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The viscosity and surface tension of the principal proteins in ice cream

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The Viscosity and Surface Tension of the
Principal Proteins in Ice Cream

Gordon Pittinger Percival

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THE VISCOSITY AND SURFACE TENSION
OF THE
PRINCIPAL PROTEINS IN ICE CREAM

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Gordon Pittinger Percival

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INTRODUCTION

Ice cream has been defined as a frozen dairy-product, with or without natural flavoring, containing sugar, and a specified amount of butterfat as required by the laws or regulations of the various states and the Federal government. Ordinarily ice cream consists of cream, sugar, flavoring, and some stabilizer which is usually gelatin. These are the principal ingredients, but rich cream may be thinned by the addition of skim milk, or skim-milk powder may be added, to build up the solids-not-fat and thus improve the body. Ice cream is truly a frozen dairy-product, although other products than cream may enter into its makeup. The different ingredients that enter into an ice cream mix exist in different grades, concentrations and forms. It is desirable, therefore, in order to obtain constructive data, to follow a logical approach which would be to study first, simple isolated portions of the system - that is, the different types of dispersed phases in the dispersion medium taken singly - and then the effects of the combinations of such systems, gradually increasing the complexity.

Also, ice cream manufacturers age their mix twenty-four hours before freezing, to improve the body of the ice cream and to increase the viscosity of the mix, a process which is generally thought to make it whip more easily.

The following research had as its object the study of

the viscosity and surface tension of water dispersions of the principal proteins present in ice cream mixes: namely, gelatin, casein, and albumin, in order that their relative values may ultimately be incorporated with data obtained from the finished product.

REVIEW OF LITERATURE.

The ice cream industry has been developed so recently that its research history is very brief and practical in nature. Early discoveries of this industry were kept secret, and scientific workers in educational institutions and private corporations, who published their findings, began their research work after the rudimentary methods of making ice cream were fairly well established.

There has been very little experimental work on the isolated proteins of milk, and as both milk and cream contain the proteins that are used in the mix, it becomes necessary to include any work done pertaining to milk and cream.

Soxhlet (48), in 1876, was one of the first to conduct investigations on the viscosity of milk, and he found that viscosity varied with changes in temperature.

The results of Babcock's (3) experiments in 1886 showed that the albuminoids of milk have a much greater influence upon the viscosity than any other constituent, and usually more than all the other solids combined. There was a slight variation with different milk which he believed to be due to the amount of albumin present or to the difference in the solubility of the casein.

Woll (52), working upon the effect of heating on viscosity,

found that heating milk to its pasteurization temperature decreased its viscosity, while higher temperatures increased viscosity. This he believed to be due to the unstable character of the proteins or to the mineral constituents. Later, Steiner (49) and Taylor (50) confirmed his results, but Jensen (24) took the opposite side and stated that the viscosity of milk or cream was not increased by heating it above the pasteurizing temperature.

Babcock and Russell (4) (5) stated that the consistency of milk and cream is due to the material which is dissolved and that which is suspended. In milk, the casein was of major importance in affecting viscosity, but in cream, fat assumed the important role.

Kobler (28) made an extensive study of the factors affecting the viscosity of milk. He found that the viscosity of milk varied with individual cows and was affected materially by the food given to the cow, pregnancy, period of lactation, and general health. Reduction in the fat or protein content of the milk reduced viscosity, and storage at a cold temperature increased it.

Oertel (39) showed experimentally that the casein and albumin content of milk affected its viscosity, but the variations in amounts of these did not influence the viscosity as noticeably as did fat. This investigation further demonstrated that the

degree of viscosity of milk is correlated very nearly with its dry matter content; but that viscosity is not a reliable index to the composition of milk, since the addition or subtraction of various components or variation in the size of the fat globules may result in the same viscosity.

Evenson and Ferris (20), in 1923, showed that there was an increase in viscosity of milk held at 30°C for over one hour. At 10°C the difference in time of flow of milk held at the different temperatures was 13.1 seconds, while at 35°C it was only 2.5 seconds. The rise of temperature markedly decreased the viscosity and likewise the difference in viscosity of the two samples held at different temperatures. They stated that "this change in the viscosity of milk held at different temperatures cannot be attributed to the effect on the fat alone since skim-milk also exhibits this phenomenon."

Dahlberg and Hening (16) working with an improved MacMichael viscosimeter in a cold room at 3° - 4°C found that, milk fat in increased percentage always increased the viscosity of milk or cream, but that its effect was most marked when the cream contained 20% - 35% fat and was aged but not pasteurized. Aging greatly increased the viscosity of rich cream but also has some effect on skim-milk.

Pasteurization slightly reduced the viscosity of fresh milk but greatly reduced the viscosity of fresh 30% - 35% cream.

In order to determine the influence of variations in percentage of milk-solids-not-fat upon viscosity, three lots of 35% cream were standardized from 40% cream. One lot was standardized with skim-milk and was normal cream. The solids-not-fat were decreased in one lot by standardizing 264 grams of 40% cream with 36 grams of water. The solids-not-fat were increased in another lot by standardizing 264 grams of 40% cream with 36 grams condensed skim-milk. The results showed that there was no marked change because of the variation made in the percentage of milk solids-not-fat.

According to Davis, Oakes and Browne (17) the viscosity of gelatin depends upon the following factors: (1) Method of effecting solution, (2) Aging of solution, (3) Concentration of hydrogen ion, (4) Concentration of gelatin. They used 4 Ostwald viscosimeters of water constants 73.8, 75.0, 78.4, and 75.8 seconds, respectively, and their results checked with a maximum error of ±0.5%. Specific gravity determinations were made by means of a pycnometer. The viscosity coefficient was calculated by the formula

$$n(\text{gelatin}) = n(\text{water}) \frac{(\text{Sec. gel. sol.}) (\text{Sp. gr. gel. sol.})}{(\text{Sec. water}) (\text{Sp. gr. water})}$$

n for water being taken as .008937 absolute units or 0.8937 centipoises

as given by Bingham (11). Though the density of 1% gelatin solution at 25°C was taken as 1.0000, actual variations were encountered from 1.0008 to .99988.

Gelatin solutions increase in viscosity with age at different rates depending upon the concentration of gelatin, hydrogen-ion concentration, and kind of gelatin. For any given gelatin dispersion the maximum viscosity is attained after aging 24 hours, although some high-grade gelatins may continue to show a slight increase after aging a longer period. A decrease in viscosity after the maximum is reached indicates bacterial decomposition.

The low-grade gelatins show a fairly rapid decrease in viscosity especially where the pH value of the solution is between 5 and 8. The increase in viscosity with age varies directly with the hydroxyl-ion concentration until a maximum is reached at $\text{pH} \approx 8.5$. At greater hydroxyl-ion concentration the increase diminishes rapidly and actually becomes a minus quantity at a pH value somewhat greater than 9. For low concentration of fairly acid solutions, the viscosity is approximately a linear function of the concentration. On the alkaline side of the isoelectric point (pH 4.7) the viscosity increases so rapidly with increasing concentration that it does not even approximate a linear function of the concentration.

Maximum viscosity was found by Davis, Oakes and Browne (17) at pH 3 - 3.5 when the viscosity is taken at an age of dispersion of 85 minutes and 25°C in a 0.50% and 0.25% solution. On the acid side the curves were essentially the same as described by Loeb (31). On the alkaline side the type of curve is quite different, since Loeb records a maximum at pH 11, approximately. Since two different methods of procedure were used in effecting solution, undoubtedly a difference in the age of the dispersion would result in the difference in the type of curve.

Manhart (34) studied the effect of gelatin on the viscosity of the ice cream mix. He made three mixes (each 0.6% gelatin by weight) using three grades of gelatin, poor, good and very good. The poor quality gelatin increased the viscosity of the mix 144.9% over that of the control, the viscosity of which was 1.67 compared with that of water at 15°C, while the good quality gelatin produced an increase of 552.6%, and the very good grade produced an increase of 834.1%. The pH of each gelatin was not given but since the pH values of the various mixes were the same the hydrogen-ion concentration was not the important factor in these viscosity values. His results show the relative values of different grades of gelatin and the importance of stating the quality of the gelatin used.

Davis and Oakes (18) in a later paper changed the method

of estimating the age of gelatin dispersions as follows. Since it is only when gelatin dispersions reach a temperature below the transition point that the viscosity begins to increase with age, they reheated the solution to 50°C after filtering and then immediately placed it in the thermostat at the desired temperature, and stirred vigorously until the temperature of the thermostat was reached. The age was then reckoned from the moment the dispersion registered 38.03°C. This change aids in securing exact checks by different workers.

Loeb (32) found that powdered gelatin in suspension resulted in a higher viscosity than did the same amount of dissolved gelatin, other conditions being the same in both cases.

Chick and Martin (14) working with casein dispersions found that the viscosity of sodium caseinogenate solutions increased rapidly with increasing concentrations, and for a given concentration with decreasing temperature. Both of these phenomena, they explain as being due to increased hydration of the colloidal particles under the changing conditions.

Zoller (54) while studying the effect of pH on the viscosity of casein found that the viscosity curves of Hammarsten and Dairy Division casein dissolved in NaOH showed a maximum viscosity in the region of pH 9. The slope of the curve is very

precipitous on either side of the maximum. The pH was measured both colorimetrically and electrometrically, the Clark electrode-vessel being employed for the latter determination. He placed a great deal of emphasis on the flattening of the viscosity curves immediately following the decline from the maximum. This he correlated with the alkaline hydrolysis and the evolution of ammonia in this zone. Solutions of casein in ammonia do not exhibit the precipitous decline from the maximum viscosity, although the maximum was in the same pH region.

Chorower (15) claims that the cause of the viscosity of condensed milk cannot be ascribed to the increase of sugar, fat content, or inorganic constituents of milk, but to the colloidal properties of the proteins present. With temperature changes, calcium salts split off, as for example $\text{Ca}_3(\text{PO}_4)_2$, the casein absorbs water and swells, resulting in the liquid becoming semi-solid in nature.

Zeller (55), continuing his previous work (54), dissolved casein in NaOH, KOH, LiOH, NH_4OH , Na_2CO_3 , Na_3AsO_4 , Na_2SiO_3 , NaF, and Na_3PO_4 , and found that the maximum viscosity occurs at nearly the same pH for each dispersion. In borax, the maximum viscosity was attained at pH 8.15 - 8.20, and the suggestion was made that casein acts like mannitol and glycerol in increasing the dissociation of boric acid. High temperature (60°C or above) affects casein to

such an extent that its alkaline dispersions have higher viscosities than unheated alkaline casein dispersions.

Loeb (32), working with casein chloride, found that the viscosity curves of 1% casein chloride at 20^o C after 22 hours show a distinct saddle at pH 2.2 where the solubility of casein chloride is at a maximum. This correlates with his belief that high viscosity is due to the swollen particles of casein since at or near 2.2 some of the particles have dissolved. That dispersion of the particles capable of swelling beneath that size where they no longer can occlude water resulted in a decrease in the relative volume of the casein; consequently a lower viscosity resulted. The maximum viscosity was at pH 2.2 - 2.8 in dispersion of various ages. From 2.7 - 2.8 to 3.1 - 3.2 the viscosity took a drop and then remained constant, not a great deal greater than that of water, up to pH 4.3, which was the limit of his experiments.

The casein used by Loeb was nearly isoelectric casein, prepared according to Van Slyke and Baker's method.

Washburn (51), working on ice cream mixes, stated that the viscosity was largely due to the casein, while Majonnier and Troy (33) found that any condition that would cause coagulation of casein or albumin would cause an increase in the viscosity.

Pauli (41) stated that the viscosimetric examination of acid albumin showed a stupendous increase in the friction up to a maximum, which is followed by a decrease when the acid becomes excessive. He worked with several acids and the effect of mineral salts. With albumin dissolved in HCl he found the maximum viscosity when the concentration of the HCl was 0.02N, while the viscosity fell sharply on both sides of this point.

As shown by Loeb (32), crystalline egg albumin dispersions have a low viscosity when compared to gelatin dispersions; also pH has little influence on the viscosity over a range of 1 - 4.4.

Even this above mentioned slight viscosity of acid albumin is higher than that of the native protein, according to Adolf and Spiegel (1).

Kobler (28) was one of the first to conduct experiments on the surface tension of milk, which he carried on in connection with his viscosity studies. His results showed that most of the factors that affected the viscosity of milk likewise affected the surface tension. He found that milk had a lower surface tension than water and that it was affected by variations in the fat and protein content.

The surface tension of milk decreased on aging and also showed a marked decline when the milk was cooled, according to the

findings of Burri and Nussbaumer (13). But if the previously cooled milk was heated to 50°C and held for half an hour, the decrease in surface tension almost disappeared. They connected the decrease in surface tension with the solidification of the fat.

Later, Bauer (7) obtained the same result as Burri and Nussbaumer (13), but Quagliariello (42) differed, as his results showed the reduction in surface tension, due to holding milk at $0^{\circ} - 10^{\circ}\text{C}$ for half an hour, was permanent and could not be restored to its original surface tension by heating.

If the protein content of milk was reduced, there resulted a considerably higher surface tension than in normal milk, according to Behrendt (8), and also that fat had no essential influence upon the surface tension.

Rahn (45) stated that there was a protein distinct from casein or albumin that surrounded the fat globules and caused foaming.

Dahlberg and Hening (16) worked on the surface tension of skim-milk, milk, and cream, using the du Nouy surface tension apparatus, and found that milk fat in increased percentages always decreased the surface tension of milk and cream, while pasteurization increased it and aging generally decreased it.

Although many have worked on the surface tension of gelatin dispersions, there is little accurate information to be found. This is due partly to the fact that there are many factors to be considered in the measurement. Quincke (43) and Zlobicki (53) worked on the surface tension of gelatin dispersions, but at that time the purity and hydrogen-ion concentration of the gelatin were not considered.

The interfacial tension between an emulsion of finely divided gelatin and oil was studied by Holmes and Childs (21) who concluded that "no concentration by adsorption" took place at the interface. They used the drop weight method.

Sheppard and Sweet (47) used a like method and measured the interfacial tension between toluene and dispersions of gelatin. They employed a high-grade gelatin and varied the hydrogen-ion concentration, but recorded no change of surface tension as the time of drop formation was varied. However, Reynolds' (46) results showed that there was a considerable change for the first fifteen minutes in the surface tension of a dispersion of gelatin and benzene, after which there was a slow change for a long time.

Mannig (35), using electrically flocculated isoelectric gelatin, found that this may be peptised or dispersed to a stable gel by very small concentrations of acid and alkali, while the

addition of relatively larger concentrations of neutral salts will produce the same effect. He concluded that the addition of neutral salts tends to increase the dispersion of the gelatin, making relatively more gelatin in sol form. This causes a lowering of the surface tension.

Bancroft (6) says, referring to Zlobicki's (53) work, "Addition of 0.5 to 0.8 grams of gelatin to 100 cc. water causes a marked decrease in the surface tension of water, while the addition of further amounts has practically no effect." This is almost the identical statement made by Alexander (2).

Davis, Salisbury, and Harvey (19), worked with the Morgan drop-weight method (36) (37) (38), which involves the formation of 15 to 20 drops in fifteen minutes. They reported their results in drop weights. Though the Morgan method gives results that are experimentally accurate, it is not agreed as to just what correction, if any, should be made to calculate the surface tension. The results of their determinations are as follows: Increased concentration causes decreased drop weight. With increased temperatures the drop weight increases in more concentrated dispersions, but finally shows decrease until the transition point is reached, above which all concentrations show no appreciable change in drop weight. With increasing pH there is a tendency for all concentrations to reach a minimum at the

neutral point. The drop weight changes slightly with age of dispersion. Also the surface tension of ash-free gelatin was much higher than that of a commercial gelatin containing impurities.

Lasnitzky and Loeb (30) used the drop-number method to determine the relative surface tension of water, gelatin dispersions, and dispersions of organic acids to which purified gelatin had been added. They found that gelatin dispersions of a concentration of 1.0%, 0.5% and 0.3% have the same surface tension and that there was but a very slight difference between these and concentrations of 0.2%, 0.1%, and 0.05% dispersions.

Johlin (25) used both the drop-weight and capillary-rise methods. His results by both methods showed that the surface tension of gelatin dispersions decreased with time, more rapidly the first fifteen minutes, but gradually reached equilibrium.

Some of the latest work on surface tension of gelatin dispersions has been done by Johnston and Pearce (27) who used Sugden's maximum bubble-pressure method. They claimed that this method was convenient, rapid, and reasonably accurate, besides being unaffected by vibration. From their results the following conclusions were drawn: (1) That the surface tension of gelatin dispersions is found to be at a maximum at the isoelectric point (pH4.7); at a minimum at pH3.8 - 4.0 on the acid side and

in the neighborhood of pH 9 on the alkaline side. A second maximum is found at pH 2.8 - 3.0, after which the surface tension decreases steadily. (2) That increase of temperature and addition of electrolytes both cause a lowering of surface tension of gelatin dispersions, and (3) that the surface tension of gelatin dispersions is little affected by time, after equilibrium is attained, which occurs in a few hours at 25°C, except in the case of isoelectric gelatin, whose surface tension slowly rises nearly to that of water as flocculation proceeds.

There has been even less work done on the surface tension of casein dispersions than there has been on the surface tension of gelatin dispersions.

Bottazzi (12) used a Traube stalagmometer and measured the surface tension of water in which casein of different origin was suspended. He found that the surface tension was lower than that of pure water, and said that it was due to the soluble impurities since the addition of caustic soda was found to cause a further decrease.

Berezeller (9) also used a Traube stalagmometer and found that casein does not lower the surface tension of water to any marked degree unless the casein has been boiled in it. Also the surface tension increased as the dispersion was allowed to

stand. Later, by the same method (10), he found that the surface tension of a casein dispersion changed as he varied the time of drop formation between 0.76 and 4.9 seconds.

Palitzsch (40) mentioned the fact that surface tension of casein dispersions change with hydrogen-ion concentrations but gave no data.

Johlin (26) has worked on the surface tension of various proteins and found that surface tension dispersions decreased with time, showing a rapid change during the first few minutes. He used two kinds of casein in order to check their solubilities. Their solubilities ranged between 0.021 and 0.024 grams per liter with no essential difference in the solubility of the casein of different origin.

Concerning the surface tension of dispersions of egg albumin there is very little available data since the purified form of this substance has been used only in recent years. Quincke (44) measured the surface tension of freshly filtered aqueous dispersions of egg-white, and found that the surface tension of these dispersions was lower than that of water. Iscovesco (23) used a stalagmometer to determine the surface tension of albumin dispersions which were prepared by dialysing egg-white. His results showed that the surface tension of these

dispersions was higher than that of water, while globulin prepared from egg-albumin had a lower surface tension.

Johlin (26) worked with crystalline egg-albumin prepared according to Hopkins and Pinkus (27). For the last recrystallization especially pure, ash-free, ammonium sulphate was used, which was removed from the purified albumin by prolonged dialysis against running distilled water. Stronger dispersions than 0.1% could not be used because of the readiness with which the substance became denatured. He made his measurements by the capillary-rise method and found that the decrease in surface tension for water dispersions was rapid at first, but gradually reached an equilibrium point. If the albumin was dispersed in a basic solution (i.e. NaOH) the extent of the decrease was not as much as in the case of the water dispersion, but approached it as a limit as the amount of alkali was decreased. When the albumin was dispersed in acid (i.e. H_2SO_4) there was an increased lowering of surface tension as the pH increased which at pH 4.3 resulted in a surface tension that was lower than that of a similar water dispersion.

From the above review it can be seen that there is a certain tying-up between viscosity and surface tension of colloidal dispersions. Also from the standpoint of the ice cream mix, they are both of importance since these are the factors which greatly

WHIPPING MIXTURE

influence the whipping properties of the mix by which air is incorporated and the texture and body of the finished product improved.

The following is a list of the ingredients of the mixture, which is used in the preparation of the mixture. The ingredients are: 1. Sugar, 2. Egg whites, 3. Cream, 4. Vanilla, 5. Lemon juice, 6. Salt, 7. Butter, 8. Flour, 9. Baking powder, 10. Cocoa powder, 11. Milk, 12. Whipped cream, 13. Egg yolks, 14. Sugar, 15. Vanilla, 16. Lemon juice, 17. Salt, 18. Butter, 19. Flour, 20. Baking powder, 21. Cocoa powder, 22. Milk, 23. Whipped cream, 24. Egg yolks, 25. Sugar, 26. Vanilla, 27. Lemon juice, 28. Salt, 29. Butter, 30. Flour, 31. Baking powder, 32. Cocoa powder, 33. Milk, 34. Whipped cream, 35. Egg yolks, 36. Sugar, 37. Vanilla, 38. Lemon juice, 39. Salt, 40. Butter, 41. Flour, 42. Baking powder, 43. Cocoa powder, 44. Milk, 45. Whipped cream, 46. Egg yolks, 47. Sugar, 48. Vanilla, 49. Lemon juice, 50. Salt, 51. Butter, 52. Flour, 53. Baking powder, 54. Cocoa powder, 55. Milk, 56. Whipped cream, 57. Egg yolks, 58. Sugar, 59. Vanilla, 60. Lemon juice, 61. Salt, 62. Butter, 63. Flour, 64. 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Milk, 463. Whipped cream, 464. Egg yolks, 465. Sugar, 466. Vanilla, 467. Lemon juice, 468. Salt, 469. Butter, 470. Flour, 471. Baking powder, 472. Cocoa powder, 473. Milk, 474. Whipped cream, 475. Egg yolks, 476. Sugar, 477. Vanilla, 478. Lemon juice, 479. Salt, 480. Butter, 481. Flour, 482. Baking powder, 483. Cocoa powder, 484. Milk, 485. Whipped cream, 486. Egg yolks, 487. Sugar, 488. Vanilla, 489. Lemon juice, 490. Salt, 491. Butter, 492. Flour, 493. Baking powder, 494. Cocoa powder, 495. Milk, 496. Whipped cream, 497. Egg yolks, 498. Sugar, 499. Vanilla, 500. Lemon juice, 501. Salt, 502. Butter, 503. Flour, 504. Baking powder, 505. Cocoa powder, 506. Milk, 507. Whipped cream, 508. Egg yolks, 509. Sugar, 510. Vanilla, 511. Lemon juice, 512. Salt, 513. Butter, 514. Flour, 515. Baking powder, 516. Cocoa powder, 517. Milk, 518. Whipped cream, 519. Egg yolks, 520. Sugar, 521. Vanilla, 522. Lemon juice, 523. Salt, 524. Butter, 525. Flour, 526. Baking powder, 527. Cocoa powder, 528. 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Milk, 595. Whipped cream, 596. Egg yolks, 597. Sugar, 598. Vanilla, 599. Lemon juice, 600. Salt, 601. Butter, 602. Flour, 603. Baking powder, 604. Cocoa powder, 605. Milk, 606. Whipped cream, 607. Egg yolks, 608. Sugar, 609. Vanilla, 610. Lemon juice, 611. Salt, 612. Butter, 613. Flour, 614. Baking powder, 615. Cocoa powder, 616. Milk, 617. Whipped cream, 618. Egg yolks, 619. Sugar, 620. Vanilla, 621. Lemon juice, 622. Salt, 623. Butter, 624. Flour, 625. Baking powder, 626. Cocoa powder, 627. Milk, 628. Whipped cream, 629. Egg yolks, 630. Sugar, 631. Vanilla, 632. Lemon juice, 633. Salt, 634. Butter, 635. Flour, 636. Baking powder, 637. Cocoa powder, 638. Milk, 639. Whipped cream, 640. Egg yolks, 641. Sugar, 642. Vanilla, 643. Lemon juice, 644. Salt, 645. Butter, 646. Flour, 647. Baking powder, 648. Cocoa powder, 649. Milk, 650. Whipped cream, 651. Egg yolks, 652. Sugar, 653. Vanilla, 654. Lemon juice, 655. Salt, 656. Butter, 657. Flour, 658. Baking powder, 659. Cocoa powder, 660. Milk, 661. Whipped cream, 662. Egg yolks, 663. Sugar, 664. Vanilla, 665. Lemon juice, 666. Salt, 667. Butter, 668. Flour, 669. Baking powder, 670. Cocoa powder, 671. Milk, 672. Whipped cream, 673. Egg yolks, 674. Sugar, 675. Vanilla, 676. Lemon juice, 677. Salt, 678. Butter, 679. Flour, 680. Baking powder, 681. Cocoa powder, 682. Milk, 683. Whipped cream, 684. Egg yolks, 685. Sugar, 686. Vanilla, 687. Lemon juice, 688. Salt, 689. Butter, 690. Flour, 691. Baking powder, 692. Cocoa powder, 693. Milk, 694. Whipped cream, 695. Egg yolks, 696. Sugar, 697. Vanilla, 698. Lemon juice, 699. Salt, 700. Butter, 701. Flour, 702. Baking powder, 703. Cocoa powder, 704. Milk, 705. Whipped cream, 706. Egg yolks, 707. Sugar, 708. Vanilla, 709. Lemon juice, 710. Salt, 711. Butter, 712. Flour, 713. Baking powder, 714. Cocoa powder, 715. Milk, 716. Whipped cream, 717. Egg yolks, 718. Sugar, 719. Vanilla, 720. Lemon juice, 721. Salt, 722. Butter, 723. Flour, 724. Baking powder, 725. Cocoa powder, 726. 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Milk, 793. Whipped cream, 794. Egg yolks, 795. Sugar, 796. Vanilla, 797. Lemon juice, 798. Salt, 799. Butter, 800. Flour, 801. Baking powder, 802. Cocoa powder, 803. Milk, 804. Whipped cream, 805. Egg yolks, 806. Sugar, 807. Vanilla, 808. Lemon juice, 809. Salt, 810. Butter, 811. Flour, 812. Baking powder, 813. Cocoa powder, 814. Milk, 815. Whipped cream, 816. Egg yolks, 817. Sugar, 818. Vanilla, 819. Lemon juice, 820. Salt, 821. Butter, 822. Flour, 823. Baking powder, 824. Cocoa powder, 825. Milk, 826. Whipped cream, 827. Egg yolks, 828. Sugar, 829. Vanilla, 830. Lemon juice, 831. Salt, 832. Butter, 833. Flour, 834. Baking powder, 835. Cocoa powder, 836. Milk, 837. Whipped cream, 838. Egg yolks, 839. Sugar, 840. Vanilla, 841. Lemon juice, 842. Salt, 843. Butter, 844. Flour, 845. Baking powder, 846. Cocoa powder, 847. Milk, 848. Whipped cream, 849. Egg yolks, 850. Sugar, 851. Vanilla, 852. Lemon juice, 853. Salt, 854. Butter, 855. Flour, 856. Baking powder, 857. Cocoa powder, 858. Milk, 859. Whipped cream, 860. Egg yolks, 861. Sugar, 862. Vanilla, 863. Lemon juice, 864. Salt, 865. Butter, 866. Flour, 867. Baking powder, 868. Cocoa powder, 869. Milk, 870. Whipped cream, 871. Egg yolks, 872. Sugar, 873. Vanilla, 874. Lemon juice, 875. Salt, 876. Butter, 877. Flour, 878. Baking powder, 879. Cocoa powder, 880. Milk, 881. Whipped cream, 882. Egg yolks, 883. Sugar, 884. Vanilla, 885. Lemon juice, 886. Salt, 887. Butter, 888. Flour, 889. Baking powder, 890. Cocoa powder, 891. Milk, 892. Whipped cream, 893. Egg yolks, 894. Sugar, 895. Vanilla, 896. Lemon juice, 897. Salt, 898. Butter, 899. Flour, 900. Baking powder, 901. Cocoa powder, 902. Milk, 903. Whipped cream, 904. Egg yolks, 905. Sugar, 906. Vanilla, 907. Lemon juice, 908. Salt, 909. Butter, 910. Flour, 911. Baking powder, 912. Cocoa powder, 913. Milk, 914. Whipped cream, 915. Egg yolks, 916. Sugar, 917. Vanilla, 918. Lemon juice, 919. Salt, 920. Butter, 921. Flour, 922. Baking powder, 923. Cocoa powder, 924. Milk, 925. Whipped cream, 926. Egg yolks, 927. Sugar, 928. Vanilla, 929. Lemon juice, 930. Salt, 931. Butter, 932. Flour, 933. Baking powder, 934. Cocoa powder, 935. Milk, 936. Whipped cream, 937. Egg yolks, 938. Sugar, 939. Vanilla, 940. Lemon juice, 941. Salt, 942. Butter, 943. Flour, 944. Baking powder, 945. Cocoa powder, 946. Milk, 947. Whipped cream, 948. Egg yolks, 949. Sugar, 950. Vanilla, 951. Lemon juice, 952. Salt, 953. Butter, 954. Flour, 955. Baking powder, 956. Cocoa powder, 957. Milk, 958. Whipped cream, 959. Egg yolks, 960. Sugar, 961. Vanilla, 962. Lemon juice, 963. Salt, 964. Butter, 965. Flour, 966. Baking powder, 967. Cocoa powder, 968. Milk, 969. Whipped cream, 970. Egg yolks, 971. Sugar, 972. Vanilla, 973. Lemon juice, 974. Salt, 975. Butter, 976. Flour, 977. Baking powder, 978. Cocoa powder, 979. Milk, 980. Whipped cream, 981. Egg yolks, 982. Sugar, 983. Vanilla, 984. Lemon juice, 985. Salt, 986. Butter, 987. Flour, 988. Baking powder, 989. Cocoa powder, 990. Milk, 991. Whipped cream, 992. Egg yolks, 993. Sugar, 994. Vanilla, 995. Lemon juice, 996. Salt, 997. Butter, 998. Flour, 999. Baking powder, 1000. Cocoa powder, 1001. Milk, 1002. Whipped cream, 1003. Egg yolks, 1004. Sugar, 1005. Vanilla, 1006. Lemon juice, 1007. Salt, 1008. Butter, 1009. Flour, 1010. Baking powder, 1011. Cocoa powder, 1012. Milk, 1013. Whipped cream, 1014. Egg yolks, 1015. Sugar, 1016. Vanilla, 1017. Lemon juice, 1018. Salt, 1019. Butter, 1020. Flour, 1021. Baking powder, 1022. Cocoa powder, 1023. Milk, 1024. Whipped cream, 1025. Egg yolks, 1026. Sugar, 1027. Vanilla, 1028. Lemon juice, 1029. Salt, 1030. Butter, 1031. Flour, 1032. Baking powder, 1033. Cocoa powder, 1034. Milk, 1035. Whipped cream, 1036. Egg yolks, 1037. Sugar, 1038. Vanilla, 1039. Lemon juice, 1040. Salt, 1041. Butter, 1042. Flour, 1043. Baking powder, 1044. Cocoa powder, 1045. Milk, 1046. Whipped cream, 1047. Egg yolks, 1048. Sugar, 1049. Vanilla, 1050. Lemon juice, 1051. Salt, 1052. Butter, 1053. Flour, 1054. Baking powder, 1055. Cocoa powder, 1056. Milk, 1057. Whipped cream, 1058. Egg yolks, 1059. Sugar, 1060. Vanilla, 1061. Lemon juice, 1062. Salt, 1063. Butter, 1064. Flour, 1065. Baking powder, 1066. Cocoa powder, 1067. Milk, 1068. Whipped cream, 1069. Egg yolks, 1070. Sugar, 1071. Vanilla, 1072. Lemon juice, 1073. Salt, 1074. Butter, 1075. Flour, 1076. Baking powder, 1077. Cocoa powder, 1078. Milk, 1079. Whipped cream, 1080. Egg yolks, 1081. Sugar, 1082. Vanilla, 1083. Lemon juice, 1084. Salt, 1085. Butter, 1086. Flour, 1087. Baking powder, 1088. Cocoa powder, 1089. Milk, 1090. Whipped cream, 1091. Egg yolks, 1092. Sugar, 1093. Vanilla, 1094. Lemon juice, 1095. Salt, 1096. Butter, 1097. Flour, 1098. Baking powder, 1099. Cocoa powder, 1100. Milk, 1101. Whipped cream, 1102. Egg yolks, 1103. Sugar, 1104. Vanilla, 1105. Lemon juice, 1106. Salt, 1107. Butter, 1108. Flour, 1109. Baking powder, 1110. Cocoa powder, 1111. Milk, 1112. Whipped cream, 1113. Egg yolks, 1114. Sugar, 1115. Vanilla, 1116. Lemon juice, 1117. Salt, 1118. Butter, 1119. Flour, 1120. Baking powder, 1121. Cocoa powder, 1122. Milk, 1123. Whipped cream, 1124. Egg yolks, 1125. Sugar, 1126. Vanilla, 1127. Lemon juice, 1128. Salt, 1129. Butter, 1130. Flour, 1131. Baking powder, 1132. Cocoa powder, 1133. Milk, 1134. Whipped cream, 1135. Egg yolks, 1136. Sugar, 1137. Vanilla, 1138. Lemon juice, 1139. Salt, 1140. Butter, 1141. Flour, 1142. Baking powder, 1143. Cocoa powder, 1144. Milk, 1145. Whipped cream, 1146. Egg yolks, 1147. Sugar, 1148. Vanilla, 1149. Lemon juice, 1150. Salt, 1151. Butter, 1152. Flour, 1153. Baking powder, 1154. Cocoa powder, 1155. Milk, 1156. Whipped cream, 1157. Egg yolks, 1158. Sugar, 1159. Vanilla, 1160. Lemon juice, 1161. Salt, 1162. Butter, 1163. Flour, 1164. Baking powder, 1165. Cocoa powder, 1166. Milk, 1167. Whipped cream, 1168. Egg yolks, 1169. Sugar, 1170. Vanilla, 1171. Lemon juice, 1172. Salt, 1173. Butter, 1174. Flour, 1175. Baking powder, 1176. Cocoa powder, 1177. Milk, 1178. Whipped cream, 1179. Egg yolks, 1180. Sugar, 1181. Vanilla, 1182. Lemon juice, 1183. Salt, 1184. Butter, 1185. Flour, 1186. Baking powder, 1187. Cocoa powder, 1188. Milk, 1189. Whipped cream, 1190. Egg yolks, 1191. Sugar, 1192. Vanilla, 1193. Lemon juice, 1194. Salt, 1195. Butter, 1196. Flour, 1197. Baking powder, 1198. Cocoa powder, 1199. Milk, 1200. Whipped cream, 1201. Egg yolks, 1202. Sugar, 1203. Vanilla, 1204. Lemon juice, 1205. Salt, 1206. Butter, 1207. Flour, 1208. Baking powder, 1209. Cocoa powder, 1210. Milk, 1211. Whipped cream, 1212. Egg yolks, 1213. Sugar, 1214. Vanilla, 1215. Lemon juice, 1216. Salt, 1217. Butter, 1218. Flour, 1219. Baking powder, 1220. Cocoa powder, 1221. Milk, 1222. Whipped cream, 1223. Egg yolks, 1224. Sugar, 1225. Vanilla, 1226. Lemon juice, 1227. Salt, 1228. Butter, 1229. Flour, 1230. Baking powder, 1231. Cocoa powder, 1232. Milk, 1233. Whipped cream, 1234. Egg yolks, 1235. Sugar, 1236. Vanilla, 1237. Lemon juice, 1238. Salt, 1239. Butter, 1240. Flour, 1241. Baking powder, 1242. Cocoa powder, 1243. Milk, 1244. Whipped cream, 1245. Egg yolks, 1246. Sugar, 1247. Vanilla, 1248. Lemon juice, 1249. Salt, 1250. Butter, 1251. Flour, 1252. Baking powder, 1253. Cocoa powder, 1254. Milk, 1255. Whipped cream, 1256. Egg yolks, 1257. Sugar, 1258. Vanilla, 1259. Lemon juice, 1260. Salt, 1261. Butter, 1262. Flour, 1263. Baking powder, 1264. Cocoa powder, 1265. Milk, 1266. Whipped cream, 1267. Egg yolks, 1268. Sugar, 1269. Vanilla, 1270. Lemon juice, 1271. Salt, 1272. Butter, 1273. Flour, 1274. Baking powder, 1275. Cocoa powder, 1276. Milk, 1277. Whipped cream, 1278. Egg yolks, 1279. Sugar, 1280. Vanilla, 1281. Lemon juice, 1282. Salt, 1283. Butter, 1284. Flour, 1285. Baking powder, 1286. Cocoa powder, 1287. Milk, 1288. Whipped cream, 1289. Egg yolks, 1290. Sugar, 1291. Vanilla, 1292. Lemon juice, 1293. Salt, 1294. Butter, 1295. Flour, 1296. Baking powder, 1297. Cocoa powder, 1298. Milk, 1299. Whipped cream, 1300. Egg yolks, 1301. Sugar, 1302. Vanilla, 1303. Lemon juice, 1304. Salt, 1305. Butter, 1306. Flour, 1307. Baking powder, 1308. Cocoa powder, 1309. Milk, 1310. Whipped cream, 1311. Egg yolks, 1312. Sugar, 1313. Vanilla, 1314. Lemon juice, 1315. Salt, 1316. Butter, 1317. Flour, 1318. Baking powder, 1319. Cocoa powder, 1320. Milk, 1321. Whipped cream, 1322. Egg yolks, 1323. Sugar, 1324. Vanilla, 1325. Lemon juice, 1326. Salt, 1327. Butter, 1328. Flour, 1329. Baking powder, 1330. Cocoa powder, 1331. Milk, 1332. Whipped cream, 1333. Egg yolks, 1334. Sugar, 1335. Vanilla, 1336. Lemon juice, 1337. Salt, 1338. Butter, 1339. Flour, 1340. Baking powder, 1341. Cocoa powder, 1342. Milk, 1343. Whipped cream, 1344. Egg yolks, 1345. Sugar, 1346. Vanilla, 1347. Lemon juice, 1348. Salt, 1349. Butter, 1350. Flour, 1351. Baking powder, 1352. Cocoa powder, 1353. Milk, 1354. Whipped cream, 1355. Egg yolks, 1356. Sugar, 1357. Vanilla, 1358. Lemon juice, 1359. Salt, 1360. Butter, 1361. Flour, 1362. Baking powder, 1363. Cocoa powder, 1364. Milk, 1365. Whipped cream, 1366. Egg yolks, 1367. Sugar, 1368. Vanilla, 1369. Lemon juice, 1370. Salt, 1371. Butter, 1372. Flour, 1373. Baking powder, 1374. Cocoa powder, 1375. Milk, 1376. Whipped cream, 1377. Egg yolks, 1378. Sugar, 1379. Vanilla, 1380. Lemon juice, 1381. Salt, 1382. Butter, 1383. Flour, 1384. Baking powder, 1385. Cocoa powder, 1386. Milk, 1387. Whipped cream, 1388. Egg yolks, 1389. Sugar, 1390. Vanilla, 1391. Lemon juice, 1392. Salt, 1393. Butter, 1394. Flour, 1395. Baking powder, 1396. Cocoa powder, 1397. Milk, 1398. Whipped cream, 1399. Egg yolks, 1400. Sugar, 1401. Vanilla, 1402. Lemon juice, 1403. Salt, 1404. Butter, 1405. Flour, 1406. Baking powder, 1407. Cocoa powder, 1408. Milk, 1409. Whipped cream, 1410. Egg yolks, 1411. Sugar, 1412. Vanilla, 1413. Lemon juice, 1414. Salt, 1415. Butter, 1416. Flour, 1417. Baking powder, 1418. Cocoa powder, 1419. Milk, 1420. Whipped cream, 1421. Egg yolks, 1422. Sugar, 1423. Vanilla, 1424. Lemon juice, 1425. Salt, 1426. Butter, 1427. Flour, 1428. Baking powder, 1429. Cocoa powder, 1430. Milk, 1431. Whipped cream, 1432. Egg yolks, 1433. Sugar, 1434. Vanilla, 1435. Lemon juice, 1436. Salt, 1437. Butter, 1438. Flour, 1439. Baking powder, 1440. Cocoa powder, 1441. Milk, 1442. Whipped cream, 1443. Egg yolks, 1444. Sugar, 1445. Vanilla, 1446. Lemon juice, 1447. Salt, 1448. Butter, 1449. Flour, 1450. Baking powder, 1451. Cocoa powder, 1452. Milk, 1453. Whipped cream, 1454. Egg yolks, 1455. Sugar, 1456. Vanilla, 1457. Lemon juice, 1458. Salt, 1459. Butter, 1460. Flour, 1461. Baking powder, 1462. Cocoa powder, 1463. Milk, 1464. Whipped cream, 1465. Egg yolks, 1466. Sugar, 1467. Vanilla, 1468. Lemon juice, 1469. Salt, 1470. Butter, 1471. Flour, 1472. Baking powder, 1473. Cocoa powder, 1474. Milk, 1475. Whipped cream, 1476. Egg yolks, 1477. Sugar, 1478. Vanilla, 1479. Lemon juice, 1480. Salt, 1481. Butter, 1482. Flour, 1483. Baking powder, 1484. Cocoa powder, 1485. Milk, 1486. Whipped cream, 1487. Egg yolks, 1488. Sugar, 1489. Vanilla, 1490. Lemon juice, 1491. Salt, 1492. Butter, 1493. Flour, 1494. Baking powder, 1495. Cocoa powder, 1496. Milk, 1497. Whipped cream, 1498. Egg yolks, 1499. Sugar, 1500. Vanilla, 1501. Lemon juice, 1502. Salt, 1503. Butter, 1504. Flour, 1505. Baking powder, 1506. Cocoa powder, 1507. Milk, 1508. Whipped cream, 1509. Egg yolks, 1510. Sugar, 1511. Vanilla, 1512. Lemon juice, 1513. Salt, 1514. Butter, 1515. Flour, 1516. Baking powder, 1517. Cocoa powder, 1518. Milk, 1519. Whipped cream, 1520. Egg yolks, 1521. Sugar, 1522. Vanilla, 1523. Lemon juice, 1524. Salt, 1525. Butter

THEORETICAL DISCUSSION.

When a liquid flows through a tube of small diameter, the velocity of flow will be governed by the force that produces the flow and by the nature of the liquid. There is not a uniform velocity throughout the tube, since a very thin layer remains in contact with the walls of the tube. Also within the column of liquid itself very thin layers of liquid move over one another with gradually increasing velocity until a maximum is reached. The internal friction which resists the movement of the different layers past one another in the direction of flow is called viscosity. If the tube is narrow, similar to the Ostwald tube, one can picture the flow of liquid through it as if the liquid was replaced by telescoping tubes sliding one past the other. The viscosity would be represented by the friction between the tubes. Now for a liquid of low viscosity (i.e. low internal friction), one could picture the flow through the tube as being retarded only near the walls of the tube while in the center the whole column falls like a solid cylinder.

The coefficient of viscosity of a liquid is defined as the tangential force per unit area of either of two horizontal planes at unit distance apart, one of which is fixed, while the other moves with unit velocity, the space being filled with the substance. It is expressed in dyne-seconds per square centimeter

or poises but for convenience may be reported in centipoises, as for example water has a viscosity of .008937 poises or .8937 centipoises at 25^oC.

With a non-colloidal solution the most important factor that governs viscosity, other than concentration, is temperature, since viscosity decreases approximately 2% per degree rise in temperature. But with colloidal dispersions other factors come into play; namely, pH and age of solution.

Now the viscosity of a colloidal dispersion is at a minimum at its isoelectric point and the protein is unionized, but if acid or alkali is added the viscosity of the protein solution increases. At first one would think that Pauli's hydration theory would account for this increase. According to his theory the ionized molecule differs from the non-ionized molecule by being surrounded by a shell of water. This adsorption of water would necessarily increase the viscosity of the solution.

With gelatin dispersions this theory applies since upon the addition of an acid or base to an isoelectric dispersion of gelatin there is an increase in viscosity. If this increase in viscosity is due to the hydration of the individual protein ions then the addition of an acid or base to any other protein should cause the same effect. However, changing the pH of an isoelectric albumin dispersion does not increase the viscosity to any marked

extent. This shows that though the hydration theory holds true in the case of gelatin, it falls short in the case of albumin. This necessitates a closer inspection of the viscosity of dispersions of the same strength of gelatin and albumin at their respective isoelectric point. The viscosity of the gelatin solution is much greater than that of the albumin solution which shows that there is some other factor governing their viscosity.

Since Pauli's theory showed that increase in size of particle caused increase in viscosity, we have the right to assume that the gelatin particle is of larger size than the albumin particle. This can be verified by seeing if Einstein's or Arrhenius's formula applies to their viscosities. Einstein's formula is $\eta = \eta_0(1 + 2.5\phi)$ where ϕ is the relative volume occupied by the protein in the solution, and η is the viscosity ratio. This formula, applied to both dispersions, gives results in the case of the albumin which are within experimental error but for gelatin the results are much too low. This shows that the albumin particle is considerably smaller than the gelatin particle. Now using Arrhenius's formula, $\log \eta - \log \eta_0 = \mathcal{J}\phi$ where ϕ is the relative volume occupied by the protein, \mathcal{J} is a constant and η and η_0 are the same as in Einstein's formula, the results are within experimental error.

To follow out the idea of differences in size of particles

we can connect up the fact that at ordinary temperature and at pH above 1.0 egg albumin solutions do not form a gel, while gelatin solutions easily gel. From this we can see that gelatin solution contains submicroscopic particles of solid jelly called micellae, while the albumin dispersions are lacking in this respect. The ability of the micellae to occlude relatively large quantities of water, resulting in a relatively larger volume occupied by the gelatin, causes the greater viscosity.

The amount of water occluded by these micellae and therefore the viscosity of the dispersion is governed by the Donnan equilibrium. This explains why the viscosity of gelatin dispersions vary with pH and the viscosity of albumin do not. Since in gelatin dispersions there is a large number of these micellae, and as electrolytes are added these micellae occlude more water therefore increasing the viscosity. We may conclude from the low viscosity of albumin dispersions that these micellae are lacking to any appreciable extent.

Casein dispersions, though they lack the tendency to set to a gel, do contain particles which have the ability to occlude water, thereby accounting for their relative high viscosity and its change with pH.

A sphere represents the smallest possible surface for a

given volume. Falling drops assume this shape as do dispersions suspended in mediums of like density. The force that governs this internal attraction is called surface tension. Within a liquid a molecule will be equally attracted in all directions, but if the molecule is at the surface it is subjected to an unbalanced force acting inward at right angles to the surface. This surface can be compared to a skin layer which is elastic and always taut. The force which acts perpendicular to a section of this surface 1 cm. long is called surface tension. It is expressed in dynes per centimeter. This force exists whenever a free surface is formed.

The addition of substances either raises or lowers the surface tension of a liquid, while an increase in temperature lowers it.

The addition of proteins lowers the surface tension of water. The extent of the lowering depends upon the protein, the concentration and the pH. The surface tension is at a maximum at the isoelectric point. This is due to the fact that, at the isoelectric point, the particles occlude the least amount of water and therefore, the surface tension approaches that of water. As to the effect of age or an addition of acid, or alkali, upon surface tension, that which tends to increase the dispersion of the colloid causes a lowering of surface tension.

CHEMICALS AND APPARATUS.

The gelatin used in this investigation was Swift and Co.'s 6A, a very high-grade product, without further purification or removal of ash ingredients, since in the ice cream mix it is not in that condition. Casein was Pfanstiehl's highest purity. The albumin used was a high-grade egg albumin in scale form. Egg albumin was used in place of milk albumin because the latter was unavailable on the market. Attempts to obtain a high-grade milk albumin from whey were unsatisfactory, but this phase of the work is being continued. Throughout the investigation chemically pure reagents were employed and also redistilled water.

A high-grade tenth-of-a-second split stop watch was used for the viscosity measurements. This watch was wound up and allowed to run for five minutes before each set of determinations. Four Ostwald tubes of water constants, 81.23, 78.88, 80.66 and 85.00 seconds respectively were employed. A du Nouy surface tension apparatus, model 10400 was used. A Freas constant temperature thermostat ($25^{\circ}\text{C} \pm 0.02$) was used which was provided with a glass window so that the flow in the viscosity tubes could be observed. Densities were determined at 25°C by means of a Westphal balance. All hydrogen-ion concentrations were determined with a Leeds and

Northrup type K potentiometer in conjunction with a Leeds and Northrup enclosed lamp and scale galvanometer and Clark's Electrode Assembly with motor driven shaker. A Weston Standard Cadmium Cell was used. Hydrogen was produced electrolytically.

PROCEDURE.

The gelatin dispersions were made up according to the method of Davis, Oakes and Browne (17). The gelatin was added to the exact amount of water to obtain the desired weight concentration. Immediately upon addition of gelatin the dispersion was placed on the hot plate and brought to 75°C in 20 minutes, stirring constantly. Upon removal from the hot plate, it was filtered and allowed to cool. When the temperature of the dispersion reached 38.03° "aging" began. The dispersions were placed in the thermostat ($25^{\circ} \pm 0.02^{\circ}$) for 24 hours and then 6 cc. of the dispersions were placed in the Ostwald viscosity tubes and their viscosities determined.

In the case of the casein which was dispersed in acid solution, four grams of casein were moistened with 10 cc. N lactic acid and then 86 cc. of distilled water were added. The dispersions, from that point on, were treated in the same manner as the gelatin dispersions. This four percent dispersion was used as a standard, and from it the dispersions of different percentages were made by dilution with distilled water.

Casein was also dispersed in a basic solution. Four grams of casein were dispersed in 96 cc. of a one percent solution of sodium carbonate and treated in the same manner as the casein dispersed in lactic acid.

Since, owing to the denaturizing effect, stronger dispersion than 0.1% cannot be made of albumin in water. It was found that egg albumin would disperse in a 0.02 N HCl solution. Then different percentage dispersions were made up directly, without heating, filtered, aged for an hour and then their viscosity determined. They were not allowed to age twenty-four hours in order to prevent any denaturizing effect.

For the determination of surface tension the dispersions were made up in like manner and aged the same time. The surface tension was determined by the du Nouy method, using a new technique, which, when used with water, gives results that are very near the results obtained by other surface tension methods.

By the old method the arm is not in the position of zero balance at the instant of rupture and this accounts, at least to some degree, for the high results obtained with this method. Using the new technique, the vessel containing the liquid is gradually lowered by means of the screw adjustment on the support, while the increasing force is being applied, all the while maintaining the arm in its position of zero balance. Thus the scale zero remains the true zero and therefore readings

on the scale will correctly represent the force at the instant of rupture.

The surface tension of water at 25^o C was taken as 71.78 dynes per cm. according to Landolt and Bornstein (29). The density of the dispersions was determined by means of a Westphal balance, the density of water at 25^o C being taken as 0.997071 according to Landolt and Bornstein (29). All the pH values were determined electrometrically.

DISCUSSION OF RESULTS.

On the following pages the results are presented in the following manner; first a table of the experimental results and then a graph of these results in order to show more clearly their relative values. The experimental results of the viscosity measurements are reported in poises, but the graphs are plotted in centipoises in order that the constants of the equations derived from the curves would be much larger than those resulting from the use of poises as a unit. These are followed by a discussion which includes a mathematical formula for the graphs whereby one can find the viscosity or surface tension values for concentrations between the points plotted.

In all cases, the acidic or basic solutions, in which the different proteins were dispersed, were tested for viscosity and surface tension and found to have only a very slight effect in comparison with the effect produced by proteins themselves.

TABLE I

Viscosity of Gelatin Dispersions

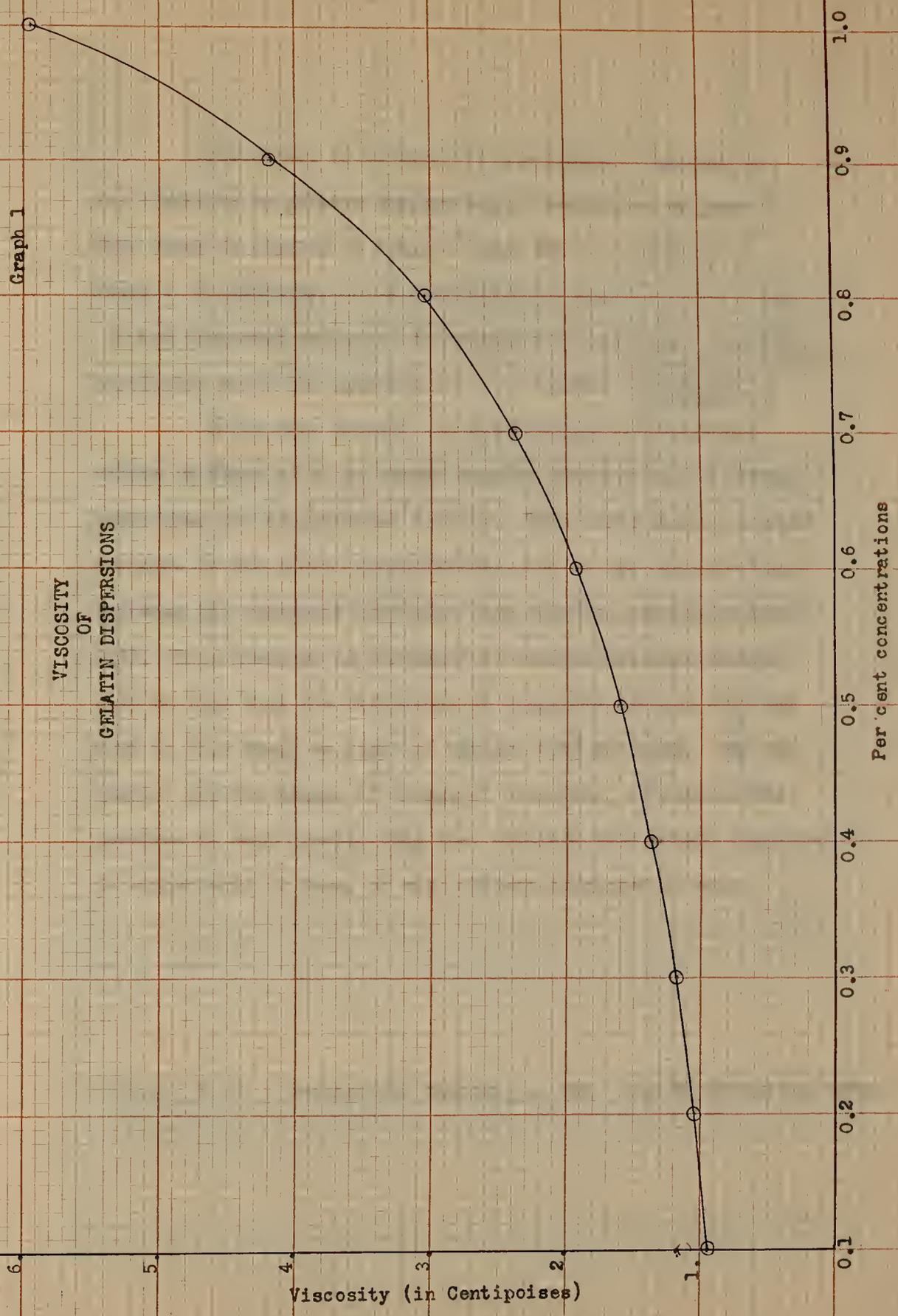
Aged 24 hrs.

pH 4.70 ± 0.1

%	Density	Viscosity in poises	Average Viscosity	%	Density	Viscosity on poises	Average Viscosity
1.0	0.9999	0.059351		0.5	0.9985	0.016174	
1.0	0.9999	0.059495		0.5	0.9985	0.016119	
1.0	0.9999	0.059471		0.5	0.9985	0.016211	
1.0	0.9999	0.059366	0.059420	0.5	0.9985	0.015995	0.0161247
0.9	0.9997	0.041817		0.4	0.9982	0.013812	
0.9	0.9997	0.041870		0.4	0.9982	0.013713	
0.9	0.9997	0.041857		0.4	0.9982	0.013776	
0.9	0.9997	0.041965	0.0418772	0.4	0.9982	0.013779	0.013770
0.8	0.9994	0.030423		0.3	0.9979	0.012003	
0.8	0.9994	0.030310		0.3	0.9979	0.011990	
0.8	0.9994	0.030418		0.3	0.9979	0.011988	
0.8	0.9994	0.030489	0.030410	0.3	0.9979	0.011996	0.0119942
0.7	0.9991	0.023801		0.2	0.9976	0.010490	
0.7	0.9991	0.023852		0.2	0.9976	0.010480	
0.7	0.9991	0.023847		0.2	0.9976	0.010566	
0.7	0.9991	0.023769	0.0238172	0.2	0.9976	0.010510	0.0104865
0.6	0.9988	0.019231		0.1	0.9974	0.0095190	
0.6	0.9988	0.019237		0.1	0.9974	0.0094969	
0.6	0.9988	0.019224		0.1	0.9974	0.0095090	
0.6	0.9988	0.019232	0.0192310	0.1	0.9974	0.0094756	0.0095001

Graph 1

VISCOSITY
OF
GELATIN DISPERSIONS



Viscosity (in Centipoises)

Per cent concentrations

The effect of varying the percentage of gelatin on the viscosity of gelatin dispersions is best shown by graph 1.

This curve is similar to Kelly's⁺ type XII $V = V_0 \left[\frac{a_1 + \chi}{a_2 - \chi} \right]^p$

Where V = viscosity, χ = concentration, and V_0 , p , and

a are constants which are determined for each case. For this particular curve the equation is $V = 0.95610 \left[\frac{1.7265 + \chi}{0.91086 - \chi} \right]^{0.3093}$

Using this formula and substituting concentration values in place of χ we obtain results that are just a little lower than the experimental results. This curve shows a gradual increase in the lower concentrations, but as the concentrations increase the viscosity increases very rapidly, especially after 0.5%. This increase in viscosity is brought out more clearly when we find that the difference in viscosity between 0.8% and 0.9% is 11.6 times as great as between 0.1% and 0.2%. The viscosity, and the degree of change of viscosity, of gelatin dispersions is much greater than that obtained with casein dispersed in either acid or base, or with albumin dispersed in acid.

⁺ Kelly, T. L. Statistical Methods, p. 131. The MacMillan Co. 1923.

TABLE II

Viscosity of Casein Dispersions

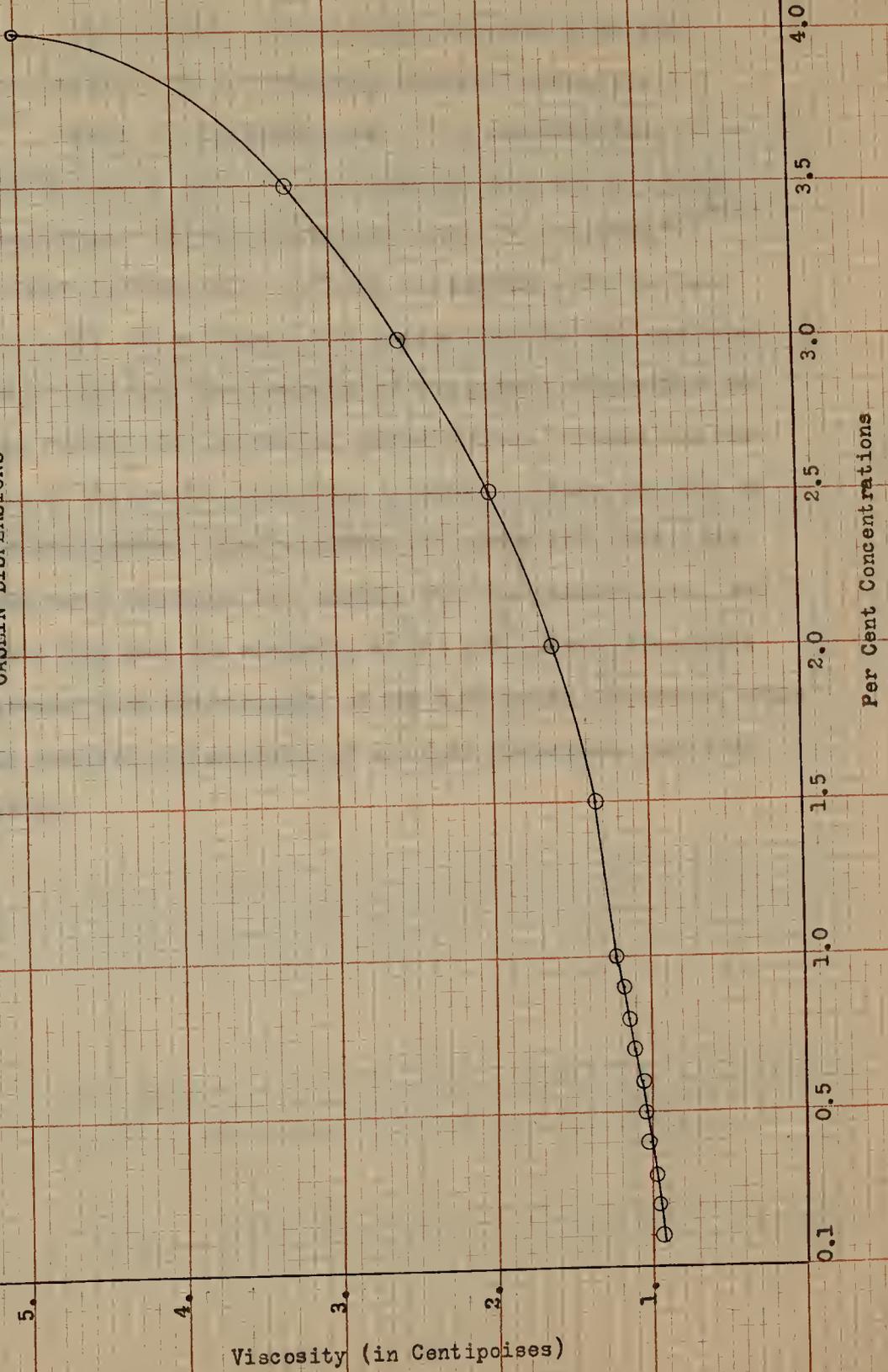
pH 3.09 ± 0.4

Aged 24 hrs.

%	Density	Viscosity in poises	Average Viscosity	%	Density	Viscosity in poises	Average Viscosity
4.0	1.115	0.050196		0.8	1.011	0.011680	
4.0	1.115	0.050109		0.8	1.011	0.011649	
4.0	1.115	0.050341		0.8	1.011	0.011717	
4.0	1.115	0.050239	0.0502312	0.8	1.011	0.011663	0.0116772
3.5	1.094	0.033136		0.7	1.009	0.011133	
3.5	1.094	0.033004		0.7	1.009	0.011121	
3.5	1.094	0.032835		0.7	1.009	0.011178	
3.5	1.094	0.032809	0.0329460	0.7	1.009	0.011119	0.01113775
3.0	1.082	0.025657		0.6	1.000	0.010681	
3.0	1.082	0.025648		0.6	1.000	0.010613	
3.0	1.082	0.025621		0.6	1.000	0.010690	
3.0	1.082	0.025660	0.0256465	0.6	1.000	0.010671	0.01066375
2.5	1.063	0.020092		0.5	0.9992	0.010463	
2.5	1.063	0.020051		0.5	0.9992	0.010377	
2.5	1.063	0.020140		0.5	0.9992	0.010479	
2.5	1.063	0.020053	0.0200840	0.5	0.9992	0.010465	0.0104460
2.0	1.042	0.016304		0.4	0.9987	0.010162	
2.0	1.042	0.016280		0.4	0.9987	0.010191	
2.0	1.042	0.016268		0.4	0.9987	0.010186	
2.0	1.042	0.016305	0.0162892	0.4	0.9987	0.010173	0.0101780
1.5	1.028	0.013657		0.3	0.9986	0.0097185	
1.5	1.028	0.013561		0.3	0.9986	0.0096900	
1.5	1.028	0.013639		0.3	0.9986	0.0097762	
1.5	1.028	0.013723	0.013645	0.3	0.9986	0.0096878	0.00971812
1.0	1.014	0.012263		0.2	0.9984	0.0094742	
1.0	1.014	0.012145		0.2	0.9984	0.0094048	
1.0	1.014	0.012259		0.2	0.9984	0.0094090	
1.0	1.014	0.012158	0.0122062	0.2	0.9984	0.0093804	0.00941710
0.9	1.013	0.011937		0.1	0.9980	0.0092612	
0.9	1.013	0.011800		0.1	0.9980	0.0092762	
0.9	1.013	0.011871		0.1	0.9980	0.0092602	
0.9	1.013	0.011878	0.0118715	0.1	0.9980	0.0092715	0.00926722

Graph 2

VISCOSITY
OF
CASEIN DISPERSIONS



The viscosity of the casein dispersed in an acid medium complies with the "compound interest" curve, i.e. $V = ae^{\lambda x}$ where V = viscosity, and x = concentration, $e = 2.7182818$, and a and λ are constants that are determined for each case. For this particular curve $V = 0.87194e^{0.381x}$. This curve is from 0.1% - 4.0% and the gelatin curve is from 0.1% - 1.0%. If we compare both curves over the same concentrations we find that the viscosity of the gelatin dispersions increase rapidly with increasing concentrations, whereas the viscosity of the casein dispersions is almost a linear function of the concentration. Upon comparing the curves as a whole, the casein curve increases less rapidly than the gelatin curve, and we also find that the viscosity of the 1.0% gelatin dispersion is greater than the viscosity of the 4.0% casein dispersion, while their respective viscosities of the 0.1% dispersions vary only slightly.

TABLE III

Viscosity of Casein Dispersions

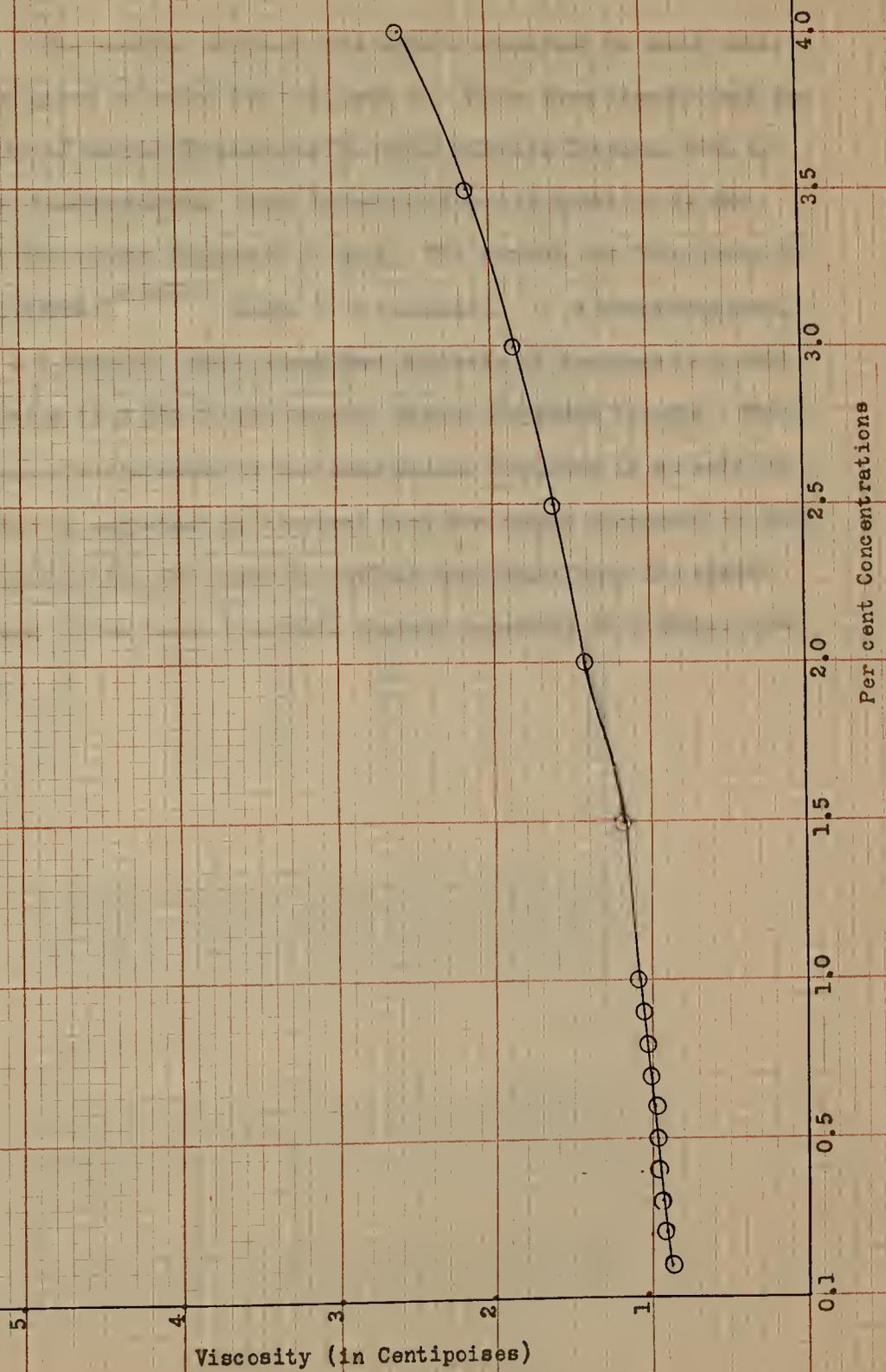
Aged 24 hrs.

pH 9.00 ± 0.2

%	Density	Viscosity in poises	Average Viscosity	Density	Viscosity in poises	Average Viscosity
4.0	1.154	0.025569	0.0256085	1.013	0.010350	0.010350
4.0	1.154	0.025675		1.013	0.010360	0.010360
4.0	1.154	0.025647		1.013	0.010356	0.010356
4.0	1.154	0.025543	0.0256085	1.007	0.010340	0.0103515
3.5	1.138	0.021495		1.007	0.010089	
3.5	1.138	0.021465		1.007	0.010081	
3.5	1.138	0.021483		1.007	0.010071	
3.5	1.138	0.021388	0.0214585	1.007	0.010090	0.010008275
3.0	1.117	0.018611		1.005	0.0098470	
3.0	1.117	0.018594		1.005	0.0098440	
3.0	1.117	0.018606		1.005	0.0098500	
3.0	1.117	0.018622	0.0186082	1.005	0.0098452	0.00984665
2.5	1.094	0.016175		1.002	0.0097295	
2.5	1.094	0.016148		1.002	0.0097235	
2.5	1.094	0.016169		1.002	0.0097135	
2.5	1.094	0.016151	0.01616075	1.002	0.0097208	0.00972632
2.0	1.075	0.014307		0.9999	0.0094995	
2.0	1.075	0.014288		0.9999	0.0094984	
2.0	1.075	0.014311		0.9999	0.0095002	
2.0	1.075	0.014317	0.01430575	0.9999	0.0094895	0.0094969
1.5	1.048	0.011807		0.9998	0.0094102	
1.5	1.048	0.011801		0.9998	0.0093952	
1.5	1.048	0.011762		0.9998	0.0093990	
1.5	1.048	0.011824	0.01179850	0.9998	0.0094040	0.0094021
1.0	1.029	0.010991		0.9997	0.0091558	
1.0	1.029	0.010991		0.9997	0.0091558	
1.0	1.029	0.011000		0.9997	0.0091538	
1.0	1.029	0.010992	0.0109935	0.9997	0.0091502	0.0091539
0.9	1.024	0.010700		0.9997	0.0089790	
0.9	1.024	0.010646		0.9997	0.0089628	
0.9	1.024	0.010696		0.9997	0.0089760	
0.9	1.024	0.010689	0.01068277	0.9997	0.0089816	0.00897485

Graph 3

VISCOSITY
OF
CASEIN DISPERSIONS



Viscosity (in Centipoises)

Per cent Concentrations

The results obtained with casein dispersed in basic solution are given on table III and graph 3. These show clearly that the viscosity of casein dispersions in basic solution increase with increasing concentration. This increase is not as great as in the case of the casein dispersed in acid. The formula for this curve is $V = 0.83189 e^{0.2811 X}$ where V = viscosity, X = concentrations, and $e = 2.7182818$. This shows that the rate of increase is 0.2811 as compared to 0.381 in the case of casein dispersed in acid. This difference in viscosity of the same casein dispersed in an acid and in a base is explained by the fact that the casein dispersed in the acid solution has the power to occlude more water than the casein dispersed in the basic solution, thereby resulting in a higher viscosity.

TABLE IV

Viscosity of Albumin Dispersions

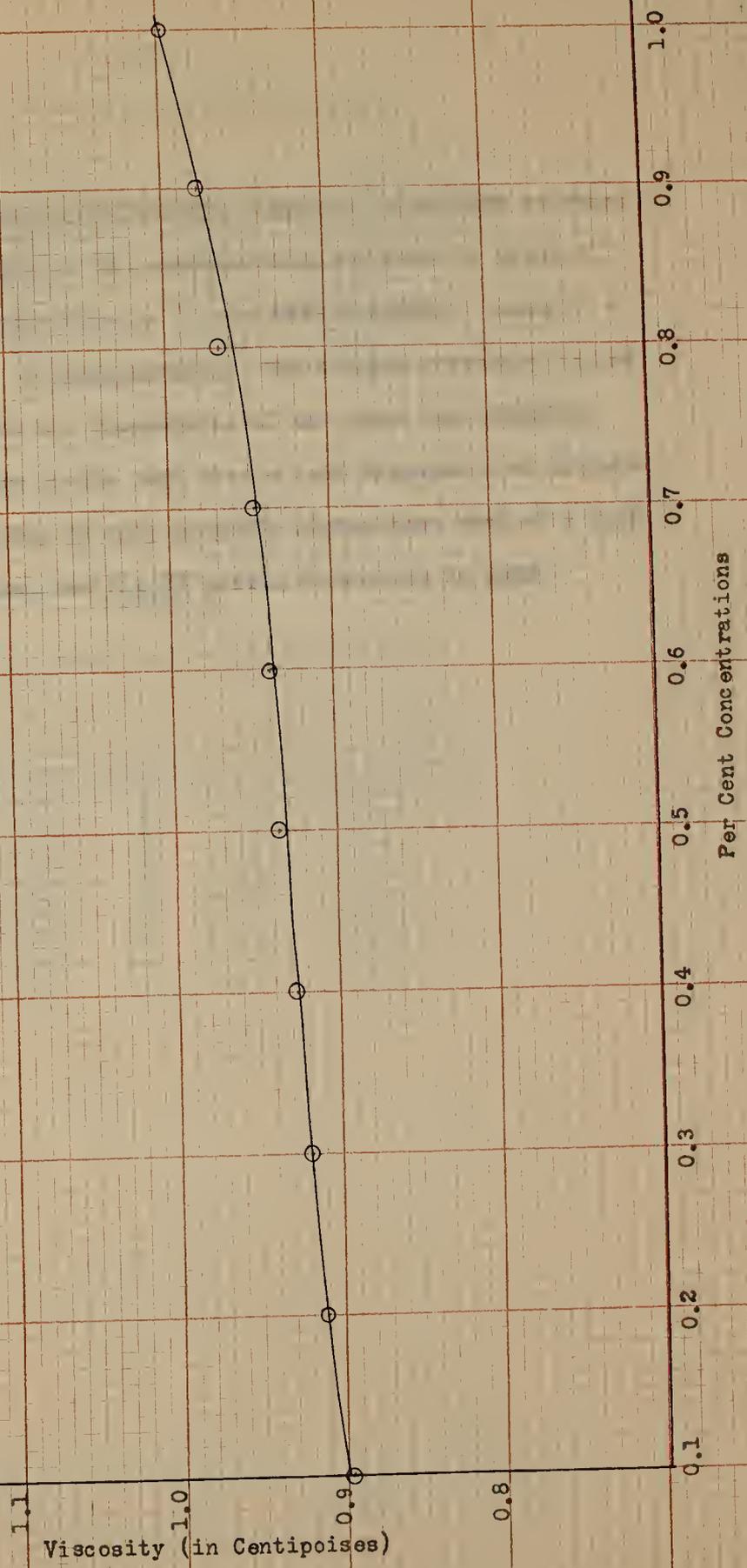
Aged 1 hr.

pH 1.97 ± 0.2

%	Density	Viscosity in poises	Average Viscosity	%	Density	Viscosity in poises	Average Viscosity
1.0	1.013	0.009480		0.5	0.9994	0.0093624	
1.0	1.013	0.009892		0.5	0.9994	0.0093688	
1.0	1.013	0.009730		0.5	0.9994	0.0093620	
1.0	1.013	0.009342	0.0099366	0.5	0.9994	0.0093688	0.0093655
0.9	1.012	0.009376		0.4	0.9992	0.0092724	
0.9	1.012	0.009744		0.4	0.9992	0.0092760	
0.9	1.012	0.009724		0.4	0.9992	0.0092712	
0.9	1.012	0.009750	0.0097899	+			
0.8	1.010	0.0096782		0.3	0.9987	0.0092018	
0.8	1.010	0.0096632		0.3	0.9987	0.0092034	
0.8	1.010	0.0096858		0.3	0.9987	0.0091890	
0.8	1.010	0.0096810	0.00967705				0.0091944
0.7	1.000	0.0094894		0.2	0.9985	0.0091112	
0.7	1.000	0.0094768		0.2	0.9985	0.0090880	
0.7	1.000	0.0094678		0.2	0.9985	0.0091206	
0.7	1.000	0.0094798	0.00947845				0.0091066
0.6	0.9996	0.0094090		0.1	0.9984	0.0090114	
0.6	0.9996	0.0093820		0.1	0.9984	0.0089962	
0.6	0.9996	0.0093972		0.1	0.9984	0.0089310	
0.6	0.9996	0.0094022	0.0093976				0.0089795

Graph 4

VISCOSITY
OF
ALBUMIN DISPERSIONS



The viscosity of albumin dispersed in an acid solution is a linear function of the concentration as shown by graph 4. The equation for the line is $\nu = 0.8859 + 0.1013 \chi$ where ν = viscosity and χ = concentration. The albumin viscosity is low in comparison with the viscosities of the other two proteins. This is best shown by the fact that a 1.0% dispersion of albumin has a viscosity that is only slightly higher than that of a 0.1% gelatin dispersion, and a 0.3% casein dispersion in acid.

TABLE VSurface Tension of Gelatin DispersionspH 4.70 \pm 0.1

Aged 24 hrs.

$\%$	Dynes per cm.	$\%$	Dynes per cm.
0.1	63.733	0.6	56.686
0.2	62.220	0.7	56.182
0.3	60.657	0.8	55.512
0.4	59.033	0.9	55.009
0.5	57.860	1.0	54.673

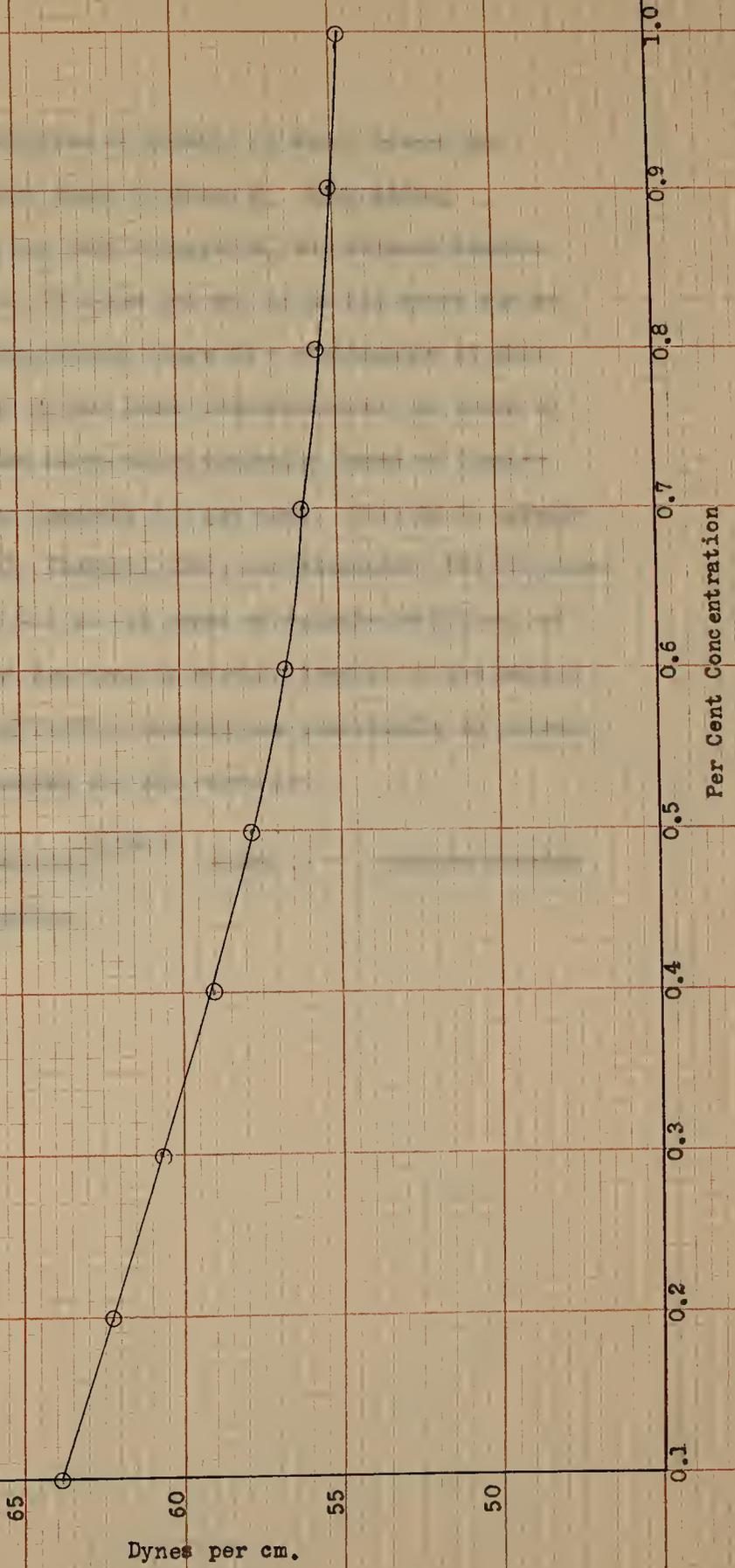
TABLE VISurface Tension of Casein DispersionspH 3.09 \pm 0.4

Aged 24 hrs.

$\%$	Dynes per cm.	$\%$	Dynes per cm.
0.1	47.630	0.9	41.592
0.2	46.288	1.0	44.611
0.3	42.263	1.5	44.946
0.4	41.258	2.0	44.946
0.5	40.921	2.5	44.946
0.6	39.579	3.0	44.946
0.7	39.245	3.5	44.946
0.8	41.258	4.0	44.946

Graph 5

SURFACE TENSION
OF
GELATIN DISPERSIONS



That the addition of gelatin to water lowers its surface tension is best shown by Graph 5. Upon adding gelatin to make a 0.1 per cent dispersion, the surface tension of water drops from 71.73 dynes per cm. to 63.733 dynes per cm. With increasing concentrations there is a continuance of this decrease, more marked in the lower concentrations, as shown by the steep slant of the curve which gradually tends to flatten as the concentrations approach 1.0 per cent. This is in accordance with Bancroft(6), Zlobicki (53), and Alexander, (2) who found that the addition of 0.5 to 0.8 grams of gelatin to 100 cc. of water causes a marked decrease in surface tension of the water, while the addition of further amounts has practically no effect. The best fitting equation for the curve is:

$$S = 64.915 e^{-0.189\chi} \quad \text{where } S = \text{ surface tension}$$

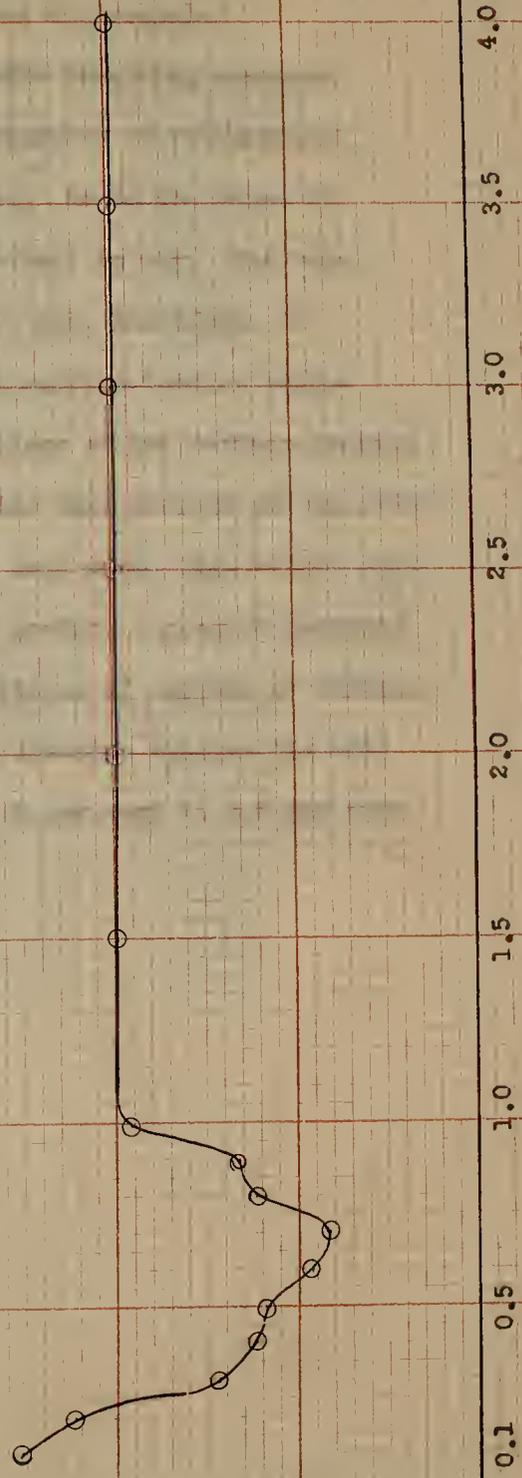
and χ = concentration.

Graph 6

SURFACE TENSION
OF
CASEIN DISPERSIONS

Dynes per cm.

Per Cent Concentration



The surface tension of the casein dispersion in acid solution as shown by Graph 6, shows an irregular decline, and then a like increase finally remaining constant from 1.5 per cent to 4.0 per cent. Naturally no mathematical formula could be derived for this curve. As to the cause of the above mentioned irregularity it is hard to say. The same solution gave normal viscosity results, and, therefore, it would be natural to expect that normal surface tension values would be obtained. Several determinations of the surface tension of casein dispersed in the acid solution were carried out in order to check on this irregularity, but in each case, like values were obtained. Acid dispersions of casein produce a greater decrease in surface tension than like concentrations of gelatin or albumin dispersions. There is only a slight variation between the acid and basic dispersion of casein from 1.5 per cent to 4.0 per cent.

TABLE VIISurface Tension of Casein Dispersions

pH 9.09 ± 0.2

Aged 24 hrs.

<u>%</u>	<u>Dynes per cm.</u>	<u>%</u>	<u>Dynes per cm.</u>
0.1	51.488	0.9	44.108
0.2	50.649	1.0	43.403
0.3	49.307	1.5	43.336
0.4	48.300	2.0	43.269
0.5	46.791	2.5	43.269
0.6	46.288	3.0	43.069
0.7	45.617	3.5	43.001
0.8	44.944	4.0	42.934

TABLE VIIISurface Tension of Albumin Dispersions

pH 1.97 ± 0.2

Aged 1 hr.

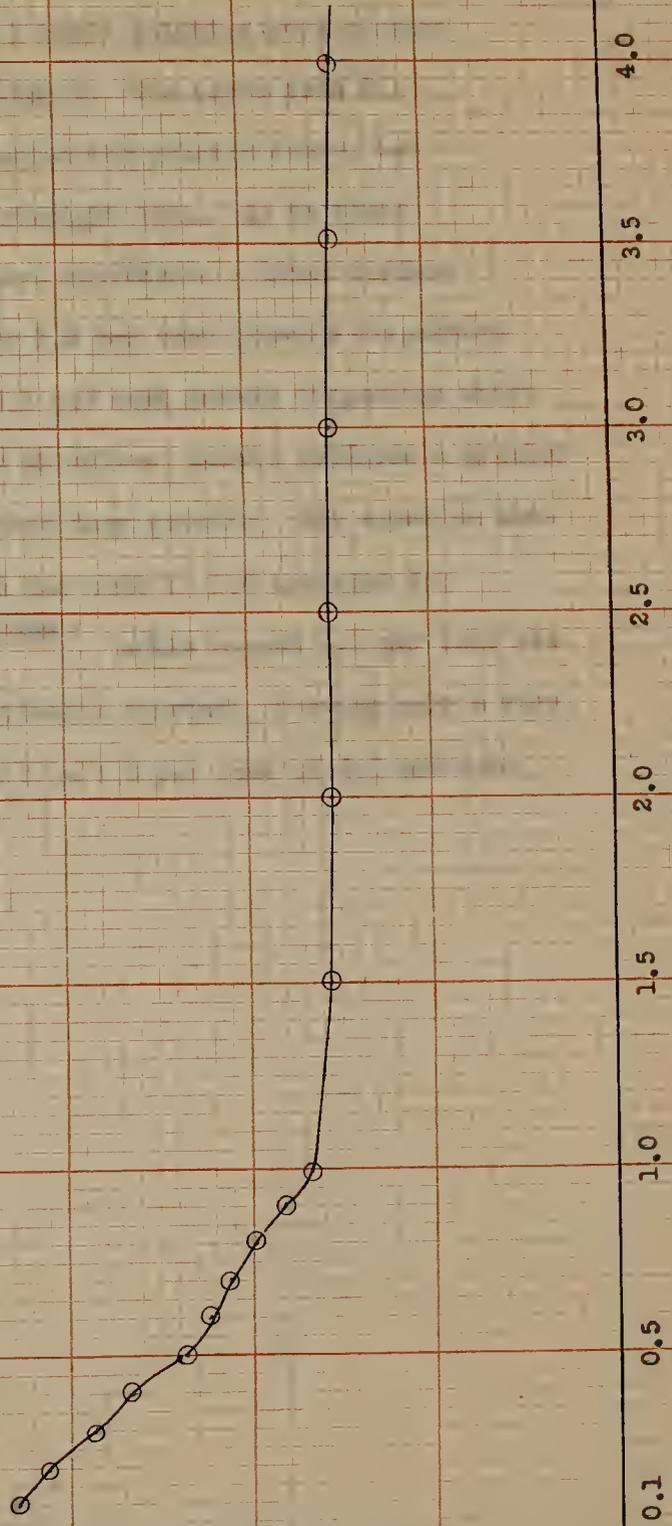
<u>%</u>	<u>Dynes per cm.</u>	<u>%</u>	<u>Dynes per cm.</u>
0.1	55.009	0.6	52.661
0.2	54.673	0.7	52.492
0.3	53.667	0.8	52.325
0.4	53.333	0.9	52.191
0.5	52.996	1.0	52.157

Graph 7

SURFACE TENSION
OF
CASEIN DISPERSIONS

Dynes per cm.

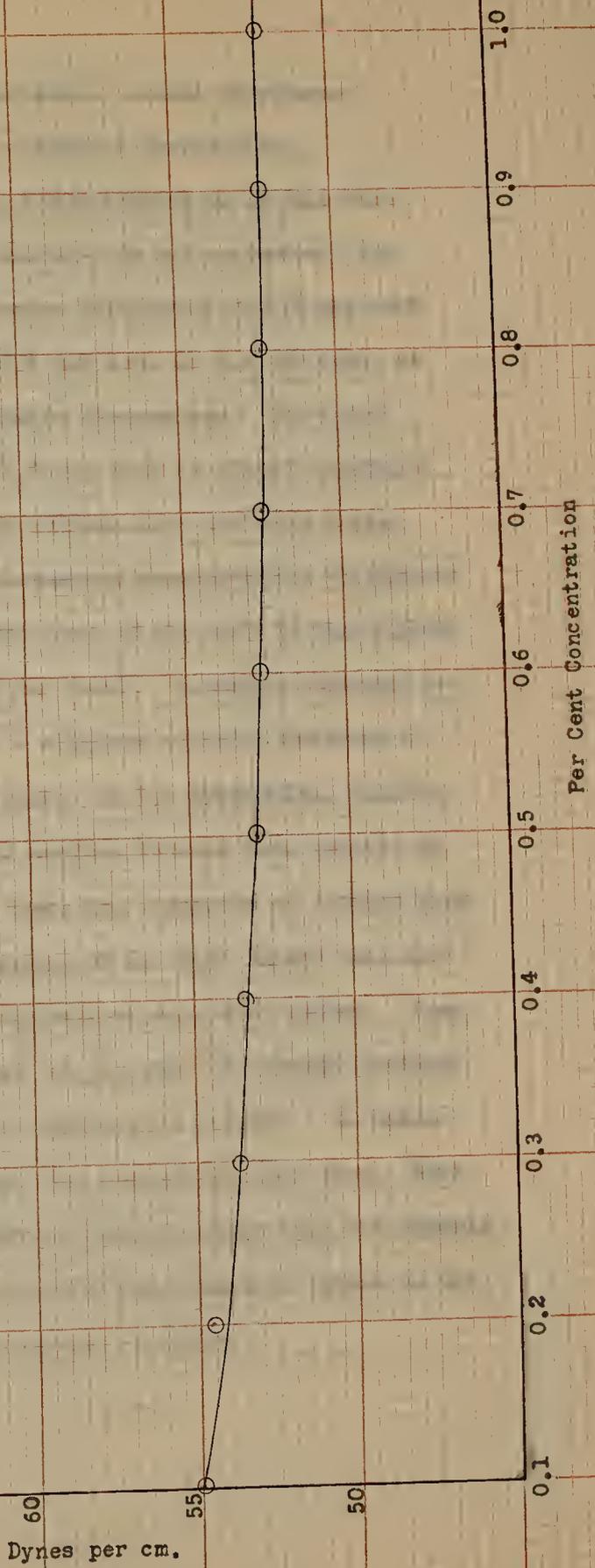
Per Cent Concentration



Casein dispersed in a basic solution gave surface tension results as shown by Graph 7. The curve from 0.1 per cent to 1.0 per cent resembles the gelatin curve, but from there on it is almost a straight line. As to their relative values the casein curve represents a lower surface tension, in fact the value for 1.0 per cent gelatin dispersion is higher than that for the 0.1 per cent casein dispersion which shows that at these respective pH values, casein produces a greater decrease in surface tension than does gelatin. The equation that best fits this curve from 0.1 per cent to 1.0 per cent is:

$S = 52.488 e^{-0.19149 X}$ while beyond 1.0 per cent the surface tension remains practically constant, showing only a very slight decrease over a range from 1.0 per cent to 4.0 per cent.

SURFACE TENSION
OF
ALBUMIN DISPERSIONS



The effect on surface tension caused by albumen is shown by Graph 8. There is a similar decrease in surface tension with increasing concentration as is the case with gelatin, but the rate of decrease is not so marked, and the "flattening out" effect becomes noticeable at 0.4 per cent to 0.5 per cent instead of at 0.8 per cent to 0.9 per cent, as observed in the case of the gelatin dispersions. The total decrease from 0.1 per cent to 1.0 per cent is almost one-third of the total decrease caused by gelatin over the same range. But the surface tension for the weakest concentration of albumin (0.1 per cent) is identical with that of the next to the highest concentration of gelatin (0.8 per cent). Therefore although increasing concentrations cause a slighter relative decrease in surface tension, however, by virtue of its properties, albumen produces a greater lowering of surface tension than gelatin at their respective pH values. Since the viscosity of albumen does not vary appreciably with changing pH we might expect that the surface tension would not be altered to any great extent. From this assumption we can say that at the same pH albumen produces a greater decrease in surface tension than gelatin. No mathematical formula could be found that would fit this line. Both of the caseins have lower surface tension values than the albumin which places albumin between gelatin and casein in regard to its ability to lower the surface tension of water.

CONCLUSIONS

Gelatin dispersions show the greatest rate of increase in viscosity with increasing concentration. A 1.0 per cent gelatin dispersion is more viscous than a 4.0 per cent dispersion of casein in acid. This shows that a low percentage of gelatin gives a marked increase in viscosity when compared with a similar percentage of the other proteins.

Casein dispersed in an acid solution results in a more viscous dispersion than does casein dispersed in a basic solution. In fact, a 4.0 per cent dispersion of casein in acid is almost twice as viscous as a 4.0 per cent dispersion of casein in base.

The viscosity of albumin dispersions is of very low magnitude, being only a little greater than that of water. Of the proteins used, albumin is the only one that has a viscosity a linear function of its concentration. This low degree of viscosity is due to the fact that the albumin dispersion contains particles of smaller size than in the case of the gelatin and casein dispersions.

Gelatin lowers the surface tension of water, but does not lower it as much as do the other proteins studied. The lowering seems to be governed by the law of diminishing returns, since the lower percentages cause more of a relative decrease than do those around 0.8 per cent and 0.9 per cent.

Casein dispersed in acid has an irregular effect on surface tension. From 1.5 per cent to 4.0 per cent the dispersions have the same surface tension which shows that above 1.5 per cent the addition of further casein has no effect on surface tension.

Casein dispersed in base shows a normal decrease in surface tension, reaching a constant value that is very near that of the casein in acid.

Albumin dispersed in acid stands between gelatin and casein in respect to its ability to lower surface tension.

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