic and even some hydrophilic molecules interact differently with micelle. Further investigations using a wider variety of surfactants in mobile phases are bound to yield interesting results.

Chromatographic behaviour of amines on thin layers are reported by various workers[3] but only a few attempts are reported on the use of surfactants in the separation of amines on impregnated silica gel thin layer chromatography[4]. Insoluble hydrated oxides have unusual ion-exchange properties and have a promising separation potentiality[5]. We observed the effect of increasing concentration of ionic surfactant on the resolution of some aliphatic and aromatic amines on hydrated stannic oxide impregnated thin layer chromatography, in various developing systems with or without 5, 10 and 15 mML^{-1} of surfactant solutions. The behaviour of amines on unimpregnated thin layer chromatography under identical conditions was also observed,

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†Department of Chemistry, D.B.S. Post Graduate College, Dehradun-249 201, India.

for comparison purpose. The advantages of aqueous miceller developing systems over traditional organic and mixed developing systems are discussed. Some of the important separations achieved are repoted.

EXPERIMENTAL

An Stahl type movable thin layer chromatographic applicator was used to prepare thin layers of absorbents on glass plates (5 cm × 20 cm). Sodium dodecyl sulphate, amines and other chemicals and solvents used were of AR grade.

Nearly 2 % test solutions of amines in 70 % alcohol or acetone were prepared and 2-4 μg amount is applied for spotting on thin layers.

Hydrated stannic oxide used as absorbent, was prepared by mixing 0.1 M solution of sodium stannate in demineralized water and 0.1 M solution of ammonium sulphate in the volume ratio of 1:1. The product was kept overnight, filtered off and washed with distilled water and then dried at 60 ºC to get white crystalline material of required grain size. Slurry of 50 g silica gel G (E. Merk) in 100 mL of demineralized water was prepared by mixing 20 g of hydrated stannic oxide, prepared as above. The slurry is spread over the glass plates, with the help of an applicator to prepare the chromatographic plates of 0.5 mm thickness. The plates were dried in open and then activated for 4 h at 60 ºC, before use.

Following developing solvent systems were employed to observe the resolution of amines, with or without 5, 10 and 15 m ML^{-1} sodium dodecyl sulphate.

(i) Chloroform: ethanol (1:1), (ii) benzene: ethanol (2:1), (iii) acetone: methanol (2:1), (iv) benzene: ethyl acetate (2:1).

RESULTS AND DISCUSSION

Table-1 presents the R_f values of amines in various developing systems. In most of the developing systems the spots of amines were found to be compact and well defined on hydrated stannic oxide thin layer chromatography in comparison to plain silica gel thin layer chromatography, in which the spots show some trailing[6]. It has been observed that in most of the cases the movement of amines is comparatively less than that observed on unimpregnated thin layer chromatography. Thus the hydrated stannic oxide thin layer chromatography serve as a good absorbent for amines and its immobilization on the thin layer chromatography retards the movement of various amines to different extent. On the unimpregnated silica gel thin layer chromatography, however, there is no such retardation force and hence a high R_f values were observed than on stannic oxide thin layer chromatography. The R_f values of amines depend on absorptivity and also on the kind of mobile phase used.

The phenomenon of partition, adsorption as well as ion-exchange mechanism play an important role and regulate the behaviour of amines on thin layer chromatography impregnated with inorganic ion-exchangers. The selectivity of the exchanger is also one of the significant advantages of the impregnated thin layer chromatography. By introducing ionic surfactants in mobile phase, the electrostatic interactions between

TABLE-1

R_f VALUES* OF AMINES ON STANNIC OXIDE IMPREGNATED THIN LAYERS

Amines	Devloping solvents															
	S1				S2				S3				S4			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Methylamine	36	36	34	34	39	38	38	36	31	27	24	22	21	19	18	16
Ethylamine	34	33	32	32	31	28	26	26	29	26	24	21	24	21	21	19
Aniline	39	39	38	38	70	64	66	63	78	64	71	67	71	68	68	66
o-Toluidine	47	47	36	44	65	65	62	59	72	68	66	63	66	64	62	62
m-Toluidine	41	41	40	40	51	57	59	58	64	61	58	58	59	56	56	54
p-Toluidine	33	32	31	31	56	56	54	53	61	58	56	56	57	54	53	51
o-Chloro aniline	72	70	71	70	78	76	74	73	83	80	78	77	78	76	76	74
m-Chloro aniline	61	61	59	58	70	68	64	61	76	73	73	69	71	68	67	64
p-Chloro aniline	56	54	54	53	69	64	59	59	73	68	66	63	66	63	62	62
o-Nitro aniline	82	80	78	78	76	69	68	68	84	79	77	75	78	74	73	73
m-Nitro aniline	71	71	69	69	63	62	60	59	71	67	64	64	63	60	58	56
p-Nitro aniline	56	55	54	54	54	54	52	51	59	56	53	53	52	52	50	49
o-Amino phenol	44	43	42	41	53	50	49	48	64	59	59	56	61	59	57	56
m-Amino phenol	36	36	34	32	48	46	43	42	64	59	59	56	61	59	57	56
p-Amino phenol	21	22	20	20	36	35	34	34	50	49	47	46	43	42	40	39
Benzyl Amine	43	39	38	37	51	49	47	46	62	61	60	59	56	55	55	53
α-Naphthyl amine	38	34	34	33	31	28	27	26	41	38	37	36	34	33	33	31

*Average of two identical runs, S1 = Chloroform: Ethanol, S2 = Benzene: Ethanol, S3 = Acetone: Methanol, S4 = Benzene: Ethyl acetate; (A = without SDS, B = 5 m ML^{-1} SDS, C = 10 m ML^{-1} SDS, D = 15 m ML^{-1} SDS).

charged solutes and ionic micelles can be achieved which not only modify partition coefficient between micelles and aqueous phase but also modify the interaction with stationary phase because the increase in polarity of the solute reduces the partition coefficient between the stationary phase and aqueous phase. The adsorption of surfactant on this phase can introduce a partial ionic character with an additional repulsive or attractive mechanism[7].

The thin layer chromatographic separation of positionally isomeric primary amines is of interest. For example in the case of *ortho*, *meta* and *para* nitro aniline, the R_f values decreased in order *i.e.*, *ortho* > *meta* > *para*[8]. Although the movement of amines is not appreciably affected by the addition of surfactants to the mobile phase solvents. However the compactness of the spots is improved. But, increasing the concentration of surfactant in the mobile phase tended to decrease the movement of the amines. The behaviour is to be expected since increasing the surfactant concentration increases number of micelles in the mobile phase[9]. Further, the observations indicated that the presence of surfactants in the mixed developing systems significantly increases the sharpness and compactness of the spots, resulting in faster and cleaner separations. Therefore the use of miceller developing systems, which increase the resolution of components, was found to offer a significant advantage over traditional developing systems[10]. Thus, due to better resolutions and compactness of the spots and the separation potentialities of aqueous solution of sodium dodecyl sulphate micelles has been found to be a novel and effective mobile phase for the separation of aliphatic and aromatic amines on thin layer chromatography impregnated with hydrated stannic oxide inorganic ion-exchangers. Some selective separations of aliphatic and aromatic amines achieved are reported in Table-2.

TABLE-2
BINARY SEPARATION OF AMINES ON STANNIC OXIDE THIN LAYER CHROMATOGRAPHY

S. No.	Separation (R_f)	From (R_f)	Solvent system
1	Aniline (39)	*o*-Chloro aniline (72)	S1A
2	Aniline (39)	*o*-Nitro aniline (82)	S1A
3	Aniline (39)	*m*-Nitro aniline (71)	S1A
4	*p*-Toluidine (32)	*o*-Nitro aniline (80)	S1B
5	*p*-Amino phenol (20)	*o*-Amino phenol (44)	S1B
6	*o*-Amino phenol (40)	*o*-Nitro aniline (82)	S1D
7	*p*-Amino phenol (36)	*o*-Chloro aniline (78)	S2B
8	α-Naphthyl amine (26)	Aniline (63)	S2D
9	α-Naphthyl amine (26)	*o*-Nitro aniline (68)	S2D
10	*p*-Nitro aniline (59)	*o*-Nitro aniline (68)	S3A
11	*p*-Amino phenol (49)	*o*-Nitro aniline (73)	S3D
12	α-Naphthyl amine (31)	Aniline (64)	S3D

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