

Plain and Ion-Pair Thin-Layer Chromatography of Synthetic Dyes on an Admixture of Silica Gel G and Barium Sulfate in an Aqueous Ethanol System

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Abstract

An easy, inexpensive, and accurate method for the analysis of synthetic dyes by means of ion-pair thin-layer chromatography (IPTLC) on mixed sorbent phases containing silica gel G and barium sulfate in an aqueous ethanol system is studied. The effect of the composition of the sorbent phases has a major effect on the hundred-fold relative migration rate, as also does the effect of the ion-pairing reagent as the impregnant. Compact and sharp spot application yields very good binary and ternary separations and enables their clear identification. IPTLC has better separations on mixed sorbent phases, which are not possible on plain mixed phases in thin-layer chromatography. The method can be applied for the trace analysis of synthetic dyes in various natural and synthetic samples.

Introduction

Synthetic dyes are used for decoration and attraction purposes for various food stuff and other substances such as syrups, medicines, leather, and clothes from ancient times. The separation of dyes is often difficult because of spot tailing and close relative migration rate (R_f) values. The separation mechanism is still complicated and not well-understood (1). Most of the dyes have diazo and amino groups and are often carcinogenic in nature with prolonged use and contact. Their use in cosmetics and other health-care products, food stuff, and toys is still prevalent. The use of banned colors and synthetic dyes that are used in biological strains and other areas may also cause health hazards, such as skin diseases or malignancies. Thus, their identification and separation is of great importance in the field of analytical chemistry. We have made some successful attempts in this direction using inorganic ion exchangers (2), reversed-phase silica gel G layers (3), and egg shell layers (4). A silica gel impregnated

with inorganic salts (5–9) that have the tendency to form complexes with dyes has also been used by several workers to obtain clear and compact spots, but a clear mechanism has not yet been given. The admixture of barium sulfate and silica gel G has shown a high potential for the separation of herbicides and related compounds (10). Barium sulfate is a highly insoluble, nontoxic, cheap, and chemically inert material (11) and can be used as an adsorbent (12–17).

The use of an ion-pair reagent is a useful method for obtaining acceptable chromatography of polar and ionizable compounds (18). The use of such reagents is possible with a wide range of stationary phases (19–23). Tetra alkyl ammonium compounds (24) have proved useful as ion-pair reagents for the separation of acids. Alkyl sulfonates (25) and alkyl sulfates (26) have been successfully used for the separation of bases. By altering the type (25), concentration of ion-pair reagents (24,26), and the composition of the solvent (27), it is possible to vary the retention of the sample substances and the selectivity of the chromatographic system. Little attention has been given to developing separations for the resolution of food dyes using ion-pair reagents (28). Soap and micellar reversed-phase thin-layer chromatography (TLC) have also been used by Lepri et al. (29) and Shtykov et al. (30), respectively, which are also types of ion-pair TLC (IPTLC). These studies have given us impetus to extend our work on chromatographic studies using impregnated mixed sorbent layers. The admixtures of silica gel G and barium sulfate of different ratios have been used after impregnation with tetra decyltrimethyl ammonium bromide as an ion-pair reagent (10). An aqueous ethanol system was selected as the mobile phase on the basis of our earlier experiences (12).

IPTLC has more possibilities for the separation of synthetic dyes on the admixture of silica gel G and barium sulfate. The spots are more compact and sharper appearing on ion-pair impregnated layers than on plain layers. Several analytically and industrially important binary and ternary separations have been actually achieved as a result of such studies. The dye mixture shows no changes in the hundred-fold R_f (hR_f) values compared with individual dyes, and the separations are reproducible. The

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method can be applied for the separation, identification, and determination of dyes in trace quantities from toys, medicines, and food stuffs after extraction.

Experimental

Apparatus

A Stahl apparatus with a universal applicator (adjustable thick-

ness of the applied layer from 0.25 to 2.00 mm), hot-air electric drier, glass plates (15 × 3 cm), glass jars (20 × 5 cm), separating funnel, graduated micropipette with vaccupet control, and a temperature-controlled electric oven (Jindal India, New Delhi, India) were used.

Chemicals and reagents

Silica gel G powder, barium sulfate, and ethanol were obtained from E Merck India (Bombay, India). The dyes were obtained

Table I. Names, Abbreviations, and Structural Formulas of the Dyes Investigated

Dye	Abbreviation	Structure	Dye	Abbreviation	Structure
Crystal violet	CrV		Pan S	PS	
Gentian violet	GnV	Mixture of CrV and MV	Methyl red	MR	
Hematoxylin	Hm		Naphthol green B	NgB	
Bismark brown	Bb		Eosin	E	
Lacmoid	La	C ₁₂ H ₉ O ₃ N	Bromothymol blue	BtB	
Resorcinol blue	Rb		Indigo carmine	IC	
Fuchsin basic	FB	C ₂₀ H ₂₀ NCl (mixture of chlorides of pararosaniline, rosaniline, and new magenta)	Rhodamine B	Rh	
Amido swatz	AS		Methyl violet	MV	
Curcumin S	CrS		Alizarin red S	ArS	
Eriochrome back T	EBT		Sudan black	SB	
Bromophenol blue	BrB				
Brilliant green	BrG				
Safranine	S				
Orange G	OrG				

Table II. hR_f Values of Synthetic Dyes on Different Mixed Stationary Phases with and without Impregnation with the Ion-Pair Reagent in the Ethanol–Water (80:20) System

Dyes*	Coatings [†]									
	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂	D ₁	D ₂	E ₁	E ₂
CrV	54 [‡]	15	60	24	62	62 [‡]	59	58	44	69
GnV	19	10	56	20	54	37	40	66 [‡]	45	49
Hm	44 [§]	39	50 [§]	42	50 [§]	42 [‡]	50 [§]	45 [‡]	50 [§]	24 [‡]
Bb	50 [§]	31 [‡]	36 [§]	16	42	45 [‡]	45 [§]	36	46 [§]	30 [‡]
La	96	41	96	94	92	95	92	86	92	68
Rb	86	64	23	12	10	4	7	0	3	0
FB	59	24	73	36	81	64 [‡]	65	50 [‡]	91	69
AS	93	55	89	34	87	84	69	37	51	29 [‡]
CrS	50 [§]	91	50 [§]	12	50 [§]	6	50 [§]	0	50 [§]	0
EBT	48	91	50 [§]	39	50 [§]	47 [‡]	50 [§]	0	50 [§]	0
BrB	96	89	93	83	91	79	88	85	95	65
BrG	51 [‡]	29 [‡]	70	29	63	55 [‡]	47	38 [‡]	75	49
S	23	19	60	22	46	59	42	69	63	63
BtB	93	91	93	84	94	87	86	84	95	59
PS	87	78	65 [‡]	33	83	77	31 [‡]	50	44 [‡]	37 [‡]
MR	89	87	86	66	88	76	65	87	92	38 [‡]
NgB	90	93	50 [§]	61	50 [§]	7	41 [§]	16 [‡]	20	21 [‡]
E	93	91	93	55	88	81	86	58	93	59
OrG	89	89	83	65	86	79	79	58	87	58
IC	91	89	50 [§]	49	50 [§]	48 [‡]	50 [§]	30 [‡]	33 [‡]	29 [‡]
Rh	32/68	66	56/75	32	27/59	44/67	54	87	86	47/58
MV	28	18	25	24	40	51 [‡]	13	43 [‡]	35 [‡]	7/45
ArS	18/85	43 [‡]	25	15	40 [§]	19 [‡]	13	19	12	0
SB	86	72	56	35	64	51 [‡]	25 [‡]	86	25 [‡]	85

* Explanation of dye abbreviations appears in Table I.

[†] As per experimental.[‡] Tailing.[§] Steak.**Table III. Various Binary and Ternary Separations of Synthetic Dyes Achieved on the Admixture of Silica Gel G and Barium Sulfate Layers Impregnated with the Ion-Pair Reagent***

Coating	Separations (R _T –R _I)	Coating	Separations (R _T –R _I)
A ₂	CrV(0.05–0.25)/S(0.13–0.25) – Rb(0.60–68)–BtB(0.88–0.93) FB(0.15–0.32)–Rh(0.58–0.74)–NgB(0.90–0.96) CrV(0.05–0.25)/GnV(0.06–0.14)–As(0.52–0.57)–CrS (0.82–1.0)/BtB(0.88–0.93) Rb(0.60–0.68)/AS(0.52–0. 57)/La(0.30–0.52)–CrS(0.82–1.0)/EBT(0.84–0.97)/BrB (0.85–0.93)/BtB(0.88–0.93)/NgB(0.90–0.96)/E(0.86–0. .95)/OrG(0.88–0.93)/IC(0.85–0.83) S(0.13–0.25)–CrS(0.82–1.0)/EBT(0.84–0.97)/BtB(0.88 –0.93)/BrB(0.85–0.93)/NgB(0.90–0.96)/E(0.88–0.95)/ OrG(0.88–0.93)/IC(0.85–0.93)/AS(0.52–0.57)/Rb(0.60 –0.68)/SB(0.57–0.86)	B ₂	CrV(0.13–0.34)–BrB(0.80–0.85)/BtB(0.78–0.90)/ MR(0.61–0.70) AS(0.26–0.41)/IC(0.42–0.52)–BrB(0.80–0.85)/ BtB(0.78–0.90)/MR(0.61–70)/ OrG(0.60–0.69)
		C ₂	Rb(0.00)–GnV(0.29–0.44)–MR(0.69–0.82) CrS(0.00–0.12)–GnV(0.29–0.44)–La(0.84–0.95) NgB(0.00–0.14)–GnV(0.29–0.44)–AS(0.81–0.86) GnV(0.29–0.44)–BrG(0.74–0.82)/BtB(0.83–0.91)/ PS(0.71–0.83)/MR(0.64–0.82)/E(0.78–0.82)/ OrG(0.74–0.84)
B ₂	E(0.45–0.64)/NgB(0.54–0.68)–La(0.88–1.0) OrG(0.60–0.69)–La(0.88–1.0) E(0.45–0.64)–BrB(0.80–0.85)	D ₂	CrS(0.00)/SB(0.00)/Rb(0.00)/EBT(0.00)–La(0.82–0.89)/ BrB(0.75–0.95)/BtB(0.82–0.86)/PS(0.34–0.66)/ MR(0.83–0.91)/OrG(0.48–67)/Rh(0.80–0.94)
		E ₂	EBT(0.00)/CrS(0.00)/ArS(0.00)/SB(0.00)–FB(0.62–0.76)

* Explanation of dye abbreviations appears in Table I.

from B.D.H. Poole (Poole, U.K.). The ion-pairing reagent (Cetrlak) was obtained from Shalaks Pharmaceuticals Pvt. Ltd. India (New Delhi, India), and all other reagents of analar grade were used.

Preparation of plates

Plates of 0.25-mm thickness were prepared by a slurry obtained by mixing silica gel G powder and barium sulfate powder in different ratios with a 1% ethanolic solution of the ion-pairing reagent and distilled water (DW). The plates were first allowed to dry at room temperature and then at 80°C for 1 h in a hot air oven.

The different coatings (12) that were made to prepare TLC plates were as follows: coating A₁ was plain silica gel G; coating A₂ was plain silica gel G + 1% ethanolic solution of the ion-

pairing reagent + DW; coating B₁ was silica gel G + barium sulfate (80:20) + DW; coating B₂ was silica gel G + barium sulfate (80:20) + 1% ethanolic solution of the ion-pairing reagent + DW; coating C₁ was silica gel G + barium sulfate (60:40) + DW; coating C₂ was silica gel G + barium sulfate (60:40) + 1% ethanolic solution of the ion-pairing reagent + DW; coating D₁ was silica gel G + barium sulfate (40:60) + DW; coating D₂ was silica gel G + barium sulfate (40:60) + 1% ethanolic solution of the ion-pairing reagent + DW; coating E₁ was silica gel G + barium sulfate (20:80) + DW; and coating E₂ was silica gel G + barium sulfate (20:80) + 1% ethanolic solution of the ion-pairing reagent + DW.

The plates of pure barium sulfate could not be made because of their cracking upon drying.

Preparation of test solutions

Test solutions of synthetic dyes (10⁻³M) were prepared in ethanol–water (4:1, v/v). All dyes are self-visualized compounds.

Method

The test solutions (500 ng) were applied on TLC plates at approximately 1.5 cm above their lower edge by means of a micropipette. The spots were dried with the help of hot air, and plates were developed with an ethanol–water (80:20) mobile phase. The solvent ascent was fixed to 10 cm above the point of application. After development the plates were removed from the jars and dried at room temperature. The spots were self-visualized. The values for the rear (R_T) and front (R_L) limits of the spot were measured in the usual way (10):

$$R_f = \frac{(R_T + R_L)/2}{10} \quad \text{Eq. 1}$$

and

$$hR_f = R_f \times 100 \quad \text{Eq. 2}$$

Results and Discussion

Table I presents the structure and abbreviations of synthetic dyes because the structure plays an important role in the migration process (31), and Tables II and III give an account of *hR_f* values in various solvent systems along with the binary and ternary separations achieved on impregnated sorbents. The *hR_f* values of the synthetic dyes were plotted against the solvent system on

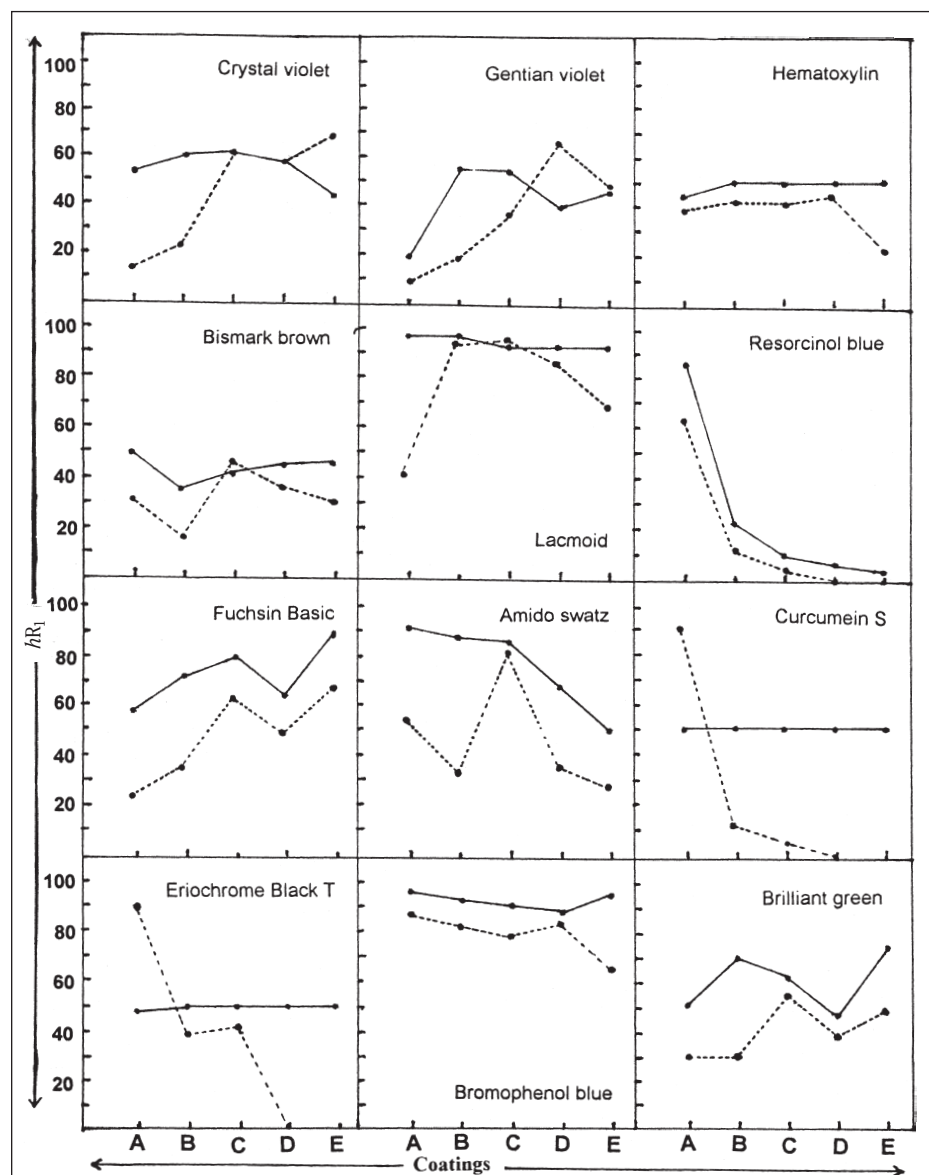


Figure 1. *hR_f* values of various dyes on plain and ion-pair reagent impregnated coatings (the solid lines are the *hR_f* values on plain layers and the segmented lines are the *hR_f* values on impregnated layers in an ethanol–water (80:20) system): (A) plain silica gel G, (B) admixture of silica gel G and barium sulfate (80:20), (C) admixture of silica gel G and barium sulfate (60:40), (D) admixture of silica gel G and barium sulfate (40:60), and (E) admixture of silica gel G and barium sulfate (20:80).

plain as well as ion-pair impregnated mixed adsorbent layers (Figures 1 and 2). The earlier investigations and the work carried out in this laboratory (2,3,10) revealed that thin layers of silica gel G do not yield satisfactory separations because of high hR_f values and tailing in several cases. Thin layers of pure barium sulfate cannot be prepared because of cracking. However, the admixture of both silica gel G and barium sulfate has some separation potential for synthetic dyes (12) and yields limited binary separations in an ethanol-water (80:20) system. Although the silica gel G ion-pair impregnated layers gave clear and satisfactory separation, the 1% impregnation gave better results because of the fact that the critical micelle concentration (CMC) value of the ion-pairing reagent was 0.036M or approximately 1%. Ethanol of an approximately 80% concentration lowers the CMC values of long-chain quaternary ammonium salts, thus the ethanol-water system (80:20) was used for this study by using a

silica-based mixed inexpensive adsorbent in IPTLC. As the barium sulfate was mixed in silica gel G, the development time was also increased. The additional increase of ion-pair reagent further increased the development time to some extent while the hR_f values decreased in comparison with the normal plates made up of mixed adsorbent. The main reason for using the TLC plates impregnated with the ion-pair reagent was that the inclusion of reagent in the solvent alone does not usually lead to acceptable chromatography. The reason appears to be that the reagent migrates more slowly than the solvent front. Thus, the sample does not have an opportunity for ion-pair formation.

Cetyl trimethyl ammonium bromide (CTMA) is asymmetrical and has its quaternary nitrogen placed at one end of a long lipophilic alkyl chain, thus its water solubility is lower than other quaternary ammonium salts. Therefore, CTMA gives a quite different layer when coated onto TLC plates. The silica gel has

silanol groups that are available to interact with the ion-pair reagent, thus a lipophilic layer is formed on the surface of the silica gel G. The tails of further CTMA molecules might sit with their hydrophilic and ion-pairing ends protruding into the aqueous mobile phase. This enables the CTMA to act with an ion-exchange (or ion-interaction) mechanism for the ionizable and polar compounds such as synthetic dyes chromatographed on such plates. This is because of the fact that the hR_f values were decreased on silica gel G impregnated with CTMA in comparison with pure silica gel G. In several cases other dyes were unaffected or developed slightly decreased hR_f values. As barium sulfate was mixed, the silanol groups were not as available for the interaction of the ion-pairing molecule, and basic dyes show an increase in hR_f values because they do not form ion pairs with CTMA (but it was less than the plain mixed adsorbent layer). With the addition of more barium sulfate (60:40) more silanol groups were covered by the barium sulfate molecules and more of the ion-pair reagent was available for the anionic dyes to form ion pairs with the CTMA and move more rapidly. It may also be possible that 0.1M CTMA is soluble in water and sufficiently polar enough to migrate in the solvent front, thus forming ion pairs with several synthetic dyes that were not affected by the admixture (60:40). This is more evident by the fact that the addition of more barium sulfate acted in the adsorption phenomenon and the admixture ratios of 40:60 and 20:80 for silica gel G-barium sulfate, respectively, gave

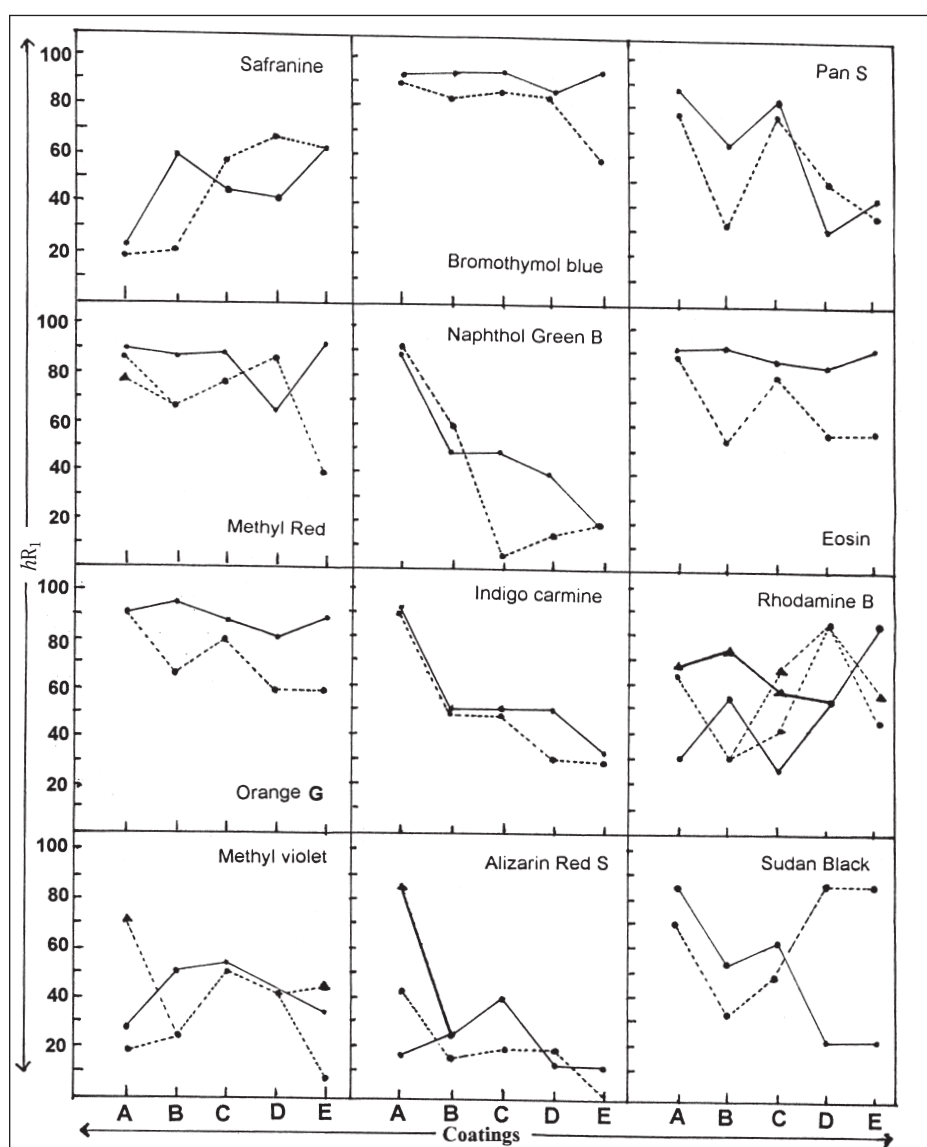


Figure 2. hR_f values of various dyes on plain and ion-pair reagent impregnated coatings (the solid lines are the hR_f values on plain layers and the segmented lines are the hR_f values on impregnated layers): (●) main spot, (▲) second spot in an ethanol-water (80:20) system, (A) plain silica gel G, (B) admixture of silica gel G and barium sulfate (80:20), (C) admixture of silica gel G and barium sulfate (60:40), (D) admixture of silica gel G and barium sulfate (40:60), and (E) admixture of silica gel G and barium sulfate (20:80).

lower hR_f values in several cases (with the exception of Sudan black and crystal violet). Fuschin basic is highly soluble in both water and alcohol and was not adsorbed on the D₁, D₂, E₁, and E₂ layers.

A close examination of Table II shows that the anionic dyes bromophenol blue, orange G, methyl red, naphthol green B, eosin, bromothymol blue, and indigo carmine had no major change in hR_f on plain and impregnated silica gel layers in the ethanol–water system. The exceptions were eriochrome black T (which showed a high increase in hR_f values on the impregnated layer) and anionic amphoteric dye amido swartz (which showed a sharp decrease in hR_f values on impregnated silica gel G layers (A₂)).

However, the cationic dyes (crystal violet, gentian violet, hematoxylin, bismark brown, fuschin basic, brilliant green, safranin, pan S, methyl violet, and nonionic Sudan black) (which do not form ion pairs with CTMA) showed a decrease in hR_f on impregnated silica gel G layers in the same solvent system.

Figures 1 and 2 depict that the basic dyes crystal violet, gentian violet, hematoxylin, lacmoid, and fuschin basic with the addition of barium sulfate in silica gel G show a sharp increase in hR_f values followed by a decrease. The hR_f values for these dyes were generally higher on coated C₂ layers. In other cases the hR_f values decreased with the addition of barium sulfate (i.e., an 80:20 ratio (B₂ layer) then increased up to a ratio of 60:40. A further addition of barium sulfate caused hR_f values to decrease or remain unaffected by the adsorbent layer as discussed previously. It can be seen that all the dyes had lower hR_f values on impregnated layers than on plain adsorbent layers without any regard to their structure and nature. Figures 1 and 2 also indicate that no definite pattern was found and several phenomena were likely involved. These include the adsorption of dyes on the different types of layers, the ion-exchange behavior of the mixed adsorbent layers resulting from the presence of the CTMA impregnant, hydrogen bonding, steric effect, and differential solubilities of dyes in the ethanol–water system. On the basis of R_T – R_L values a large number of binary and ternary separations have been achieved, which cannot be achieved on plain admixed layers of silica gel G and barium sulfate (10) (represented in Table III).

Conclusion

The ion-pair impregnated silica gel G and barium sulfate admixed layers have a better separation potential for the synthetic dyes, and the ion-pair separations of dyes of analytical and industrial importance can be easily achieved. Plain admixed layers show very limited separations.

This method is useful for separating dyes from toys, cosmetics, food stuffs, and drugs after extraction with the help of this ion-pair reagent (28). Further studies in this direction are in progress with real samples.

Acknowledgments

The authors are thankful to Prof. K.G. Varshney (Professor & Head Department of Applied Chemistry, Faculty of Engineering

& Technology, Aligarh Muslim University, Aligarh, India) for his helpful suggestions and discussion. Thanks are also due to the State Council of Science & Technology (U.P., India) for financial support.

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Manuscript accepted February 25, 2002.