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Determination of Sorption Equilibria in Gels

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A procedure for the determination of sorption equilibria in gels and porous substances has been worked out. It has been used to study the partition of various solutes in the systems gel cellulose-water and gel cellulose-cyclohexane. It was found that in water moderate sorption effects occurred with polar solutes and that the sorption isotherms were in general linear. In cyclohexane the sorption effects were much more pronounced than in water, and the sorption isotherms exhibited a marked nonlinearity. In this case very strong sorption effects occurred with substances which could form hydrogen bonds with the gel matrix.

The partition of solutes between a gel phase and a solution constitutes the basis of many important separation processes. To these belong gel chromatography and processes which make use of solute permeation through gel membranes, such as dialysis and ultrafiltration. These methods normally make use of the steric exclusion of solutes from the gel phase and therefore allow the separation of solutes according to their molecular size. However, the situation is often complicated by the occurrence of sorption phenomena, encountered especially with polar solutes. An example is the "aromatic adsorption" in Sephadex gels.[1–8] In chromatographic investigations some information of the sorption phenomena can be obtained from the elution diagrams, since the elution volume of a substance depends explicitly on its partition coefficient.[9,10] However, for a complete determination of the sorption isotherm direct determinations of the partition equilibria are necessary. In the methods usually employed in this connection the gel phase is separated from the solution after the equilibrium has been established and the amount of solute in the gel phase is determined.[11–17] The main disadvantage of this procedure is the difficulty of obtaining a complete separation of the gel phase from the solution. Although it is possible to correct for the incomplete separation of the phases [16–17] the method becomes quite laborious when the measurements are extended over a wide range of concentrations. In the present investigation a new method for the determination of partition equilibria has been worked out and it has been used for studying partition equilibria for various solutes in the systems gel cellulose-water and gel cellulose-cyclohexane.

THEORETICAL

In this treatment we consider a two-phase system consisting of a gel phase and a solution phase in contact with it, and we restrict the treatment to the case of a single solute. Thus, the system has three components: solvent, solute, and gel matrix. Since it is difficult to determine accurately the volumes of the constituent phases we will express the compositions of the phases on the weight basis. The following symbols will be used

m_1'	mass of solvent in the solution phase
m_2'	mass of solute in the solution phase
$w_2' = m_2'/(m_1'+m_2')$	weight fraction of solute in the solution phase
m_1''	mass of solvent in the gel phase
m_2''	mass of solute in the gel phase
m_3	mass of the gel matrix
$w_2'' = m_2''/(m_1''+m_2''+m_3)$	weight fraction of solute in the gel phase
$w_3 = m_3/(m_1''+m_2''+m_3)$	weight fraction of gel matrix
γ	partition coefficient
ε	excess solute in the gel phase
$m_1 = m_1'+m_1''$	total mass of solvent
$m_2 = m_2'+m_2''$	total mass of solute
γ_c	partition coefficient for volume concentration
c'	solute concentration in the solution phase (g/l)
c''	solute concentration the gel phase (g/l)
ϱ'	density of the solution phase
ϱ''	density of the gel phase

To express the partition of the solute between the solution and the gel phase we will use the partition coefficient. Since in the absence of appreciable sorption effects the solute in the gel phase is present mainly in the solution filling the interstices of the gel matrix, it is appropriate to define the partition coefficient with the aid of the weight fractions of solute in the interstitial and external solutions. Thus

$$\gamma = \frac{m_2''}{m_1''+m_2''} \Big/ \frac{m_2'}{m_1'+m_2'} \tag{1}$$

It should be noted that for an inert, noninteracting lattice (including steric interactions) the interstitial solution is identical to the external solution and, hence, γ is unity.

Eqn. (1) may be rearranged by expressing the weight fraction of solute in the interstitial solution by its total weight fraction in the gel phase. Observing that

$$m_2''/(m_1''+m_2'') = w_2''/(1-w_3) \tag{2}$$

we get

$$\gamma = w_2''/w_2'(1-w_3) \tag{3}$$

The quantities in the right members of eqns. (1) and (3) referring to the gel phase are not easily determined directly, and therefore an indirect proce-

dure for the determination of γ has to be adopted. We therefore define a new quantity, the excess solute in the gel phase:

$$\varepsilon = m_2 - (m_1 m_2'/m_1') = m_2 - [m_1 w_2'/(1-w_2')] \quad (4)$$

This quantity is a measure of sorption of solute in the gel phase and it can obviously be determined if the total amounts of solute and solvent in the system are known, and the composition of the solution phase is determined. It should be noted that the determination of ε is not influenced by the swelling of the gel.

From eqn. (1) we get

$$\gamma - 1 = m_1'[m_2'' - (m_1'' m_2'/m_1')]/m_2'(m_1'' + m_2'') \quad (5)$$

Using the definitions of m_1 and m_2 we may rearrange eqn. (4) and get

$$\varepsilon = m_2'' - (m_1'' m_2'/m_1') \quad (6)$$

Combining (5) and (6) we get

$$\gamma - 1 = m_1'\varepsilon/m_2'(m_1'' + m_2'') = (1-w_2')\varepsilon/w_2'(m_1'' + m_2'') \quad (7)$$

In dilute solutions the factor $(m_1'' + m_2'')$ in (7) is very nearly constant and a possible variation of the partition coefficient is then reflected in a curvature in a plot of ε *v.* w_2'. Under these circumstances the sorption isotherm may be expressed directly in terms of ε. However, for an explicit determination of γ the factor $(m_1'' + m_2'')$ in (7) has to be evaluated. In dilute solutions m_1'' is much larger than m_2'' and is in general constant. It can be evaluated by determining ε for a polymeric solute, which is excluded from the gel phase. Then γ and m_2'' in (7) are zero and m_1'' is readily obtained. This procedure is analogous to the polymetaphosphate method introduced by Samuelson.[18] The parameter m_1'' can also be determined by drying the gel, although this procedure is in general less satisfactory, since it is not possible to remove completely the adhering solvent from the surface of the gel. The situation is more complicated when the sorption of solute changes the swelling of the gel. Then measurements with the polymeric solute have to be carried out in the presence of various amounts of the solute being sorbed.

It is also of some interest to compare the partition coefficient γ, defined by eqn. (1), with the partition coefficient γ_c, relating the volume concentrations in the solution and the gel phase, which is used in chromatographic theory.[9] From the definitions and eqn. (3) we get

$$\gamma_c = \frac{c''}{c'} = \frac{\varrho'' w_2''}{\varrho' w_2'} = \frac{\varrho''(1-w_3)}{\varrho'}\,\gamma \quad (8)$$

In dilute solutions and in the absence of specific swelling effects, the parameters ϱ', ϱ'', and w_3 in the right member of this equation are very nearly constant and hence the two partition coefficients may be considered as being proportional.

EXPERIMENTAL

The gel cellulose used in this investigation was commercial cellophane (cellulose casing, from Union Carbide Corp., Chicago).

The polymeric solutes used were hydroxyethyl cellulose and polystyrene, which had the molecular weights $M_v = 520\,000$ and $M_v = 115\,000$, respectively.

The partition experiments were carried out in a glass-stoppered cylindrical bottle of pyrex glass, which contained weighed amounts of the cellophane and the solution. Before measurements were started the cellophane was purified by extracting it in the bottle overnight with a continuous stream of water at 50°C. In the case of measurements in aqueous solutions the same procedure was used for the regeneration of pure gel cellulose between different sets of measurements. In the case of measurements in cyclohexane the cellophane was freed from water by placing the bottle with the cellophane sample into a Soxhlet extractor and extracting it with acetone, which was dried with anhydrous potassium carbonate. The extraction was later repeated with cyclohexane and this procedure was also used to regenerate the pure gel cellulose between different sets of measurements. To the gel cellulose in pure solvent a small amount of a standard solution containing the solute was then added with a pipette and the system was allowed to reach equilibrium. The equilibration was carried out in an air thermostat at 25°C, where the flask was kept in steady rotation. As a rule the equilibrium was established in about 2—3 h. A portion of the solution was then removed for analysis and a new portion of the standard solution was added. This procedure was repeated until a sufficient range of concentrations was covered. To check the reversibility of the sorption reaction, the

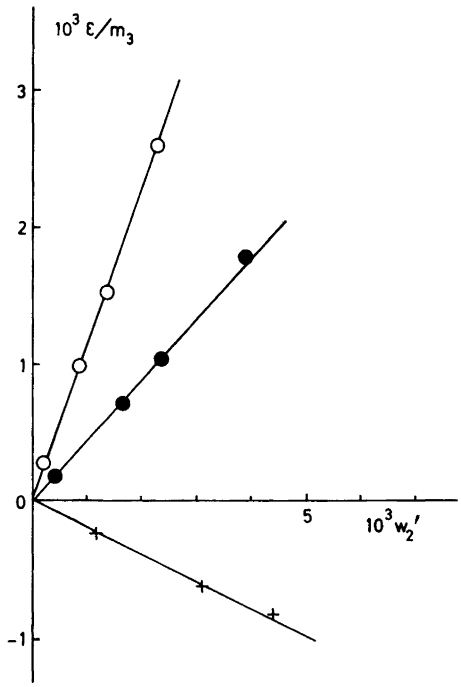

Fig. 1. Sorption isotherms in the system gel cellulose-water: ○ for *p*-nitrophenol, ● for phenol, and + for raffinose.

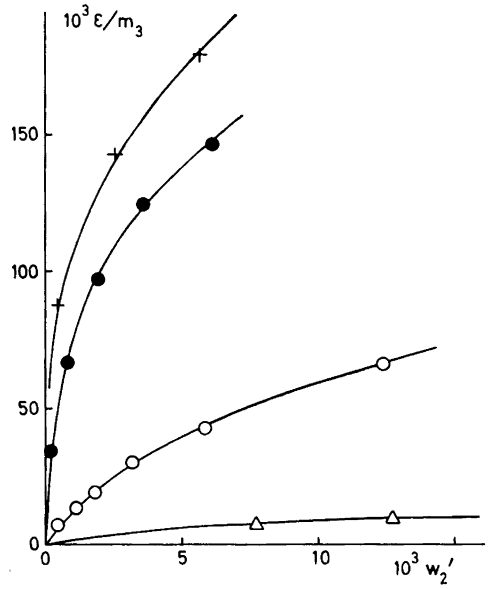

Fig. 2. Sorption isotherms in the system gel cellulose-cyclohexane: + for phenol, ● for ethanol, ○ for *p*-nitrotoluene, and △ for benzene.

experiments were sometimes reversed by adding pure solvent, instead of the standard solution, to the system.

The concentration determinations were carried out with a Water's differential refractometer, which was used as a digital reading instrument. The differential measurements were carried out against standard solutions having concentrations close to those of the solutions to be analyzed. With the instrument refractive index differences could be determined with an accuracy of about 1 part in 10^6, which yielded an accuracy better than 0.5 % in the concentration determinations over the entire range of concentrations covered by the experiments. With phenol and *p*-nitrophenol in the low concentration range the concentration determinations were carried out spectrophotometrically, using a Zeiss PMQ II model spectrophotometer. Also in these measurements an accuracy better than 0.5 % in the concentration determinations was attained.

RESULTS AND DISCUSSION

The results of the measurements are shown in Figs. 1 and 2, where the specific excess solute in the gel phase ε/m_3 is plotted against the weight fraction of solute in the solution phase. The primary data are listed in Tables 1 and 2, which also contain values of the partition coefficient γ. The latter were

Table 1. Sorption data for various solutes in the system gel cellulose-water. $m_3 = 13.38$ g; $m_1'' = 16.6$ g.

Solute	$10^3\ w_2'$	m_1 g	m_2 g	$10^3\ \varepsilon$ g	γ
Ethanol	2.972	72.25	0.2131	− 2.3	0.95
	8.115	53.61	0.4296	− 9.0	0.93
	37.89	51.72	1.9838	−52.9	0.92
Glucose	1.082	50.71	0.05411	− 1.10	0.94
	2.265	52.64	0.1177	− 1.8	0.95
	10.48	52.30	0.5425	−11.3	0.94
	15.72	54.97	0.8618	−16.1	0.94
	22.49	54.67	1.2371	−20.7	0.95
Raffinose	1.154	64.50	0.07138	− 3.1	0.84
	3.090	64.38	0.1912	− 8.4	0.84
	4.402	64.26	0.2730	−11.1	0.85
Phenol	0.1114	71.26	0.008646	0.708	1.38
	0.4062	68.56	0.03012	2.26	1.34
	1.645	72.50	0.12893	9.45	1.35
	2.350	68.26	0.1746	13.8	1.35
	3.902	67.98	0.2900	23.7	1.36
p-Nitrophenol	0.1112	71.95	0 009919	1.92	2.04
	0.1952	68.14	0.01681	3.51	2.08
	0.8483	67.99	0.07090	13.2	1.94
	1.355	69.26	0.1144	20.4	1.90
	2.275	69.07	0.1921	34.6	1.91
NaCl	1.501	49.81	0.07118	− 3.63	0.85
	2.635	56.92	0.1445	− 5.9	0.87
	5.427	49.66	0.2643	− 6.6	0.93
	11.92	56.75	0.6752	− 9.4	0.95
Hydroxyethyl cellulose	0.8103	62.48	0.03718	−13.49	0

Table 2. Sorption data for various solutes in the system gel cellulose-cyclohexane. $m_3 = 11.16$ g; $m_1'' = 4.56$ g.

Solute	$10^3\ w_2'$	m_1 g	m_2 g	ε g	γ
Ethanol	0.1873	46.80	0.3926	0.3838	450
	0.852	46.75	0.7837	0.7436	192
	1.973	45.28	1.170	1.080	121
	3.575	44.85	1.547	1.386	86
	6.122	40.58	1.885	1.635	59
Phenol	0.438	51.28	0.9973	0.9748	489
	2.544	53.91	1.732	1.595	138
	5.649	53.33	2.305	2.002	78
Benzene	7.720	43.16	0.4150	0.0792	3.23
	12.72	42.82	0.6565	0.1050	2.79
	25.59	42.10	1.264	0.158	2.32
p-Nitrotoluene	0.4630	50.25	0.1036	0.0803	39
	1.132	50.12	0.2054	0.1486	30
	1.838	49.50	0.3046	0.2135	26
	3.203	49.45	0.4976	0.3387	24
	5.858	52.62	0.7835	0.4734	19
	12.38	44.67	1.2983	0.7386	14
Polystyrene	1.769	42.89	0.06792	−0.00808	0

calculated with the help of the m_1''-values obtained from measurements with the polymeric solutes hydroxyethyl cellulose and polystyrene in aqueous solutions and cyclohexane, respectively. In this connection swelling effects were probably negligible in all cases, except possibly with ethanol and phenol in cyclohexane solutions. Also, in all cases the sorption reactions were found to be reversible.

We find that in aqueous solutions the sorption isotherms are linear and yield essentially constant partition coefficients. On the other hand the sorption isotherms in cyclohexane exhibit a pronounced nonlinearity and the partition coefficients decrease markedly with increasing concentration. Also, the partition coefficients for polar solutes are much higher in cyclohexane than in water. This behaviour may be understood from the general characteristics of the gel-solvent systems under consideration. Thus, in aqueous solutions the cellulose in the gel matrix is highly solvated by water, which hinders the interaction between the gel matrix and polar solute molecules. The values of the partition coefficients for relatively unpolar solutes, such as ethanol and glucose, indicate that they may penetrate most of the solvent in the gel phase, the amount of water from which the solute is excluded being of the order of 5 %. With raffinose a somewhat lower value is observed, which indicates a beginning steric exclusion. Also with sodium chloride at low concentrations a lower value of the partition coefficient is observed. This is probably due to the Donnan effect arising from the presence of small amounts of carboxyl groups in the cellulose.[19] The effect of "aromatic adsorption"

is clearly displayed by the aromatic substances investigated, and the effect is seen to increase with the polarity of the substance.

In cyclohexane the gel matrix is not appreciably solvated by the solvent and therefore the interaction between the gel matrix and polar solutes is much more pronounced than in water. In this case a direct interaction between the gel matrix and polar solutes seems to occur, which is indicated by the marked nonlinearity of the sorption isotherms. A very strong interaction is found with substances containing hydroxyl groups, which may be explained by their ability to form hydrogen bonds with the hydroxyl groups of the cellulose in the gel matrix. Thus, in unpolar solvents gel cellulose is a very efficient sorbent for substances capable of forming hydrogen bonds. The present results are in agreement with those obtained with Sephadex gels in the previously mentioned chromatographic investigations.[1-8] This is of course expected in view of the chemical similarity of cellulose and dextran gels.

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