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ADSORPTION ELUTION CHROMATOGRAPHY OF NITROGEN-CONTAINING HETEROCYCLES ON ALUMINA

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SUMMARY

The adsorption energies of three acidic and five basic nitrogen-containing heterocycles on aluminas with surface pH values of 4, 7.5 and 10 were measured. Mixtures of 10% diethyl ether and 10% methylene chloride with *n*-pentane were used for elution. The calculated values of the adsorption energies of the basic nitrogen compounds depend on the adsorbent surface pH and show the advantage of using acidic alumina for the separation of nitrogen bases from aromatic hydrocarbons. It was observed that the use of diethyl ether as an eluent considerably lessens the effect of the acidic surface of the adsorbent on basic substances.

INTRODUCTION

The separation of aromatic hydrocarbons by adsorption elution chromatography on alumina has been described in earlier communications[1,2]. Natural mixtures of aromatic hydrocarbons (oil distillates, tar fractions) usually contain a certain amount of nitrogen-containing compounds. In most instances, nitrogen-containing heterocycles are adsorbed on alumina more firmly than hydrocarbons with four aromatic rings. The retention volumes of a number of nitrogen-containing heterocycles and of polycyclic aromatics are, however, very similar. The S° and A_s parameters, characterizing the adsorption properties of a molecule (see below), correspond approximately to the values that are valid for polycyclic aromatics[3,4]. Polycyclic aromatics and nitrogen-containing heterocycles may interfere with each other in those instances when the specific properties of the heterocyclic molecules cannot assert themselves.

Nitrogen-containing heterocyclic substances are usually weakly acidic or basic, which can be quantitatively expressed by the negative logarithm of their dissociation constant, the pK_a value[4,5]. These properties can be utilized to improve the separation of aromatic hydrocarbons and heterocycles. The adsorption energy of a substance which has acidic or basic character depends, among other factors, on the pH of the surface of the adsorbent used and on the pK_a value of the substance. If an adsorbent with a non-neutral surface ($pH \neq 7$) is used for separating a mixture of nitrogen-containing compounds and hydrocarbons, an improved separation of a certain type of nitrogen-containing substance from the hydrocarbon fraction may result, depending on the pH of the adsorbent used. The success of this separation depends, however, on the basicity or acidity of the nitrogen-containing compound, since, in the case of a substance with a very low dissociation constant, the acid–base interactions cannot operate. Moreover, among polycyclic aromatics, tetracene and pentacene are marked by high retention volumes, so that in most instances they interfere with nitrogen-containing heterocycles.

The present paper deals with the adsorption elution chromatography of several nitrogen-containing heterocycles, using three kinds of alumina that differ in their surface pH values.

EXPERIMENTAL

Adsorbents

Alumina, Woelm Eschwege, was used, in acidic, neutral and basic forms. Prior to use, the adsorbents were deactivated by addition of 6% (w/w) of water.

Columns

Columns of lengths 36, 24 and 12 in., I.D. 4 mm, were obtained from Pye Unicam Ltd., Great Britain. The columns contained *ca.* 12, 8.5 and 4.5 g of adsorbent, respectively. The amounts of substances introduced were 0.5–1 mg. The eluent flow-rate was 60 ml/h. A guard column containing active silica gel was placed before the column during elutions with *n*-pentane.

Detector

An SP800B UV spectrophotometer (Pye Unicam) with a flow-through quartz cell, path length 2 mm, and dead volume 0.2 ml, was used. The wavelengths range of 240 to 265 nm were chosen for the detection.

Eluents

n-Pentane was used only for testing the adsorbents. The nitrogen-containing compounds were eluted either with a mixture of 10% of diethyl ether in *n*-pentane or with 10% of methylene chloride in *n*-pentane. All the solvents used were dried and distilled. The eluent purity was checked with the UV spectrophotometer.

The R°_{ab} values reported later in Table II are free from the effect of removing water. The precision and reproducibility of the results were checked by two methods. Firstly, no more than four samples were injected into the column. Secondly, the first injected sample was introduced again as the last one. The procedure was repeated by injecting samples in a different order.

HANDLING OF RESULTS

From the elution measurements, the equivalent retention volume, R°, defined as the retention volume of the substance from the dry column (ml) divided by the weight of adsorbent (g), was calculated.

The theoretical calculation of the equivalent retention volumes in adsorption chromatography is, according to SNYDER[3], described by eqn. 1 for a given adsorbent:

$$\log R^\circ = \log V_a + \alpha(S^\circ - \varepsilon^\circ A_s) + \Delta_{eas} \qquad (1)$$

where V_a is the surface volume of the adsorbent, α is the activity of the adsorbent, $S°$ is the adsorption activity of the sample, A_s is the molecular area of the adsorbed molecule, $\varepsilon°$ is the solvent strength parameter and Δ_{eas} is a complex term including the secondary effects of adsorbent, solvent and the adsorbed sample molecule.

As the Δ_{eas} factor is difficult to express, let us suppose that the effects of the adsorbent surface and the pK_a of the substance measured are implicitly included in the change, $\Delta Q°_i$, of the adsorption energy, $S°$:

$$S°_M = S° + \Delta Q°_i \tag{2}$$

The $S°_M$ value can be calculated from the measured equivalent retention volume of the substance with *n*-pentane, the $\varepsilon°$ value of which is defined as zero, or, if a mixture of two solvents is used for elution, the solvent strength, ε_{ab}, is calculated from eqn. 3:

$$\varepsilon_{ab} = \varepsilon_a + \frac{\log\,(N_b \cdot 10^{\alpha n_b(\varepsilon_b - \varepsilon_a)} + 1 - N_b)}{\alpha n_b} \tag{3}$$

where ε_a is the strength of solvent A, ε_b is the strength of solvent B, N_b is the mole fraction of solvent B in the binary mixture and n_b is the effective area of the adsorbed solvent B molecule.

The adsorption energy is calculated from the equivalent retention volume, $R°_{ab}$, with a mixture of solvents A and B:

$$S°_M = \frac{\log R°_{ab} - \log V_a}{\alpha} + \varepsilon_{ab} \cdot A_s \tag{4}$$

The characteristic values of the adsorbents, α and log V_a, required for calculation of $S°_M$ were obtained for all the adsorbents by measuring the equivalent retention volumes for naphthalene, phenanthrene and benzo[*a*]pyrene with *n*-pentane (Table I). The ε_{ab} values were calculated for the adsorbents and eluents used according to eqn. 3.

TABLE I

PARAMETERS OF ADSORBENTS AND ELUENTS

Alumina	*pH*	α	*log* V_a	ε_{ab} *pentane–10% diethyl ether*	ε_{ab} *pentane–10% methylene chloride*
Acidic	4	0.394	−1.873	0.116[a] 0.083[b]	0.131
Neutral	7.5	0.376	−1.852	0.112[a] 0.081[b]	0.128
Basic	10	0.504	−1.979	0.142[a] 0.100[b]	0.152

[a] Values for non-hydrocarbon samples.
[b] Values for hydrocarbon samples.

TABLE II

EQUIVALENT RETENTION VOLUMES, R°_{ab}, OF NITROGEN HETEROCYCLES ON ALUMINA

Sample	S°[a]	A_s[a]	pK_b[b]	R°_{ab}					
				Acidic alumina		*Neutral alumina*		*Basic alumina*	
				Pentane–10% CH_2Cl_2	*Pentane–10% diethyl ether*	*Pentane–10% CH_2Cl_2*	*Pentane–10% diethyl ether*	*Pentane–10% CH_2Cl_2*	*Pentane–10% diethyl ether*
Pyrrole	5.9	8.0	−0.3	2.70	1.32	3.36	1.78	8.57	3.38
Indole	6.8	10.0	−2.4	4.78	2.59	6.65	3.55	14.43	6.81
Carbazole	7.7	12.0	−1.9	6.86	2.82	8.18	3.68	17.40	9.40
Pyridine	6.3	6.0	5.4	23.2	4.60	12.36	3.14	14.5	5.15
Quinoline	6.2	8.0	5.0	21.40	3.42	11.68	2.58	17.44	4.12
Acridine	6.7	10.0	4.7	12.1	3.61	8.0	2.86	10.46	5.00
Isoquinoline	7.0	8.0	5.3	39.0	7.80	22.64	4.85	28.93	8.15
7,8-Benzoquinoline	5.8	10.0	4.3	4.62	0.88	3.37	0.77	4.76	1.60
Benzo[*a*]pyrene	6.4	13.0	—	0.62	0.28	0.54	0.25	1.54	0.79
Coronene	7.4	13.8	—	1.19	0.57	1.02	0.49	3.82	1.79

[a] Values from refs. 3 and 4.

[b] Values from refs. 4 and 5.

RESULTS AND DISCUSSION

The results obtained from the adsorption chromatography of nitrogen-containing heterocyclic substances on alumina adsorbents with different surface pH and using two kinds of eluents, *i.e.*, *n*-pentane with 10% of diethyl ether and *n*-pentane with 10% of methylene chloride, are summarized in Table II. As an example of the separation of aromatic hydrocarbons and nitrogen-containing heterocycles, the values for two hydrocarbons, benzo[*a*]pyrene and coronene, are also tabulated. The results in Table II are given in terms of equivalent retention volumes, $R°_{ab}$. Free adsorption energies, $S°$, areas of adsorbed substance molecules, A_s, and the pK_a values taken from the literature[3-5], are also tabulated. By using the characteristic values of the adsorbents, α and V_a, and the solvent strength values, ε_{ab}, from Table I, the corresponding $S°_M$ values for the nitrogen-containing substances measured were calculated by eqn. 4. Some of the $S°_M$ values obtained in this way are plotted against

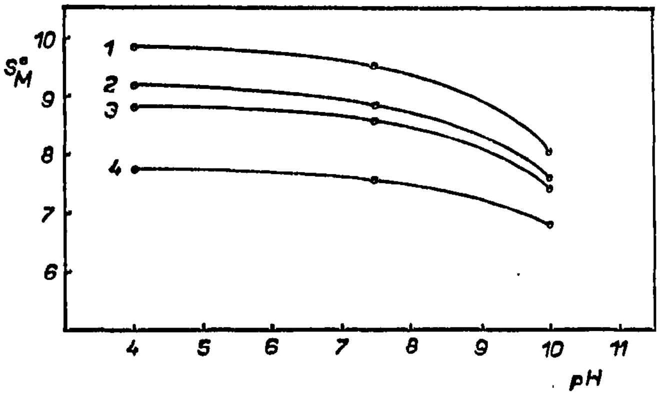

Fig. 1. Dependence of adsorption energies of basic nitrogen compounds on the pH of the adsorbent surface. 1 = Isoquinoline; 2 = quinoline; 3 = acridine; 4 = 7,8-benzoquinoline. Eluent: *n*-pentane–10% of methylene chloride.

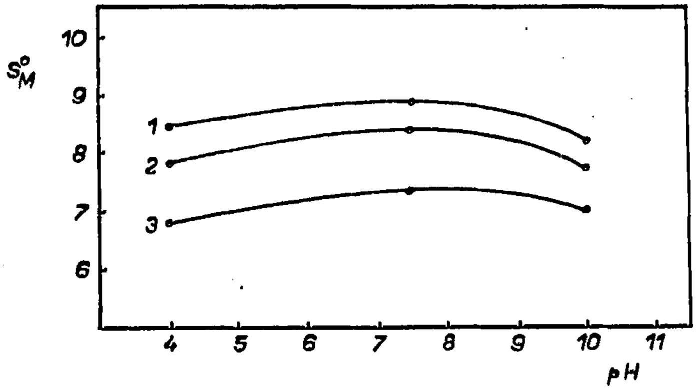

Fig. 2. Dependence of adsorption energies of non-basic nitrogen compounds on the pH of the adsorbent surface. 1 = Carbazole; 2 = indole; 3 = pyrrole. Eluent: *n*-pentane–10% of methylene chloride.

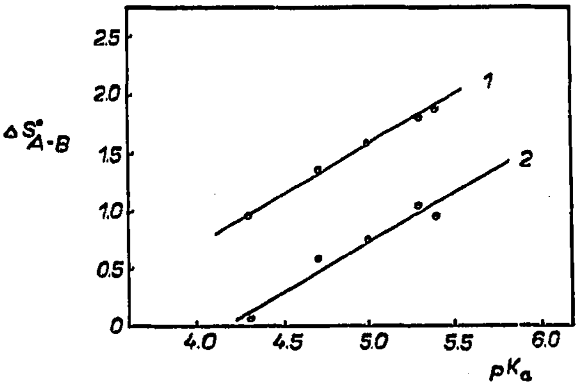

Fig. 3. Excess adsorption energies of basic compounds on acidic alumina. 1 = Eluent, *n*-pentane–10% of methylene chloride; 2 = Eluent, *n*-pentane–10% diethyl ether.

the pH values of the adsorbents used in Figs. 1 and 2. In Fig. 3, the values $\Delta S°_{A-B}$, *i.e.*, the difference between the $S°_M$ values on acidic and basic alumina, are plotted against the pK_a value of the corresponding nitrogen-containing base. From Table II, it follows that, by using acidic and neutral alumina, good separation of hydrocarbons and nitrogen-containing heterocycles can be achieved with the two eluents used. Further, it can be seen that interference between coronene and 7,8-benzoquinoline occurs on basic alumina. It is expected that this interference would be even more pronounced with other weakly basic substances.

The results show disagreement between the calculated ε_{ab} values (Table I) and the actual solvent strength found during the determination of equivalent retention volumes, $R°_{ab}$ (Table II). While the calculation suggests that the solvent strength of the mixture pentane–10% of methylene chloride is in all instances higher than that of the mixture *n*-pentane–10% of diethyl ether, the experiment showed the opposite, even if a higher solvent strength of diethyl ether for substances other than hydrocarbons was assumed in the calculation of ε_{ab} (ref. 6). Certain differences between calculated and observed ε_{ab} values for 10% methylene chloride can be explained by the uncertainty in the α values. The differences in ε_{ab} values for 10% diethyl ether can be partially explained by eluent localization.

The results show that the use of the mixture *n*-pentane–methylene chloride and of acidic alumina as an adsorbent is advantageous for separating nitrogen-containing basic substances and aromatic hydrocarbons. While the adsorption energy increase, $\Delta S°_{A-B}$, is 1–2 units when using the mixture *n*-pentane–methylene chloride, this increase is, on average, 0.8 unit less for the *n*-pentane–diethyl ether eluent. For weakly acidic nitrogen-containing substances (pyrrole, indole and carbazole), no dependence was found on the surface pH of the adsorbent. It is probable that the pK_a values of these substances are so low that there is no acid–base interaction. The effect of the surface pH of the adsorbent is proved unambiguously for basic nitrogen-containing substances. The increased adsorption energy on acidic alumina is due to acid–base interactions between the lone pair of electrons on the nitrogen atom and the positive charge concentrated on the aluminium atoms of the adsorbent. A closer study of this interaction would require a more precise determination of the character of the acidic centres on the alumina surface.

From a comparison of the results obtained by elution with mixtures of diethyl ether and methylene chloride with *n*-pentane (Table II), substantial differences in the effects of the surface pH on the adsorption energy (or log $R°_{ab}$) are evident. The explanation of this follows from a correlation of the structures of both of the solvents with the properties of the adsorbent surface. Comparing the two eluents used (diethyl ether and methylene chloride), a symmetrical electron cloud around the chlorine atoms can be assumed, while the oxygen atom has two lone pairs of electrons. Alumina belongs to the group of polar adsorbents with very complex surfaces, containing both acidic and basic centres. KISELEV[7] distinguishes between adsorbents with so-called positive and negative surface fields. For an adsorbent with a positive field, an interaction with electron donors occurs (π-electrons, lone pairs of electrons). Therefore, the assumption is substantiated that lone pairs of electrons will be more easily polarizable and diethyl ether, as an electron donor, will occupy the acidic centres of the adsorbent. As there is simultaneously an acid–base interaction of the surface with nitrogen-containing basic substances on the acidic centres, it can be stated that the use of diethyl ether as an eluent suppresses to a considerable extent this interaction and decreases the effect of the pH of the adsorbent surface. This is a typical example of eluent–adsorbent interaction, which was noted earlier by SNYDER[6] as an ether anomaly. In the present case, the connection of this interaction with the acidity of the alumina was definitely proved. This ether effect will take place even in adsorption of relatively strong bases (*e.g.*, pyridine). Comparing the results in Table II, it is necessary to consider the different parameters of the individual adsorbents. For pyridine, the $R°_{ab}$ values for the 10% diethyl ether mixture are approximately the same for acidic and basic alumina, while for the 10% methylene chloride mixture a large difference is observed. This depends on the pK_b value, *i.e.*, a solute of low pK_b decreases the effect of the acidic surface of alumina when using the 10% methylene chloride mixture as solvent. When methylene chloride is used as an eluent, the total adsorption energy of nitrogen-containing bases on alumina is the sum of the physical adsorption energy and an energy accompanying the charge transfer in the interaction of the π-electrons of nitrogen with the acidic centres of the adsorbent. The magnitude of the energy liberated during a charge-transfer interaction is directly proportional to the pK_a of the adsorbed base and inversely proportional to the pH of the adsorbent surface (Fig. 3). The results obtained show that the surface pH effect cannot be neglected when eluents occupying the acidic centres of alumina are used.

REFERENCES

1 M. POPL, J. MOSTECKÝ AND Z. HAVEL, *J. Chromatogr.*, 53 (1970) 233.
2 M. POPL, V. DOLANSKÝ AND J. MOSTECKÝ, *J. Chromatogr.*, 59 (1971) 329.
3 L. R. SNYDER, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
4 L. R. SNYDER AND B. E. BUELL, *J. Chem. Eng. Data*, 11 (1966) 545.
5 C. A. STREULI, *Anal. Chem.*, 30 (1958) 997.
6 L. R. SNYDER, *J. Chromatogr.*, 16 (1964) 55.
7 A. V. KISELEV, *Zh. Fiz. Khim.*, 38 (1964) 2753.