CHROM. 3717

The separation of polyols by thin-layer chromatography*

Many procedures have recently been proposed for the separation of polyols by thin-layer chromatography on silica gel, alumina or Kieselguhr G plates using various developing solvents[1]. In some cases, adsorbents modified with complexing agents such as boric acid[2] or ammonium borate[3] have also been tried.

In previous work[4–6] it has been shown that in an alkaline medium complex formation takes place between lead(II) and polyols (P) containing at least two adjacent hydroxyl groups, according to the following equilibrium:

$$Pb(OH)_3^- + P \rightleftharpoons PbP^- + nH_2O.$$

Because the complex formation is affected by the number and position of the hydroxyl groups and the equilibrium constants are quite different, lead(II) has been used here as a complexing agent in the adsorbent layer to separate polyols by thin-layer chromatography. The influence of complex formation with lead(II) and of eluent composition on the mobility of polyols has been studied.

Experimental

Thin-layer plates were prepared according to the following procedure: 30 g of Silica Gel H (Merck) were mixed with 70 ml 0.1 *M* $Pb(NO_3)_2$ (Erba RP, Milan) or 70 ml water (untreated plates) by shaking in a stoppered conical flask, and were then transferred to the spreader (Chemetron, Milan). The thickness of the layer was set at 0.25 mm. All the plates were activated by heating at 110° for 30 min. Samples were applied to the starting line of the chromatograms as dilute solutions in alcohol or water–alcohol, in chromatography tanks. Alcohol–ammonia or alcohol–ammonia–water mixtures were used as developing solvents, and the polyols were detected by spraying with potassium permanganate containing sodium carbonate solution. Experiments carried out with Silica Gel G plates have not given satisfactory results. This seems to be due to the reaction of lead(II) with calcium sulfate present in the Silica Gel G.

TABLE I

FORMATION CONSTANTS WITH LEAD (II) OF POLYOLS IN ALKALINE MEDIUM

Polyol	*log K*
1,3-Propanediol	−0.20
Ethylene glycol	0.30
1,2-Propylene glycol	0.30
1,2,5-Trihydroxypentane	0.40
1,2,4-Butanetriol	0.45
Glycerol	1.15
meso-Erythritol	1.93
d-Mannitol	2.78
Dulcitol	2.90
d-Sorbitol	3.42

* Work carried out with the aid of the "Consiglio Nazionale delle Ricerche".

Results

The polyols listed in Table I were examined, their formation constants, K, with lead(II) in alkaline medium (0.1 M OH^-) having been previously determined.

Typical chromatograms of some polyols on untreated Silica Gel H and lead(II)-impregnated Silica Gel H for three developing solvent systems are reproduced in Fig. 1. The influence of lead(II) is evident: the mobility of the polyols decreases with an increase of the number of adjacent hydroxyl groups, as the formation constants between lead(II) and polyols become larger.

In Table II the R_F values measured for the polyols investigated are collected. The R_F values for glycols are slightly affected by the presence of lead(II) in the adsorbent layer, while the mobility of other polyols is considerably decreased by

TABLE II

R_F VALUES × 100 OF THE INVESTIGATED POLYOLS ON SILICA GEL H (A) AND LEAD(II)-IMPREGNATED SILICA GEL H (B)

Developing solvents: (I) ethanol saturated with gaseous ammonia; (II–VII) ethanol–conc. ammonia (32 %)–water, respectively: II (21:2:0), III (23.5:2.2:1), IV (23:2.2:2), V (21:2:2.4), VI (21:2:3.5) and VII (20:2:4).

Polyols	*I*		*II*		*III*		*IV*		*V*		*VI*		*VII*	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
1,3-Propanediol	76	68	82	75	80	78	86	79					82	82
Ethylene glycol	62	59	67	60	64	60	66	62	66	62	74	68	71	66
1,2-Propylene glycol	69	65	73	67	72	67	73	69	72	70	80	76	77	74
1,2,5-Trihydroxypentane	65	61	69	64	68	64		66	70	65	78	73	76	74
1,2,4-Butanetriol	60	53	62	60	64	60	66	62	65	62	73	68	71	67
Glycerol	48	22	53	42	50	46	56	48	57	52	62	54	63	55
meso-Erythritol	33	6	39	22	38	30	45	34	49	39	51	43	56	45
d-Mannitol	7	0	14	3	15	6	22	9	30	14	27	17	37	22
Dulcitol	4	0	12	0	14	3	21	3	29	8	24	10	35	18
d-Sorbitol	4	0	11	0	12	2	17	5	26	7	22	9	34	14

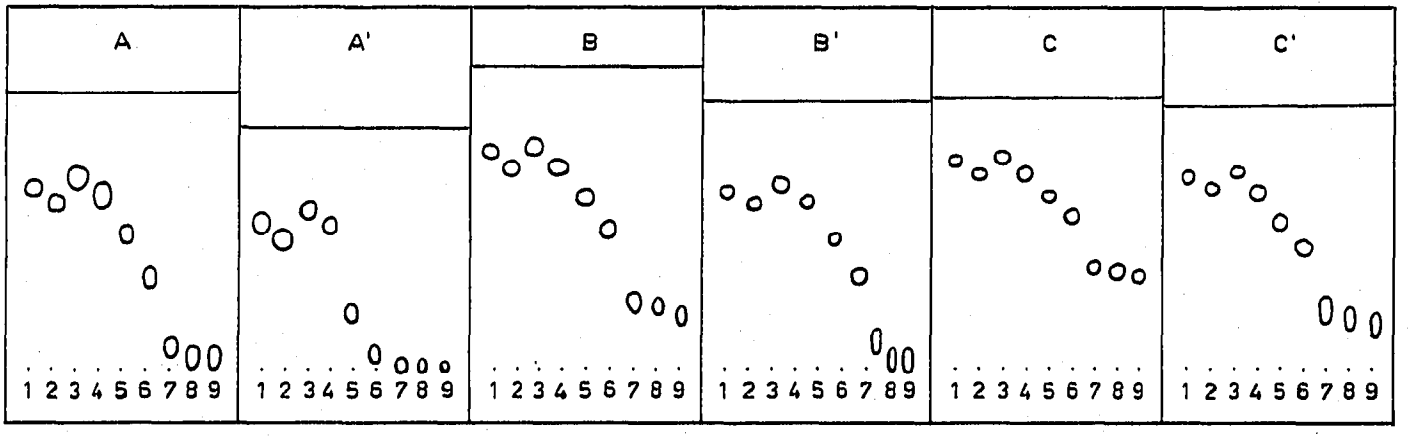

Fig. 1. Thin-layer chromatograms on Silica Gel H (A, B, C) and lead(II)-impregnated Silica Gel H (A', B', C') of the following polyols: (1) 1,2,5-trihydroxypentane; (2) 1,2,4-butanetriol; (3) 1,2-propylene glycol; (4) ethylene glycol; (5) glycerol; (6) *meso*-erythritol; (7) *d*-mannitol; (8) dulcitol; (9) *d*-sorbitol. Developing solvents: (A,A') ethanol saturated with gaseous ammonia; (B,B') ethanol–conc. ammonia (32 %)–water (23:2.2:2); (C,C') ethanol–conc. ammonia (32 %)–water (20:2:4).

the presence of the metal. A marked influence of the complexing ability of the added metal can be observed by running compounds that do not bind lead(II) on the two types of plates. Amines such as benzylamine yield identical R_F values when 95 % ethanol–25 % ammonia (4:1) is used as eluent.

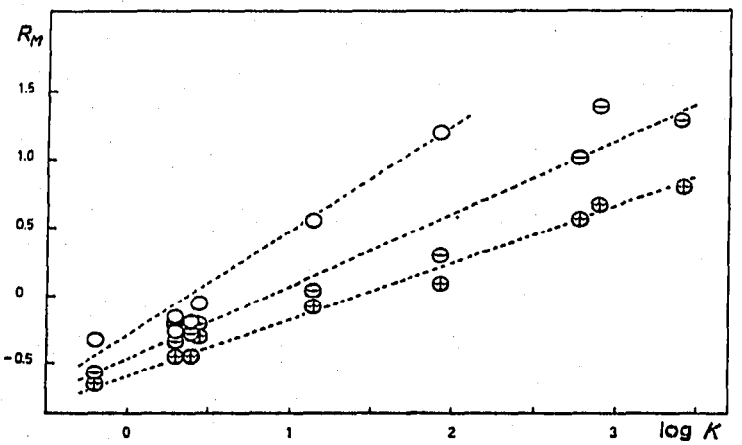

Fig. 2. R_M values plotted *versus* logarithm of the formation constants with lead(II). Developing solvents: (○) ethanol saturated with gaseous ammonia; (⊖) ethanol–conc. ammonia (32 %)–water (23:2.2:2); (⊕) ethanol–conc. ammonia–water (20:2:4).

The mobility of the polyols changes noticeably with the eluent composition. Since the polyol–lead(II) complexes are polar, their migration is affected by the polarity of the elution medium consisting of ethanol and ammonia, with and without water. The migration of glycols is slightly affected by the eluent composition. Glycerol and erythritol exhibit a large difference in the R_F values when they are chromatographed on untreated and lead(II)-treated silica gel plates when water is present in the eluent. Higher polyols show a larger difference in the R_F values on the two types of plates when the eluent does not contain water.

More favourable conditions for the separation of triols and higher polyols from diols are obtained when anhydrous ethanol saturated with ammonia is used. In this medium the higher polyols have a smaller mobility because their complexes with

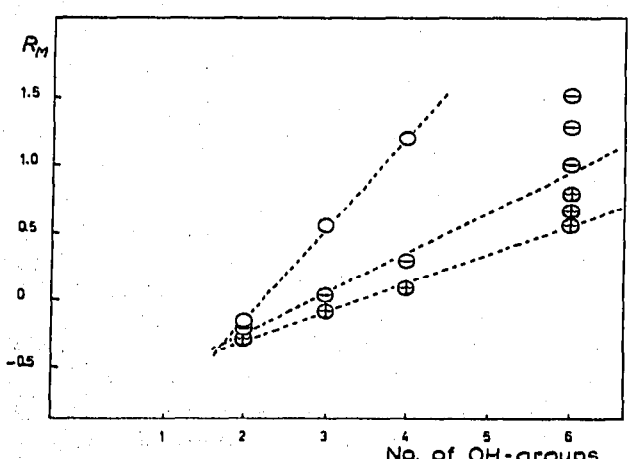

Fig. 3. R_M values plotted *versus* number of hydroxyl groups of various polyols. Developing solvents: (○) ethanol saturated with gaseous ammonia; (⊖) ethanol–conc. ammonia (32 %)–water (23:2.2:2); (⊕) ethanol–conc. ammonia–water (20:2:4).

lead(II) are stronger and very slightly soluble. It is possible to separate glycerol from erythritol and the latter from hexahydric alcohols by increasing the eluent polarity by adding water.

The dependence of the chromatographic behaviour on the formation constants of lead(II)-polyol complexes is readily observed in Fig. 2, where the R_M values obtained for three different eluents have been plotted *versus* the logarithm of the formation constants reported above. The plot is only of a qualitative nature because the formation constants were obtained under different experimental conditions (0.1 *M* OH^- and 1 *M* Na^+). It clearly shows, however, that the R_M values increase gradually as log *K* increases. From this plot the effect of the eluent is quite clear because the slopes of the hypothetical curves drawn through the experimental points are different.

Since R_M is a linear function of the number of equal groups responsible for the chromatographic behaviour, the R_M values obtained on lead (II)-treated plates have been plotted *versus* the number of hydroxyl groups of the polyols investigated. There is a linear relationship for diols, triols and tetrols, whereas deviations are observed for the hexahydric alcohols; this is probably due to interactions among -OH groups which influence each other.

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First received July 10th, 1968; revised manuscript received July 29th, 1968