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Synthetic and chromatographic studies on silica polyaniline: A new approach

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Abstract

A new adsorbent, silicapolyaniline has been synthesized. The material was characterized on the basis of FTIR, XRD and SEM studies. X-ray diffraction study of silica polyaniline reveals mixed crystalline and amorphous phases indicating its semi crystalline nature. The analytical applicability of this newly synthesized material has been established by using it as stationary phase in thin layer chromatographic analysis of nine surfactants (both non-ionic and cationic), amino acids and metal ions with different solvent systems. This material was found useful for the separation of cationic surfactants from non-ionic surfactants with 1.0 M aqueous formic acid or sodium formate solution. However, the separation of L-alanine or L-glycine from L-leucine or other amino acids could be possible with 1.0 M aqueous formic acid whereas for the separation of metal ions, mixture of 1.0 M aqueous solutions of formic acid and sodium formate in 1:1 volume ratio was most suitable. Ni^{2+} with higher R_F value can be well separated from Hg^{2+} and Zn^{2+} .

Keywords: Synthesis, Characterization, Silica-Polyaniline, Separation, Surfactants, Amino Acids, Metal Ions.

INTRODUCTION

In recent years thin layer chromatography (TLC) has grown much in status and has experienced a dramatic surge due to its simplicity, versatility and low cost. TLC provides colorful separations with good resolution and easier manipulation of mobile and stationary phases. With optimization of techniques, new layer materials can be applied for the analysis of various compounds present in environmental, geological and biological samples. The separation by TLC is generally controlled by a mutual action of the stationary and mobile phases with the analyte. As a general practice, the composition of mobile phases is usually altered to obtain a desired separation on a

particular adsorbent. The development of thin layer chromatography (TLC) and its suitability to the analysis of surfactants [1-6], amino acids [7-12] and metal ions [13-16] has been well documented in many papers and reviews. Modern instrumental techniques such as spectrophotometry, densitometry, atomic absorption spectrophotometry (AAS) etc. have also been used in the analysis of biological, pharmaceutical, biomedical and environmental samples. With the exception of TLC, other techniques are expensive and require the use of specialized equipment. Because of the rapidity, cost effectiveness, reasonable separation power and broader applicability, TLC has retained its status as a valid and simple analytical technique for qualitative and quantitative analysis of surfactants [17-22]. In general separations of surfactants have been performed on TLC plates coated either with a polar stationary phase most frequently silica gel [23] or on non polar phases like RP-18 [24]. However, other layer materials like cellulose alumina and kieselguhr etc [25, 26] have also been used. In the absence of an ideal sorbent, the use of an inexpensive, reproducible and readily available stable sorbent phase for TLC has always been felt.

In order to explore new adsorbent having better separation ability, silica-polyaniline has been synthesized. Silica-polyaniline has been characterized on the basis of FTIR, XRD and SEM studies. The material was utilized for separation and detection of surfactants, amino acids and metal ions.

MATERIALS AND METHODS

Apparatus

A TLC applicator (Toshniwal, India) was used for the preparation of layers on a supporting glass plate surface (20 x 3.5 cm). Glass jars (24 x 6 cm) were used for development of the plates. A glass sprayer was used to spray reagents on the plates to locate the position of the spot of analyte.

Reagents

Sodium format and formic acid were obtained from Merck (India).

Test Solutions

- The test solutions (2%) of metal ions were the chloride, nitrate or sulfate salts of nickel, cobalt, mercury, thallium, lead, silver, thorium, copper and zinc. The solutions were prepared in double distilled water.
- Solutions (0.5%) of the surfactants were prepared in methanol. Surfactants studied were Triton X-100 (TX-100), Brij-35 (BJ-35), Brij-57 (BJ-57), Tween-20 (TW-20), Cween-40 (CW-40), Cween-60 (CW-60), cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium chloride (HDTAC).
- Test solutions (1%) of amino acids (L-alanine, L-leucine, L-isoleucine, L-valine, L-glycine and L-methionine) were prepared in double distilled water.

Detectors

All the metal ions were detected with dithizone (0.1%) in carbon tetrachloride which appeared as light brown spots on the plate. Surfactants were detected with Dragendroff reagent as orange spots. Amino acids were self detected on TLC plates as black spots.

Synthesis

Light green colored gel of silica-polyaniline was prepared by mixing different volume ratios of 10% aniline and 0.1 M potassium persulfate in different amount of silica gel under continuous stirring with the aid of magnetic stirrer. The product (adsorbent) was kept below 10°C for an h. The gel was washed with demineralized water till the filtrate become neutral. The product was dried in an oven at 50°C.

Characterization**FTIR analysis**

For FTIR analysis, 10 mg (dry mass) of the adsorbent was thoroughly mixed and powered with 100 mg (dry mass) of KBr. A transparent disc was formed by applying a pressure of 80 psi (1 psi = 6894.76pa) in a moisture free atmosphere. The FTIR absorption spectrum was recorded in between 500-4000 cm^{-1} .

X-ray studies

The x-ray diffraction pattern of the adsorbent material was recorded using X Pert diffractometer with $\text{CuK}\alpha$ radiation with 2θ value in the region 10-80°. The applied current and voltage were kept at 30 mA and 40 KV respectively.

Scanning electron microscopy

Electron micrographs were recorded for silica, polyaniline and silica-polyaniline by using scanning electron microscope at 20.0 KV. The magnification was kept constant at 20,000 X.

Chromatography**Preparation of TLC Plates**

TLC was performed on 20 x 3.5 cm glass plates coated with 0.5 mm layers of stationary phase. The plates were prepared by mixing silica-polyaniline with water in 1:3 ratios with constant shaking until homogenous slurry was obtained. The resultant slurry was applied on the glass plate with the help of TLC applicator to give 0.5 mm thick layer. The plates were dried in air at room temperature and then activated by heating for 1 h at $100 \pm 2^\circ\text{C}$ in an electrically controlled oven. The activated plates were stored in a close chamber at room temperature until used.

Procedure

Test solutions (1.0 μL) of analytes were applied by means of Tripette (GmbH, Werthlim, Germany) approximately 2.0 cm above the lower edge of the plate. The plates were developed by ascending technique in glass jars previously saturated with mobile phase vapor by equilibrium for approximately (30 min). The development distance was fixed to 10 cm from the origin in all cases. After development, the plates were dried at room temperature and the spots were visualized by the use of the appropriate reagent.

R_F values were calculated by use of the formula $R_F = 0.5 (R_L + R_T)$, where R_L and R_T are, respectively the R_F values of the leading and trailing edges of the spots.

For the separation of analyte mixtures, equal volumes of the analytes were mixed and 1.0 μL of the resultant mixture was applied on a TLC plate. The plate was developed with the chosen mobile phase. The spots were detected and R_F values of the separated spots were calculated.

RESULTS AND DISCUSSION

A number of samples of silica-polyaniline (adsorbent) were prepared and the mobility of surfactants, amino acids and metal ions was examined. The adsorbent sample that is capable to activate differential migration of analytes along with their clearer detection was selected for use as stationary phase.

FTIR spectrum of silica-polyaniline indicates strong and broad band in the region $3500\text{-}3000\text{cm}^{-1}$ may be assigned to interstitial water molecules and OH groups. Another strong and sharp peak at 1625 cm^{-1} is due to H-O-H bending. A strong band due to Si-H stretching vibration is found at $2250\text{-}2100\text{ cm}^{-1}$. An assembly of two peaks in the region $1200\text{-}1400\text{ cm}^{-1}$ may be ascribed due to the stretching vibration frequency of C-N which indicates that silica-polyaniline contains considerable amount of aniline. The spectrums of silica-polyaniline also exhibit strong bands at 1087 cm^{-1} and 975 cm^{-1} indicating the presence of silicate groups. Another band maximum at a 585 cm^{-1} is due to the presence of metal oxide bond.

X-ray diffraction studies of silica-polyaniline are shown in Fig. 1. Some broad intensity peaks at $14, 16 \text{ \& } 22\ 2\theta$ and weak intensity signals at $38, 44$ and $65\ 2\theta$ shows its semi crystalline nature.

The SEM photographs of silica gel, polyaniline and silica-polyaniline is shown in Fig. 2 (a-c). The SEM pictures shows difference in surface morphology of inorganic, organic and composite material. The presence of impure phases indicates the absence of impurities.

TLC

TLC of nine surfactants, six amino acids and nine metal ions was performed on modified silica layers using DMW (A), 1.0 M aqueous formic acid (B), 1.0 M aqueous sodium formate (C) and 1.0 M aqueous formic acid + 1.0 M aqueous sodium formate (1+1 v/v) D as mobile phases to study the chromatographic performance of newly developed layer material. The obtained R_F values for surfactants, amino acids and metal ions are recorded in Tables 1-3 respectively. The chromatography of six nonionic and three cationic surfactants were performed using the chromatographic behavior of surfactants using three mobile phases A, B, and C respectively. On using mobile phase A i.e. DMW all the surfactants remain at the point of application. On using B mobile phase system nonionic surfactants move with higher R_F values ranging from 0.70 to 0.92 along with tailed spots. TX-100, BJ-57 and CW-60 show tailed spots. All the cationic surfactants remain at the point of application with lower R_F values ranging from 0.04 to 0.09. Similarly, the mobility pattern of non-ionic surfactants appeared almost same with slight change in the R_F values on using C mobile phase system. TX-100 and BJ-57 show tailed spots. The cationic surfactant show mobility with R_F value ranging from 0.08 to 0.15 as given in Table 1. Amino acids also remain at the point of application on using DMW as mobile phase. On using B solvent system amino acids move with R_F values ranging from 0.40 to 0.69 whereas on using C mobile phase system amino acid move with higher R_F values ranging from 0.88 to 0.94. The R_F values

are given in Table 2. Metal ions also remain at the point of application and show 0.00 R_F value on using DMW as eluent. On using B mobile phase system metal ions move with higher R_F values ranging from 0.80 to 0.98. All the metal ions remain at the point of application when 1.0 M aqueous sodium formate i.e. C mobile phase is used. D (1.0 M aqueous formic acid + 1.0 M aqueous sodium formate (1+1, v/v) was used to check the mobility pattern of metal ions. Higher R_F values were found using D mobile phase system as compared to C solvent system. Zn^{2+} and Hg^{2+} show low R_F values 0.52 and 0.56 respectively.

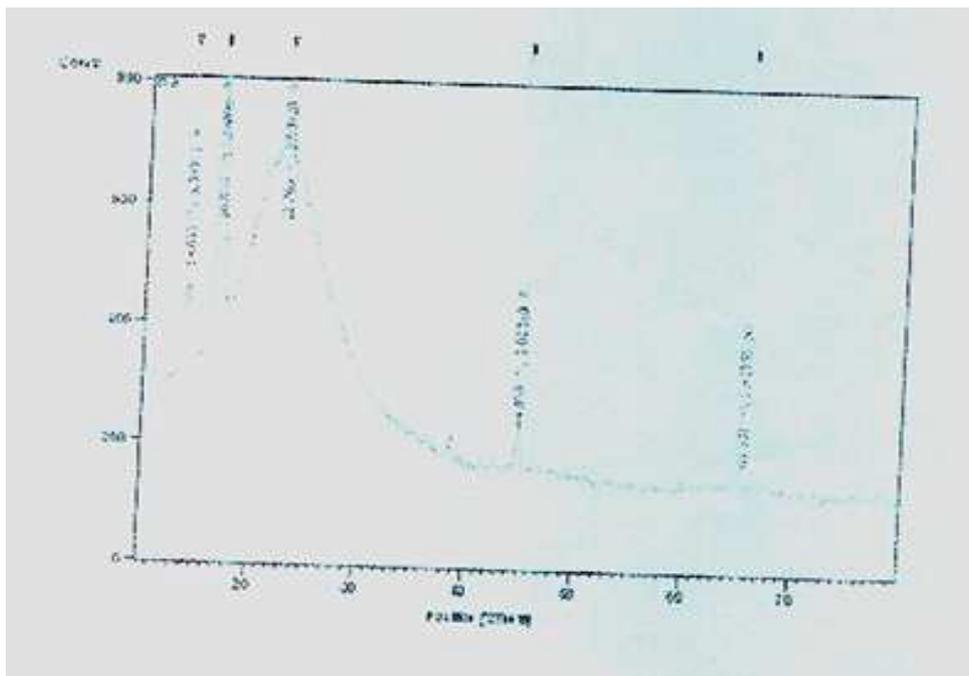


Fig. 1: X-ray Diffraction Pattern of Silica-Polyaniline

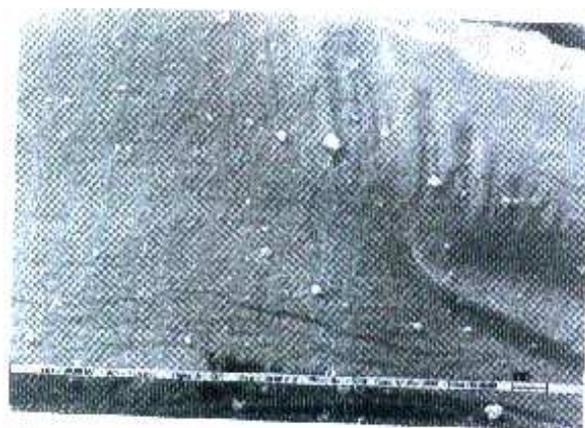


Fig. 2 (a): Sem Photograph of Silica Gel

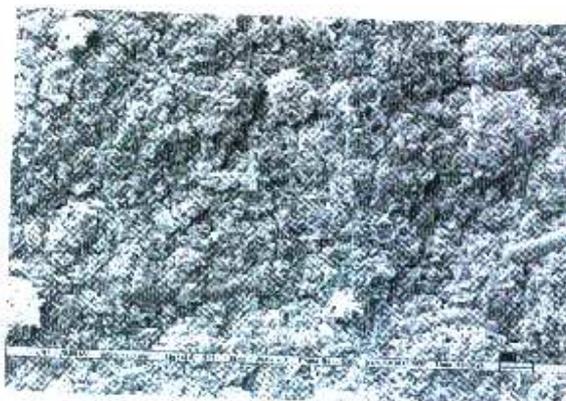


Fig. 2 (b): Sem Photograph of Polyaniline

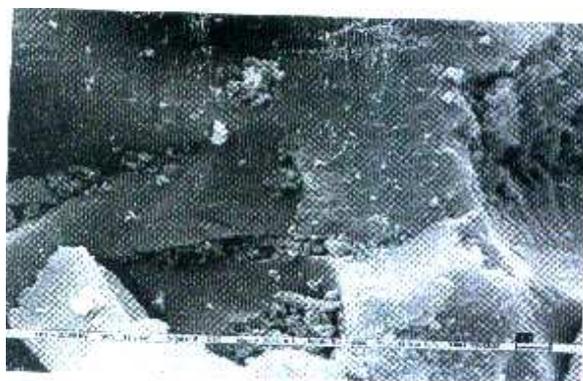


Fig. 2 (c): Sem Photograph of Silica-Polyaniline

Tl³⁺ and Th⁴⁺ show 0.72 and 0.75 R_F values; Cu²⁺, Ag⁺ and Co²⁺ show mobility with R_F value 0.80, 0.86 and 0.87 respectively and Pb²⁺ and Ni²⁺ show higher R_F values (0.90 and 0.95) as compared to other metal ions.

Table 1 R_F Values of Surfactants on Silica-Polyaniline Thin Layers

S. No.	Surfactants	R _F Value		
		Solvent System		
		A	B	C
1.	TX-100	0.0	0.85T	0.84 T
2.	BJ-35	0.0	0.87	0.72
3.	BJ-57	0.0	0.74 T	0.76 T
4.	TW-20	0.0	0.70	0.94
5.	CW-40	0.0	0.91	0.87
6.	CW-60	0.0	0.87 T	0.78
7.	CPC	0.0	0.04	0.15
8.	TTAB	0.0	0.09	0.23
9.	HDTAC	0.0	0.06	0.08

T = Tailed Spot

Table 2 R_F Values of Amino Acids on Silica-Polyaniline Thin Layers

S. No.	Amino Acids	R _F Value		
		Solvent System		
		A	B	C
1.	L-Alanine	0.0	0.69	0.90
2.	L-Leucine	0.0	0.34	0.94
3.	L-Isoleucine	0.0	0.40	0.90
4.	L-Valine	0.0	0.47	0.96
5.	L-Glycine	0.0	0.69	0.88
6.	L-Methionine	0.0	0.43	0.92

A = DMW, B = 1.0 M aqueous formic acid, C = 1.0 M aqueous sodium formate

Table 3 R_F Values of Metal Ions on Silica-Polyaniline Thin Layers

S. No.	Metal Ions	R _F Value			
		Solvent System			
		A	B	C	D
1.	Ni ²⁺	0.0	0.95	0.0	0.95
2.	Co ²⁺	0.0	0.80	0.0	0.87
3.	Hg ²⁺	0.0	0.92	0.0	0.56
4.	Tl ³⁺	0.0	0.98	0.0	0.72
5.	Pb ²⁺	0.0	0.85	0.0	0.90
6.	Ag ⁺	0.0	0.90	0.0	0.86
7.	Th ⁴⁺	0.0	0.91	0.0	0.75
8.	Cu ²⁺	0.0	0.89	0.0	0.80
9.	Zn ²⁺	0.0	0.88	0.0	0.52

A = DMW, B = 1.0 M aqueous formic acid, C = 1.0 M aqueous sodium formate, D = 1.0 M aqueous formic acid + 1.0 M aqueous sodium formate (1+1, v/v)

Table 4 Separation Data for the Analytes on Silica Modified Layers

Analyte	Mobile Phase	Separation (R _F)
Surfactants	B	BJ-57 (0.86) – CPC (0.04) TW-20 (0.70) – TTAB (0.08) CW-40 (0.91) – CPC (0.04) CW-40 (0.90) – TTAB (0.09) TW-20 (0.71) – HDTAC (0.05)
	C	BJ-35 (0.72) – CPC (0.15) TW-20 (0.94) – TTAB (0.23) CW-40 (0.87) – CPC (0.15) CW-60 (0.78) – TTAB (0.22)
Amino Acids	B	L-alanine or L-glycine (0.69)–L-leucine (0.32) or L-isoleucine (0.40)
Metal Ions	D	Ni ²⁺ (0.95) – Hg ²⁺ (0.56) Ni ²⁺ (0.94) – Zn ²⁺ (0.52)

The separations achieved on modified silica layers are summarized in Table 4. The mutual separation of nonionic from cationic surfactants was achieved using two mobile phase system B and C. On using B as eluent BJ-57 was successfully separated from CPC, TW-20 was separated from TTAB and HDTAC respectively and CW-40 was separated from CPC and TTAB respectively. On using C as mobile phase system BJ-35 was separated from CPC, TW-20 from TTAB, CW-40 from CPC and CW-60 from TTAB. Amino acid L-alanine and L-leucine was separated on using B mobile phase system. Ni²⁺ was separated from Hg²⁺ and Zn²⁺ respectively on using D mobile phase as eluent. The R_F values of the separated spots are given in Table 4.

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