WATER DEACTIVATED MAGNESIA AS A CHROMATOGRAPHIC ADSORBENT

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(Received October 20th, 1966)

INTRODUCTION

Magnesia (magnesium oxide or hydroxide) has been used as a chromatographic adsorbent principally in the separation of the carotenoids (see review of RAGAZZI et al.[1]), with only occasional application to other sample types (e.g. alkaloids[1], porphyrins[2]). By comparison with such adsorbents as silica, alumina or charcoal, magnesia is scarcely used at all today in adsorption chromatography. The lack of interest in magnesia as adsorbent can be traced to several factors: no obvious advantages over the more common adsorbents; reports by different workers that different batches of magnesia are highly variable; the availability of most commercial chromatographic magnesias as fine powders rather than in larger particle sizes which are more popular for column chromatography; the early failure[3] of magnesia in thin-layer chromatography (TLC) applications (but note later success with magnesia in TLC[1]). Despite these apparent shortcomings of magnesia, a number of isolated observations in the literature emphasize its uniqueness with respect to other polar adsorbents. Most polar adsorbents strongly adsorb compounds containing polar substituents such as hydroxyl or keto, and it is possible to separate different compound groups according to the type and number of polar substituents. The presence of one or two vinyl groups in such compounds frequently has only a slight effect on their relative adsorption. STRAIN[4] has noted, however, that the relative adsorption of the carotenes on magnesia is determined largely by the number of olefinic double bonds, with polar groups playing a less important role. Similarly NICHOLAS[2] has shown that the relative adsorption of the porphyrins on most polar adsorbents increases with increasing number of ester substituents on the porphyrin molecule, while for adsorption on magnesia a reverse separation sequence is observed. SCHWARTZ AND PARKS[5] were able to separate homologous carbonyl compounds *as a class* from corresponding monounsaturated compounds on magnesia, a separation which does not appear possible on other polar adsorbents and which again demonstrates the preferential adsorption of unsaturated compounds on magnesia. Finally SABACKY et al.[6] have reported that ethyl ether and acetone are weaker solvents (*i.e.* give larger sample adsorption) for adsorption on magnesia than is benzene, while on other polar adsorbents ether and acetone are always stronger solvents than is benzene. Again this can be interpreted as preferential adsorption of an unsaturated compound (*i.e.* benzene) on magnesia since solvent strength has been related to solvent adsorption energy[7].

The purpose of the present study was to evaluate the chromatographic proper-

ties of magnesia in terms of a previous theoretical model for other polar adsorbents (e.g. refs. 8, 9 and preceding papers in that series), and to compare the types of separations which can be obtained on magnesia relative to other adsorbents.

EXPERIMENTAL

The major part of the present investigation was based on an adsorbent composed of two parts by weight of Sea Sorb 43 "Adsorptive Magnesia" (Fisher Scientific) plus one part of Celite 545 (Johns Manville). The dry adsorbent mixture was first blended with water, dried on an air filter, and heated overnight in air at 130°. Limited studies were also carried out on a granular magnesia (West Vaco) which was ground to 100–200 mesh and heated as above. Unless otherwise specified, all of the data reported in following sections refer to the Sea Sorb Magnesia–Celite mixture rather than to the West Vaco magnesia. Dry adsorbent was further activated by heating in air for 16 h at various temperatures. Water deactivated adsorbent samples were prepared from activated adsorbent by adding liquid water and equilibrated in closed containers for 24 h or longer. The experimental data reported in following sections refer generally to adsorbent with a final activation at 300°, with the indicated amount of added water (as % H_2O–MgO); this material (Sea Sorb Magnesia–Celite) had a BET surface area of 90 m^2/g prior to deactivation by water.

The measurement of equivalent retention volumes $\underline{R}°$ (ml/g) for various sample compounds was carried out as previously[10]. Sample was charged to prewet columns and used columns were normally discarded after one separation. All measurements refer to separation in the linear isotherm region (linear elution adsorption chromatography, LEAC). The linear capacity[11] of 3 % H_2O–MgO was approximately $2 \cdot 10^{-5}$ g/g.

IRREVERSIBLE SAMPLE ADSORPTION ON MAGNESIA

It was observed at the beginning of the present study that irreversible adsorption of aromatic samples on magnesia can occur under certain conditions. This effect, which has been referred to as "chemisorption" previously[12], can severely limit the usefulness of a separation technique. Typically it was found that elution of a sample such as anthracene or phenanthrene from fresh columns of 3 % H_2O–MgO by (dry) pentane gave quantitative sample recoveries, but low recoveries resulted if the process was repeated a second time on the same column. Recovery during the second elution from a given column varied with sample size; e.g. for anthracene a sample size of $8 \cdot 10^{-7}$ g/g gave 4 % recovery, rising to 33 % recovery for $8 \cdot 10^{-6}$ g/g sample. Water wet pentane increased sample recovery as shown in Table I. Only with water saturated pentane was quantitative sample recovery achieved, however. These observations suggest that elution with dry pentane removes water from the magnesia surface, and that the resulting dry surface can irreversibly hold the sample by strong adsorption or chemical reaction. A similar effect has been noted by BRIERLY AND SMITH[13] in the separation of rotenone on alumina, and several other workers have noted the drying of water deactivated adsorbents by column washing. The unusual aspect of the present phenomenon involving magnesia is the ease with which it occurs. Water is normally removed from alumina and silica only by fairly polar solvents[7,9,14], although extensive washing of heavily deactivated alumina by pentane

TABLE I

SAMPLE RECOVERY IN THE ELUTION OF ANTHRACENE FROM 3 % H_2O–MgO BY PENTANE CONTAINING VARYING AMOUNTS OF WATER[a]

Pentane water content[b] (% saturation)	Sample recovery (%)	
	First elution	Second elution[c]
0	100	4
30	100	11
60	100	35
100	100	100

[a] Sample size $8 \cdot 10^{-7}$ g/g.
[b] Solvent prepared by mixing indicated proportion of water saturated pentane with dry pentane.
[c] Repeated separation after initial elution, fresh sample charged.

results in a gradual dehydration of the adsorbent[10]. Possibly this reflects a lower affinity of the magnesia surface for water and a higher affinity for aromatic molecules, relative to other polar adsorbents. Such an explanation agrees with the various observations cited in the Introduction.

Samples with large retention volumes ($R° > 20$) gave incomplete sample recoveries even for initial elution from a fresh column. For example, the pentane elution from 3 % H_2O–MgO of anthracene ($R° = 6.7$), pyrene ($R° = 29.6$) and chrysene ($R° = 174$) gave recoveries, respectively, of 100, 80, and 3 %. Further elution of the column to which chrysene was charged, using benzene solvent, gave only 35 % additional sample recovery, despite the fact that benzene is a much stronger solvent. This behavior makes it impractical to use dry solvents in the study or practical application of magnesia in adsorption chromatography. However, use of water wet solvents eliminated this problem. Consequently all of the following studies were carried out using 100 % water saturated solvents unless otherwise stated. Where $R°$ values were determined using both dry and water wet solvents, it was found that $R°$ values for a given compound and solvent did not vary by more than 10–15 % (i.e. elution by dry and wet solvents from fresh columns is quite similar). Whereas water wet solvents on other adsorbents[7,9] generally give lower $R°$ values than do dry solvents, both higher and lower $R°$ values were observed on magnesia with wet solvents. All of the present studies were carried out with water immiscible solvents. It is not known how much (if any) water would have to be added to such solvents as acetone or the lower alcohols to avoid the problem of irreversible sample adsorption on magnesia. The West Vaco magnesia appeared to give less of a problem with irreversible sample asorption than did the Sea Sorb magnesia.

At first glance it appears odd that the problem of irreversible adsorption on magnesia has escaped previous notice in the literature. However most previous separations on magnesia have involved either column or plate development, where extensive washing of the adsorbent in front of the sample does not occur. In unreported studies LIJINSKY[15] has noted that the pentacyclic aromatic hydrocarbons are held on magnesia so tightly, following normal elution of the lower aromatics, that they can be recovered only by chemical destruction of the adsorbent. In conclusion

it seems apparent that in elution from columns of magnesia it is generally wise to use water saturated solvents.

SAMPLE RETENTION VOLUME AS A FUNCTION OF SEPARATION CONDITIONS

Adsorbent activation temperature

All polar adsorbents undergo similar surface changes upon being heated (*i.e.* activated) at moderate temperatures. Activation at temperatures below 150° removes varying amounts of physically adsorbed water from the adsorbent surface, and adsorbent activity increases with increasing activation temperature. At temperatures above 150° more drastic changes in adsorbent surface structure begin to occur: surface hydroxyls react to form oxide groups and liberate water, and other forms of chemically bound water are similarly lost. This process can lead either to an increase or decrease in adsorbent activity, depending upon the importance of surface hydroxyls as adsorption sites. In the case of silica, surface hydroxyls are strong adsorption sites, and above 150° adsorbent activity decreases with higher activation temperature[16]. Alumina, on the other hand, shows a continuing increase in adsorbent activity as activation temperature is increased from room temperature to 1000°[17]. The effect of activation temperature on the activity of magnesia was briefly studied, using the pentane elution of styrene from samples of activated adsorbent. Under these conditions the adsorption isotherm was markedly nonlinear for at least some of the adsorbent samples, and the experimental results are only qualitatively significant. Adsorbent activity was observed to decrease continuously with higher activation temperature over the interval 130–500°. Equivalent retention volumes (ml/g) for styrene ($8 \cdot 10^{-6}$ g/g) eluted from adsorbent activated at the following temperatures were: 130° (12.5), 200° (10.4), 300° (8.4) and 500° (6.6). KISELEV *et al.*[18] have noted a similar decline in the activity of magnesia with higher temperature of activation. Interestingly the elution band obtained with the 500° band was quite symmetrical and sharp while the corresponding bands for the lower temperature adsorbents were quite broad and tailing (compare Fig. 1). Quite limited data suggest that 500° water deactivated magnesias preserve these differences to some degree and are less subject to irreversible sample adsorption. Activation of magnesia at 500° may therefore give a chromatographic adsorbent of generally better performance than is the case for acti-
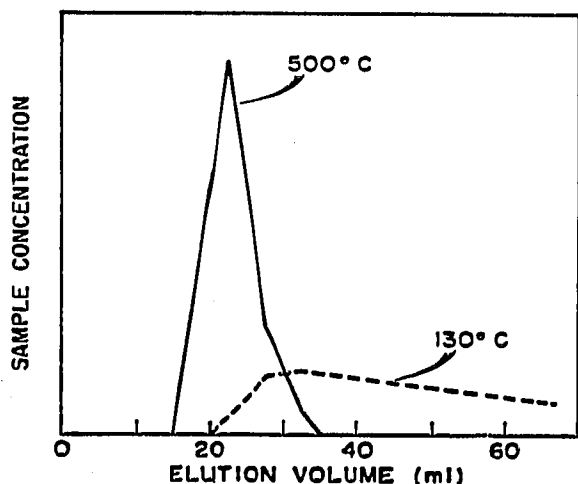

Fig. 1. Effect of magnesia activation temperature on band shape; elution of styrene ($8 \cdot 10^{-6}$ g/g) by pentane.

vation at lower temperatures. The decrease in activity of magnesia with increasing activation temperature suggests (but does not prove) that surface hydroxyls are important adsorption sites.

Adsorbent activity versus water deactivation

Addition of water to an activated adsorbent generally results in adsorption onto the strongest surface sites, resulting in a loss in the surface available for adsorption of sample molecules and a decrease in average surface activity. The results of water deactivation may be interpreted in terms of changes in two adsorbent parameters: the adsorbent surface volume V_a and the surface activity function α. A previous relationship (*e.g.* refs. 7, 8) gives sample $\underline{R}^\circ$ values as a function of these two adsorbent parameters:

$$\log \underline{R}^\circ = \log V_a + \alpha \, f \, (S,E) \tag{1}$$

For a particular adsorbent type (*e.g.* silica, magnesia, etc.), the function $f(S,E)$ depends only upon the sample and eluent corresponding to $\underline{R}^\circ$. Eqn. 1 therefore describes the variation of $\underline{R}^\circ$ with adsorbent activity. Eqn. 1 has been corroborated for previous adsorbents, and the parameters V_a and α have been determined as a function of adsorbent water content, by determining $\underline{R}^\circ$ values for various sample–eluent combinations on several adsorbent samples of differing water content (*e.g.* ref. 10). This procedure is impractical in the case of magnesia, primarily because of the problem of irreversible sample adsorption on adsorbents of reduced water content. A further complication is a quite rapid increase in $\underline{R}^\circ$ values with decreasing magnesia water content. This precludes the possibility of comparing $\underline{R}^\circ$ values for the same sample and solvent over the full range of adsorbent activity. These problems were circumvented to some extent by noting that $f(S,E)$ is a linear function of carbon number for the unsubstituted aromatic hydrocarbons, as discussed in a later section. Assuming that the adsorbent parameters V_a and α are smooth functions of adsorbent activity, the data of Table II could then be used to derive V_a and α *versus* adsorbent water content in a straightforward manner. The resulting adsorbent parameters are tabulated in Table III and plotted *versus* % H_2O–MgO in Fig. 2. The parameter

TABLE II

VARIATION OF RETENTION VOLUME WITH MAGNESIA WATER CONTENT[a]

Sample	Log $\underline{R}^\circ$[b]				
	0.0 % H_2O–MgO[c]	0.5 % H_2O–MgO[c]	1.5 % H_2O–MgO[c]	3.0 % H_2O–MgO	6.7 % H_2O–MgO
Styrene	1.03	0.24			
Naphthalene		1.02	0.24		
Acenaphthylene			1.04	0.41	
Phenanthrene				1.11	0.49
Fluoranthene					1.03
Chrysene					1.83

[a] Adsorbent activated at 300° before addition of water.
[b] Pentane elution.
[c] Dry pentane used.

TABLE III

ADSORBENT PROPERTIES OF WATER DEACTIVATED MAGNESIA[a]

% H_2O-MgO	Log V_a	α	R_s[b]		
			Styrene	Ace-naphthylene	Fluor-anthene
0.0	—2.2	1.00	1.03		
0.5	—2.97	1.00	0.24		
1.0	—3.44	1.00		1.33	
1.5	—3.76	0.99		1.04	
2.0	—3.95	0.98		0.73	
3.0	—4.18	0.95		0.41	1.91
4.0	—4.32	0.93		0.14	1.63
5.0	—4.39	0.91			1.41
6.0	—4.44	0.88			1.19
7.0	—4.49	0.86			1.00

[a] 2:1 MgO–Celite activated at 300°.
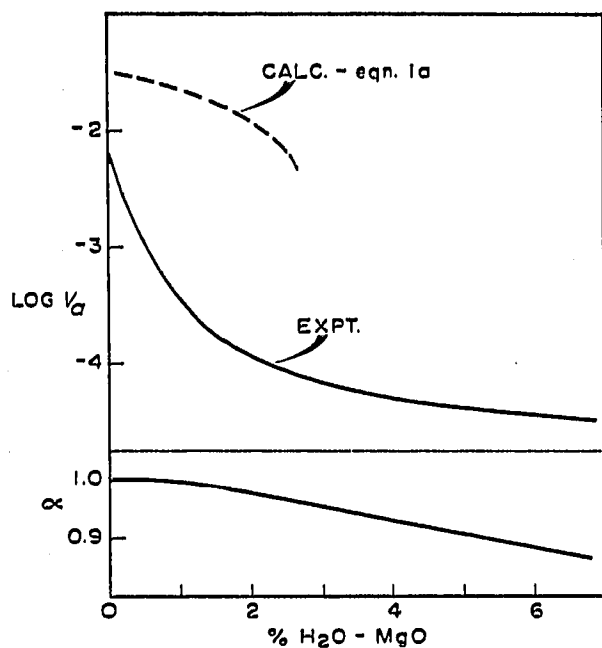[b] $R^°$ value for indicated sample; pentane elution.

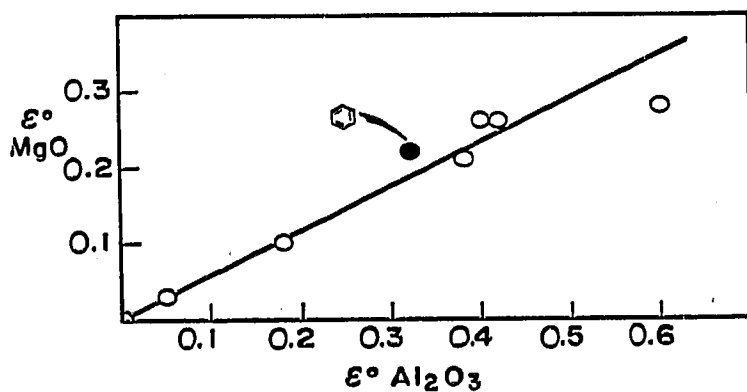Fig. 2. Adsorbent parameters for water deactivated magnesia.

Fig. 3. Eluent strengths of various solvents on magnesia versus alumina.

V_a can also be calculated from the BET surface area of the activated adsorbent (90 m²/g) and the added water (% H_2O) in terms of a previous relationship[10]:

$$V_a \text{ (ml/g)} = 0.00035 \text{ surface area} - (\% H_2O). \tag{1a}$$

Comparison of calculated values of V_a from eqn. 1a (dashed curve of Fig. 2) with experimental values (solid curve of Fig. 2) shows a large discrepancy between these two plots. The experimental V_a values are considerably smaller, and this may be the result of restricted access to part of the adsorbent surface; i.e. nitrogen molecules may be able to adsorb in small pores which cannot accommodate the larger sample molecules of Table II. A microporous adsorbant structure might also account for the chemisorption of aromatics on magnesia. Alternatively the linear relationship between sample molecule carbon number and log $\underline{R}°$ may break down for smaller sample molecules (compare adsorption energy of aromatic hydrocarbons on silica *versus* alumina[10]). Whatever the reason for this anomaly involving V_a values for magnesia, the practical consequences are unimportant and the adsorbent parameters of Table III can be used with eqn. 1 to predict the effect of adsorbent activity on $\underline{R}°$ values. Because of the problem of irreversible sample adsorption, 3–7 % H_2O–MgO appears to represent an optimum adsorbent activity range. Adsorbent linear capacity is also expected to be greater in this range, relative to more active adsorbent samples[11]. Table III presents $\underline{R}°$ values for standard sample–solvent systems (R_s values) which can be used to measure the chromatographic activity (as % H_2O–MgO) of a magnesia sample[10].

Role of the solvent

For elution from other polar adsorbents (e.g. ref. 19) the effect of the solvent on sample retention volumes can be expressed in terms of eqn. 2, which is derivable from eqn. 1:

$$\log \underline{R}° = \log V_a + \alpha (S° - \varepsilon° A_s). \tag{2}$$

Here $S°$ is the adsorption energy of the sample in a standard chromatographic system (activated adsorbent, pentane solvent), $\varepsilon°$ is the eluent strength of the solvent, and A_s is the adsorbed volume of the sample molecule (proportional to the area a sample molecule requires upon the adsorbent surface). In most cases values of A_s can be calculated[10] for a given sample molecule. Eqn. 2 can be simplified for purposes of examining the solvent effect *per se*, by defining the retention volume R_p of a sample molecule eluted by pentane:

$$\log \underline{R}° = \log R_p - \alpha\varepsilon° A_s. \tag{2a}$$

For elution from 6.3 % H_2O–MgO, values of $\alpha\varepsilon°$ for several solvents and solvent binaries were obtained from $\underline{R}°$ values of the samples shown in Table IV (using eqn. 2 a). These $\alpha\varepsilon°$ values are also shown in Table IV, along with values of A_s and R_p for each sample. R_p values were either measured directly (pentane solvent) or else calculated from an $\underline{R}°$ value for another solvent using eqn. 2a. The resulting $\alpha\varepsilon°$ values for the various solvent binaries could also be calculated from a previous relationship[10] between the $\alpha\varepsilon°$ values of a solvent mixture ($\alpha\varepsilon°_{AB}$) and the corresponding values for the pure solvents composing that mixture ($\alpha\varepsilon°_A$ and $\alpha\varepsilon°_B$):

$$\alpha\varepsilon°_{AB} = \alpha\varepsilon°_A + \frac{\log X_B \, 10^{\alpha n_b (\varepsilon°_B - \varepsilon°_A)} + 1 - X_B}{n_b} \tag{3}$$

TABLE IV

ELUTION STRENGTH OF VARIOUS SOLVENTS AND SOLVENT BINARIES: ELUTION FROM 6.3 % H_2O–MgO[a]

Solvent	Sample	$\alpha\varepsilon^\circ$	
		Exptl.	Calc.[b]
CCl_4	Chrysene[c]	0.091	
Ethyl ether	1,2,3,4-Dibenzanthracene[d]	0.184	
Benzene	1,2,3,4-Dibenzanthracene[d]	0.189	
Chloroform	2-Aminochrysene[e]	0.224	
Cyclopentane	Fluoranthene[f]	0.026	
10 % v Ether–pentane	Anthracene[g]	0.052	0.047
25 % v Ether–pentane	Pyrene[h]	0.092	0.091
5 % v Benzene–pentane	Pyrene[h]	0.037	0.041
20 % v Benzene–pentane	Benzanthracene[i]	0.089	0.100
50 % v Benzene–pentane	Benzanthracene[i]	0.156	0.149
5 % v CH_2Cl_2–pentane	Chrysene[c]	0.043	0.049[k]
15 % v CH_2Cl_2–pentane	Chrysene[c]	0.098	0.106[k]
35 % v CH_2Cl_2–pentane	1,2-Benzpyrene[j]	0.163	0.163[k]
70 % v CH_2Cl_2–pentane	2-Aminochrysene[e]	0.220	0.209[k]
10 % v Methyl acetate–pentane	Chrysene[c]	0.093	0.097[l]
25 % v Methyl acetate–pentane	1,2-Benzpyrene[j]	0.153	0.154[l]
40 % v Methyl acetate–pentane	1,2,3,4-Dibenzanthracene[d]	0.187	0.183[l]

[a] Water saturated solvents.
[b] Eqn. 3.
[c] Log R_p 1.80, A_s 12
[d] Log R_p 3.12, A_s 14
[e] Log R_p 4.1 , A_s 13.5
[f] Log R_p 1.13, A_s 11
[g] Log R_p 0.39, A_s 10
[h] Log R_p 1.05, A_s 11
[i] Log R_p 1.77, A_s 12
[j] Log R_p 2.50, A_s 13
[k] Assumes $\alpha\varepsilon^\circ$ for CH_2Cl_2 equals 0.230.
[l] Assumes $\alpha\varepsilon^\circ$ for methyl acetate equals 0.244.

TABLE V

THE ELUENT STRENGTH OF VARIOUS SOLVENTS ON MAGNESIA: COMPARISONS WITH VALUES FOR ALUMINA

Solvent	ε°		
	MgO (exptl)	Al_2O_3[a]	MgO (calc.)[b]
Pentane	0.00	0.00	0.00
Cyclopentane	0.03	0.05	0.03
CCl_4	0.10	0.18	0.10
Ethyl ether	0.21	0.38	0.22
Benzene	0.22	0.32	0.19
$CHCl_3$	0.26	0.40	0.23
CH_2Cl_2	0.26	0.42	0.24
Methyl acetate	0.28	0.60	0.35

[a] Values of Table II, ref. 7.
[b] Calculated for elution from MgO, as 0.58 times value for Al_2O_3.

Here X_B refers to the mole fraction of the stronger solvent component B in the binary solvent, and n_b refers to the area or A_s value of component B. The agreement between experimental $\alpha\varepsilon^\circ$ values for the binary solvents of Table IV and values calculated from eqn. 3 is quite satisfactory: ± 0.007 units standard deviation. Values of $\alpha\varepsilon^\circ$ for the solvents CH_2Cl_2 and methyl acetate were calculated from the best fit of the corresponding binary data to eqn. 3.

In Table V the derived ε° values for the pure solvents of Table IV are summarized, along with values of ε° for elution from alumina. As seen in Fig. 3 the alumina and magnesia ε° values are approximately proportional. (Magnesia ε° values equal 0.58 times alumina values). This permits the estimation of other magnesia ε° values from corresponding values for alumina[7]. Table V compares ε° values for magnesia with values calculated in this fashion from the alumina ε° values. The standard deviation of the calculated and experimental ε° values is ± 0.03 units.

The data of Table V and Fig. 3 do not suggest that benzene is an anomalously strong solvent on magnesia, relative to other adsorbents, as suggested by the data of SABACKY et al.[6]. It instead appears that ethyl ether and acetone may have appeared as weak solvents in the latter study because of adsorbent drying by solvent during separation. The resulting increase in adsorbent activity would of course reduce sample R° values, which is equivalent to the solvent appearing weaker than it actually is. SABACKY et al. and other workers have questioned the general value of eluotropic series or relative solvent strength values as in Table V. In general it is claimed that such series or relative values are inapplicable to different adsorbents and/or different sample types. It has now been established that essentially the same series of relative ε° values and the same eluotropic series exists for alumina[7], Florisil[12], silica[9] and magnesia (Table V). While some variations in apparent eluent strength with sample type have been noted (e.g. refs. 7, 8), these have been related to specific interactions between sample, adsorbent and/or solvent which can be predicted in advance. Hence the concept of a single eluotropic series which is valid for all polar adsorbents and most sample types seems quite acceptable as a first approximation and should continue to find use by practical chromatographers.

The application of eqns. 2 and 2a to adsorption on silica (and Florisil to a lesser extent) is complicated by the fact that sample A_s values in some case do not correspond to simple molecular size[19]. Strongly adsorbing substituents appear to contribute much more to A_s than their actual size would suggest. This effect was briefly examined for adsorption onto magnesia. Table VI presents R° values for a few samples which give anomalous A_s values on silica, and apparent A_s values (on magnesia) are derived. Comparison of these magnesia A_s values in Table VI with the normal values for alumina and the anomalous values for silica shows that the magnesia A_s values agree much more closely with the alumina values than with the silica values. We tentatively conclude that the anomalous A_s effect does not apply to adsorption on magnesia, and that A_s values for different sample molecules can be calculated in the same way as for alumina[10].

RETENTION VOLUME AS A FUNCTION OF SAMPLE STRUCTURE

Previous papers (e.g. refs. 8, 19) have developed a general theory for the dependence of sample retention volume on sample structure in adsorption chromato-

TABLE VI

APPARENT SAMPLE A_s VALUES FOR ADSORPTION ON MAGNESIA; 6.3 % H_2O–MgO

Sample	Log $\underline{R}^\circ$			A_s		
	Pentane	5 % v CH_2Cl_2– pentane	15 % v CH_2Cl_2– pentane	MgO^a	$Al_2O_3^b$	SiO_2^b
m-Nitroacetophenone	1.82	1.17	0.53	13.2	10.5	22.4
1,4-Dinitronaphthalene	0.83	0.41		9.8	13.0	22.4
2-Aminonaphthalene	1.74		0.74	10.2	9.5	16.0
ε°	0.000	0.043	0.098			

a Calculated from above $\underline{R}^\circ$ values and Eqn. 2a.
b Calculated as in ref. 19.

graphy. The standard adsorption energy S° of a sample molecule expresses the major contribution of sample structure to $\underline{R}^\circ$. S° is related to the adsorption energies Q°_i of the different groups i which constitute the sample molecule:

$$S^\circ = \sum^i Q^\circ_i - f(Q^\circ_k) \sum^{i \neq k} Q^\circ_i \qquad (4)$$

Here S° is given as the sum of group adsorption energies for every group i in the sample molecule, minus an adsorption energy loss due to localization of certain sample types on strong adsorbent sites. The localization function $f(Q^\circ_k)$ in eqn. 4 depends upon the adsorption energy Q°_k of the strongest adsorbing group k in the sample molecule. Relative separation order on different adsorbents is largely determined by the values of Q°_i for different sample groups i and by the relative extent of sample localization.

Retention volume data for a variety of sample types were collected and reduced to values of S° by means of eqn. 2. These data are summarized in Table VII. Table VII permits a fairly detailed examination of the role of sample structure in determining $\underline{R}^\circ$ values on magnesia.

Aromatic hydrocarbons

The S° values for the aromatic hydrocarbons of Table VII are plotted *versus* the number of aromatic carbon atoms in each molecule in Fig. 4. The various points fall on top of a straight line through the origin. This correlation is predicted by eqn. 4 when no sample localization occurs (*i.e.* f[Q°_k] equal zero). A value of Q°_i for an aromatic carbon atom (—C=) adsorbed on magnesia can be derived, equal 0.40. The adsorption of the aromatic hydrocarbons onto alumina, Florisil and "X" sieve is similar in this respect[20]. The aromatic hydrocarbons adsorb on silica with localization, and as a result the S° value for a nonfused aromatic such as dibenzyl is much larger than is S° for fused aromatics of similar aromatic carbon number (*e.g.* acenaphthylene). As seen in Table VII and Fig. 4, this is not the case for the adsorption of hydrocarbons onto magnesia. We therefore conclude that localization of hydrocarbons on magnesia does not occur.

TABLE VII

RELATIVE SAMPLE ADSORPTION AS A FUNCTION OF SAMPLE STRUCTURE: $S°$ VALUES FOR DIFFERENT SAMPLES (6.3 % H_2O–MgO)

Sample	Solvent[a]	Log $\underline{R}°$	$S°$ Exptl.[b]	$S°$ Calc.[c]
Acenaphthylene	P	—0.32	4.8	4.8
Dibenzyl	P	0.34[d]	4.1	4.8
Anthracene	P	0.39	5.6	5.6
Phenanthrene	P	0.47	5.7	5.6
Fluoranthene	P	1.13	6.4	6.4
Pyrene	P	1.05	6.3	6.4
Chrysene	P	1.80	7.2	7.2
Triphenylene	P	1.76	7.1	7.2
Benzanthracene	P	1.77	7.2	7.2
1,2-Benzpyrene	15 % M–P	1.23	8.0	8.0
1,2,3,4-Dibenzanthracene	35 % M–P	0.84	8.7	8.8
Methyl benzoate	P	—0.5	4.5	5.0
Acetophenone	P	0.37	5.5	5.3
Aniline	P	0.68	5.9	5.8
Phenol	35 % M–P	1.31	7.9	7.4
Phenylacetone	P	0.74	6.0	5.7
1-(1-Thiapropyl)-naphthalene	P	0.12	5.3	5.0
2-Methoxynaphthalene	P	0.08	5.2	5.2
1-Nitronaphthalene	P	0.47	5.7	5.8
Methyl-2-naphthoate	P	0.73	6.0	6.1
2-Acetonaphthone	P	1.18	6.5	6.4
1-Naphthaldehyde	P	0.70	5.9	6.2
2-Aminonaphthalene	see Table VI	—	7.1	6.9
2-Aminoanthracene	35 % M–P	0.97	8.4	8.0
Pyridine	P	0.63	5.8	5.7
Isoquinoline	P	1.10	6.4	6.7
Quinoline	P	1.00	6.3	6.2
Phenanthridine	P	1.85	7.3	7.3
1-Azapyrene	35 % M–P	0.49	7.7	7.9
7,8-Benzoquinoline	5 % M–P	0.71	6.4	6.5
Acridine	15 % M–P	0.60	6.9	7.2
m-Nitroacetophenone	see Table VI	—	7.0	6.8
p-Nitroaniline	35 % M–P	1.05	8.2	7.3
m-Nitromethylbenzoate	5 % M–P	0.85	6.7	6.5
m-Nitroanisole	P	0.52	5.7	5.6
2,5-Dimethoxyacetophenone	15 % M–P	0.35	6.7	7.2
Dimethylisophthalate	15 % M–P	0.34	6.9	6.9
p-Dinitrobenzene	5 % M–P	0.63	6.4	6.2
2,4-Dinitroanisole	15 % M–P	0.98	7.6	7.3
m-Nitrobenzaldehyde	5 % M–P	0.96	6.7	6.6
p-Methoxyacetophenone	5 % M–P	0.84	6.5	6.3
1,4-Dinitronaphthalene	see Table I	—	6.1	7.2

[a] P = pentane; 5 % M–P = 5 % v methylene chloride–pentane; 15 % M–P = 15 % v methylene chloride–pentane; 35 % M–P = 35 % v methylene chloride–pentane.
[b] From $\underline{R}°$ values and eqn. 4.
[c] From eqn. 4 and alumina data, as described in the text.
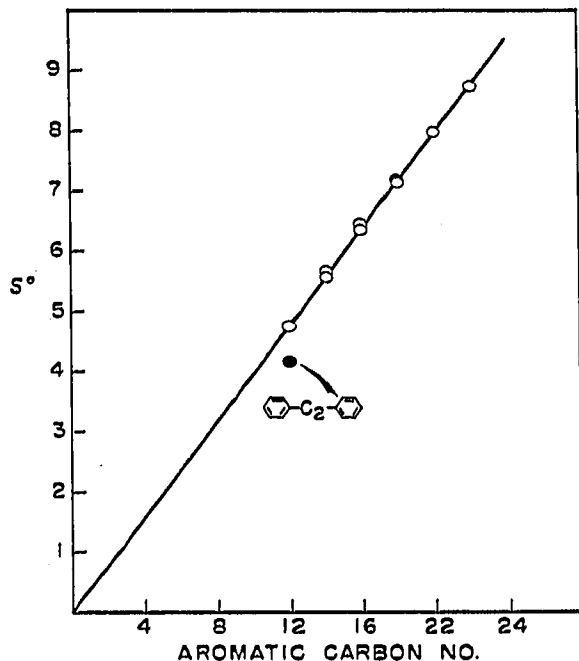[d] Value for 1.5 % H_2O–MgO.

Fig. 4. Dependence of hydrocarbon $S°$ values on aromatic carbon number; data of Table VII.
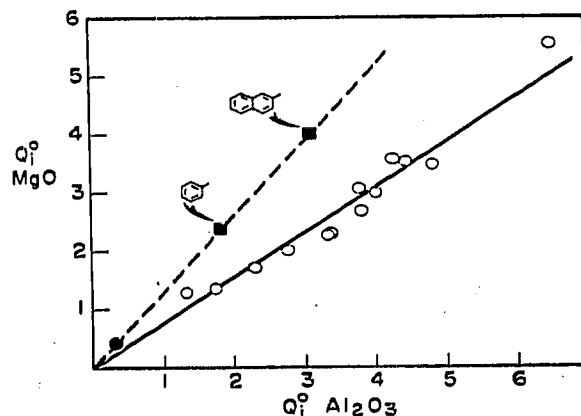
Fig. 5. Group adsorption energies on magnesia *versus* alumina; data of Table VIII.

TABLE VIII

SAMPLE GROUP ADSORPTION ENERGIES $Q°_i$ ON MAGNESIA *versus* ALUMINA

Group	$Q°_i$			$f(Q°_k)$	
	MgO (exptl.)[a]	Al_2O_3[b]	MgO (calc.)[c]	Al_2O_3[d]	MgO[e]
—C=	0.40	0.31	0.24	0.00	0.00
Ar)—SR	1.26	1.32	1.02	0.00	0.00
Ar)—OR	1.34	1.77	1.36	0.10	0.08
Ar)—NO₂	2.00	2.75	2.12	0.31	0.21
AR)—CO₂R	2.26	3.32	2.56	0.39	0.26
Ar)—CHO	2.29	3.35	2.58	0.35	0.23
Ar)—COR	3.03	3.74	2.88	0.44	0.29
Ar)—NH₂	3.50	4.41	3.40	0.45	0.30
Ar)—OH	5.54	6.5	5.01	0.45	0.30
—N=[f]	3.50	4.8	3.70	0.45	0.30
—N=[g]	2.99	4.0	3.08	0.45	0.30
—N=[h]	2.68	3.8	2.93	0.35	0.30
—N=[i]	1.71	2.3	1.77	0.22	0.15
Ar)—CH₂COR	3.57	4.28	3.30		

[a] Derived from $R°$ values of Table VII for monosubstituted aromatics.
[b] Ref. 8
[c] 0.77 times value for alumina.
[d] Ref. 21.
[e] 0.67 times alumina value.
[f] As in pyridine.
[g] As in quinoline.
[h] As in acridine.
[i] As in 7,8-benzoquinoline.

Substituted aromatics

Q°_i values for different groups i can be derived most readily from $\underline{R}^\circ$ data for the monosubstituted benzenes (C_6H_5-i) or paraffins (R-i). Extensive data for compounds of this type could not be obtained in the present study because of experimental limitations. Alternatively group Q°_i values can be derived from compounds such as the monosubstituted naphthalenes or other more complex sample molecules if we know the value of the localization function $f(Q^\circ_k)$. Examination of the data of Table VII suggests that the localization function for adsorption on magnesia is given approximately as 0.67 times the corresponding value for adsorption on alumina. This fits the same pattern already noted for adsorption on silica and Florisil[19], where the respective localization functions are 0.4 and 0.65 times the alumina values. Using this approximation to $f(Q^\circ_k)$ on magnesia, the Q°_i values of Table VIII were derived from the S° values of Table VII for the monosubstituted aromatics (*e.g.* acetophenone, 1-nitronaphthalene, acridine). The previous convention[19] with respect to not counting the delocalization of the benzene ring attached to the localizing group was followed in this procedure. Comparison of these magnesia Q°_i values with corresponding values for alumina (Table VIII and circles in Fig. 5) shows a close correspondence. The magnesia values can in fact be calculated from values for alumina within a standard deviation of ± 0.25 units, using the relationship: Q°_i (MgO) equals 0.77 Q°_i (Al_2O_3). With the exception of acidic and basic sample molecules, this similarity of group adsorption energies on different polar adsorbents now appears to be quite typical. Similar quantitative correlations between Q°_i values on different adsorbents have already been noted for alumina, silica and Florisil[22] and BROCKMANN[23] has reported the same qualitative sequence of group adsorption energies on alumina, silica, magnesia, calcium sulfate and copper sulfate. The Q°_i value for the one acidic group of Table VIII, aromatic hydroxyl, is relatively larger on magnesia than on alumina, compared to neutral sample groups. This confirms that magnesia, like alumina[22], is a basic adsorbent which preferentially adsorbs acidic samples.

The correlation of Fig. 5 does not suggest a large preference for the adsorption of a single aromatic carbon on magnesia relative to alumina. However the dashed curve in Fig. 5 for aromatic nucleic of varying size emphasizes the preferential adsorption of aromatic rings on magnesia relative to alumina (and other adsorbents), confirming the observations collected in the Introduction.

The overall applicability of eqn. 4 for adsorption on magnesia, and the similarity of Q°_i values on magnesia *versus* alumina, was further checked as follows. All Q°_i values were assumed equal to 0.77 times the alumina values, except for aromatic carbon (Q°_i equal 0.40); $f(Q^\circ_k)$ was assumed equal to 0.67 times the value for the same substituent on alumina (Table VIII); S° values for the compounds of Table VII were calculated using eqn. 4. The resulting 42 calculated S° values are shown in Table VII. The standard deviation of calculated from experimental values was found to be ± 0.3 units. This agreement is not significantly worse than in similar calculations of S° for other adsorbents, and confirms our ability to calculate S° values on magnesia by means of eqn. 4.

The variability of different magnesia samples was briefly studied with respect to changes in sample separation order (*i.e.* relative $\underline{R}^\circ$ values). $\underline{R}^\circ$ values for several of the compounds of Table VII (Sea Sorb MgO) were redetermined on a sample of the West Vaco magnesia under approximately the same separation conditions (same

TABLE IX

SAMPLE RETENTION VOLUMES ON 3% H_2O–MgO (WEST VACO)[a]; PENTANE ELUENT

Sample	Log $\underline{R}^{\circ}$ [b]
Acenaphthylene	—0.35
Phenanthrene	0.34
Fluoranthene	1.07
Acetophenone	—0.06
Aniline	0.47
1-Nitronaphthalene	0.23
2-Acetonaphthone	0.86
Methyl-2-naphthoate	0.40
Quinoline	0.54
Isoquinoline	0.55
m-Nitroanisole	0.09

[a] Adsorbent heated to 300° and 3% water added.
[b] Corrected to 67% w MgO basis (2:1 MgO–Celite) by subtraction of 0.18.

eluent, similar adsorbent activity). These values are reported in Table IX. A linear relationship between the latter log $\underline{R}^{\circ}$ values and corresponding values from Table VII is predicted by eqn. 1. As seen in Fig. 6 the anticipated relationship between log R°
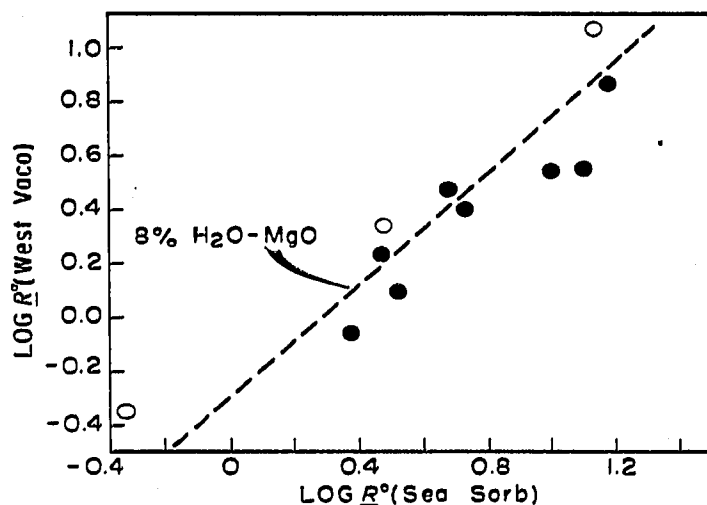

Fig. 6. Log $\underline{R}^{\circ}$ data of Table IX versus corresponding values from Table VII. (O) Hydrocarbons; (●) substituted aromatics.

values on the two adsorbents is observed approximately. The dashed curve of Fig. 6 is that predicted for a sample of 8% H_2O–MgO (Table III). The standard deviation of the points of Fig. 6 from the dashed curve is ±0.18 log units. Considering the different sources of these two magnesia samples, (and corresponding differences in their processing) the scatter of points in Fig. 6 does not indicate any marked variation in the adsorptive properties of the two adsorbents. The data of Fig. 6 for the aromatic hydrocarbons (open circles) tend to lie significantly higher than corresponding data for the substituted aromatics (closed circles). This suggests that the preferential adsorption of aromatic rings on magnesia (relative to other sample groups) is somewhat intensified on the West Vaco magnesia relative to Sea Sorb magnesia.

PRACTICAL APPLICATIONS OF SEPARATION ON MAGNESIA

The correlational model developed in this and preceding papers does not have as its primary aim the precise calculation of $R°$ values in chromatographic systems of possible interest. In fact the experimental data collected and correlated to date suggest that such a goal is in general beyond the capability of any relatively simple theory of adsorption chromatography. A more reasonable, and in fact more useful goal of a general theory of adsorption chromatography is the classification of different separation systems with regard to *general* differences in sample $R°$ values. In this way we can tell how an unsatisfactory separation can be improved by systematic changes in separation conditions. Our initial guess of separation conditions for a particular sample can also be made more intelligent. The primary role of adsorbent type, in this connection, is in the selective adsorption of certain sample types by various adsorbents. Thus basic adsorbents such as alumina and magnesia selectively retain acidic samples[22], and for some separation problems this factor might be decisive in the selection of adsorbent type. A previous paper[12] has examined certain other general differences in separation on alumina, silica and Florisil. In the present paper we have seen that separation on magnesia is for the most part quite similar to separation on alumina, with the one exception that olefinic and aromatic groups are preferentially held on magnesia, relative to other sample groups. Because magnesia is less convenient to work with than is alumina, separations on magnesia should be restricted to those cases where it is advantageous to have selective adsorption of unsaturated molecules. Certainly the separation of compounds differing only in the total number of carbon-carbon double bonds can be better carried out on magnesia than on such adsorbents as alumina, silica or Florisil. Silver impregnated adsorbents are of course competitive with magnesia for selective retention of unconjugated olefins.

For quite complex samples which are composed of many compounds of differing type, it is frequently found that no single adsorbent can provide adequate separation of all compounds or compound types. It is then advantageous to make use of a two dimensional chromatographic system, where initial separation on one adsorbent yields fractions which are each further separated on a second adsorbent (or by another chromatographic method, *e.g.* partition). In using this technique it is important that the selectivity of each adsorbent type chosen be complementary with respect to the chosen sample. One example is provided by certain compound type separations of petroleum. On alumina the alkyl substituted naphthalenes, benzothiophenes, sulfides, and diphenyl alkanes separate together as a single fraction. On silica as adsorbent aromatic types are localized, with the result that polycyclic aromatics are less strongly adsorbed relative to other compound types. Consequently it is possible to further separate the above group of compounds from an alumina separation by reseparation on silica: the naphthalenes and benzothiophenes will be separated as an initial fraction from the diphenyl alkanes plus sulfides. Or the same alumina fraction might be reseparated on magnesia, which selectively retains all aromatic types: an initial sulfide fraction and a final naphthalene–benzothiophenes–diphenyl alkane fraction would result in this case. These various possibilities are illustrated in Fig. 7 for an actual petroleum sample. A typical gas oil (200–350.° boiling range) was first separated on alumina (Fig. 7a) to give a concentrate "A" (cross hatched) of naphthalenes, diphenyl alkanes, benzothiophenes and sulfides. Ultraviolet (U.V.) absorbance
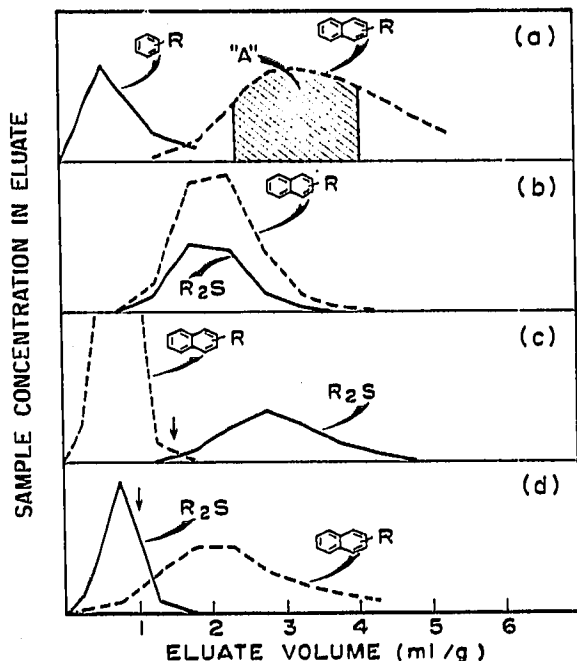
Fig. 7. Successive separation of a petroleum gas oil on alumina, silica, and magnesia. (a) = Initial separation on alumina; (b) = reseparation of cross hatched fraction "A" from (a) on alumina; (c) = reseparation of fraction "A" from (a) on silica; (d) = reseparation of fraction "A" from (a) on magnesia.

of the eluate is plotted in Fig. 7a, in order to distinguish the latter group of compounds from the initially eluting benzene derivatives. Reseparation of fraction "A" on alumina was followed by U.V. and iodine complex absorbance to distinguish sulfides from naphthalenes plus benzothiophenes (Fig. 7b). No further separation of these two compound groups resulted, as expected. In Fig. 7c reseparation of the initial alumina fraction on silica is shown, and as predicted the sulfides (plus undetected diphenyl alkanes) are cleanly separated from the naphthalenes plus benzothiophenes, which elute first. Using the cutpoint indicated by the arrow in Fig. 7c, 99 % of each compound type was recovered in its respective fraction. Finally in Fig. 7d the corresponding reseparation on magnesia is shown. Again the sulfides are cleanly separated (94 % in each fraction) from the aromatic types, but the elution order is now reversed relative to separation on silica (as predicted). Progressive separation on alumina, silica and magnesia could give almost complete breakdown into sample types, with only the naphthalenes and benzothiophenes remaining unresolved. Use of a fourth, sulfur selective adsorbent (e.g. ref. 24) might then provide complete compound type separation.

SUMMARY

Linear elution adsorption chromatography on water deactivated magnesia has been used to evaluate the unique characteristics of this adsorbent. Water is washed from the magnesia surface by all solvents quite readily, and the resulting dry surface irreversibly adsorbs aromatic compounds. Complete sample recovery is possible, however, using water wet solvents. With respect to the effect of the solvent on sample separation order (retention volume values) and the relationship of sample adsorption to sample structure, magnesia resembles alumina rather closely. The major difference between these two adsorbents is a stronger relative adsorption of the carbon–carbon double bond on magnesia. Magnesia has a general tendency to

adsorb olefins and aromatics more strongly than other adsorbents, leading to some useful separation possibilities with magnesia alone or in combination with other adsorbents.

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