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Title "Effect of pH on Viscosity of Gelatin Solutions
in Alcohol-Water Systems"

Abstract approved _____

Major Professor

Numerous investigations have been made on the stability of hydrophilic sols through viscosity determinations. The stability of hydrophilic sols when under the influence of alcohol has been measured; however, no mention has been made of the effect of pH on the above influence. This experiment was done in order to determine the effect of pH on the specific viscosity of gelatin solutions in alcohol-water systems.

Nondialyzed gelatin was weighed out in portions of 2.000 g. protein per 100 g. solvent whose viscosity had previously been determined at 40°C. The solvent consisted of alcohol and water, with the alcohol replacing the water in 5%-by-weight increments. The gelatin was allowed to swell overnight in 25 g. water. The following day the remainder of the solvent was added, and enough acid was included to attain the proper pH. The pH and the density of each solution was determined after it had been in a water bath for two hours at 40°C. After these determinations, the viscosity was measured at 40°C. with Ostwald type viscosimeters.

The results have been tabulated in Tables 1-10 inclusive and plotted in Figures I-VI inclusive. At pH 5.2, pH 6.3, and pH 7.2 the specific viscosity decreases steadily with increasing amounts of alcohol. At pH 5.2, however, the trend is not so pronounced. At pH 2.3, pH 3.5, pH 4.0, and pH 4.5 there is a maximum in each curve at increasing percentages of alcohol.

The results are explained by Smoluchowski's equation. Where the specific viscosity is a maximum, the combined effects of the zeta potential and dehydration by alcohol is a maximum. An increase in zeta potential increases the specific viscosity, while an increase in the dehydration by alcohol decreases the specific viscosity.

EFFECT OF pH
ON VISCOSITY OF GELATIN SOLUTIONS
IN ALCOHOL-WATER SYSTEMS

by

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EFFECT OF pH ON VISCOSITY OF GELATIN SOLUTIONS IN ALCOHOL-WATER SYSTEMS

INTRODUCTION

The stability of hydrophilic sols has been the subject of many investigations, a decrease in stability being manifested by a lowering in the viscosity of the sol. Since gelatin is easily made into a stable hydrophilic sol, it is considered a good material with which to study the stability factors, which are: (1) the electric charge on the particles and (2) the hydration shell.

Einstein has developed an equation for the viscosity of a suspension of rigid spheres in a liquid (15, p.207), which is

$$\frac{\eta_s}{\eta_m} = k\phi + 1$$

where η_s is the viscosity of the suspension,

η_m is the viscosity of the medium,

k is a constant which Einstein gave the value of 2.5,

ϕ is the volume of the dispersed phase.

This equation has been proved valid for hydrophobic sols, but deviations were found in the case of hydrophilic sols. The equation does not account for the effect of charge and solvation on the particles.

Smoluchowski modified Einstein's equation (15, p.208) to give

$$\eta_{sp} = 2.5\phi \left[1 + \frac{1}{\lambda \eta_m r^2} \left(\frac{D^2}{2\gamma} \right)^2 \right]$$

where λ is the specific conductivity of the medium,

D is the dielectric constant of the medium,

ζ is the electrokinetic potential,

r is the radius of the particles of sol.

Smoluchowski's equation has been found valid for hydrophilic as well as hydrophobic sols.

When a determination of viscosity of gelatin is made, it must be remembered that the viscosity is affected by several things, the previous mechanical and thermal treatment of the gelatin, the temperature of solution, the age of the solution, the purity of the original gelatin, and the presence of added electrolytes (15, p.208). Gelatin shows the property of plastic flow at high concentration and at a temperature less than 35°C. (3, p.1313).

Gelatin flakes, when allowed to stand in water for several hours, swell to several times their original size. After the gelatin has swelled, it may be made into a stable hydrophilic sol by warming to 40°C. and shaking. If enough alcohol is added to the gelatin sol, the gelatin is precipitated. In examining the stability of hydrophilic sols, at least one investigator has shown the decrease of specific viscosity of a sol of low concentration to be continuous with the addition of alcohol (15, p.301), (5, p.143). However, no mention was made of the role that pH might play on specific viscosity and stability of a

hydrophilic sol in an alcohol-water medium. Therefore, determinations of specific viscosity have been made at various pH values in order to determine the effect of pH on the specific viscosity of gelatin solutions in alcohol-water media.

EXPERIMENTAL PROCEDURE

Materials and apparatus. Gelatin was obtained in nondialyzed flake form from the United States Gelatine Company, Milwaukee, Wisconsin. The gelatin contained 12.99% moisture, on a wet basis, as determined by drying in an oven at 100-105°C. for 72 hours. It contained 1.75% ash, on a wet basis, as determined by ignition to constant weight over a Meker burner.

Other materials used were boiled distilled water, ethyl alcohol (93% by weight), 1N HCl, 6N HCl, 0.02N NaOH, and toluene.

The liquids were added from burettes, the densities of the liquids being used to determine the volumes to be added. The densities of the solutions were found by means of a Westphal balance.

The pH of each solution was determined with a Beckman pH meter.

Ostwald type viscosimeters were used to determine the viscosities. The equation $\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$ (9, p.104) was made the basis for all calculations of viscosity, the viscosity of water at 40°C., 6.536 millipoises, being taken as the standard (14, p.10).

Determination of viscosity of alcohol-water solvent.
Enough alcohol was run from a burette into a flask to

give a certain weight of alcohol. Then water was added from a burette until the alcohol was a given percent by weight of the solution. In all cases the water (7% by weight) in the original alcohol solution was accounted for in the calculations of volumes to be added. The density of the solution was determined at 40°C., a portion added to the viscosimeter, and the viscosity determined at 40°C.

Determination of viscosity of gelatin solutions.

Sufficient gelatin was weighed into a flask to give $2.000 \pm .002$ g. of protein. 25 ml. of water and 1-2 drops of toluene were added to the flask and the stoppered material allowed to stand overnight at room temperature. The following day enough water plus acid (or base), or water plus alcohol plus acid (or base), was added to give approximately 99 g. of solvent. The stoppered flask was placed in a constant temperature bath maintained at $40 \pm 0.1^\circ\text{C}$. After a period of 30-45 minutes, the material was shaken to give a uniform sol. Two hours after being placed in the bath, the flask was removed and the pH of the contents determined. Sufficient additional acid or base was added to arrive in the desired pH range, and then water was added to give 100 g. of solvent. The pH was again taken, after which the density of the sol was measured. 1N HCl was used to

adjust the pH in all but three cases. At pH 6.3 no acid or base was added; at pH 7.2, 0.02N NaOH was used; and at pH 1.3, 6N HCl was necessary. After the density measurements, a portion of the sol was placed in the viscosimeter and the viscosity determined when the sol reached the bath temperature.

EXPERIMENTAL RESULTS

The densities of the alcohol-water solvent were measured at 40°C. and agreed with International Critical Table values within the range of experimental error. International Critical Table values, shown in Table 1, were therefore used to calculate the viscosities of the solvent (13, pp.116-117). These viscosities were then plotted on a large sheet of graph paper, as shown by Figure I, and values taken from the curve, given in Table 1, were used in the calculation of the specific viscosity of the gelatin solutions.

The densities of the gelatin solutions were measured at four different pH values, and the average values, shown in Table 2, were made the basis for calculating the viscosities of the gelatin solutions. The densities at all pH values agreed within experimental error when checks were made.

The viscosities of the gelatin solutions in water were determined at eight different pH values covering the range pH 1.3 to pH 7.2. The viscosities were then re-determined at each pH as the solvent water was replaced by alcohol in 5%-by-weight increments until the addition of sufficient alcohol caused the precipitation of gelatin. The results are given in Tables 3-10 inclusive and are shown graphically in Figures II and III.

The individual pH values shown in Tables 3-10 were determined with an accuracy of ± 0.03 pH unit; however, since it would have been an extremely tedious task to bring each of the solutions to exactly the same pH, it was decided that the pH should be adjusted to within ± 0.1 of a pH unit of the desired value.

The minimum and maximum amounts of acid or base needed to attain each pH are shown in Table 11.

In Figures IV and V, specific viscosity values of the gelatin solutions at constant alcohol percentages have been plotted against pH.

The percentage alcohol points at which the maximum specific viscosity has been found are plotted against pH in Figure VI.

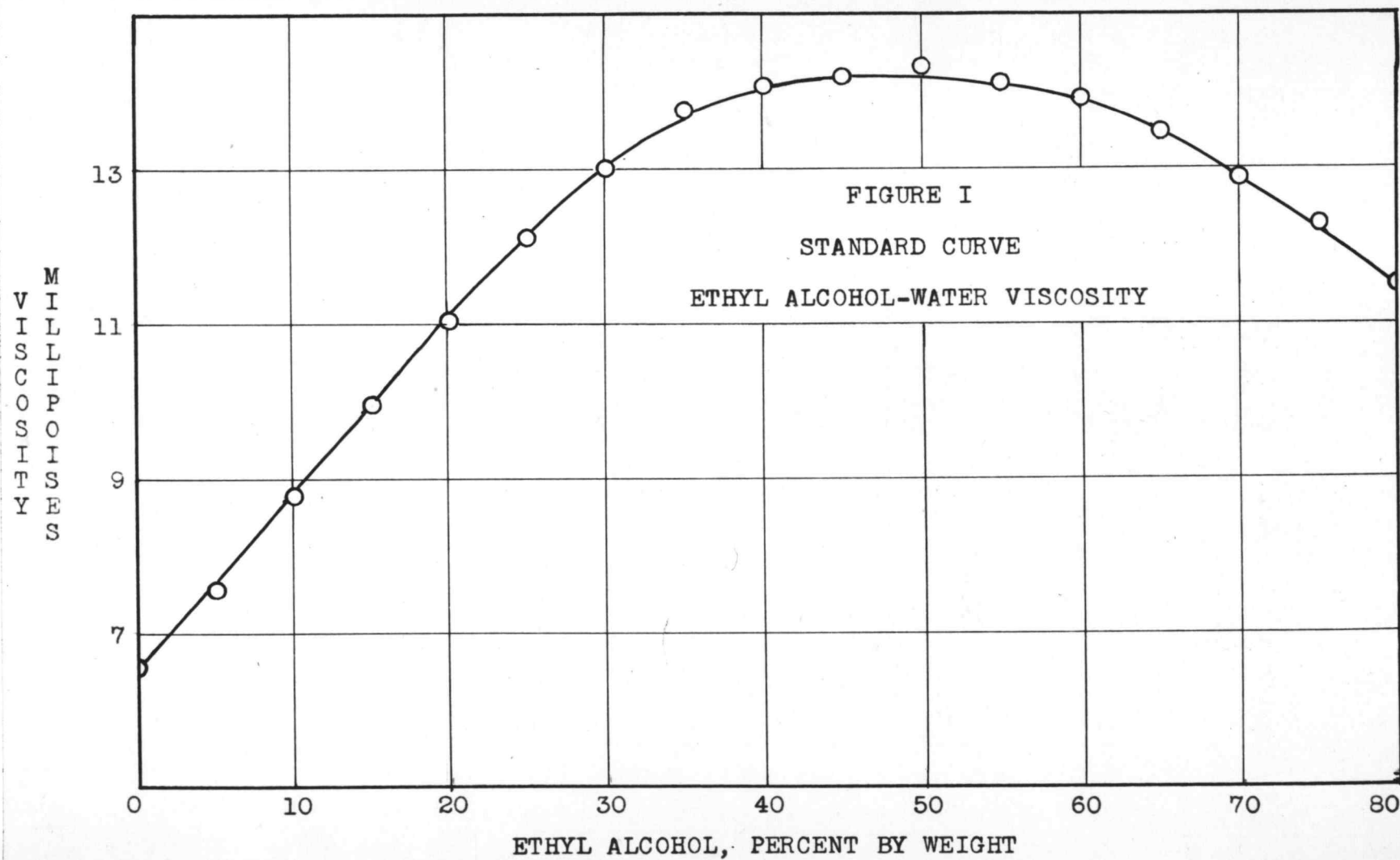


TABLE 1
DENSITIES AND VISCOSITIES OF SOLVENT

Alcohol % by wt. -----	Density grams/ ml. -----	Viscosity millipoises -----
0	0.9922	6.54
5	0.9831	7.67
10	0.9748	8.80
15	0.9667	9.94
20	0.9586	11.04
25	0.9499	12.10
30	0.9406	13.04
35	0.9305	13.67
40	0.9199	14.04
45	0.9088	14.18
50	0.8975	14.17
55	0.8859	14.10
60	0.8742	13.87
65	0.8623	13.47
70	0.8503	12.86
75	0.8381	12.18
80	0.8258	11.50

TABLE 2
DENSITIES OF GELATIN SOLUTIONS

Alcohol % by wt. -----	Density g./ml. -----
0	0.9990
5	0.9900
10	0.9814
15	0.9742
20	0.9662
25	0.9575
30	0.9479
35	0.9386
40	0.9275
45	0.9174
50	0.9063
55	0.8943
60	0.8835
65	0.8711
70	0.8589
75	0.8466
80	0.8335

TABLE 3

VISCOSITIES OF GELATIN SOLUTIONS AT pH 1.3

Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
-----	-----	-----	-----
0	1.28	22.67	2.46
5	1.34	26.82	2.50
10	1.37	30.74	2.50
15	1.35	33.60	2.38
20	1.30	34.35	2.11
25	1.10	36.39	2.08
30	1.20	38.94	1.99
35	1.27	40.82	1.98
40	1.10	37.16	1.65
45	1.18	35.60	1.51
50	1.35	34.87	1.46
55	1.30	32.28	1.29
60	1.37	28.54	1.06
65	1.20	21.46	0.59
70	1.38	19.22	0.46

TABLE 4

VISCOSITY OF GELATIN SOLUTIONS AT pH 2.3

Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
-----	-----	-----	-----
0	2.30	32.54	3.98
5	2.29	38.82	4.06
10	2.36	45.22	4.14
15	2.31	50.39	4.07
20	2.32	56.68	4.14
25	2.30	61.21	4.06
30	2.38	63.84	3.90
35	2.33	65.37	3.78
40	2.36	65.11	3.64
45	2.39	62.48	3.41
50	2.36	60.11	3.24
55	2.35	52.58	2.73
60	2.31	43.41	2.13
65	2.35	37.02	1.75
70	2.36	30.93	1.35
75	2.34	25.32	1.08
80	2.36	18.93	0.65

TABLE 5

VISCOSITY OF GELATIN SOLUTIONS AT pH 3.5

Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
-----	-----	-----	-----
0	3.54	28.54	3.37
5	3.48	35.71	3.66
10	3.53	40.37	3.59
15	3.50	46.55	3.68
20	3.50	51.41	3.66
25	3.48	58.96	3.87
30	3.52	61.80	3.74
35	3.35	65.03	3.76
40	3.48	65.68	3.68
45	3.50	64.22	3.53
50	3.55	60.11	3.24
55	3.46	57.39	3.07
60	3.50	55.49	3.00
65	3.35	49.80	2.69
70	3.55	42.56	2.24

TABLE 6
 VISCOSITY OF GELATIN SOLUTIONS AT pH 4.0

Alcohol % by wt. -----	pH -----	Viscosity mpoises -----	Specific Viscosity -----
0	4.00	23.54	2.60
5	4.03	26.50	2.46
10	4.00	32.04	2.64
15	4.01	37.89	2.81
20	4.00	43.64	2.96
25	4.00	49.17	3.06
30	4.02	50.47	2.87
35	4.03	54.06	2.95
40	4.04	55.41	2.95
45	4.02	55.35	2.92
50	4.02	52.44	2.70
55	4.05	49.06	2.48
60	4.06	46.35	2.34

TABLE 7
 VISCOSITY OF GELATIN SOLUTIONS AT pH 4.5

Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
-----	-----	-----	-----
0	4.46	19.12	1.93
5	4.49	23.01	2.00
10	4.47	26.55	2.02
15	4.47	31.32	2.15
20	4.42	35.70	2.21
25	4.50	38.50	2.18
30	4.52	41.69	2.20
35	4.49	44.32	2.24
40	4.50	48.64	2.46
45	4.52	47.71	2.36
50	4.45	45.28	2.20
55	4.56	43.51	2.09

TABLE 8
 VISCOSITY OF GELATIN SOLUTIONS AT pH 5.2

Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
0	5.10	17.08	1.61
5	5.12	20.04	1.61
10	5.14	22.32	1.54
15	5.14	24.54	1.47
20	5.22	27.38	1.48
25	5.20	29.41	1.43
30	5.20	31.86	1.44
35	5.20	33.17	1.43
40	5.25	32.36	1.30
45	5.27	31.45	1.22
50	5.25	29.97	1.11
55	5.26	29.64	1.10

TABLE 9
VISCOSITY OF GELATIN SOLUTIONS AT pH 6.3

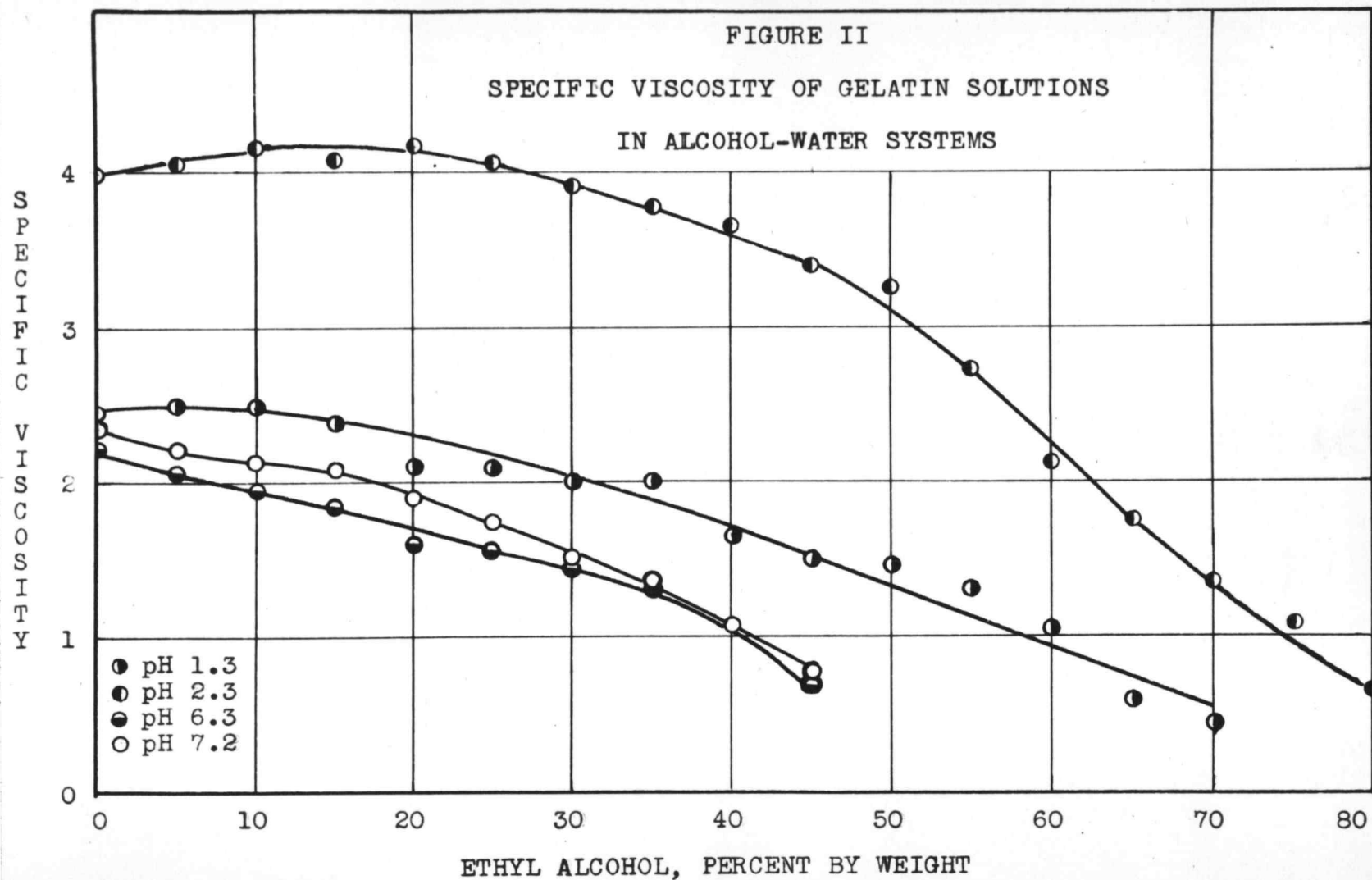
Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
0	6.20	20.99	2.21
5	6.20	23.38	2.05
10	6.23	25.85	1.94
15	6.24	28.14	1.83
20	6.33	28.71	1.60
25	6.40	30.87	1.55
30	6.40	31.61	1.42
35	6.40	31.39	1.30
40	6.40	38.85	1.06
45	6.40	23.99	0.69

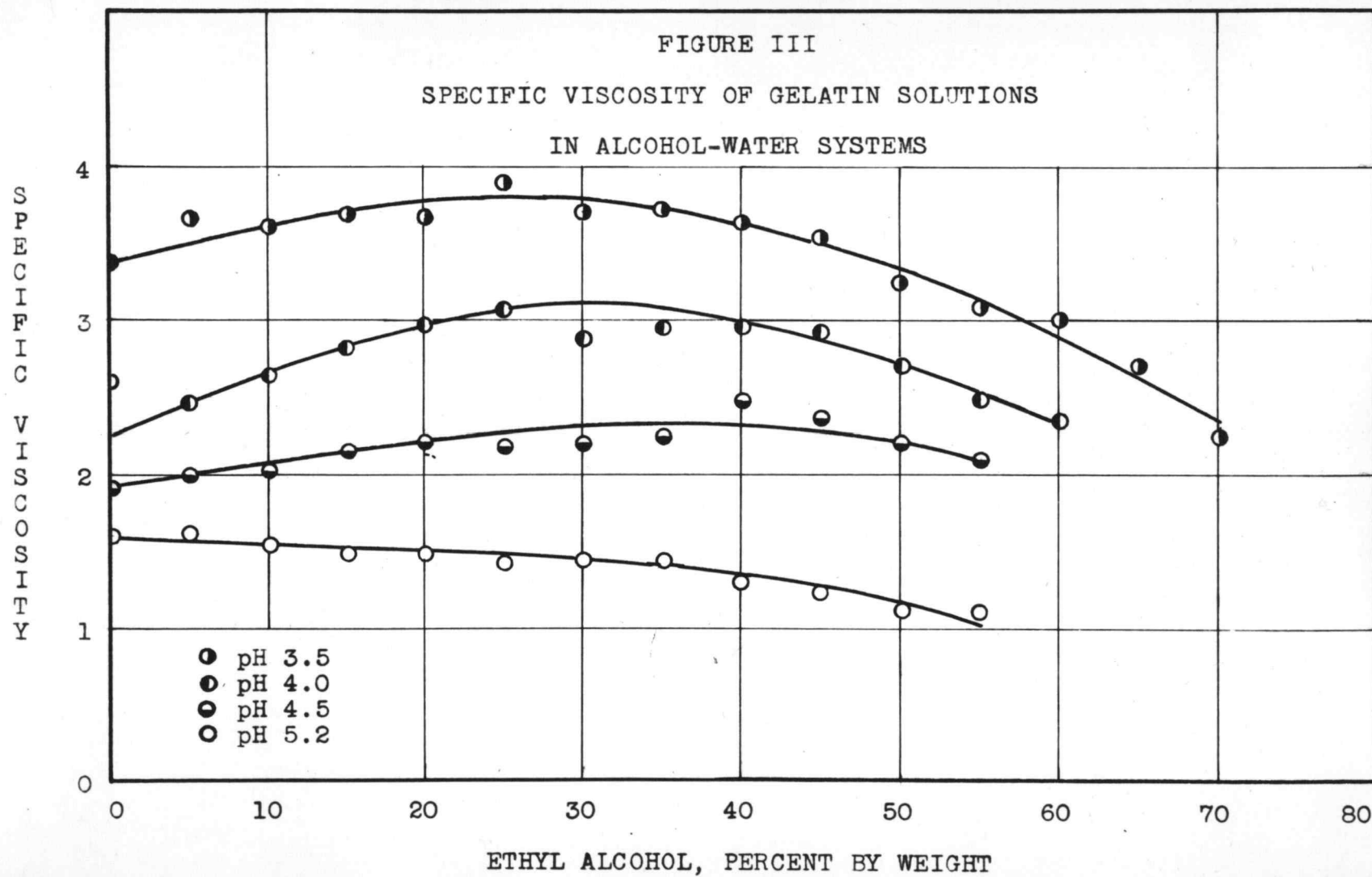
TABLE 10
 VISCOSITY OF GELATIN SOLUTIONS AT pH 7.2

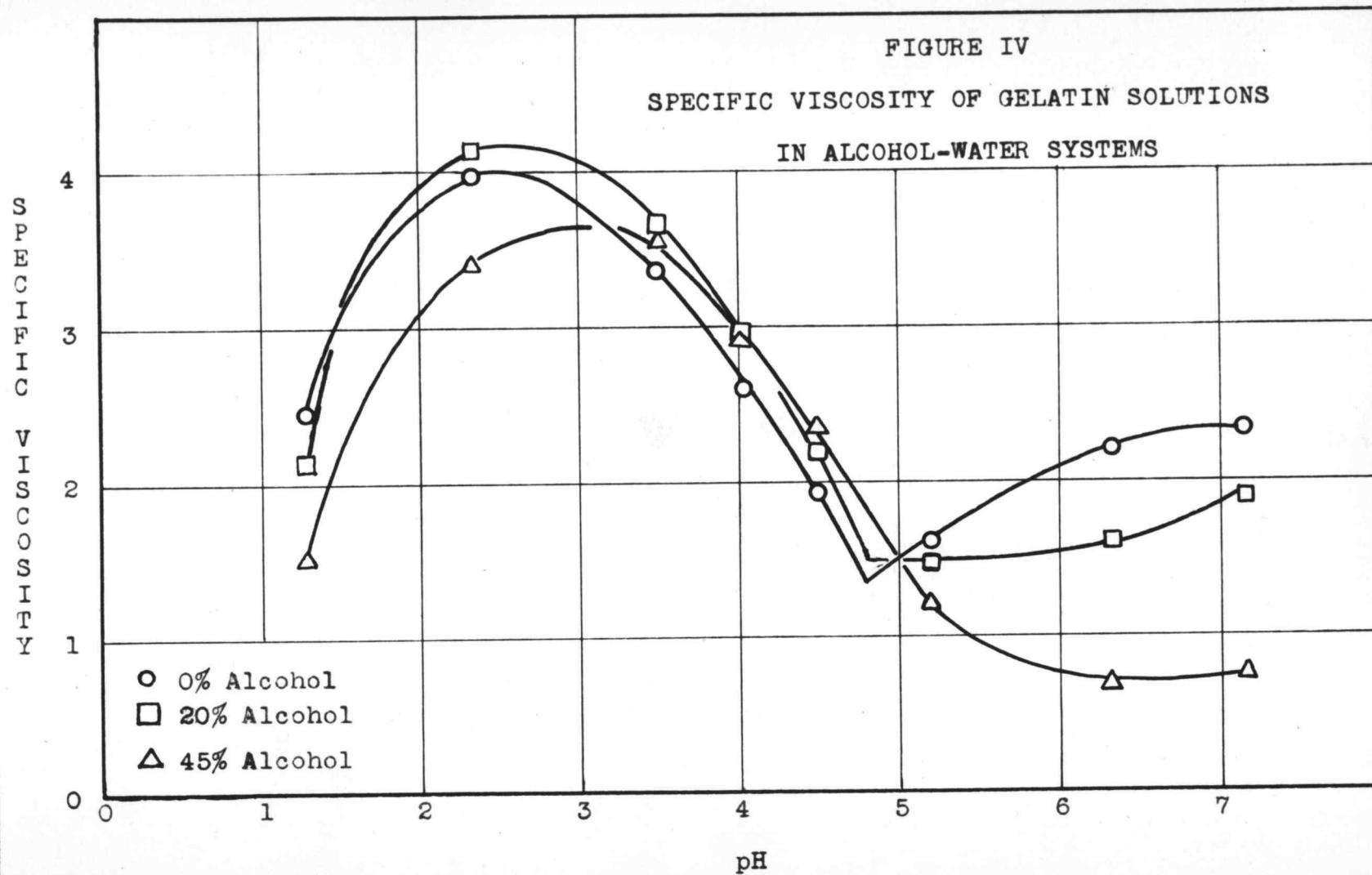
Alcohol % by wt.	pH	Viscosity mpoises	Specific Viscosity
-----	-----	-----	-----
0	7.20	21.85	2.34
5	7.10	24.55	2.20
10	7.08	27.63	2.13
15	7.10	30.58	2.08
20	7.22	31.90	1.89
25	7.09	33.00	1.73
30	7.11	32.72	1.51
35	7.18	31.99	1.34
40	7.17	29.04	1.07
45	7.24	25.00	0.76

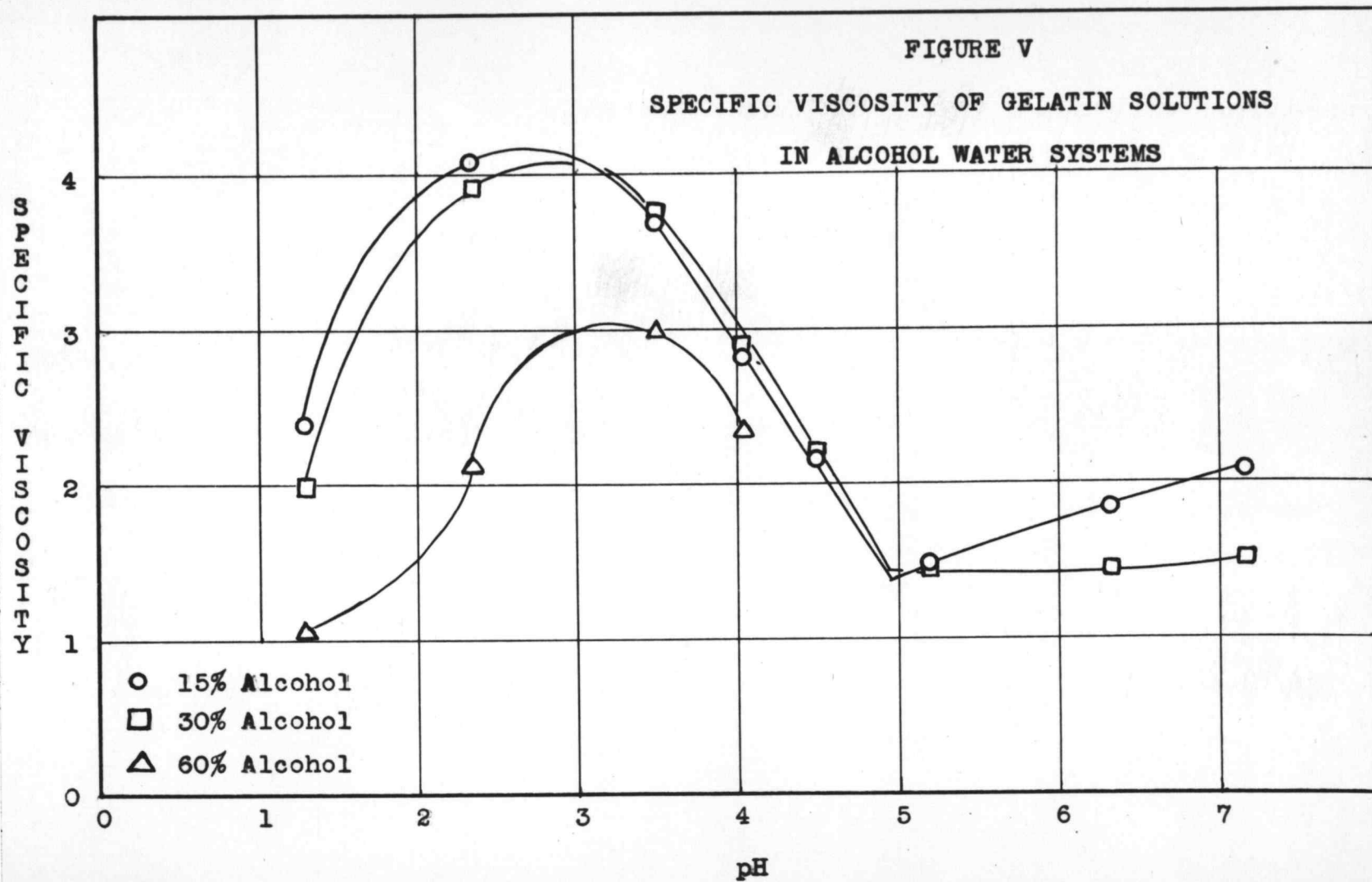
TABLE 11
ACID OR BASE VERSUS pH

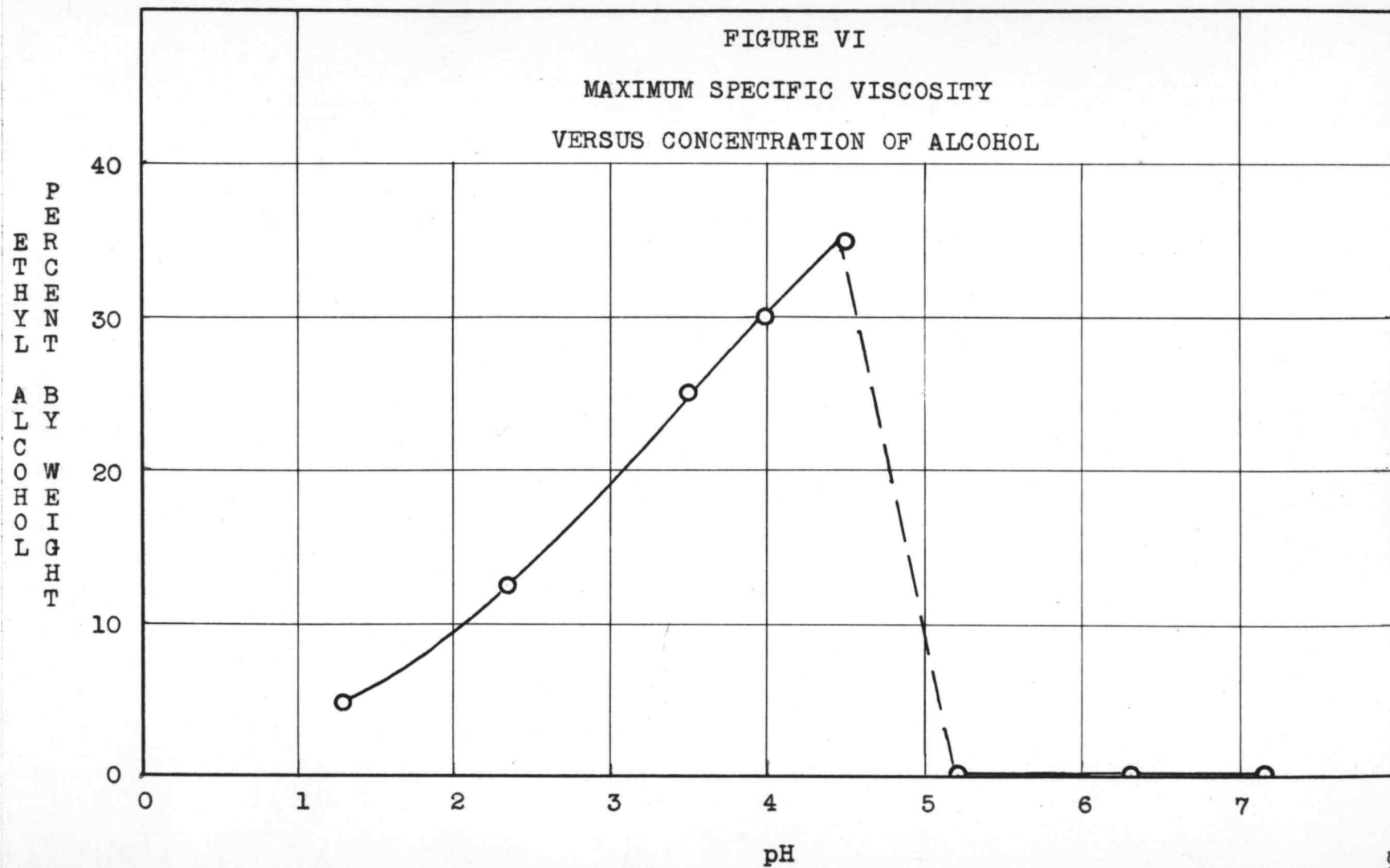
pH	Alcohol %	Acid or Base ml.
1.3	0-70	1.5-2.2 6N HCl
2.3	0-80	3.0-4.5 1N HCl
3.5	0-70	1.8-2.6 1N HCl
4.0	0-60	1.3-1.9 1N HCl
4.5	0-55	0.8-1.4 1N HCl
5.2	0-55	0.4-0.9 1N HCl
6.3	0-45	None
7.2	0-45	1.1-1.3 .02N NaOH











DISCUSSION OF RESULTS

The curve at pH 6.3 in Figure II shows the effect of adding alcohol to a gelatin solution containing no stabilizing electrolyte (aside from ash impurity in the gelatin). Pure gelatin would be slightly negative in charge and would have a pH a little above that of the isoelectric point but below pH 7. The pH of the solutions used for this experiment was a little higher than would be expected for pure gelatin due to the small amount of ash present. It is to be noted that the specific viscosity of the gelatin solutions decreases continuously with the increase in concentration of alcohol at pH 6.3, presumably the result of reduction in size of the gelatin particles caused by dehydration by the alcohol.

At a pH of 5.2 the aqueous solution has been brought closer to the isoelectric point but is still on the alkaline side. In the aqueous solution the gelatin particles should therefore have a smaller charge and smaller hydration than at pH 6.3. As is to be expected, the specific viscosity in water was lower at pH 5.2 than at pH 6.3. The outstanding differences at these two pH's is that at pH 5.2 an increase in the concentration of alcohol decreases the specific viscosity to a much lesser degree than at pH 6.3, and at pH 5.2 the

precipitation of the gelatin does not occur until the alcohol concentration reaches 60%, against precipitation at 50% alcohol at pH 6.3. From the amounts of acid or base added to achieve a given pH (see Table 11) we see that at pH 5.2 and 55% alcohol enough acid has been added to give the particles of gelatin a charge greater than was imparted to the particles at pH 4.5 and 0% alcohol. Also, the particles are now negatively charged and in a region of higher zeta potential. This charge will be enhanced by the fact that at 55% alcohol and pH 5.2 the particles are more hydrophobic and the charge density greater. On the other hand, the dehydrating action of the alcohol on the particles is enough to keep the viscosity from rising at this zeta potential. The specific viscosities of the solutions at pH 5.2 and pH 6.3 are approximately equal at 30-35% alcohol; therefore, at this concentration of alcohol the zeta potentials must be approximately equal.

At pH 4.5, Figure III, the specific viscosity in aqueous solution is greater than in aqueous solution at pH 5.2, as is expected from the increase in zeta potential. As alcohol is added at pH 4.5, more acid must be added to reach this pH. A point is attained where the electrokinetic potential is greater than at pH 4.0 in aqueous solution. At pH 4.5 the combined effect of

increased zeta potential and the dehydrating nature of the alcohol reaches a maximum at 35% alcohol, as is shown by the specific viscosity at this point.

At pH 4.0, Figure III, the specific viscosity in aqueous solution is greater than at pH 4.5, and at pH 4.0 the specific viscosity increases more rapidly than at pH 4.5 with the addition of alcohol. This is due to the fact that a greater amount of acid must be added in the presence of alcohol at pH 4.0 than at pH 4.5. At pH 4.0 the maximum combined effect of electrokinetic potential and dehydration by alcohol occurs at 30% alcohol.

At pH 3.5 the specific viscosity is greater in aqueous solution than at pH 4.0 because of the increase in electrokinetic potential. As alcohol is added, more acid must be added to reach this pH, and once again the addition causes an increase in electrokinetic potential great enough to counterbalance the effect of the dehydration by alcohol until the alcohol concentration has become 30% by weight.

At pH 2.3 the specific viscosity in aqueous solution is higher than at any other point in this experiment. The addition of alcohol and consequent increase in amount of acid necessary to reach this pH causes an increase in the specific viscosity, for the zeta

potential has been increased. Between 10% and 15% alcohol the specific viscosity levels off and starts downward. The dehydration by alcohol at higher percentages is greater than the effect of the zeta potential.

At pH 1.3 the specific viscosity has decreased, due to a decrease in the zeta potential. In this region the zeta potential decreases with increasing concentration of acid (6, p.122). The increase in specific viscosity at 5% and 10% alcohol is due either to experimental error or to a decrease in the hydrolysis of the gelatin by the acid when alcohol is present.

At pH 7.2 the specific viscosity in aqueous solution is slightly higher than at pH 6.3, as is to be expected from the increase in electrokinetic potential. The gelatin is negatively charged, with no change in the sign of the charge resulting from the addition of base. With addition of alcohol the amount of base necessary to achieve a pH of 7.2 is not significantly different from that necessary in aqueous solution, and hence the zeta potential will not be significantly different. The dehydrating effect of the alcohol is the most predominant effect, just as at pH 6.3.

The curve of 0% alcohol on Figure IV may be taken to represent the zeta potential to the second power.

No alcohol is present to dehydrate the particles. The only factor affecting the specific viscosity is the charge on the particles, if the hydrolysis of the gelatin is disregarded (8, p.742). The other curves on Figures IV and V, however, do not represent zeta potential alone. Alcohol is present, and hence the curves represent the combined effect of zeta potential and the dehydrating effect of the alcohol.

The points on Figure VI show at what percent alcohol the maximum specific viscosity is found at each pH. The maximum at each pH is due to a maximum in the combined effect of electrokinetic potential plus dehydration by alcohol. In Smoluchowski's equation

$$2.5\phi \left[1 + \frac{1}{\lambda \eta_m r^2} \left(\frac{D\zeta}{2\pi} \right)^2 \right] \quad \text{is a maximum.}$$

CONCLUSIONS

As is to be expected, the specific viscosity varies with the pH and with the concentration of alcohol.

The specific viscosity at a given pH is a maximum at a point determined by the electrokinetic potential and dehydration by the alcohol, following Smoluchowski's equation.

The electrokinetic potential is determined primarily by the acid or base which is added.

In aqueous solution the zeta potential is a maximum at approximately pH 2.5.

The isoelectric point of the gelatin used in this experiment is in the range pH 4.8-5.0.

SUMMARY

Nondialyzed gelatin was weighed out in portions of 2.000 g. protein per 100.0 g. solvent whose viscosity had previously been determined at 40°C. The solvent consisted of alcohol and water, with the alcohol replacing the water in 5%-by-weight increments. The gelatin was allowed to swell overnight in 25 ml. water. The following day the remainder of the solvent was added, and enough acid was included to attain the proper pH. The pH and the density of each solution was determined after it had been in a water bath for two hours at 40°C. After these determinations, the viscosity was measured at 40°C. with Ostwald type viscosimeters.

The results have been tabulated in Tables 1-10 inclusive and plotted in Figures I-VI inclusive. At pH 5.2, pH 6.3, and pH 7.2 the specific viscosity decreases steadily with increasing amounts of alcohol. At pH 5.2, however, the trend is not so pronounced. At pH 2.3, pH 3.5, pH 4.0, and pH 4.5 there is a maximum in each curve at increasing percentages of alcohol.

The results are explained by Smoluchowski's equation. Where the specific viscosity is a maximum, the combined effects of the zeta potential and the

dehydration by alcohol give a maximum. An increase in electrokinetic potential increases the specific viscosity.

BIBLIOGRAPHY

1. Beckman, A. O. The development of pH instrumentation. Bulletin, reprint no. R-36. South Pasadena, Beckman Instruments, Inc., 1950. 17p.
2. Bogue, Robert Herman. The viscosity of gelatin sols. Journal of the American chemical society 43:1764-1773. 1921.
3. Bogue, Robert Herman. The sol-gel equilibrium in protein systems. Journal of the American chemical society 44:1313-1322. 1922.
4. Davis, Clarke E., Earle T. Oakes, and Harry H. Browne. Viscosity of gelatin solutions. Journal of the American chemical society 43:1526-1538. 1921.
5. Gemant, Andrew. Frictional phenomena. Brooklyn, Chemical, 1950. 497p.
6. Loeb, Jacques. Proteins and the theory of colloidal behavior. New York, McGraw-Hill, 1922. 292p.
7. Mahin, Edward G. Quantitative Analysis. Fourth Edition. New York, McGraw-Hill, 1932. 623p.
8. Northrop, John H. The role of the activity coefficient of the hydrogen ion in the hydrolysis of gelatin. Journal of general physiology 3:715-742. 1921.
9. Prutton, Carl F. and Samuel H. Maron. Fundamentals of physical chemistry. New York, Macmillan, 1944. 780p.
10. Ruyssen, R. G. Electrokinetic potentials of barium sulfate in solutions of electrolytes and in 50% ethanol. Journal of physical chemistry 44:265-274. 1940.
11. Shchelkanovtseva, A. Ya. The change in zeta potential of some colloids in mixtures of water-alcohol-ether. Chemical abstracts 37:4951. 1943.

12. Taylor, Hugh S. (ed.). A treatise on physical chemistry. New York, D. Van Nostrand, 1924. Two volumes, 1359p.
13. Washburn, Edward W. (ed.). International critical tables of numerical data. New York, McGraw-Hill, 1928. Volume 3, 444p.
14. Washburn, Edward W. (ed.). International critical tables of numerical data. New York, McGraw-Hill, 1929. Volume 5, 470p.
15. Weiser, Harry Boyer, A textbook of colloid chemistry. Second edition. New York, Wiley, 1949. 444p.