Synthesis of silica gels containing imidazole groups and their binding affinity for methyl orange in water

Yukihiko Ueno, Hazime Yoshio, Manshi Ohyanagi, Koji Ikeda and Yoshiro Sekine
Department of Chemistry, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 160, Japan

(Received 16 January 1985; revised 10 March 1985)

Silica gels containing imidazole groups or hexyl groups whose compositions are well controlled have been prepared. The imidazole group in the gel was quaternized with C_4H_9Br, $C_6H_{13}Br$ or $C_{12}H_{25}Br$ to obtain gels that are charged and have an alkyl chain. Their binding affinities for methyl orange in water were then investigated.

We aimed to clarify the relation between the structure of the gel and its binding behaviour for small molecules in water. So the binding affinities of the unquaternized and quaternized gels were compared for methyl orange in water at various temperatures and we obtained the thermodynamic parameters for this binding. It was found that in silica gel the alkyl chain that is bound chemically to the charged site is very efficient for binding the dye in water.

(Keywords: silica; adsorption; affinity; methyl orange; chromatography; hydrophobicity)

INTRODUCTION

A great many investigations on thin-layer chromatography (t.l.c.) have been made and t.l.c. has been used in many fields because it has selectivity of detection reagents. For example, it is used for the separation of drugs and poisons[1,2], antibiotics[3], metal ions[4,5], detergents[6] and synthetic food dyes[7]. So it is very interesting to introduce various functional groups into silica gel, because there is a good possibility of preparing a stationary silica phase of t.l.c. which has an affinity for some chemical.

Here, the binding affinities of silica gels for methyl orange in water, closely related to t.l.c., were investigated at various temperatures. It is interesting to study the relation between the structure of silica gel and its dye binding behaviour. According to published reports[8-11], it is strongly suggested that hydrophobic interaction is one of the most important interactions in dye binding.

A silica gel that has imidazole or hexyl groups in it is synthesized from trimethoxyorganosilanes containing these groups and tetramethoxysilane, and the compositions of the gel are satisfactorily controlled. The imidazole group of the gel was quaternized with alkyl bromide (C_4H_9Br, $C_6H_{13}Br$, $C_{12}H_{25}Br$). Thus unquaternized and quaternized gels whose hydrophobicities are different from each other were obtained. One type of gel is uncharged and has hydrophobicity corresponding to its content of hexyl groups. Another type of gel is charged because the imidazole group in it is quaternized with C_4H_9Br and has hydrophobicity corresponding to its content of hexyl groups. The third type of gel is charged because the imidazole group in it is quaternized with C_4H_9Br, $C_6H_{13}Br$ or $C_{12}H_{25}Br$ and does not have hexyl groups, which are not bound to the charged site.

From the binding affinity of the gel and the thermodynamic parameters of dye binding, it is suggested that in silica gel the alkyl chain that is bound chemically to the charged site is very efficient for binding the dye in water.

EXPERIMENTAL

Materials

Organosilanes were supplied by Chisso Corporation, methyl orange was purchased from Eastman Kodak Company and other materials were purchased from Kanto Chemical Corporation.

Syntheses of gels

The compositions of the gels are shown in *Figure 1*. To a mixture of pure water (14 ml), ethanol (100 ml) and 28% aqueous ammonia (10 ml), a mixture of *N*-(trimethoxysilylpropyl)imidazole (10 ml), tetramethoxysilane, hexyltrimethoxysilane (if needed) and methanol (35 ml) was added and stirred for 24 h at room temperature. The reaction mixture was evaporated to remove any alcohol and aqueous ammonia. The gel was washed several times with diethyl ether and dried for 24 h *in vacuo* at 60°C.

Quaternization

The gel and alkyl bromide were carefully degassed and stood for 5 days at 70°C. After cooling, the gel was washed with diethyl ether and dried. The scheme is shown in *Figure 2*. In *Figure 2* gel I is quaternized with alkyl bromide ($C_nH_{2n+1}Br$). The quaternized gel is indicated as I*n* ($n=4$, 6 or 12). Similarly the gels synthesized by quaternizing gels II(1) and II(2) with C_4H_9Br are indicated as II4(1) and II4(2) respectively.

0032-3861/86/040627-04$03.00

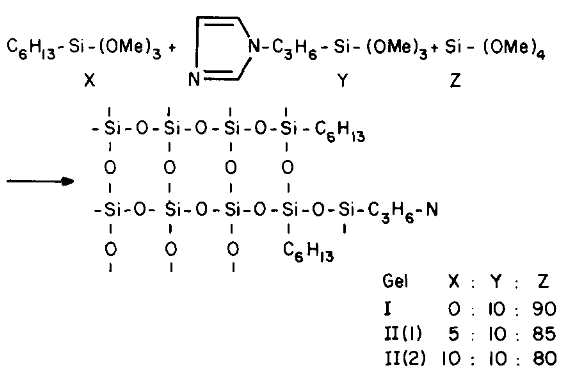


Figure 1 The scheme for the preparation of gels from methoxysilanes and their ratios

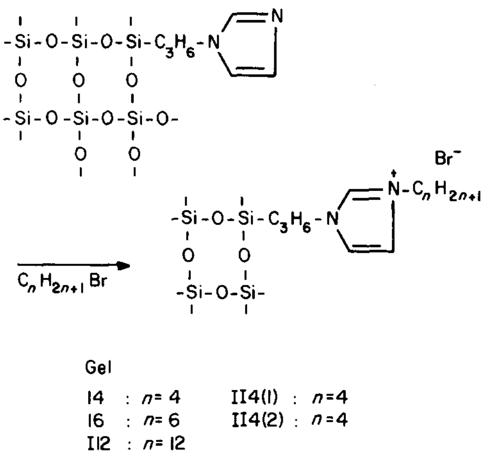


Figure 2 The scheme for the quaternization of gels with alkyl bromide ($C_nH_{2n+1}Br$)

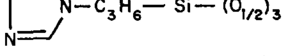
Binding experiment

Equilibrium data were obtained by an equilibrium technique[12]. About 20 mg of the gel and 5 ml of methyl orange aqueous solution (buffered to pH 7.0 with 0.1 M Tris–HCl) were put into a cellulose casing and 10 ml of the same solution was put into the test tube. The test tube that contained the solution and the cellulose casing was gently shaken in a water bath incubator at 15, 25, 35 or 45°C. Equilibration was attained after 60 h. At equilibrium the dye concentration external to the cellulose casing, which is called the free dye concentration F, was determined by an absorbance measurement using a Shimadzu Type 240 spectrophotometer. To exclude the amount of dye bound on the cellulose casing, blank tests were done. In the blank tests, the relationship between the dye bound on the cellulose casing and the free dye concentration F was obtained.

RESULTS AND DISCUSSION

Syntheses of gels

The results of elemental analyses are shown in *Table 1*. If all the methoxy groups of the organosilanes react completely and the organosilanes change into the substances indicated in equations (1), (2) and (3):

 (1)

$$C_6H_{13}—Si—(O_{1/2})_3 \quad (2)$$

$$Si—(O_{1/2})_4 \quad (3)$$

the percentages of each element in the gel can be calculated, and these values are shown in parentheses in *Table 1*. In *Table 1* the values from elemental analyses are not completely coincident with the calculated values, but the maximum differences are 2.3% in gel II(2) (carbon), 1.40% in gel I (hydrogen), 3.43% in gel II(2) (O + Si) and 1.40% in gel 11(2) (nitrogen).

The yields of the gels are about 100%. Gels I, II(1) and II(2) were synthesized three times and the differences in the values from elemental analyses (in *Table 1*) are small. So, these facts indicate that the compositions of the gel can be controlled to a good extent.

The elemental analyses of the quaternized gels are shown in *Table 2*.

Binding experiments

In the binding of methyl orange in water, the dye is bound on both the gel and the cellulose casing. So it is necessary to exclude the amount of dye bound on the latter. *Figure 3* shows the results of blank tests. In *Figure 3* there is a relation:

$$F_0 - F = aF \quad (4)$$

where F_0 is the initial dye concentration (mol l^{-1}), F is the free dye concentration (the dye concentration external to the cellulose casing at equilibrium) (mol l^{-1}) and a is a constant. From equation (4) the amount of dye bound on the cellulose casing is proportional to the free dye concentration in this region. It is thought that this relation

Table 1 The percentages of elements in unquaternized gels[a,b]

Gel	Element (%) C	H	O+Si	N
I	(10.26)	(1.28)	(84.47)	(3.99)
	10.66	2.61	83.71	3.02
	10.18	2.51	84.63	2.68
	10.32	2.68	84.19	2.81
II(1)	(14.59)	(2.09)	(79.59)	(3.78)
	14.31	2.95	79.44	3.20
	12.95	2.84	81.49	2.72
	14.00	2.92	79.87	3.21
II(2)	(18.49)	(2.82)	(75.10)	(3.59)
	18.51	3.45	75.06	3.60
	16.24	3.04	78.53	2.19
	18.84	3.14	74.52	3.50

[a] Gels were prepared three times
[b] The values in parentheses are calculated on the assumption that all the methoxy groups react completely and organosilanes exist as in equations (1), (2) and (3)

Table 2 The percentages of elements in quaternized gels

Gel[a]	Element (%) C	H	O+Si+Br⁻	N	Content of Br⁻ (mmol g^{-1})[b]
I4	12.55	3.01	81.35	3.09	1.67
I6	12.84	3.03	81.18	2.95	1.33
I12	20.39	4.39	72.83	2.39	1.26
II4(1)	15.70	3.29	77.59	3.42	1.39
II4(2)	19.22	3.38	74.30	3.10	1.27

[a] The number following the Roman numeral(s) indicates the number of carbon atoms of alkyl bromide used for quaternization
[b] By the Volhard method

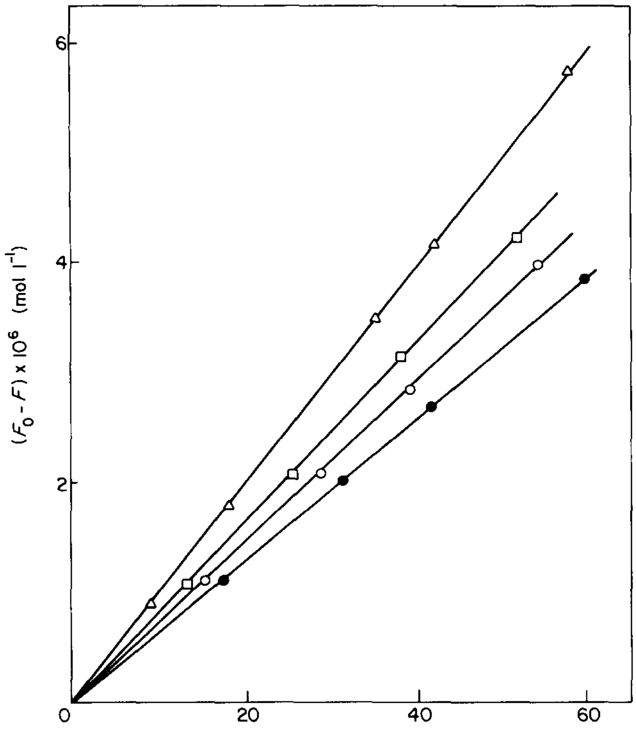


Figure 3 Results of the blank tests. Relationships between F and $(F_0 - F)$ for the binding of methyl orange by the cellulose casing in 0.1 M Tris–HCl buffer, pH 7.0: (△) 15°C, (□) 25°C, (○) 35°C, (●) 45°C. F_0 is the initial dye concentration; F is the free dye concentration

is also true in the presence of the gel. So the amount of dye bound on the cellulose casing is equal to $15aF/1000$ (mol) and the dye bound on the gel is given by:

$$(F_0 - F - aF) \times 15/1000 \quad \text{(mol)} \qquad (5)$$

To facilitate comparison of the gels, the extent of binding has been expressed in terms of a common unit of weight of 10^5 g of gel (indicated with R).

In the aggregation of anion dye molecules on polycation, when the concentration of dye in the solution is low, the dye molecules are bound individually to the charged sites of the polymer. When the concentration of dye is high, the dye molecules are sometimes bound to the charged sites lying one upon another; this is called stacking[11,13-15]. So at low concentrations of free dye the relationship between $1/F$ and $1/R$ was investigated to eliminate stacking. Typical examples of these relationships are shown in *Figures 4*, *5* and *6*. In these figures the relationships show good linearities. The values of the first binding constant K_1 (equal to nK, where K and n represent the intrinsic binding constant and the number of binding sites per 10^5 g of gel, respectively) for the binding of methyl orange by the gels can be obtained from the slope of the linear relationship[16]. The binding affinities can be compared quantitatively in terms of the first binding constant K_1. The values of K_1 are shown in *Table 3*. In *Table 3* the dye binding affinities are II(2)>II(1)>I, II4(2)>II4(1)>I4, I12>I6>I4. For the same type of gel an increase in their carbon content causes an increase in the dye binding affinities. The binding affinities of I12 and I6 are very large and these affinities are larger than those of II4(2) and II4(1).

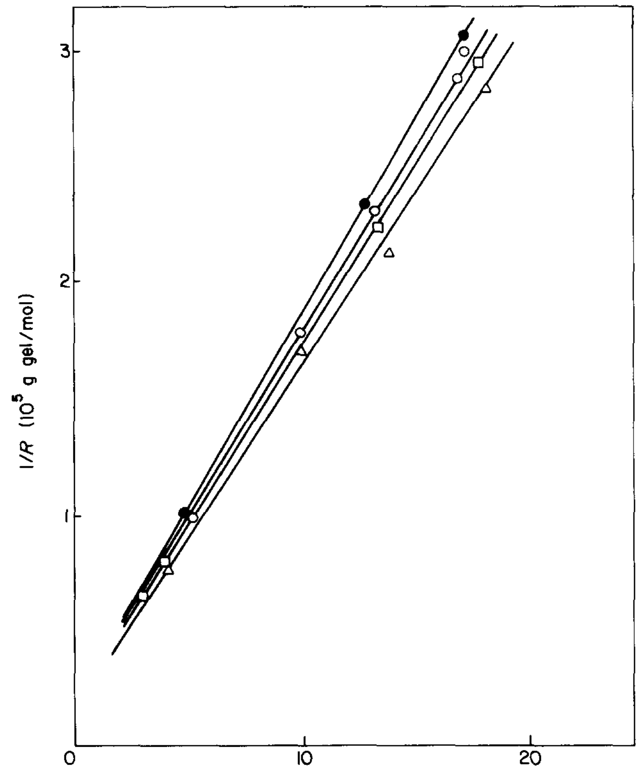


Figure 4 Relationships between $1/F$ and $1/R$ for the binding of methyl orange by gel II(2) in 0.1 M Tris–HCl buffer, pH 7.0. Symbols as for *Figure 3*

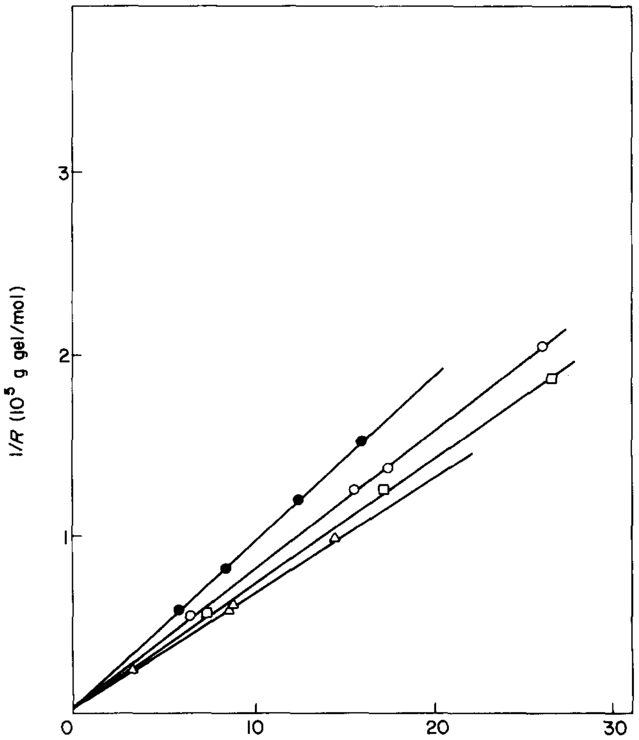


Figure 5 Relationships between $1/F$ and $1/R$ for the binding of methyl orange by gel II4(2) in 0.1 M Tris–HCl buffer, pH 7.0. Symbols as for *Figure 3*

The first binding constant for the binding of methyl orange in 0.1 M Tris–acetate buffer (pH 7.0) by polyion complexes consisting of a piperidinium polycation and polyanion (PAS complex) and crosslinked poly(vinyl-

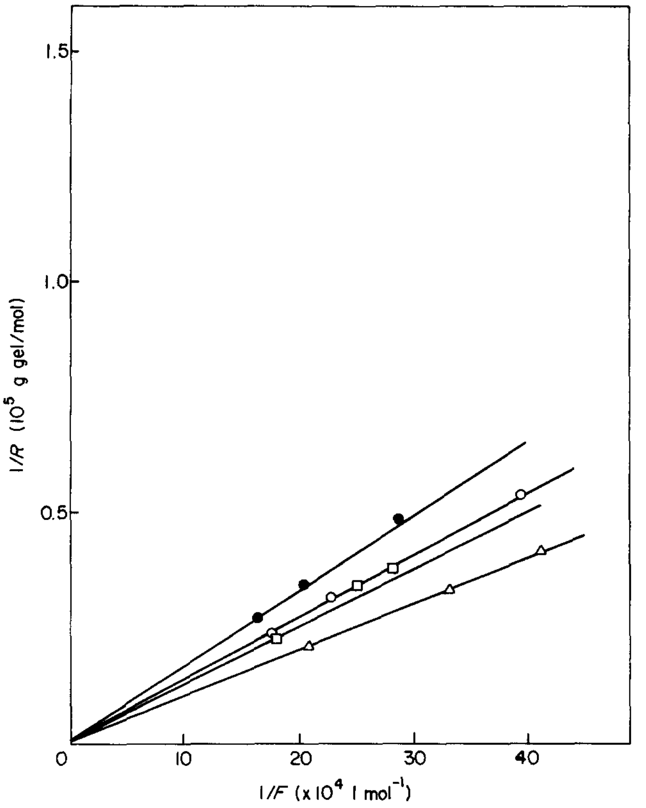


Figure 6 Relationships between $1/F$ and $1/R$ for the binding of methyl orange by gel I12 in 0.1 M Tris–HCl buffer, pH 7.0. Symbols as for *Figure 3*

Table 3 First binding constants for binding of methyl orange in water by gels at various temperatures

Gel	K_1 ($\times 10^4$)			
	15°C	25°C	35°C	45°C
I	0.934	0.776	0.625	0.522
I4	1.12	0.939	0.753	0.669
I6	22.2	17.4	14.9	10.9
I12	25.3	20.1	18.7	15.4
II(1)	2.66	2.33	2.27	2.20
II4(1)	12.0	10.9	8.93	6.00
II(2)	6.78	6.41	6.20	5.99
II4(2)	15.9	15.3	12.7	10.4

Calculated from R values computed for 10^5 g of gel. Measurements in 0.1 M Tris–HCl buffer, pH 7.0

Table 4 Thermodynamic parameters for binding of methyl orange in water by gels

Gel	$\Delta F°$ (cal mol^{-1})	$\Delta H°$ (cal mol^{-1})	$\Delta S°$ (eu)
I	−5310	−2340	9.97
I4	−5420	−2920	8.39
I6	−7160	−3980	10.7
I12	−7240	−2590	15.6
II(1)	−5960	−1040	16.5
II4(1)	−6880	−1990	16.4
II(2)	−6560	−926	18.9
II4(2)	−6970	−1100	19.7

Measurements at 25°C in 0.1 M Tris–HCl buffer, pH 7.0

pyrrolidone) (crosslinked PVP) were reported. The first binding constants are:

for PAS complex[15]	(11.8–23.5) × 10^4 (25°C)
for crosslinked PVP[17]	4.55 × 10^4 (15°C)
	3.86 × 10^4 (25°C)
	3.25 × 10^4 (35°C)

Comparing these data with *Table 3*, the binding affinities of gels I, I4 and II(1) are smaller than those of crosslinked PVP and PAS complex, but those of the other gels are comparable.

Thermodynamic parameters for the binding can be obtained from the first binding constants and their temperature dependences[8] and are listed in *Table 4*. In *Table 4* the contributions of $\Delta S°$ to $\Delta F°$ are II(2) > II(1) > I, II4(2) > II4(1) > I4, I12 > I6 > I4. These orders are the same as those of the carbon contents in the gels (shown in *Tables 1* and *2*). In *Table 4* the contribution of $\Delta H°$ to $\Delta F°$ for the charged gel is larger than that for the uncharged gel: I4 > I, II4(1) > II(1), II4(2) > II(2). Thus it is clear that the negatively charged sulphonate groups of the dye used are attracted to the charged site of the gel. These facts suggest that hydrophobic interaction and electrostatic interaction play an important role in dye binding and that the hydrophobic interaction increases according to the carbon content in the gel.

It was reported that a polysoap whose polymer chain is flexible and whose pendant alkyl groups are not bound to the charged site has a good binding affinity[18]. But these gels are crosslinked and rigid, so the dye binding affinities of II4(1) and II4(2) are smaller than those of I6 and I12.

It is suggested that both the alkyl chain bound chemically to the charged site and the alkyl chain not bound to the charged site in the gel are efficient for the hydrophobic interaction between the gel and the dye and that the binding affinity of the former is larger than that of the latter.

REFERENCES

1 Stead, A. H., Gill, R., Wright, T., Gibbs, J. P. and Moffat, A. C. *Analyst* 1982, **107**, 1106
2 Wilson, I. D. *J. Chromatogr.* 1984, **291**, 241
3 Hendrickx, S., Roets, E., Hoogmartens, J. and Vanderhaeghe, H. *J. Chromatogr.* 1984, **291**, 211
4 Kovâcs, J. and Kiss, P. 'Proc. Symp. on Advances in Liquid Chromatography', 1982, p. 191
5 Qureshi, M., Sethi, B. M. and Sharma, S. D. *J. Liq. Chromatogr.* 1984, **7**, 1345
6 Yagami, K., Yokota, Y., Iwashita, S. and Nakayama, M. *Yakagaku* 1984, **33**, 284
7 Steele, J. A. *J. Assoc. Off. Anal. Chem.* 1984, **67**, 540
8 Takagishi, T. and Kuroki, N. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 1889
9 Takagishi, T., Takami, T. and Kuroki, N. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 437
10 Takagishi, T., Imajo, K., Nakagami, K. and Kuroki, N. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 31
11 Takagishi, T., Kozuka, H. and Kuroki, N. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 3237
12 Hughes, T. R. and Klotz, I. M. *Meth. Biochem. Anal.* 1956, **3**, 265
13 Bradley, D. F. and Wolf, M. K. *Proc. Natl. Acad. Sci. USA* 1959, **45**, 944
14 Klotz, I. M., Royer, G. P. and Sloniewsky, A. R. *Biochemistry* 1969, **8**, 4752
15 Takagishi, T., Kozuka, H. and Kuroki, N. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 447
16 Klotz, I. M., Walker, F. M. and Pivan, R. B. *J. Am. Chem. Soc.* 1946, **68**, 1486
17 Takagishi, T., Naoi, Y., Sonoda, I. and Kuroki, N. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2323
18 Niino, M., Ueno, Y., Araki, T. and Sekine, Y. *Polymer* 1983, **24** (*Commun.*), 124