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IMPORTANCE AND USE OF INCLUSION COMPOUND FORMATION IN GAS–SOLID CHROMATOGRAPHY

E. SMOLKOVÁ, L. FELTL and J. VŠETEČKA

Department of Analytical Chemistry, Faculty of Science, Charles University, 12840 Prague 2, Albertov 2030 (Czechoslovakia)

SUMMARY

Gas chromatography can supply useful information on the course of clathration, and the formation of inclusion compounds can be utilized in the chromatographic separation of substances. In addition to the interactions common in gas–solid and gas–liquid chromatographic systems, specific properties of inclusion compounds play a role and can sometimes be used with advantage for analytical purposes. Systems containing wide-pore silica (Silochrom S-80) or Chromosorb W coated with urea or thiourea as hosts were investigated. The measurements were carried out by using sorbates selected on the basis of their clathrating ability. The temperature dependence of V_g was determined over the temperature range 40–140° on a monomolecular layer of urea on silica. Comparison of the retention data on pure silica and Chromosorb W and on these substances coated with urea or thiourea indicated that the formation of inclusion compounds contributes to the retention of sorbates that are capable of clathration. Although this process is less pronounced in the gaseous phase than in the liquid phase, it is still advantageous for certain types of substances that can be analysed very rapidly, in short columns and at lower temperatures than on common chromatographic packings.

INTRODUCTION

The principal use of inclusion compounds on laboratory and industrial scales is in the separation of substances with different molecular structures. Separations based on the formation of inclusion compounds are usually carried out in liquid systems and their study has been described in many papers (*e.g.*, refs. 1–3). The formation of inclusion compounds is also utilized in modern analytical separation methods, especially in liquid[4–6] and gas chromatography[7–10]. Gas chromatography is a method that permits modelling of the experimental conditions over a wide range and hence enables detailed studies of the formation and properties of clathrates to be carried out. From gas chromatographic data, conclusions can then be drawn about the physico-chemical properties of inclusion compounds and about the possibilities of using them analytically as selective stationary phases.

In view of the importance of inclusion compounds in petrochemistry, we recently studied especially urea adducts with C_8–C_{16} *n*-alkanes[11,12], using more than 30 alkanes with various structures as sorbates. The main factors affecting clathration were followed, *viz.*, the chain length of the guest *n*-alkane molecules, the vapour pressure of the guest molecules and temperature. These studies confirmed that the stability of the adduct increases with increasing chain length. If the adducts are employed as stationary phases, their partial dissociation can be used for the formation of further adducts with the sorbates studied, which can be employed analytically.

The temperature dependences indicated that the urea adducts with *n*-alkanes are decomposed below the melting point of urea and that the decomposition temperature increases with increasing chain length of the *n*-alkanes.

The relatively stable urea adduct with *n*-hexadecane[13] was used for a deeper study of these dependences, not only for *n*-alkanes and branched alkanes, but also for other compounds that can behave as guests, namely olefins, ketones and *n*-alkanols. Depending on the temperature, either the clathrate itself can be used in the gas–solid chromatographic (GSC) system, transition phenomena (*i.e.*, decomposition of the clathrate) can be studied, or its decomposition products (*n*-hexadecane) can be employed as liquid stationary phases in the gas–liquid chromatographic (GLC) system.

In connection with these studies and with published work in which the host was used as a stationary phase for analytical purposes[10,14,15], we have further studied interactions that take place in the GSC system involving a common adsorbent or support coated with the clathrating component. The aim of these experiments was to establish the extent to which the specific properties of inclusion compounds contribute to interactions common in GSC and to ascertain their possible analytical uses.

EXPERIMENTAL

Silochrom S-80 wide-pore silica (particle size 0.16–0.25 mm) (Reakhim, U.S.S.R.) and Chromosorb W (60–80 mesh) coated with 10–20% urea or thiourea to ensure complete coverage of the surface were used.

The sorbates were selected to represent various types of compounds (aliphatic and aromatic hydrocarbons, halogen derivatives, alcohols, ethers and ketones) from the point of view of their various activities in the formation of inclusion compounds. All of the substances used were commercial preparations of analytical-reagent grade.

The measurements were carried out on a Chrom 4 chromatograph (Laboratorní přístroje, Prague, Czechoslovakia) with flame-ionization detection, using stainless-steel columns of length 85 cm and I.D. 6 mm. Nitrogen was used as the carrier gas.

RESULTS AND DISCUSSION

The experiments were based on the properties of sorbents obtained by depositing a monomolecular layer of a strongly adsorbed substance on a strongly adsorbing surface, in this instance wide-pore silica. Then adsorption on a solid sorbent was replaced by adsorption on a monolayer, the volatility of which was substantially decreased by adsorption forces. In this way, the specific properties of the substance

adsorbed on the monolayer can be utilized, while the main advantage of GSC, *viz.* the rapid partition kinetics, permitting rapid analyses, is preserved.

The Silochrom S-80 was coated with a monomolecular layer of urea and the retentions of a wide range of substances of various structural types were measured at 40–140°. Measurements on the original Silochrom S-80 were carried out in parallel. The results of these measurements are summarized in Tables I and II.

A comparison of the data obtained on Silochrom S-80 with those obtained on Silochrom S-80 coated with a monolayer of urea shows that the specific retention volumes are lower on the urea-coated adsorbent, which is caused, for most polar substances, by blocking of the surface hydroxyl groups of silica. This decrease is not strongly affected by a decrease in the surface area, as the retentions of non-specifically interacting substances, *i.e.*, of substances that do not form hydrogen bonds or clathrates, are virtually identical on the two adsorbents.

However, the assumed greater thermal stability of urea adsorbed as a monolayer has not been confirmed. Changes in the properties of the column due to decomposition of urea occur even below the melting point of urea, which is probably caused

TABLE I

SPECIFIC RETENTION VOLUMES ON SILOCHROM C-80 FOR VARIOUS TYPES OF SORBATE

Column: Silochrom S-80 silica gel, particle size 0.16–0.25 mm, length 85 cm, I.D. 6 mm, weight of the packing 9.60 g.

Sorbate	*Column temperature (°C)*					
	40	*60*	*80*	*100*	*120*	*140*
n-Pentane	14.30	7.38	4.02	2.59	1.50	0.94
n-Hexane	37.88	16.87	8.63	4.89	2.71	1.57
n-Heptane	99.09	39.54	18.42	9.49	5.12	2.83
n-Octane	260.65	91.73	38.56	18.13	8.73	4.72
Benzene	138.23	55.88	25.32	11.22	5.72	3.46
Toluene	—	159.21	62.73	27.34	12.34	6.61
Nitromethane	—	264.11	96.68	38.85	15.35	7.87
Dichloromethane	152.28	60.10	25.89	12.37	6.32	2.83
Chloroform	53.95	22.14	10.93	5.47	3.31	2.20
Carbon tetrachloride	38.88	18.45	9.21	5.47	3.31	2.20
1,1-Dichloroethane	71.50	30.05	13.81	7.19	3.91	2.20
1,2-Dichloroethane	145.75	58.52	25.32	12.37	6.32	3.46
1,1,1-Trichloroethane	72.50	31.10	14.96	7.77	4.51	2.83
1,1,2-Trichloroethane	—	117.56	48.34	21.58	9.93	5.35
1,1,1,2-Tetrachloroethane	—	148.14	58.12	26.18	11.74	6.61
1,1,2,2-Tetrachloroethane	—	—	112.22	46.32	18.96	9.76
Vinyl chloride	—	4.22	2.30	1.44	0.90	0.31
1,1-Dichloroethylene	15.80	8.43	4.60	2.59	1.50	0.94
Trichloroethylene	60.46	29.52	12.66	6.62	3.91	2.20
Perchloroethylene	—	42.70	19.57	10.07	5.12	2.83
1,2-Dibromomethane	—	135.48	54.10	24.46	11.14	5.98
Fluorobenzene	144.75	57.46	25.90	12.37	6.32	3.46
Chlorobenzene	—	—	54.67	24.46	11.14	5.98
Bromobenzene	—	—	87.48	37.69	16.56	9.13
Diethyl ether	—	—	—	151.07	51.47	21.09
Acetone	—	—	—	233.94	70.14	36.20

TABLE II

SPECIFIC RETENTION VOLUMES ON A MONOMOLECULAR LAYER OF UREA ON SILOCHROM S-80 FOR VARIOUS TYPES OF SORBATE

Column: Silochrom S-80 silica gel + 12.3% urea, particle size 0.16–0.25 mm, length 85 cm, I.D. 6 mm, weight of the packing 8.80 g.

Sorbate	*Column temperature (°C)*					
	40	*60*	*80*	*100*	*120*	*140*
n-Pentane	11.83	6.99	3.66	1.88	2.17	1.50
n-Hexane	33.30	18.05	8.53	4.39	3.61	2.25
n-Heptane	93.84	42.50	19.50	9.42	6.51	3.75
n-Octane	242.99	103.05	42.04	18.83	11.57	6.00
Benzene	76.23	34.93	16.45	8.79	5.06	3.75
Toluene	239.69	96.64	40.83	18.83	10.12	6.75
Nitromethane	—	132.74	54.84	25.11	12.29	7.50
Dichloromethane	91.09	43.08	20.11	10.67	5.78	3.75
Chloroform	44.30	22.70	11.58	6.28	3.61	2.25
Carbon tetrachloride	36.05	18.63	9.75	5.02	3.61	2.25
1,1-Dichloroethane	50.36	25.03	11.58	6.28	3.61	3.00
1,2-Dichloroethane	90.56	43.08	20.11	10.67	5.78	3.75
1,1,1-Trichloroethane	60.27	30.27	14.62	7.53	5.06	3.00
1,1,2-Trichloroethane	—	114.11	48.72	23.23	10.85	6.75
1,1,1,2-Tetrachloroethane	—	156.61	65.81	30.76	14.46	8.25
1,1,2,2-Tetrachloroethane	—	—	151.12	64.04	23.86	12.00
Vinyl chloride	—	2.91	1.83	1.25	0.72	0.72
1,1-Dichloroethylene	11.83	6.40	3.66	2.51	0.72	0.72
Trichloroethylene	55.86	26.78	13.40	6.28	4.34	3.00
Perchloroethylene	—	44.24	21.33	10.67	7.23	4.50
1,2-Dibromomethane	—	100.72	44.48	21.97	10.85	6.75
Fluorobenzene	84.48	43.08	17.06	10.67	5.78	3.75
Chlorobenzene	—	—	50.57	23.23	12.29	6.75
Bromobenzene	—	—	82.26	30.13	18.08	11.25
Diethyl ether	—	—	90.18	29.51	23.14	21.00
Acetone	—	—	187.68	67.80	45.55	31.30

by catalysis by silica acidic sites. Ammonia was detected in the carrier gas at 120° and for this reason the retention data obtained at 120° and 140° deviated from a linear dependence of log V_g *versus* $1/T$.

It follows from the temperature dependences of the specific retention volumes of substances capable of clathration, *i.e.*, *n*-alkanes and chlorinated hydrocarbons, and of inactive substances, *e.g.*, benzene, toluene and cyclohexane, that these two groups of sorbates behave differently. While the decrease in V_g for inactive substances (Fig. 1) is caused by their inability to interact with the hydroxyl groups over the whole temperature range, hydrocarbons (Fig. 2) and chlorinated hydrocarbons (Fig. 3) exhibit higher V_g values on urea-coated silica than on uncoated silica. This phenomenon can only be explained by assuming that the total energy of interaction determined by non-specific forces is increased by a contribution from a specific interaction due to the formation of the inclusion compounds with urea. This contribution increases with increasing numbers of carbon atoms in *n*-alkane molecules and of chlorine atoms in chloroethanes and chloroethylenes, as illustrated by the dependences in Figs. 1 and 2 and the data in Tables I and II. These conclusions also con-

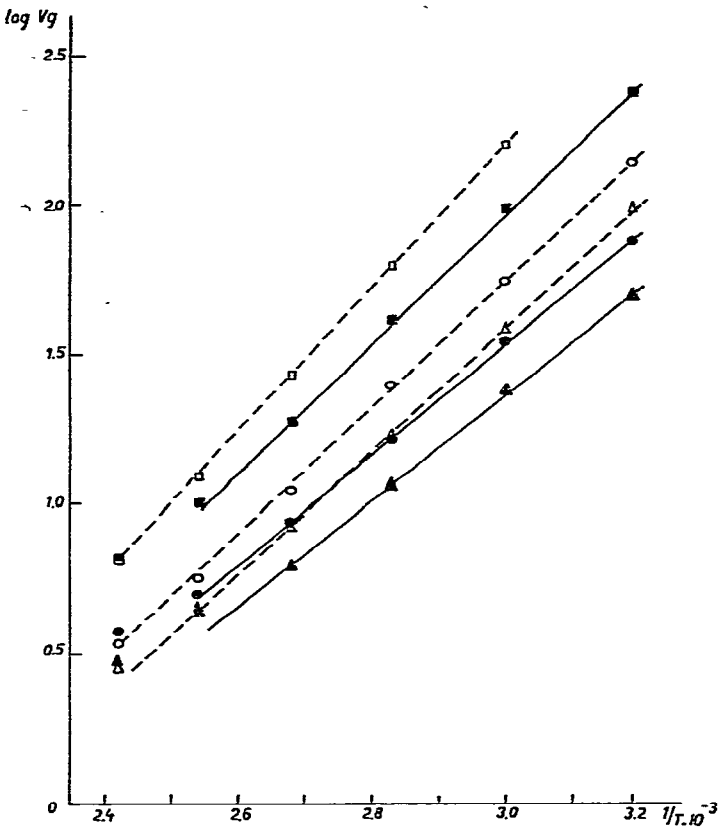

Fig. 1. Temperature dependences of V_g for non-clathrating sorbates on Silochrom S-80 and on a monomolecular layer of urea on Silochrom S-80. ○, Benzene; □, toluene; △, cyclohexene.

firm the results of previous experiments, in which the effect of the carbon chain length on the formation and stability of the adducts was shown. Chlorinated hydrocarbons, in agreement with the behaviour in the liquid phase, also change their elution order compared with the V_g values on silica only from tetrahalogeno derivatives onwards.

Similar experiments were carried out with urea deposited on a common chromatographic support, Chromosorb W. Further, thiourea was selected as a type of host that is capable of forming inclusion compounds with substances of different structural types. Reference experiments were carried out on the two columns.

A contribution from clathration to the overall retention of active sorbates, which can be used analytically, was also verified in these systems. An example is the separation of cyclohexane and *n*-hexane on urea deposited on Chromosorb W at 40° (Fig. 4), where the substances are eluted in the opposite order to that of their boiling points; this behaviour cannot be assigned to other interactions. Another example is analysis of light petroleum under identical conditions on columns with urea and thiourea deposited on Chromosorb W (Fig. 5). Whereas the separation is poor on the urea column, the individual components can readily be differentiated on the

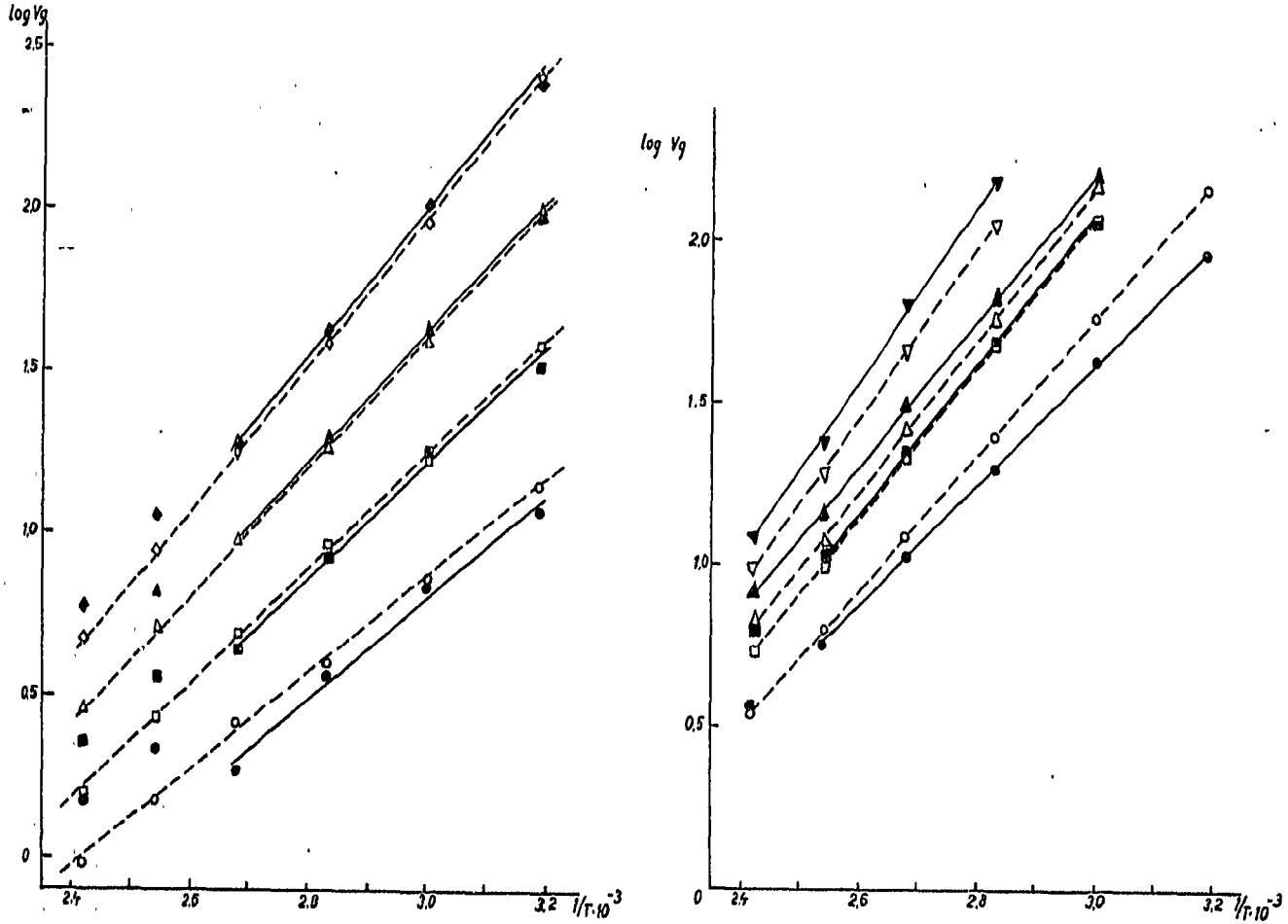

Fig. 2. Temperature dependences of V_g for *n*-alkanes on Silochrom S-80 and on a monomolecular layer of urea on Silochrom S-80. ○, *n*-Pentane; □, *n*-hexane; △, *n*-heptane; ◇, *n*-octane.

Fig. 3. Temperature dependences of V_g for chlorinated ethanes on Silochrom S-80 and on a monomolecular layer of urea on Silochrom S-80. ○, 1,2-Dichloro-; □, 1,1,2-trichloro-; △, 1,1,1,2-tetrachloro-; ▽, 1,1,2,2-tetrachloroethane.

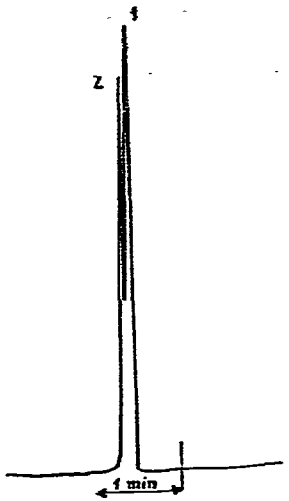

Fig. 4. Separation of cyclohexane and *n*-hexane on urea deposited on Chromosorb W.

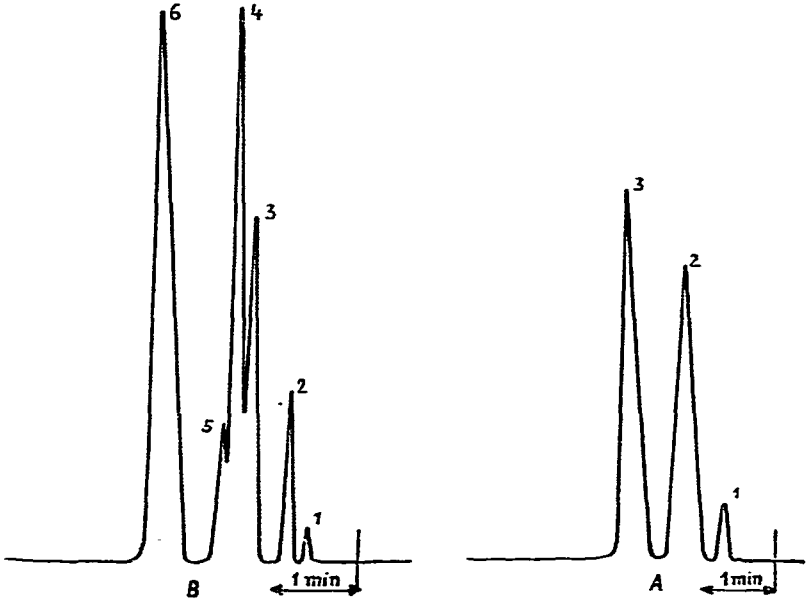

Fig. 5. Chromatograms of light petroleum on (A) urea and (B) thiourea deposited on Chromosorb W.

thiourea-coated column because of the formation of clathrates with the branched alkanes that constitute light petroleum.

In many other analytically useful systems the retention of individual substances cannot be unambiguously ascribed to the formation of inclusion compounds. It can rather be assumed that the separation mechanism is affected by the medium polarity of urea or thiourea. Orientative experiments indicated that these substances might be used with advantage as adsorbents, because of the rapidity of the analyses and the high peak symmetry obtained.

The results obtained confirmed that gas chromatography can detect even interactions as weak as the formation of inclusion compounds from the gaseous phase and that these compounds can sometimes be useful for selective separations.

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