

given series of like structure, such as the alkyl-1,2-benzanthracene derivatives, compounds of lowest water solubility are least carcinogenic. Such a parallel cannot be drawn when considering compounds of more widely differing structures. The solubility is regarded, by the present authors, as merely one of a large number of factors which may have to be taken into account in considering the mechanism of hydrocarbon carcinogenicity. It may be that certain hydrocarbons will prove to be too soluble to be retained long enough to exhibit carcinogenesis except following repeated applications, while other hydrocarbons cannot exhibit carcinogenesis because they are so insoluble that they cannot reach a potential site of action rapidly enough to exceed their rate of destruction there.

From a purely chemical point of view certain of the results are interesting because they show that introducing a methyl group may either raise or lower the solubility of a given compound. For example, the 1'-, 9- and 10-methyl-1,2-benzanthracenes have solubilities of 55, 66 and 55 micrograms per liter, respectively, as compared with 11 for 1,2-benzanthracene. Likewise, the values for the 5- and 6-methylchrysenes are 62 and 65, respectively, as compared with 1.5 for chrysene. On the other hand, 5-methylbenzpyrene, with 0.8, is lower than 3,4-benzpyrene with 4. Since the extent of the solubility is determined by the excess of energy liberated by attraction of hydrocarbon for water molecules over that necessary to remove it from the particles of the hydrocarbon, the increased solubilities of the methyl-1,2-benzanthracenes and methylchrysenes as compared to those of the respective parent hydro-

carbons may be provisionally accounted for by a decrease in the energy required to remove the molecules of the methyl derivatives from the solid, rather than by increase in attraction of the methyl derivatives for water. This suggestion is supported qualitatively by the fact that the methyl derivatives have lower melting points than the parent hydrocarbon. In the case of 5-methyl-3,4-benzpyrene and its parent hydrocarbon, the introduction of the methyl group apparently has little effect on the energy of binding of the hydrocarbon in the solid; consequently the solubility of the methyl derivative is decreased because of decreased water affinity. In a similar way, the solubilities of the 10-methyl-, 10-ethyl-, 10-butyl- and 10-amyl-1,2-benzanthracenes decrease as the water affinity of the whole molecule decreases with increasing length of side chain, even though the energies required to remove the hydrocarbon molecules from their respective solids, as indicated qualitatively by the melting points, decrease in the same order.

The authors are indebted to Mr. T. V. Parke for his cooperation in certain phases of the experimental work here described.

Summary

By means of the nephelometric method described in the preceding paper,² the approximate solubilities of thirty-one polycyclic hydrocarbons in pure water have been measured at 27°. These were found to vary from about 0.5 microgram per liter for 1,2,5,6-dibenzanthracene up to about 1600 micrograms per liter for phenanthrene.

INDIANAPOLIS, INDIANA

RECEIVED JULY 14, 1941

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Studies on the Hydrogel of Zirconia. I. The Time of Set

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Introduction

Although the literature contains a number of observations of the formation of a hydrogel of zirconia, apparently only Prakash³ has determined the time of set. His data do not show the relation of temperature to time of set.

(1) Present address: Eastman Kodak Company, Rochester, N. Y.

(2) Present address: General Chemical Company, New York City.

(3) Prakash, *J. Phys. Chem.*, **36**, 2483 (1932).

A series of determinations of the time of set of zirconia hydrogels under carefully controlled conditions should prove interesting, because of the relations between zirconium, titanium, and silicon, and because of the large amount of data available on time of set of hydrogels of silica, often called silicic acid gels.

It has been found much more difficult to control the setting of these hydrogels of zirconia than the corresponding silicic acid gels. Nevertheless,

the present paper presents data showing certain relations between time of set, temperature, pH and concentration of electrolyte in some gels of hydrated zirconia.

Historical

The hydrogel of zirconia has usually been reported as being formed from the hydrosol simply upon standing, in some cases, or by a change in pH of the hydrosol. It thus resembles in its formation the hydrogels of titania and silica.

Methods of formation of the hydrosol have been reviewed by Weiser⁴ and Fricke.⁵ Briefly, the hydrosol is prepared by hydrolysis and dialysis of zirconium nitrate,⁶ of the tetrachloride or oxychloride,⁷ or of the acetate.⁸ By the addition of alkaline solutions to solutions of zirconium salts,^{3,9} zirconia hydrosols are prepared. Dialysis of a zirconium salt solution, by removing acid, also raises the pH of the solution.

Since sodium zirconate is practically insoluble, the analog of the most commonly used method for making silica hydrosol cannot be used for zirconia, namely, mixing solutions of sodium zirconate and an acid.

There is no agreement in the literature concerning the composition of hydrous zirconia.¹⁰ It is apparent that one form is easily soluble in dilute acid while the other dissolves very slowly.⁴

Experimental

In order to determine time of set accurately, some practically instantaneous method of forming the hydrosol must be found. Methods involving dialysis are useless here.

Of the four zirconium compounds supplied by the Titanium Alloy Manufacturing Company, namely, the oxychloride, hydroxide and sulfate of zirconium and sodium zirconate, we have found the oxychloride most useful.

An aqueous solution of the oxychloride (analysis ZrO_2 , 40%; Cl , 22%; Fe , 0.05%; and Ti , 0.05%) containing 385 g. per liter in distilled water was prepared and filtered. This solution showed a total increase from $pH = 0.10$ to 0.12 in three days with no further change over seven weeks. This change, though slight, agrees with the literature.

Since hydrogels were prepared either by addition of solutions of sodium carbonate or sodium acetate to the zirconium oxychloride solution, and since the results were somewhat different, the two methods are described separately.

(4) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1935, pp. 264-271.

(5) Fricke and Hüttig, "Handbuch der allgemeinen Chemie," (Walden) Vol. IX, Acad. Verlag., Berlin, 1937, pp. 219-227.

(6) Biltz, *Ber.*, **35**, 4431 (1902).

(7) Adolf and Pauli, *Koll. Z.*, **29**, 173 (1921).

(8) Rosenheim and Hertzmann, *Ber.*, **40**, 813 (1907).

(9) Szilard, *J. Chim. Phys.*, **5**, 488 (1907).

(10) Venable, "Zirconium," Chemical Catalog Co., Inc., New York, N. Y., 1922, p. 41.

A. Gels Prepared by Mixing Solutions of Sodium Carbonate and Zirconium Oxychloride.—To one liter of the solution containing 385 g. of zirconium oxychloride, 75 g. of sodium carbonate was added with rapid stirring. No gelation occurred. The pH was 1.19. Such a solution was found to stand for over a month without gelation and with only a very slight change in pH . To avoid any difficulty due to age of this solution, runs at two different temperatures were made all on the same day. To determine time of set, 25 cc. of this standard solution was mixed with 40 cc. of 0.20 N sodium carbonate solution. The time of set was determined in a 100-cc. beaker by the tilted rod method. Solutions were carefully thermostated before and after mixing. The pH was measured in separate samples at 25° by the quinhydrone method. It was found that rapid stirring during the addition of the 0.20 N sodium carbonate to the zirconium oxychloride solution was necessary in order to dissolve the fine precipitate which formed, and also that an increase in the time of stirring caused a small decrease in time of set. Hence the stirring time was also recorded. The times of set in Table I are an average of several determinations.

TABLE I

TIME OF SET OF HYDROGELS OF ZIRCONIA MADE BY MIXING SOLUTIONS OF SODIUM CARBONATE AND ZIRCONIUM OXYCHLORIDE

Temp., °C.	Stirring time, minutes	Time of set, minutes
34.6	2	20.25
	3	17.80
	6	16.65
25.0	2	88.00
	3	86.00
	4	79.65
	6	78.00

pH of mixture was 2.68. Concentration of zirconium dioxide = 0.48 g. mole per liter.

By plotting the logarithm of time of set against reciprocal temperature, as first shown by Hurd and Letteron,¹¹ and by multiplying the slope by 2.30 R , one may obtain the energy of activation. This is given in Table II.

TABLE II

ENERGY OF ACTIVATION OF THE FORMATION OF THE HYDROGELS OF ZIRCONIA FROM MIXTURES OF SODIUM CARBONATE AND ZIRCONIUM OXYCHLORIDE SOLUTIONS

Time of stirring, min.	Energy of activation, cal.
2	28,800
3	29,200
6	29,400

It should be noted here that in these gels a thin film appears to form on the surface. This causes a little uncertainty in the determination of the time of set.

The effect of addition of a salt, potassium chloride, upon the time of set of these zirconia gel mix-

(11) Hurd and Letteron, *J. Phys. Chem.*, **36**, 604 (1932).

tures was determined at 25°. The concentration of zirconium oxychloride and sodium carbonate was kept constant. These gels contained 0.45 g. mole of zirconium dioxide per liter.

TABLE III

EFFECT OF POTASSIUM CHLORIDE ON TIME OF SET OF ZIRCONIA HYDROGELS AT 25°

Concn. KCl, g. mols. per liter	pH	Time of set, minutes
0.00	2.72	450
.06	2.68	146
.12	2.72	105
.18	2.89	70
.24	2.86	46
.30	2.89	28

These data show that the salt added causes a considerable decrease in time of set of the gel without changing the pH sensibly. The irregularity in pH values is due to the difficulty of reproducing the zirconium oxychloride and sodium carbonate mixtures exactly in this unbuffered mixture. This effect of a salt in decreasing the time of set of the zirconia gel mixtures agrees with the results for similar studies on silicic acid gels.¹²

These gel mixtures, produced by mixing solutions of sodium carbonate and zirconium oxychloride solutions, set more rapidly as temperature increased. Above 90°, however, the gels were re-liquefied.

B. Gels Prepared by Mixing Solutions of Sodium Acetate and Zirconium Oxychloride.—

Gel mixtures were also prepared by mixing solutions of sodium acetate and zirconium oxychloride. The method was similar to the method described under the preceding heading and resembled that reported by Prakash and Dhar.¹³ The same solution of zirconium oxychloride was used here as with sodium carbonate, namely, one containing 385 g. of zirconium oxychloride per liter. A 1.5 molar sodium acetate solution also was used. To facilitate some studies on re-liquefaction here, the gels were allowed to set in eight-inch test-tubes. Time of set was determined by the "tilted tube" method of Flemming,¹⁴ which has been used in this Laboratory in the study of the setting of titania hydrogels.¹⁵ The results are given in Table IV.

The energy of activation was calculated, although only two temperatures were available and the mixture number 1 did not set at 25°. The

(12) Hurd, Raymond and Miller, *J. Phys. Chem.*, **38**, 663 (1934).

(13) Prakash and Dhar, *J. Ind. Chem. Soc.*, **7**, 591 (1930).

(14) Flemming, *Z. physik. Chem.*, **41**, 427 (1902).

(15) Hurd, Jacober and Godfrey, *THIS JOURNAL*, **63**, 723 (1941).

TABLE IV

TIME OF SET OF HYDROGELS OF ZIRCONIA MADE BY MIXING SOLUTIONS OF SODIUM ACETATE AND ZIRCONIUM OXYCHLORIDE

Gel number	Concn. NaAc g. moles per liter	Temp., °C.	pH	Time of set, minutes
1	0.725	25.0	3.33	Did not set
2	.750	25.0	3.50	3.50
3	.775	25.0	3.65	2.00
4	.800	25.0	3.80	1.67
1	.725	40.0	3.33	0.59
2	.750	40.0	3.50	.50
3	.775	40.0	3.65	.43
4	.800	40.0	3.80	.33

Concn. of ZrO₂ = 0.42 g. mole per liter in all.

energy of activation obtained was 25,800 calories for number 2, 21,000 for number 3, and 21,400 for number 4.

These same mixtures were run at 0°, but none of them set. Only the last mixture showed even a trace of opalescence.

In order to study the effect of concentration of zirconia or of zirconium oxychloride on the time of set, a series was run at 25°. The data are shown in Table V. It should be noted here that with varying concentration of the zirconium oxychloride solution and constant concentration of sodium acetate, the pH has varied also.

TABLE V

TIME OF SET OF ZIRCONIA HYDROGELS AS A FUNCTION OF CONCENTRATION OF ZIRCONIA

Concn. of ZrO ₂ g. mole per liter	pH	Time of set, minutes
0.126	4.98	14.25
.167	4.88	6.50
.209	4.70	3.50
.251	4.60	2.25
.293	4.35	2.00
.335	4.18	2.25
.376	4.00	4.33
.418	3.60	9.17

Concentration of NaAc = 0.75 g. mole per liter throughout.

These data are listed in Fig. 1, which shows the minimum of time of set at a concentration of about 0.3 g. mol. per liter of zirconium dioxide.

Reliquefaction of Zirconia Hydrogels.—The phenomenon of reliquefaction of these hydrogels of zirconia was encountered often in the gels made by mixing solutions of sodium acetate and zirconium oxychloride. The phenomenon occurred as follows. When the solutions of sodium acetate and zirconium oxychloride were mixed, the result, a hydrosol of zirconia, was clear. It soon became opalescent and set, usually, in a few

minutes. The material appeared to be a gel, although softer than the silicic acid gels. After a longer interval of standing in the thermostat, usually one to three hours, the gels became liquid. They were water-clear once more.

If they were now placed in a bath at a higher temperature, 50–60°, the mixtures would regel. They would reliquefy again if cooled for some time. We have repeated this process more than ten times on a single sample and it can be repeated many more times, apparently. The same effect for the hydrogel of titania has been reported from this Laboratory.¹⁵

One table of data giving the time of reliquefaction in terms of concentration of zirconia, sodium acetate and *p*H is included, Table VI.

TABLE VI

TIME OF SET AND OF RELIQUEFICATION OF HYDROGELS OF ZIRCONIA AT 25°

Concn. NaAc, g. mole per liter	<i>p</i> H	Time of set, minutes	Time of reliquefaction, minutes
0.56	3.83	2.66	125
.64	4.10	1.75	131
.71	4.28	1.25	140
.79	4.43	1.25	130
.86	4.58	1.86	100
.94	4.68	2.09	90
1.01	4.78	2.09	80
1.09	4.84	2.17	68

Concn. ZrO₂ = 0.31 g. mole per liter throughout.

It is easily seen here from Table VI that the faster these gels have set where *p*H = 4.3 to 4.4, the longer it has taken for them to reliquefy.

Discussion

Some discussion of the data in this paper has necessarily accompanied the data. We shall attempt here to formulate a theory for the mechanism of setting of these zirconia hydrogels.

It is probably impossible to give any completely satisfactory discussion. The best zirconium compounds available are not chemically pure, hence two observers may not have worked with exactly the same material. It is difficult to compare the results of different observers also because of different methods used.

From our data it is evident that aqueous solutions of zirconium oxychloride of *p*H = 0.10 do not set in any reasonable time to form gels. When the *p*H is raised to values from 2.0 to 5.0, the sols set to form gels which are softer than silicic acid gels of equivalent concentration. A rise of temperature causes a decrease in time of set. Addi-

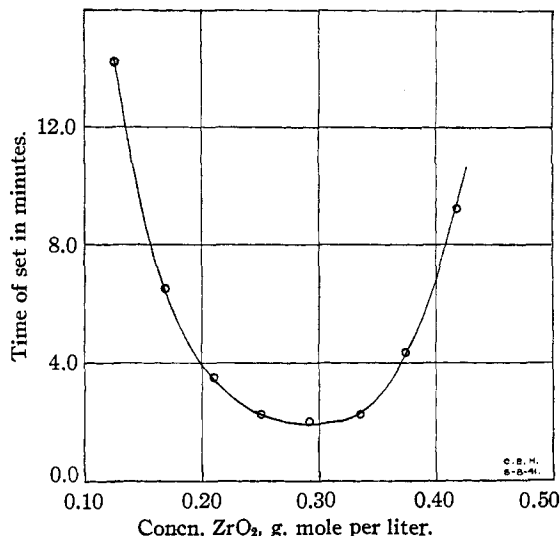


Fig. 1.—Time of set of zirconia gels as a function of the concentration of zirconia.

tion of potassium chloride to the zirconia hydrosol decreases time of set markedly, although no change in *p*H occurs. Increase in concentration of zirconium oxychloride causes a decrease in *p*H, but gives a minimum in time of set. The liquefaction, regelation and reliquefaction phenomena are rather confusing.

Unfortunately, with zirconia hydrosols we have no data on the apparent molecular weight of the zirconium oxide or hydroxide such as we have for silicic acid,^{16,17} which showed a molecular weight of silicic acid when first formed of from 60 to 100, suggesting a monosilicic acid. Hurd¹⁸ has suggested that silicon hydroxide is amphoteric and undergoes condensation, building up polysilicic acids to form the gel.

Most observers believe that zirconium hydroxide is amphoteric, although Venable¹⁰ and Owens and Morris¹⁹ believe ZrO(OH)₂ is more certain to be formed than Zr(OH)₄, owing to the stability and persistence of the —ZrO— group in zirconium compounds. We shall assume that hydrolysis of the zirconium salt gives zirconyl hydroxide, ZrO(OH)₂. This compound is undoubtedly amphoteric. In solutions of *p*H = 0.10 very little hydrolysis can occur and the acidic ionization of this compound is certainly negligible. Hence conditions do not favor condensation and no gel forms. When, by addition of sodium carbonate or acetate or by removal by dialysis of the hydro-

(16) Gruner and Elbd, *Z. anorg. Chem.*, **208**, 317 (1932).

(17) Brintzinger and Brintzinger, *ibid.*, **196**, 44 (1931).

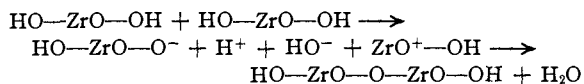
(18) Hurd, *Chem. Reviews*, **22**, 403 (1938).

(19) Owens and Morris, *J. Phys. Chem.*, **42**, 563 (1938).

chloric acid, produced in the hydrolysis of $ZrOCl_2$, the pH is increased, conditions more favorable to the condensation are present. A gel is therefore formed.

In comparing the formation of the hydrogels of zirconia and silica it should be noted that if both hydroxides are amphoteric, the silicon hydroxide is a stronger acid than base, while the reverse is true of the zirconium hydroxide. Thus silicic acid gels set easily at $pH = 0.1$ or lower,²⁰ while with the zirconia gel, setting does not occur at $pH = 0.1$, in fact not until the pH is more than 2.

Although others have suggested the mechanism of condensation to explain the formation of zirconia hydrogels, we wish to suggest here that the condensation of zirconyl hydroxide would give long chains with no cross linkages, such as are probably present in silicic acid gels. The zirconia hydrogels would thus be soft and weak, which fact is observed to be true. The process would be



The effect of stirring the mixtures of zirconium oxychloride and sodium carbonate is simply to dissolve the precipitate formed on mixing. This is a fine white precipitate and is probably present in colloidal-sized particles even after all visible particles have disappeared.

A rise of temperature, producing greater activity in the particles, causes more frequent collisions and causes more rapid setting. The energy of activation of the setting process was found to be from 21,000 to 29,000 calories. It is to be regretted that greater accuracy could not be attained, but it is plain to see that this value is considerably higher than the much more accurate value of 17,000 for silicic acid gels in the medium pH range or from 9000 to 11,000²⁰ in the extremely acid range.

The liquefaction, regelation and reliquefaction have been described. The process may apparently go on indefinitely through successive increase and decrease of the temperature. It is under careful study now in this Laboratory, but we can as yet offer no explanation. Other known

(20) Hurd and Barclay, *J. Phys. Chem.*, **44**, 847 (1940).

systems show this effect, such as nitrated cellulose in alcohol.²¹

The action of potassium chloride in decreasing time of set is apparently related to the Hofmeister series. Biltz⁶ found with his zirconia hydrosols that certain chlorides had more coagulating power than did potassium nitrate sodium nitrate or potassium iodide. Ruer²² found sodium chloride or potassium chloride caused coagulation of his zirconia hydrosols. Others⁸ have reported similarly. The chloride ion probably influences the degree of hydration of the zirconia, possibly through influence on the hydrol equilibrium.²³ Schalek and Szegvari²⁴ mention the effect of electrolytes on the formation of zirconia hydrogel.

Toward electrolytes the zirconia hydrosol resembles in behavior the hydrosol of ferric oxide²⁴ rather than that of silica.

Summary

Hydrogels of zirconia have been prepared by mixing solutions of sodium carbonate or sodium acetate and zirconium oxychloride. This raises the pH of the latter solution from 0.1, where it does not set, up to values from 2.0 to 5.0.

The time of set was found in terms of temperature, pH and concentration of added electrolyte. The energy of activation varied from 21,000 to 29,000.

The gels are softer than corresponding silicic acid gels, show some syneresis, but do not hold their form.

Gels which have formed at 25° in a few minutes were found to reliquefy at constant temperature in a few hours. Raising the temperature to 60° caused regelation and subsequent cooling caused reliquefaction. The process may be repeated.

The time of set is very much decreased by adding potassium chloride, in low concentrations, to the mixture.

A theory for the setting process, involving condensation of zirconyl hydroxide is suggested. The amphoteric nature of zirconyl hydroxide makes this possible.

SCHENECTADY, NEW YORK RECEIVED SEPTEMBER 25, 1941

(21) Hartman, "Colloid Chemistry," Houghton-Mifflin Company, Boston, Mass., 1939, p. 406.

(22) Ruer, *Z. anorg. Chem.*, **43**, 282 (1905).

(23) Bancroft and Gould, *J. Phys. Chem.*, **38**, 197 (1934).

(24) Schalek and Szegvari, *Koll. Z.*, **33**, 326 (1923).