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REVERSED-PHASE ION-PAIR LIQUID CHROMATOGRAPHIC SEPARATIONS OF SOME HETEROBORANE ANIONS

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SUMMARY

Separation of 23 heteroborane anions by reversed-phase ion-pair liquid chromatography on C_1-bonded-phase columns using C_{12} or C_6 *n*-alkylamine pairing ion is reported. The elution was monitored with a UV detector at 235, 254 or 280 nm well below microgram sensitivity level. The effects of the concentrations of the pairing ion and the inert salt, the pH, the pairing ion length, the stationary phase material and the methanol–water ratio on retention and selectivity were investigated.

INTRODUCTION

In the past two decades, a great variety of borane anionic species have been synthesized, ranging from polyhedral borane anions to sandwich cage heteroborane complexes. Some of these compounds were successfully applied in neutron capture therapy[1], as extraction reagents in processing spent nuclear fuel[2,3] and in homogenous catalysis[4]. Despite the fact that many closely related compounds were prepared, which differ structurally in a very subtle way, a speedy and efficient analytical method for purity assay, reaction monitoring and isolation of reaction products is still lacking. The only report dealing with separation of these compounds is the study of Wellum *et al.*[5], who separated some polyhedral borane anions using ion-exchange and partition thin-layer chromatography (TLC) systems.

Ion-pair reversed-phase high-performance liquid chromatography is now a well established technique for the analysis of many organic and biochemical systems[6,7], but reports of its application to analysis of inorganic and organometallic compounds are relatively scarce[8–10].

The present article is aimed at demonstrating the convenience of the reversed-phase ion-pair technique for direct analysis of some heteroborane anions, and at investigating the effect of factors governing the separation process.

EXPERIMENTAL

The home-made chromatograph described previously[11] comprised a VCM 300 membrane pump, a UV detector operating at 254 nm, a UVM-4 variable-wavelength

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(235–380 nm) detector (Development Works of Czechoslovak Academy of Sciences, Prague, Czechoslovakia), a U6K injector (Waters Assoc., Milford, MA, U.S.A.) and a differential refractometer (Model 2025/50; Knauer, Oberursel, G.F.R.).

All samples were obtained from laboratory stocks; the methods of preparation are listed in Table I. Laurylamine (Lachema, Brno, Czechoslovakia) and hexylamine (Koch-Light Labs., Colnbrook, Great Britain) were converted into hydrochloride salts and purified by crystallization from dry diethyl ether–absolute ethanol mixture. All other chemicals were p.a. grade. Methanol was passed through a column of activated silica and distilled in glass before use. Water was deionized and double distilled from all-glass still.

Packing materials were C_1-bonded phase (C_1-BP) prepared from Kieselgel for TLC (Merck, Darmstadt, G.F.R.); a fraction with average particle size 14.3 μm

TABLE I

CAPACITY RATIOS OF HETEROBORANE ANIONS

System I: column, 150 × 3.8 mm; sorbent, C_1-BP on silica (14.3 μm); eluent, $2.70 \cdot 10^{-3}$ *M* n-$C_{12}H_{25}NH_2 \cdot HCl$ in methanol–water (6:4); flow-rate, 0.92 ml/min; pressure drop, 4.8 MPa; UV detection. System II: eluent, $2.70 \cdot 10^{-3}$ *M* n-$C_{12}H_{25}NH_2 \cdot HCl$ in methanol–water (7:3); flow-rate, 1.19 ml/min; pressure drop, 5.8 MPa; other parameters as in system I. System III: eluent, $2.70 \cdot 10^{-3}$ *M* n-$C_{12}H_{25}NH_2 \cdot HCl$ in methanol–water (8:2); flow-rate, 0.93 ml/min; pressure drop, 3.7 MPa; other parameters as in system I.

Anion	*Cation*	*k′ value*			*Reference to method of preparation*
		System I	*System II*	*System III*	
$7,8\text{-}C_2B_9H_{12}^-$	K^+	6.83	0.89	—	12
$7,8\text{-}C_2B_9H_{12}^-$	$N(CH_3)_4^+$	6.39	0.84	—	12
$7,8\text{-}C_2B_9H_{12}^-$	Na^+	—	0.84	—	12
$5\text{-HS-}7,8\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	—	1.05	—	13
$5\text{-iso-}C_3H_7\text{-}7,8\text{-}C_2B_9H_{11}^-$	Cs^+	16.8	1.49	—	13
$5\text{-I-}7,8\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	10.4	1.16	—	13
$5\text{-Cl-}7,8\text{-}C_2B_9H_{11}^-$	K^+	—	1.08	—	13
$9\text{-Cl-}7,8\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	—	1.03	—	13
$9\text{-I-}7,8\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	13.1	1.22	—	13
$9\text{-OH-}7,8\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	12.1	1.32	—	13
$5,6\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}^-$	$N(CH_3)_4^+$	16.1	1.54	—	13
$5,6\text{-}Cl_2\text{-}7,8\text{-}C_2B_9H_{10}^-$	Na^+	—	1.11	—	13
$9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}^-$	$N(CH_3)_4^+$	—	2.03	—	13
$9,11\text{-}Cl_2\text{-}7,8\text{-}C_2B_9H_{10}^-$	$N(CH_3)_4^+$	—	1.22	—	13
$7,9\text{-}C_2B_9H_{12}^-$	Cs^+	7.00	0.86	—	14
$10\text{-OH-}7,9\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	2.87	0.48	—	13
$10\text{-}CH_3O\text{-}7,9\text{-}C_2B_9H_{11}^-$	$N(CH_3)_4^+$	6.35	0.89	—	13
$CB_{10}H_{13}^-$	Cs^+	6.65	0.84	—	15
$CB_9H_{12}^-$	$N(CH_3)_4^+$	6.91	0.87	—	16
$(1,2\text{-}C_2B_9H_{11})_2Co^-$	Na^+	—	2.95	—	17
$(1,2\text{-}C_2B_9H_{11})_2Co^-$	Cs^+	—	2.89	0.21	
$8,8'\text{-S-}(1,2\text{-}C_2B_9H_{10})_2Co^-$	$N(CH_3)_4^+$	—	2.03	0.28	18
$8,8'\text{-}C_6H_4\text{-}(1,2\text{-}C_2B_9H_{10})_2Co^-$	Cs^+	—	2.62	0.29	18
$(1,2\text{-}C_2B_9H_{11})_2Fe^-$	Cs^+	—	4.08	—	17
$(1,2\text{-}C_2B_9H_{11})_2Fe^-$	$N(C_4H_9)_4^+$	—	4.05	0.50	17
$(1,2\text{-}C_2B_9H_{10}I)_2Co^-$	Cs^+	—	22.8	1.83	13
$(1,2\text{-}C_2B_9H_{11})_2Ni^-$	Cs^+	—	4.68	—	17

(obtained by sorting with Alpine MZR air classifier) was used. The sorbent was treated in toluene with trimethylchlorosilane–hexamethyldisilazane mixture in the usual manner[19]. The prepared material contained 5.84% C and exhibited a capacity ratio (k') of 0.23 for nitrobenzene in heptane and negative methyl red test[20]. Separon SI C_1 and Separon SI C_{18} (Laboratorni Přistroje, Prague, Czechoslovakia) are sorbents based on spherical silica with average particle size 10 μm, and with carbon content 6 and 20% C, and specific surface area 200 and 300 m^2/g, respectively. Both exhibit k' values less then 0.6 for nitrobenzene in heptane and negative methyl red test.

The columns were prepared by the slurry packing technique using an apparatus described by Coq *et al.*[21]. Equilibration of the eluent with the column packing was relatively rapid; 30 column volumes were sufficient to achieve constant k' values. The system was washed with a minimum of 50 column volumes of pure methanol prior to leaving out of operation. The capacity factor values k' were calculated in a usual way from triplicate measurements of retention times, and the hold-up time was determined by the method of Bristow and Knox[22] from baseline disturbance of the UV trace. Fresh 0.1–0.5% solutions of borane salts in methanol–water mixture corresponding to the given eluent composition were used; for sparingly soluble samples the pure methanolic solution was preferred.

RESULTS AND DISCUSSION

The chromatographic conditions used and k' data for heteroborane anions are summarized in Table I. Figs. 1–4 show some typical separations of borane anion mixtures and demonstrate the separation power of the method. Heteroborane anions are relatively strongly retained on hydrocarbonaceous bonded phase, and a methylated silica gel C_1-bonded phase was preferred to the more conventional C_{18}-bonded phase to lower the required methanol content and improve peak shapes for strongly

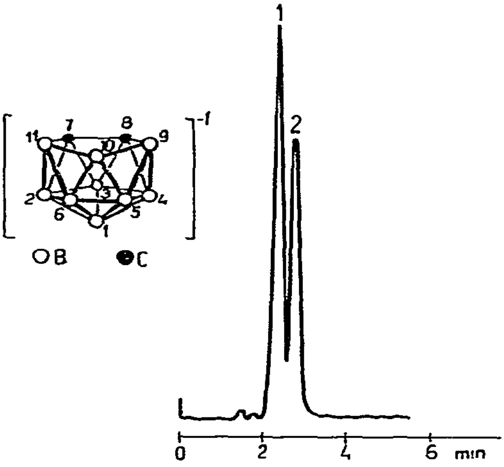

Fig. 1. Separation of 7,8-$C_2B_9H_{12}^-$ iodine derivatives: 1, 5-I-7,8-$C_2B_9H_{11}^-$; 2, 5,6-I_2-7,8-$C_2B_9H_{10}^-$. Hydrogen atoms are omitted from the structural formula. Operating conditions: sorbent, C_1-BP (14 μm); column, 150 × 3.8 mm; eluent, $2.7 \cdot 10^{-3}$ *M* *n*-$C_{12}H_{25}NH_2 \cdot HCl$ in methanol–water (7:3); flow-rate, 1.09 ml/min; pressure drop, 5.3 MPa; detector, UV 254 nm.

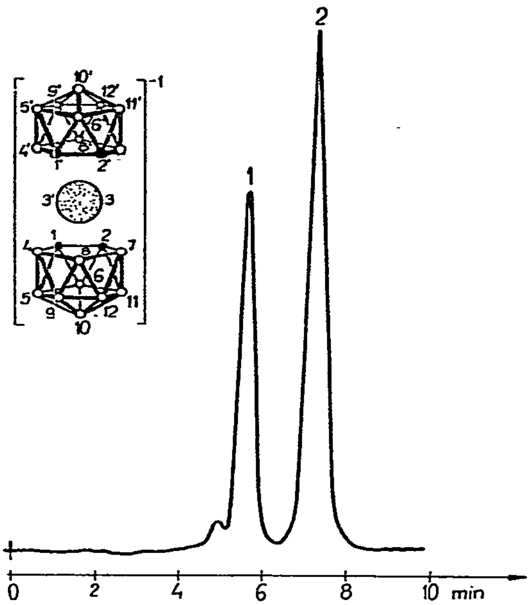

Fig. 2. Separation of sandwich complexes $(1,2\text{-}C_2B_9H_{11})_2M^-$, where M = Co (1) or Fe (2). Operating conditions: flow-rate, 0.84 ml/min; pressure drop, 4.0 MPa; other conditions as in Fig. 1.

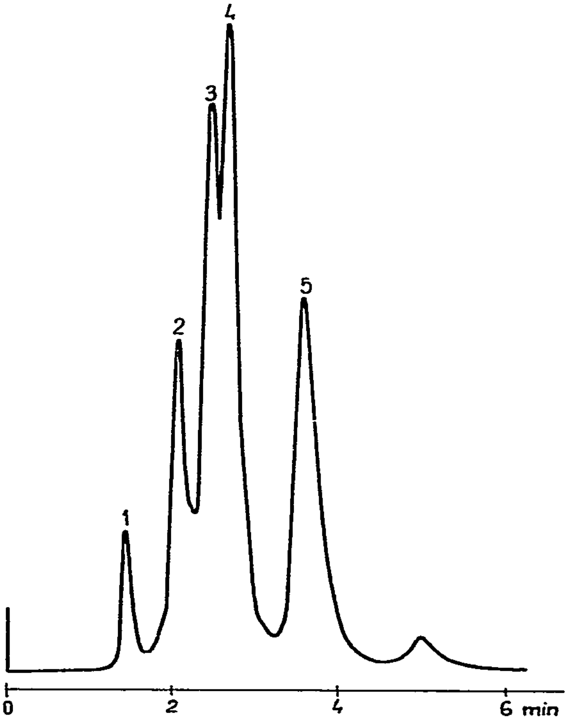

Fig. 3. Separation of a mixture of borane anions. 1 = Unknown; 2 = $7,8\text{-}C_2B_9H_{12}^-$; 3 = $5\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}^-$; 4 = $9\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}^-$; 5 = $9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}^-$. Operating conditions: sorbent Separon SI C_1 (10 μm); column, 200 × 3.8 mm; eluent, $2.7 \cdot 10^{-3}$ *M* $n\text{-}C_{12}H_{25}NH_2 \cdot HCl$, 0.02 *M* $NaClO_4$ in methanol–water (6:4); flow-rate, 1.15 ml/min; pressure drop, 8.5 MPa; detector, UV 254 nm.

retained solutes. Column efficiencies of 6000 theoretical plates per metre were achieved for ionic compounds, as compared with 11,500 theoretical plates per metre for the non-ionic test substance anisole on the C_1-BP sorbent. The spherical commercial sorbent Separon SI C_1 exhibited the same selectivity, the retention ratios being *ca.* 50% of the value obtained with irregular C_1-BP material.

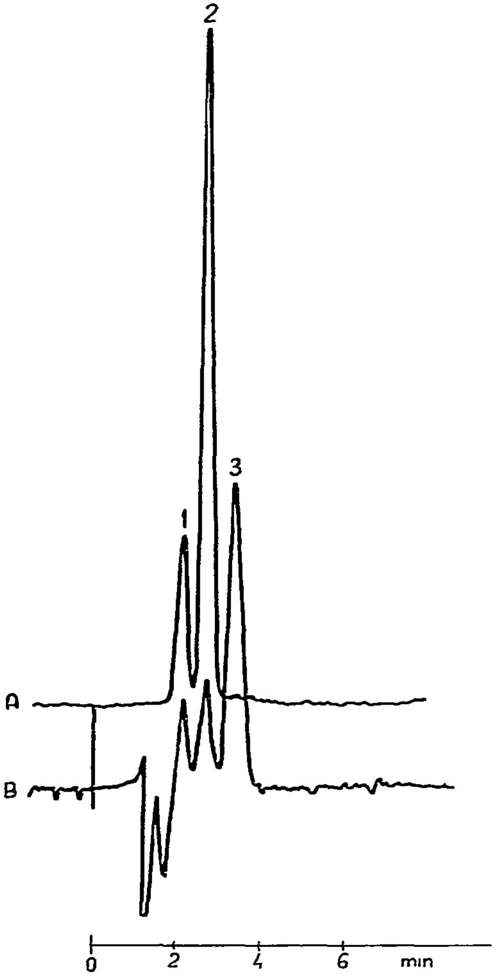

Fig. 4. Separation of non-ionic *o*-carborane from borane anion reaction products. 1 = $7,8\text{-}C_2B_9H_{12}^-$; 2 = $9\text{-OH-}7,8\text{-}C_2B_9H_{11}^-$; 3 = $1,2\text{-}C_2B_{10}H_{12}$ (*o*-carborane). Operating conditions: detection A, UV 254 nm; B, refractive index; other conditions as in Fig. 2.

All borane anions studied exhibit absorption in the low UV region. For the $C_2B_9H_{12}^-$ anion and its derivatives, the absorption maximum lies below 240 nm and, when working with a variable-wavelength UV detector, the lowest available value (235 nm) was used. Sandwich heteroborane complexes exhibit absorption maxima near 280 nm. For comparison, Table II presents the minimum detectable amount of solute that causes a detector signal of double the noise intensity. However, the gain in signal intensity of the single beam variable-wavelength detector is partially de-

TABLE II

MINIMUM DETECTABLE AMOUNTS (IN μg) OF SOME BORANE ANIONS

For chromatographic conditions see Table I, system II.

Species	*UV detection wavelength*		
	*254 nm**	*280 nm***	*235 nm***
$7,8\text{-}C_2B_9H_{12}K$	0.250	–	0.105
$5\text{-iso-}C_3H_7\text{-}7,8\text{-}C_2B_9H_{11}Cs$	0.580	–	0.360
$5\text{-I-}7,8\text{-}C_2B_9H_{11}N(CH_3)_4$	0.120	–	0.167
$9\text{-I-}7,8\text{-}C_2B_9H_{11}N(CH_3)_4$	0.093	–	0.065
$10\text{-OH-}7,9\text{-}C_2B_9H_{11}N(CH_3)_4$	0.370	–	0.096
$(1,2\text{-}C_2B_9H_{11})_2CoCs$	0.030 0.139**	0.036	–
$(1,2\text{-}C_2B_9H_{11})_2FeN(C_4H_9)_4$	0.062	0.130	–
$8,8'\text{-}S(1,2\text{-}C_2B_9H_{10})_2CoN(CH_3)_4$	0.100	0.095	–
$8,8'\text{-}C_6H_4(1,2\text{-}C_2B_9H_{10})_2CoCs$	0.068	0.083	–

* Fixed-wavelength detector.
** UVM detector.

preciated by its relatively high noise level. But even with this instrumentation, including very short column, sufficient sensitivity can be routinely achieved.

For some borane anions under certain but different conditions peak splitting was observed. Similar behaviour was described in the reversed-phase ion-pair separation of benzenesulphonic acids[23] and the phenanthroline complex of ruthenium[10]. The phenomenon, which is not due to bad column performance, can be easily identified by changing the amount of sample injected, as seen in Fig. 5. Not all the principles governing the observed peak splitting are clear, but from the experiments it follows that the main factors determining the extent of peak splitting are the ratio of the concentrations of the solute and the counter ion, the composition of the mobile phase and the chemical nature of the solute.

To gain insight in chromatographic factors in ion-pair chromatography that can be used to optimize the separation process, we studied the effect of the concentra-

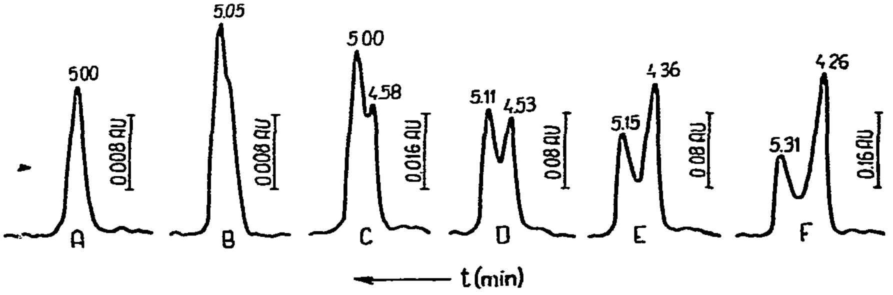

Fig. 5. Effect of a sample amount on splitting of the $9,11\text{-}I_2\text{-}7,8\text{-}C_2B_9H_{10}^-$ peak. Sample size: A, 11.4 μg; B, 28.5 μg; C, 57 μg; D, 136.8 μg; E, 285 μg; F, 570 μg. Operating conditions: sorbent C_1-BP (14 μm); column, 300 × 3.8 mm; eluent, $2.7 \cdot 10^{-3}$ *M* $n\text{-}C_{12}H_{25} \cdot HCl$, 0.02 *M* $NaClO_4$ in methanol–water (65:35); flow-rate, 1.26 ml/min, pressure drop, 7.8 MPa; detector, UV 254 nm. The numbers above the peaks denote corresponding *k'* values.

tion of the pairing ion (Fig. 6) and methanol content in mobile phase (Fig. 7) on retention behaviour of borane solutes. In addition, the effect of the inert salt concentration, the pH of mobile phase (Table III) and the effect of the lengths of the pairing-ion chain and the bonded-phase hydrocarbon chain were examined.

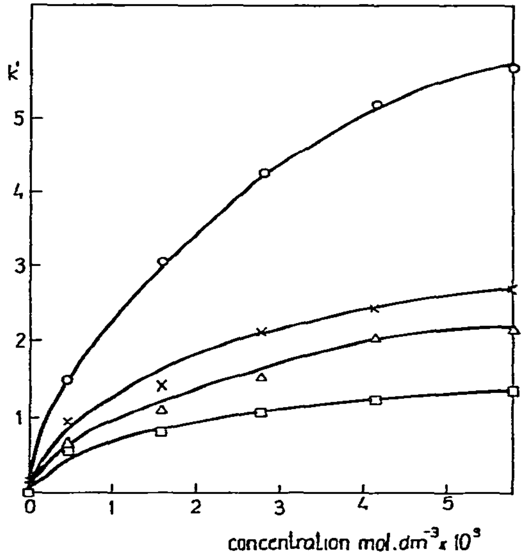

Fig. 6. Effect of the concentration of the pairing agent (laurylamine hydrochloride) on borane anion capacity ratios: △, 5-I-7,8-$C_2B_9H_{11}^-$; ×, 5-iso-C_3H_7-7,8-$C_2B_9H_{11}^-$; □, 7,8-$C_2B_9H_{12}^-$; ○, (1,2-$C_2B_9H_{11})_2Co^-$. Operating conditions: sorbent, C_1-BP (14 μm); column, 150 × 3.8 mm; eluent, methanol–water (7:3); flow-rate, 1.35–1.40 ml/min; pressure drop, 6.5–7.0 MPa; detector, UV 254 nm.

Fig. 6 shows that the addition of pairing ion sharply increases the retention of borane anions which are practically not retained in methanol–water solvent system. Further increase in pairing-ion concentration increases retention without any change in elution order. The retention of borane cage anions is very sensitive to the amount of methanol in the mobile phase, as seen from Fig. 7. The observed phenomena, which are consistent with observations on other ion-pair reversed-phase systems[24], can be rationalized in terms of solvophobic theory[25,26]. Despite the fact that the exact mechanism for ion-pair chromatography has not been clearly established to date, a model involving the formation of ion pairs in the mobile phase, followed by distribution of the ion peaks to the hydrophobic stationary phase, is the easiest framework for rationalizing the observed phenomena. Thus, the decrease in methanol concentration increases the surface tension of methanol–water eluent and increases the repulsive interaction of hydrophobic ion pairs with the eluent, resulting in increased k' values. As seen from Table III, the addition of neutral salt decreases the k' values of borane anions. Added salt can compete in forming ion pairs with the pairing ion, thus decreasing the thermodynamic activity of the pairing ion. The observed decrease in retention is dependent also on the chemical nature of the anion added. The perchlorate anion is known to be a good ion-pairing agent, and its effect is thus stronger than that of the sulphate anion.

The conjugated acids of the borane anions under study are generally strong

TABLE III

EFFECT OF ACIDITY OF ELUENT AND INERT SALT CONCENTRATION ON CAPACITY RATIOS OF SOME BORANE ANIONS

Chromatographic conditions: sorbent, Separon SI C_1 (10 μm); column, 200 × 3.8 mm; eluent, $2.7 \cdot 10^{-3}$ *M* $n\text{-}C_{12}H_{25}NH_2 \cdot HCl$ in methanol–water (6:4); flow-rate, 1.25 ml/min; detector, UV 254 nm.

Species	*k′ value*				
		pH 6.8	*pH 3.6*	*pH 5.6*	
	$c_{H_2SO_4}$ *(M)*				
	0.000	*0.000*	*0.002*	*0.000*	*0.000*
	$c_{inert\ salt}$ *(M)*				
	0.000	*0.020* (Na_2SO_4)	*0.020* (Na_2SO_4)	*0.020* ($NaClO_4$)	*0.040* ($NaClO_4$)
$7,8\text{-}C_2B_9H_{12}K$	2.29	0.95	1.03	0.33	0.36
$5\text{-iso-}C_3H_7\text{-}7,8\text{-}C_2B_9H_{11}Cs$	4.83	2.02	2.24	0.77	0.85
$5\text{-I-}7,8\text{-}C_2B_9H_{11}N(CH_3)_4$	3.82	1.62	1.75	0.59	0.61
$9\text{-I-}7,8\text{-}C_2B_9H_{11}N(CH_3)_4$	4.32	1.93	2.03	0.71	0.73
$5\text{-Cl-}7,8\text{-}C_2B_9H_{11}K$	2.64	1.16	1.22	0.40	0.44
$9\text{-Cl-}7,8\text{-}C_2B_9H_{11}N(CH_3)_4$	2.96	1.29	1.37	0.47	0.53
$(1,2\text{-}C_2B_9H_{11})_2CoCs$	12.00	6.24	6.63	2.10	2.22

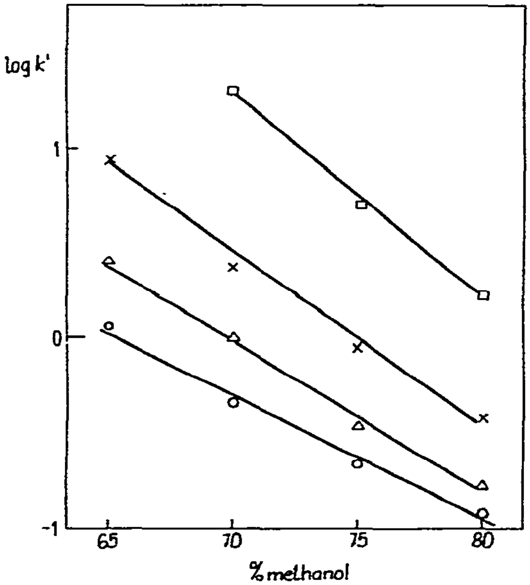

Fig. 7. Relationship between log *k′* and the amount of methanol in the mobile phase for some borane anions: ○, $7,8\text{-}C_2B_9H_{12}^-$; ×, $(1,2\text{-}C_2B_9H_{11})_2Co^-$; □, $(1,2\text{-}C_2B_9H_{10}I)_2Co^-$; △, $9\text{-I-}7,8\text{-}C_2B_9H_{11}^-$. Operating conditions: sorbent, C_1-BP (14 μm); column, 300 × 3.8 mm; eluents $2.7 \cdot 10^{-3}$ *M* $n\text{-}C_{12}H_{25}NH_2 \cdot HCl$ and 0.02 *M* $NaClO_4$ in methanol–water; flow-rate, 1.25–1.30 ml/min; pressure drop, 6.3–7.8 MPa; detector, UV 254 nm.

acids in a Brönsted sense, *e.g.* $7,8\text{-}C_2B_9H_{13}$ can be titrated in methanol–water (1:2) solution[12] with apparent pK_a of 2.95. As might be expected, the influence of the acidity of the eluent on k' values was minimal, as demonstrated in Table III. The reproducible k' values of borane anions and symmetrical peaks can be obtained without using complicated buffer system.

Table IV shows the influence of changing the lengths of the pairing-ion chain and bonded-phase hydrocarbon chain on the retention and selectivity of some borane anions. The group contribution term, τ, is defined[25] as $\tau = \log k'_j/k'_i$, where k' are capacity ratios of solutes j and i which differ by a functional group. In this present study, the reference solute i was taken to be the unsubstituted $7,8\text{-}C_2B_9H_{12}^-$ anion, and the sandwich complexes are formally considered as derivatives of this anion. From the results it follows that a decrease in the length of alkyl chain of the counter ion produces a corresponding decrease in the retention of a given solute, but the elution order of solutes remains unchanged. The order of the retention power of the stationary phases, $C_{18} > C_1$, can be related to the carbon loading of the support. However, the higher carbon content of the C_{18} sorbent does not bring about a corresponding increase in selectivity. To obtain a reasonable retention, mobile phases of different polarity were used. The linear relationship between τ and the surface

TABLE IV

FUNCTIONAL BEHAVIOUR OF SOME $7,8\text{-}C_2B_9H_{12}^-$ SUBSTITUTION DERIVATIVES DETERMINED USING VARIOUS ALKYLSILICA STATIONARY PHASES AND VARIOUS PAIRING IONS

Column 150 × 3.8 mm; methanol–water eluent; pairing ion concentration, $2.70 \cdot 10^{-3}$ *M*; flow-rate, 1.20 ml/min. $7,8\text{-}C_2B_9H_{12}^-$ structure drawing: Fig. 1.

	Sorbent					
	C_1-BP		*C_1-BP*		*Separon SI C_{18}*	
	Pairing agent					
	$n\text{-}C_{12}H_{25}NH_2$		*$n\text{-}C_6H_{13}NH_2$*		*$n\text{-}C_{12}H_{25}NH_2$*	
	Methanol concentration (%) (v/v)					
	70		*60*		*75*	
Substituent	k'	τ	k'	τ	k'	τ
H	0.89	0.00	0.72	0.00	0.89	0.00
5-Cl	1.08	0.08	0.92	0.11	1.14	0.11
5-I	1.16	0.11	1.08	0.18	1.28	0.16
5-iso-C_3H_7	1.49	0.22	1.62	0.35	1.56	0.24
5-HS	1.05	0.07	0.89	0.09	–	–
9-I	1.22	0.14	1.33	0.27	1.44	0.21
9-Cl	1.03	0.06	0.97	0.13	1.06	0.08
9-OH	1.32	0.17	1.47	0.31	1.44	0.21
9,11-I_2	2.03	0.36	2.94	0.61	2.46	0.44
9,11-Cl_2	1.22	0.14	1.25	0.24	1.28	0.16
$3\text{-}C_2B_9H_{11}Fe^-$	4.05	0.66	8.86	1.09	5.14	0.76
$3\text{-}C_2B_9H_{11}Co^-$	2.89	0.51	5.53	0.89	3.73	0.62

tension of the eluent was demonstrated by Riley *et al.*[26], and for the C_1 bonded phase–hexylamine counter-ion system the effect of the more polar eluent with higher surface tension dominates. Thus, for a given class of compounds, the C_1-bonded phase seems to be more useful than the C_{18}-bonded phase in terms of selectivity.

When we try to discuss the relationship between the chemical nature of the compounds under study and their retention behaviour, we are handicapped by the fact that, for these compounds, only a few physical data are available. Despite this fact, two general trends are obvious. As the surface area of the molecule increases so the retention increases, which is demonstrated by high positive τ values of sandwich complexes and $C_2B_9H_{12}^-$ iodine derivatives (see Table IV). Substitution of hydrogen in 7,9-$C_2B_9H_{12}^-$ by a more polar group leads, for 10-OH and 10-CH_3O groups, to a decrease of retention and, for 5-HS group in the 7,8-$C_2B_9H_{12}^-$ skeleton, to only a small increase in retention in comparison with the retention of the parent anion. The k' values of 9-OH-7,8-$C_2B_9H_{12}^-$ are higher than one might expect on the basis of the ideas given above.

CONCLUSION

Ion-pair liquid chromatography with *n*-alkylamine pairing ions, C_1-bonded phase on silica and a methanol–water eluent system presents a powerful and relatively simple analytical method for separating heteroborane anions. The methanol–water ratio, the *n*-alkylamine chain length, and the concentrations of the pairing ion and the inert salt can be varied, to achieve the required separation for the broad range of borane anions. The separation of non-ionic heteroboranes and heteroborane anions can be performed in a single analysis. The great separation efficiency allows the routine separation of structurally closely related species, including geometrical isomers, on a sub-microgram scale.

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