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Solidified Alcohols

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SOLIDIFIED ALCOHOLS

by

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PREFACE

The relatively new field of science, colloid chemistry, has risen to become an important addition to man's knowledge of the behavior of matter in the natural world and in the laboratory. Although it can no longer be viewed as a new science, it is still new enough to contain unexplored fields and to intrigue the investigator.

The study of gel formation has been received with interest by chemists of the nineteenth and twentieth centuries. This phenomenon of sudden gel formation instead of the expected crystalline precipitate while extracting with alcohol was encountered often in experimental work.

The inquisitive mind would enhance investigation; and so it was that a use of the alcohol gel, commonly termed "solid alcohol", came into prominence. The nature of alcohol itself suggests inflammibility, rapid evaporation, and superior penetrating action for cleansing and medicinal preparations.

This solid form of alcohol was unique. The addition of a small amount of solidifying agent such as soap, calcium acetate, or sodium benzoate, caused the entire liquid content of alcohol to set to a solid mass.

And what of the physical and chemical nature of these gels? Much theorizing has been done attacking the problem from the point of view of the alcohol itself and, also, the gelling agent.

The project at hand is an opportunity to learn. No definite conclusion has previously been stated to explain these false gels. The field of "solid alcohol" is waiting for extension and further research. Higher chain alcohols and various gelling agents will be employed experimentally and the results presented.

The author wishes to express her sincere appreciation to Dr. S. Kittsley for reading this manuscript and for the many helpful suggestions which he has made.

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INTRODUCTION

Schiller has well said: "To one man science is a sacred God, to whose service he is happy to devote his life; to another she is a cow who provides him with butter."(16)So it was with alchemy,and so it is with most scientific developments that man's needs are viewed and developments spring forth from the concept of supply and demand. A chemist searches for new substances and, possessing a knowledge of the properties of the elements and innumerable compounds, he contemplates new uses for those things which are already known. The experimental science of chemistry advocates the proposition that the only way to find out whether something is practical is to try it.

The actual discovery of "solidified alcohol" is said to be the outcome of an attempt on the part of an unscrupulous person to fool the Paris custom officials. He mixed white graded soap with alcohol and produced an homogenous solution which when set to a solid, was cut into small cakes. These passed the custom without difficulty and all that remained was for the alcohol to be distilled from the solid. This scheme was uncovered and the inventor found his ingenuity rewarded by a term of imprisonment at Fresnes.(1) While there is no valid reason for doubting this story, it is certain that this is not the first occasion which solidified alcohol was mentioned. Work upon this subject began in Germany in 1887, at least twenty years before that attempted fraud on the Paris Customs.

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(16) Moore, F. J. History of Chemistry, New York, McGraw-Hill Book Co., Inc., (1939) 16.

(1) Alexander, J. (ed) Colloid Chemistry, New York, Chemical Catalog Company, (1932) 617.

Preparations using alcohol in a hardened form may be grouped into two classes according to the use for which they are intended. Most of the early patents had as their object the making of a solid fuel and employed soaps as their hardening agents. By varying the amounts of soap, products were obtained which could equally well serve as detergent agents. As a result of this, the first class has been further subdivided into a group comprising fuels, which could be used as soaps by varying the amounts of hardening materials and into a group of fuels proper. The second class comprising more recent patents, includes soaps, and medicinal and toilet preparations.

Since the War of 1914-1918, there have been few patents for solid alcohol fuels. Two outstanding reasons have rendered the solid fuel of limited practical value; improvements in the methods of transporting liquid fuels; and the ease with which the liquid fuels may be utilized in internal combustion engines. Solid fuels consisting of hardened liquids have been used for curling tong heaters, laundry irons, portable spirit stoves and firelighters, but on the larger scale, coal briquelles, prepared from small coal or coal dust and suitable binding compositions, have completely displaced solidified alcohol.

Quite to the contrary, medicinal and toilet preparations having alcohol as their bases are being used to an increasing extent due to their superior cleansing and astringent properties. The early transparent soaps were usually made by shredding and drying the soap, and dissolving it in alcohol or methylated alcohol. The bulk of the spirit was distilled off and so recovered, the resultant mass being dried in the air to enable the residual alcohol to evaporate at normal temperature. As the soap was kept it became more and more transparent. The reason for this transparency was supposed to be the separation of the soap from the solution as a "true colloid."(14-17)A more recent investigation tends toward the view that soap exists as a simple unpolymerized electrolyte in true solution in alcohol.

This is especially the case with the oleates and there is little doubt that they are very much simpler in alcoholic solutions than other soaps. This fact accounts for the indifferent value of oleates as solidifying agents in comparison with stearates and palmitates. Potassium oleate is a typical simple electolyte moderately dissociated, whereas oleic acid although a normal electrolyte is very ionized. The sodium salt is so strongly ionized, especially near the boiling point of the solution that it does not obey the Ostwald dilution law. The amount of theoretical work done upon this subject is very small, but it shows that although it is possible to obtain gels by "salting out" sodium oleate solutions in water by the addition of alcohol, those gels are not very stable and are of little commercial value. This fact seems to have been known to the earliest workers in this

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(14) Laing, M. E., Trans. Chem. Soc., 113, (1918).

(17) Patrick, W. A., J. Phys. Chem., 29, (1925).

field, principally as a result of experimental work undertaken without any theoretical background, for every attempt to solidify alcohol with soap employed the harder soaps rather than the oleates, which tend to soften the final product.

Considering now soap as a solidifying agent for alcohol the earliest attempts to prepare a solid fuel from an alcohol were due to R. Hirsch, who in conjunction with Otto N. Witt, pointed out that a transparent soap containing small quantities of spirt did not differ essentially from mixtures containing larger quantities. They were all solid solutions. He succeeded in preparing a solid solution containing 99.5% alcohol and 0.5% soap. Small portions of water free sodium soap were dissolved in water free alcohol. The mass solidified when cool and had a melting point near the boiling point of the alcohol. On the addition of water greater amounts of soap were dissolved, but with increasing amounts of water the product became softer and softer and finally did not set. Moreover the amount of soap which could be dissolved and the hardness of the end product depended upon the fat in the soap. Fats such as coconut fat gave hard products. The most stable products and those with the highest melting points were given by stearic acid soaps, which were also very suitable for the preparation of alcohol soaps for toilet purposes. (12)

In 1898 H. Hempel attempted to put the production of solidified alcohol upon a commercial basis. In several

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(12) Hirsch, R. & Witt, O. N. Chem. Ind. 18. 475. (1895).

patents, he described methods of making it from ordinary animal fats, which were cheap and easily obtained.(1) According to the earliest of his patents, Hempel employed saponified animal tallows, obtained from sheep and deer especially, and stearic acid. One hundred parts of the tallow were warmed with twelve and one-half parts of stearic acid until molten. The mass was then thoroughly mixed by stirring. On cooling it was saponified with sodium hydroxide and the cold mass pulverized. One part of the pulvarized mass was dissolved by warming in about twenty-five parts of 80% alcohol. On cooling a solid alcohol was obtained. On account of the small proportion of solidifying material used, this fuel burnt with very little residue. (24)

Another hardening material prepared in a similar manner to that of Hempel, utilized coconut oil and sodium laurate. The soap became, to a certain extent, spongy in appearance and absorbed the alcohol into its pores, the resulting product having a fairly good lasting properties when placed in air-tight containers. (8)

E. Skriwan modified this method by employing with his soap-producing substances, certain inorganic materials and wood pulp(1) while H. Mayer employed paraffin wax and resin. (1)

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(1) Alexander, J. (ed) <u>Colloid Chemistry</u>. New York. Chemical Catalog Company. (1932). <u>Vol</u>. <u>4</u>. 619.

(24) Hempel, H. D. R. P. 152,682. 1898.

(8) Hempel, H. <u>Seifensieder Ztg</u>. <u>31</u>. 33. (1904).

(1) Alexander, J. <u>Ibid</u>. 620.

Instead of the latter two, gums were also used, the effect being to prevent rapid evaporation of the alcohol.

It was found that if the soap itself is produced in the alcohol while warm, the solution sets on cooling and R. Fallnieht employed this reaction. (3)

An outstanding disadvantage of the solid fuels previously described was that in burning they produced a large amount of soot and left a bulky residue behind them. Strobl found that the sooty flame was due to the ethyl alcohol in denatured alcohol (90% ethyl alcohol, 10% methyl alcohol with a trace of benzene).(1)Consequently, he used methyl alcohol, either alone or mixed with the denatured alcohol. The greater the proportion of methyl alcohol used, the less the amount of soot formed during combustion of the fuel.(19)This idea was still further exploited by H. L. Fisher. He mixed ethyl and methyl alcohol in the proportion of 3 to 1 containing about 4% water, which improved the product. (4)

A more recent patent of H. S. Mork and G. J. Esselen sought to embody in one fuel the various improvements outlined by previous patentees. The objects of the patent were to prepare a fuel which would burn quietly, and not liquify during the process. This liquifying had not been realized by any of the foregoing patents. The fuel was to be readily ignited and to leave but small residue. Attention was focused on economical manufacture, evaporation losses being reduced to a

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(3) Fallnicht, R. English Pat. 15030. (1899).

(1) Alexander, J. (ed) *Colloid Chemistry. 4.* New York. Chemical Catalog Company. (1932). 621.

(19) Strobl, A. U. S. Pat. 1,277,149. (1918).

(4) Fisher, H. L. U. S. Pat. 1,389,638. (1921).

minimum. The fuel being non-explosive, presented no outstanding transport difficulties. It comprised three substances: a saponaceous base, a combustible alcohol solvent, and a volatile combustible liquid or mixture of liquids, the major portion of which was non-alcoholic in character and function. Stearic or any other saturated non-volatile fatty acid was dissolved in alcohol, and the solution heated to a temperature just below the boiling point of alcohol. A non-volatile alkali was added in sufficient quantity to neutralize the acid giving us the saponaceous base in alcohol.

$$C_{17}H_{35}COOH + NaOH \quad \overset{\text{alcohol}}{\text{sol.}} \quad C_{17}H_{35}COONa \quad H_2O$$

A slight excess of alkali was not detrimental. The third substance, a non-solvent for the soap was added, (example-acetone) and any soap which may have been thrown out of solution during the addition of this substance was redissolved by heating the mixture.

It was then poured into cans, in which it congealed on cooling. Since the acetone was a non-solvent for the soap, it helped to retain it in the solid form during burning and, moreover, modified the surface crust, making it less dense. Owing to the higher vapor pressure of acetone, than either methyl or ethyl alcohol, acetone facilitated the relighting of the fuel. Either alcohol might be used instead of both, and little water was permissible. Liquids other than acetone, having the effect of reducing the solubility of the soap and raising the gelatinizing temperature could be used, e.g.

commercial acetone, or methyl acetate. Palmitic acid ($C_{15}H_{31}COOH$) may replace the stearic, being saturated and possessing one less CH_2 group, while the soap, itself, could be used instead of its being prepared in the alcohol. Potassium hydroxide might be used as an alternate neutralizing agent. (15)

Having viewed soap as a solidifying agent for alcohol, the conclusion is that there is a definite disadvantage in the use of soap for production of fuels in that the calorific value of the fuel is considerably reduced by the addition of soap. Also, there is a disadvantage arising from the porosity of the soap, for the alcohol tended to separate from the solidifying agent and sink to the bottom of the container. Due to this the flame might spread quickly over the fuel, with every possibility of explosion. This disadvantage was mitigated by the introduction of wool into the fuel. This absorbed the liquid as it separated. Unfortunately such fuels left residues which made the container very dirty. To overcome this, fixing materials have been used in conjunction with the hardening material having soap as a basis. The success of some of these substances has emboldened patentees to use them by themselves without the soap, so that the majority of the recent patents dispense with soap altogether.

Consider now the use of other solidifying agents for alcohol. Organic materials which leave no residue on burning have been generally, although not exclusively, employed. Compounds which contain oxygen are especially useful in so far that they provide the oxygen necessary for burning, and

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(15) Mark, H. S. & Esseln, G. U.S. Pat. 1,545,595. (1925).

hence promote rapid and uniform combustion.

There are many patents making use of cellulose derivatives of which nitrocellulose in various forms and cellulose acetate are the most favored because of their superior oxygen content and the consequent more complete gasification of the fuel. The property of nitrocellulose of giving gels in alcohol-ether solution has been utilized for the manufacture of a solid fuel for many years. In his book on "Industrial Alcohol" published in 1907, Brachvogel described solid fuel, which uses alcohol containing a little ether and gun cotton. This fuel is said to keep for upwards of twelve months in closed vessels, although the alcohol evaporates on exposure to air. The fuel was marketed under the name of "Smaragdin."

E. Raynaud made use of sodium silicate as a fixing material to be used in conjunction with soap. Of interest here is the fact that this was the first time that a purely inorganic material was used for the preparation of solid fuel. Use was made of the gelatinous properties of the silicates, and it is not surprising to find that the hardening mixture was principally sodium silicate. The larger the proportion of the silicate, the smaller the amount of mixture that had to be used for solidifying a definite weight of alcohol. Such a mixture was used for hardening other hydrocarbons especially petroleum products. (18)

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(18) Raynaud, E. U. S. Pat. 879,193. (1903).

A complete departure in the method of hardening fuels was attempted by C. Baskerville, who used a quasi-inorganic substance as his hardening agent. To the alcohol he added about 10% of a saturated solution of calcium acetate with a trace of stearic acid. The purpose of the acid was not to harden the alcohol, but to neutralize the alkali produced during combustion. When calcium acetate is burnt calcium carbonate and acetone are produced. The acetone is consumed, but provided the temperature is high enough, the carbonate decomposes to lime and carbon dioxide. The lime reacts with the water present producing an alkali. (2)

Thorne and Smith in their investigation, also, found that the addition of dehydrating agents, acetone and pyridine, for example, have the effect of increasing remarkably the stability of the gel by delaying the process of crystalization(20-21

Sufficient has been written upon the methods of solidifying alcohol to show the agents employed are drawn from almost every class of substances. Many of them depend upon their natural gelatinous properties while others cause solidification because of their insolubility in alcohol. This is especially the case of the behavior of calcium acetate, which is not alone in promoting gel formation in alcohol. Other organic compounds found to form gels are l-arabinosazone, camphoryl phenyl thiosemi-carbazide,

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(2) Baskerville, C. U.S. Pat. 1,208,265. (1916).

(20) Thorne & Smith. *Kolloid Z.* *48*. 113. (1919).

(21) Thorne & Smith. *Kolloid Z.* *54*. 181. (1913).

5-dimethyl-amino-anilino-3-3 diphenyl cyclo-pentane-1-2-dione, benzoylcystine, benzoyltyrosine, sorbitol acetate, eucupine acetate, and quinine sulfate. (7)

In 1933, Henstock began a series of papers concerned primarily with alcogels, the dispersion medium being the alcohol and the dispersed parts composed of the simple organic acid salts of the alkali metals and of calcium. The first of this series was discovered when an attempt was made to purify calcium acetate, obtained from another experiment, by precipitating it from concentrated aqueous solution on the addition of absolute alcohol. Instead of the expected crystalline salt, a translucent, but not quite transparent jelly appeared. (9)

Henstock investigated calcium acetate gels with ethyl alcohol and mixtures of methyl alcohol and lower aliphatic alcohols. He devoted special attention to methanol gels. Although methyl alcohol, alone, does not form a gel with calcium acetate, the salt being soluble in the alcohol, the addition of other alcohol to methanol produced gels on the addition of the salt. In a brief resume of his paper in 1938, he summarized by saying that gels were formed by some of the simpler organic acid salts of the alkali metals and of calcium (examples: calcium acetate, sodium benzoate, and potassium ethyl sulfate) in methanol solution, on the addition of a suitable organic liquid as a dispersion medium.

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(7) Hartman, R. J. Colloid Chemistry. New York. Riverside Cambridge Press. (1939). 408.

(9) Henstock, H. Trans. Faraday Soc. 29. 1101. (1933).

(usually lower chain alcohols). The ultimate seat of gel formation was the salt solutions which were investigated by means of adsorption experiments. He proposed that the idea of molecular aggregation in varying degrees as the reason for gelation, which is, also, partly due to the large atomic volume of the metals concerned.(11)

The problem in this project will be the investigation of calcium acetate gels using lower and higher chain aliphatic alcohols, an aromatic alcohol, and, also, an unsaturated alcohol as a dispersion medium for the gelation process. Various acetates will be investigated for their gelling property. Saturated aqueous solutions of the salts will be employed as hardening agents. This is contrary to Henstock's thorough investigations using methanol solutions. He did use aqueous solutions of calcium acetate with ethyl alcohol, but his interests were directed toward the methyl alcohol gels. He states that those liquids which form gels with saturated calcium acetate solution are miscible with water and include the lower chain aliphatic alcohols except methanol, acetone, ethylacetate, and others. In this paper each alcohol will be examined for its gelling power separately by varying the composition and determining which composition, if any, gives the solid gel. Also, various metallic acetates will be tested in like manner.

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(11) Henstock, H. J. Am. Chem. Soc. 61. (1939). 673.

Another project of interest is the use of sodium benzoate as a gelling agent. Henstock began this investigation and concluded that ethanol and the series of saturated alcohols up to a butanol formed fairly solid white opaque gels with six volumes of precipitant to one volume of saturated solution.(10) This will be investigated further with aromatic and higher chain and aliphatic alcohols and the required composition for gelation determined.

Henstock introduced the method of using the methanol solutions of the salts and adding a suitable organic liquid as dispersion medium. In this study of gels, 1,1, 1 trichloro, 2 methyl propanol^{2} in methanol solution will be tested for solid gels by the addition of calcium acetate and sodium benzoate.

The previous work done will be correlated, and the conclusions that were drawn, will be compared to the results here obtained. Some new conclusions may be drawn, and the findings should affirm or deny the previous conclusions.

As a conclusion to the preview of the work done to date in the field of "solidified alcohols", the alcoholic soaps should be mentioned. Anything which would increase the foam, would increase the washing powers of soap. Since alcohol reduces the surface tension of aqueous solutions and water, itself, and, therefore, increases the foam, it should enhance the washing power of a soap. Such is found to be

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(10) Henstock, H. *Trans. Faraday Soc. 30.* 560. (1934).

its behavior when incorporated in the soap. Moreover, owing to their greater power of dissolving fats, soaps containing alcohol possess distinct advantages over the ordinary aqueous soaps. Due to its superior wetting powers, alcohol can penetrate further into the pores of the skin. It, therefore, extracts the dirt particles from the depth of the pores, and introduces them into the foam. If the hands are washed with ordinary soap and then dried, and the apparently clean hands rewashed in alcohol soap, the water from the second washing will contain as much or even more dirt than the water from the first.

A. Kolliger has given a very valuable resume of the work done upon the germicidal properties of alcohol regarded from the medical standpoint. Alcoholic soaps are especially adapted for the admixture of disinfecting agents. This is due to the superior dissolving powers of the alcohol toward the bactericides, which are usually organic compounds (like dissolves like). (13)

It was very necessary that the soap should be solid or at least semi solid. This solid form of alcohol has at the present day more importance commercially than the fuel due to the disadvantages previously enumerated. A drawback possessed by many of these soaps was that syneresis set in on standing, or when they were subjected to pressure. This difficulty was overcome by carrying out the preparation in an autoclave under pressure instead of under a reflux condenser,

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(13) Kolliger, A. Chem. Ztg. 45. 649. (1921).

the usual method of preparing the soaps. Owing to the use of high pressure, six atmospheres as a rule, it was possible to carry out the preparation at a much higher temperature. The effect of this seemed to be to give the soap a definite structure in which the alcohol was firmly retained. The foam building and cleansing properties of the soap were twice as powerful as those of ordinary aqueous soaps. The quality of the soap was still further improved by using soaps prepared in alcoholic medium rather than soaps prepared in water.

The alcoholic base has been used as an improvement in many face creams. The ordinary cream applied in a thin layer to the skin is impervious to the air, and tends to open the pores of the skin promoting an unnatural and unpleasant sweat. The presence of an astringent closes the pores and gives the skin a soft and natural appearance. The use of astringent alone would cause dryness of the skin, which is equally undesirable. By incorporating with the cream a substance such as eau de cologne, which has an alcoholic base, both of these unpleasant features are obviated. In addition, the presence of the saponaceous base with the cream produces a cleansing effect, which could not be obtained by eau de cologne alone. "Frozocolone" is a preparation of this type. (22)

Alcohol has been employed as a base for medical preparations because of its superior penetrating power. These medical

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(22) Weeks, C. English Pat. 251,948. (1927.)

preparations have as their object the relief of various muscular disorders and rheumatism.

II EXPERIMENTAL WORK

A. The rapid mixing of the solutions was done effectively in six inch test tubes. A cork was provided. Erlenmeyers were first employed, but the original proportions (7) described wasted the chemicals,so smaller portions, maintaining the same ratios of alcohol to gelling agent, were found to give just as satisfactory results.

B. Saturated aqueous solutions of the following chemicals were prepared:

Table I

	Solubility in one hundred parts of solvent	
Name	Sol./water	Sol./alcohol
calcium acetate	52.0^{0°; 45.5^{80°	sl.s.alc.
sodium benzoate	62.5^{25°; 76.9^{100°	2.3^{25°
methyl acetate	57.1^{20°; 33^{22°	infinitely
sodium acetate	119^{0°; 170.15^{100°	$2.1^{1.8^\circ}$
zinc acetate	40^{25° 66.6^{100°	vs alc.
barium acetate	75^{30° 79^{40°	insoluble
aluminum acetate	s.cold; d (hot)	insoluble
dromic acetate	s. cold	-

The following alcohols were used:

Table II

	Solubility in one hundred parts of solvent	
Name	Sol/water	Sol/alcohol
methyl alcohol	infinitely	infinitely
ethyl alcohol	infinitely	
propyl alcohol	infinitely	infinitely
isopropyl alcohol	infinitely	infinitely

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(7) Hartman, R. J. Colloid Chemistry. New York. Riverside Cambridge Press. (1939). 407.

Name	Sol/water	Sol/alcohol
N butyl alcohol	9.0(15°)	infinitely
secondary butyl alcohol	12.5(20o)	infinitely
isobutyl alcohol	10.0(15°)	infinitely
tertiary butyl alcohol	infinitely	infinitely
amyl alcohol	2.7(22°)	infinitely
pentanol - 2	4.0(20°)	infinitely
2-methyl - butanol - 4	2.0(14°)	infinitely
benzyl alcohol	4.0(17°)	infinitely
hexyl alcohol	0.6(20°)	infinitely
octyl alcohol	sl.s	infinitely
allyl alcohol	infinitely	infinitely
trichloro-tertiary butyl alcohol	insoluble	vs

C. TYPICAL EXPERIMENT

To 45 milliliters of secondary butyl alcohol was added five milliliters of a saturated aqueous solution of calcium acetate. (ration of 9:1) Immediately the solution was shaken and a rigid white gel formed. The gel was stable for less than 16 hours. Liquid was extruded from the gel. Small nodules formed in the gel as it started to decompose. As these nodules grew they went to the bottom of the test tube,and the liquid rose to the top. In the growth of these particles they changed from amorphous substances into crystalline substances.

TABLE III

TABULATED RESULTS

EXPERIMENTAL DATA AND RESULTS III

Alcohol	gelling agent	Vol. of alcohol ratio(to vol.g.agent)	Result
N propyl alcohol	sat.aq.sol. calcium acetate	9:1	rigid, clear, colorless gel
	sat.aq.sol. MeAcetate	9:1	clear liquid-no gel
	sat.aq.sol. NaAcetate	9:1	clear liquid-no gel
	sat.aq.sol. ZnAcetate	9:1	turbid sol.-no gel
	sat.aq.sol. BaAcetate	9:1	wt.ppt.-no gel
	sat.aq.sol. AlAcetate	9:1	emulsion-no gel
	sat.aq.sol. CrAcetate	9:1	no gel
	sat.aq.sol. NaBenzoate	6:1	rapid addition - no gel dropwise addition - borderline gelatinous ppt. - gel
isopropyl alcohol	sat.aq.sol. CaAcetate	9:1	rigid, clear, gel.
	sat.aq.sol. MeAcetate	9:1	clear liquid - no gel
	sat.aq.sol. NaAcetate	9:1	turbid suspension- no gel
	sat.aq.sol. ZnAcetate	9:1	turbid solution - no gel
	sat.aq.sol. BaAcetate	9:1	wt. ppt. - no gel
	sat.aq.sol. AlAcetate	9:1	no gel
	sat.aq.sol. CrAcetate	9:1	no gel
	sat.aq.sol. NaBenzoate	6:1	rigid white gel

Alcohol	gelling agent	ratio vol. of alcohol to vol. of gelling agent	Results
butyl lcohol	sat.aq.sol CaAcetate	9:1	rigid gel
	sat. aq.sol MeAcetate	9:1	clear sol. - no gel
	sat.aq.sol NaAcetate	9:1	cloudy sol. - no gel
	sat.aq.sol ZnAcetate	9:1	no gel
	sat.aq.sol BaAcetate	9:1	cloudy,viscous sol.-no gel
	sat.aq.sol AlAcetate	9:1	ppt. - no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	varied	no gel
ec.butyl alcohol	sat.aq.sol CaAcetate	9:1	rigid white gell
	sat.aq.sol MeAcetate	9:1	clear sol. - no gel
	sat.aq.sol NaAcetate	9:1	cloudy sol. - no gel
	sat.aq.sol ZnAcetate	9:1	two layers - no gel
	sat.aq.sol BaAcetate	9:1	clear-ten/sec. wt. ppt. no gel
	sat.aq.sol AlAcetate	9:1	cloudy sol. - no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	4:1	solid white gel

Alcohol	Gelling Agent	ratio volume of alcohol to vol. of gelling agent	results
rtiary butyl alcohol	sat.aq.sol CaAcetate	45:7	rigid gel
	sat.aq.sol MeAcetate	9:1	clear - no gel
	sat.aq.sol NaAcetate	9:1	clear, viscous sol. no gel
	sat.aq.sol ZnAcetate	9:1	turbid - no gel
	sat.aq.sol BaAcetate	9:1	turbid-five sec. ppt - no gel
	sat.aq.sol AlAcetate	9:1	turbid - no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	Varied	solid white gel
obutyl alcohol	sat.aq.sol CaAcetate	9:1	gelatinous ppt.
	sat.aq.sol.MeAcetate	9:1	clear - no gel
	sat.aq.sol NaAcetate	9:1	cloudy, viscous - no gel
	sat.aq.sol ZnAcetate	9:1	turbid - no gel
	sat.aq.sol BaAcetate	9:1	gelatinous ppt.
	sat.aq.sol AlAcetate	9:1	wt.ppt - no gel
	sat.aq.sol CrAcetate	9:1	no gel

Alcohol	Gelling Agent	ratio (volume of alc. to volume of gelling agent)	Result
butyl alcohol	sat.aq.sol NaBenzoate	1 millimeter 1 drop	solid gel
myl alcohol	sat.aq.sol CaAcetate	9:1	no gel - cloudy
	sat.aq.sol MeAcetate	9:1	no gel - turbid
	sat.aq.sol NaAcetate	9:1	cloudy - no gel
	sat.aq.sol ZnAcetate	9:1	immiscible-no gel
	sat.aq.sol.BaAcetate	9:1	turbid - no gel
	sat.aq.sol AlAcetate	9:1	ppt. - no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenz	3 millimeters: 1 drop	wt. solid gel
c.amyl alcohol	sat.aq.sol CaAcetate	9:1	no gel
	sat.aq.sol MeAcetate	9:1	no gel
	sat.aq.sol NaAcetate	9:1	no gel
	sat.aq.sol ZnAcetate	9:1	immiscible - no gel
	sat.aq.sol BaAcetate	9:1	no gel
	sat.aq.sol AlAcetate	9:1	two layers - no gel
	sat.aq.sol CrAcetate	9:1	ppt. - no gel
	sat.aq.sol NaBenzoate	6:0.2	wt.solid gel

lcohol	Gelling Agent	ratio (volume of alc. to vol. of gelling agent	Result
amyl alcohol	sat.aq.sol CaAcetate	9:1	cloudy - no gel
	sat.aq.sol MeAcetate	9:1	no gel
	sat.aq.sol NaAcetate	9:1	cloudy - no gel
	sat.aq.sol ZnAcetate	9:1	no gel
	sat.aq.sol BaAcetate	9:1	turbid - no gel
	sat.aq.sol AlAcetate	9:1	wt.ppt - no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	3 millimeters: 1 drop	white gel
xyl alcohol	sat.aq.sol CaAcetate	9:1	no gel
	sat.aq.sol MeAcetate	9:1	no gel
	sat.aq.sol NaAcetate	9:1	no gel
	sat.aq.sol ZnAcetate	9:1	two layers - no gel
	sat.aq.sol BaAcetate	9:1	no gel
	sat.aq.sol AlAcetate	9:1	no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	9:0.1	rigid, blue luminous gel

Alcohol	Gelling Agent	ratio(volume of alc. to volume of gelling agent)	Result
ctyl alcohol	sat.aq.sol CaAcetate	9:1	no gel
	sat.aq.sol MeAcetate	9:1	no gel
	sat.aq.sol NaAcetate	9:1	no gel
	sat.aq.sol ZnAcetate	9:1	no gel
	sat.aq.sol BaAcetate	9:1	no gel
	sat.aq.sol AlAcetate	9:1	no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	varied	ppt. - no gel

Alcohol	Gelling Agent	ratio (volume of alc. to volume of gelling agent	Result
lyl alcohol	sat.aq.sol CaAcetate	9:0.6	rigid, clear gel
	sat.aq.sol NaAcetate	9:1	no gel
	sat.aq.sol ZnAcetate	9:1	no gel
	sat.aq.sol BaAcetate	9:1	no gel
	sat.aq.sol AlAcetate	9:1	no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaZenzoate	Varied	no gel
enzyl alcohol	sat.aq.sol CaAcetate	9:1	particles - no gel
	sat.aq.sol MeAcetate	9:1	no gel
	sat.aq.sol NaAcetate	9:1	no gel
	sat.aq.sol ZnAcetate	9:1	no gel
	sat.aq.sol BaAcetate	9:1	no gel
	sat.aq.sol AlAcetate	9:1	no gel
	sat.aq.sol CrAcetate	9:1	no gel
	sat.aq.sol NaBenzoate	varied	no gel

Alcohol	Gelling Agent	ratio(volume of Alc. to volume of gelling agent	Result
,1,1, trichloro, methyl, propanol 2 ethanol solvent)	sat.aq.sol. CaAcetate (acetone added)	varied	solid gel
	sat.aq.sol. NaBenzoate	varied	no gel
vol. isobutyl alc. vol. tertiary alc.	sat.aq.sol. CaAcetate	9:1	permanent, clear gel
vol. tertiary tyl alcohol vol. isobutyl alc.	sat.aq.sol.CaAcetate	9:1	clear gel stable for 10 sec. then decomposed

IV Discussion

In 1864, Graham introduced the now universally used terms of "sol", "gel", and "peptization", and in each instance commented on the analogies to physiological processes. Thus in his paper dealing with the properties of silic acid he says:

> If I may be allowed to distinguish the liquid and gelatinous hydrates of silicic acid by the irregularly formed term of hydrosol and hydrogel of silicic acid, the two corresponding alcoholic bodies now introduced may be named the alcosol and alcogel of silicic acid. (6)

Gels are coherent systems composed of dispersion medium and dispersed parts, the latter having particles of colloidal dimension. They consist of semi-rigid, jelly-like masses which entrap the whole of the liquid present. Depending on their nature, they may be prepared by cooling, double decomposition, or change of solvent. A good example of the latter is a gel of calcium acetate. When alcohol is added to a saturated solution of calcium acetate the salt is thrown out of solution and sets to a gel. This type of gel comes under the heading of "false gel" because it is found to be unstable, that is, upon standing it breaks down into crystals and supernatant liquid.(7) The commercial name of"solidified alcohol" was adapted for this type of alcohol gel.

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(6) Graham, T. J. Chem. Soc. 17. 318. (1864).

(7) Hartman, R. J. Colloid Chemistry. New York. Riverside Cambridge Press. (1939). 407.

Gels may be subdivided into hydrogels, alcogels, benzpgels, etc., depending upon the nature of the dispersion medium. Presumably all gels possess a structure and require a finite amount of energy to distort this structure. The more rigid gels show many of the characteristics of solids, but it has been emphasized that there is a borderline region where the sols grade almost imperceptibly into gels. There is no sharp line of demarcation between the two classes.(5)

Time is an important fourth dimension which must be considered in the study of colloid systems. The term "hysteresis" as used by the workers in the field of colloids refers to the effect of past mechanical, thermal, etc., treatment on the present behavior of the colloid system and naturally involves predominately the effect of time. It has been allegorically spoken of as the "memory of colloid system", the reflection of the past treatment on present behavior.(5)

Hysteresis is a characteristic phenomenon of gels. Therefore, gel behavior is very difficult to predict or to control. In addition to knowing the exact compsition of the present system, we should, also, know the past treatment that some particular constituent has had in the factory. I want to emphasize again that the time factor is important. Unquestionably a great many of the divergent results, which

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(5) Gortner, R. A. Selected Topics in Colloid Chemistry. Ithaca, New York. Cornell University Press. (1937). 29.

(5) Gortner, R. A. Ibid. 65.

different workers have reported in the literature on what appears to be comparable series of experiments with colloid gels, would be explainable if one knew the exact history of the systems and the constituents of the system under investigation.

The term "syneresis", the extrusion of liquid from a gel, was described as characteristic of the calcium acetate gel. Ostwald has stated that syneresis is probably the most characteristic property of a gel and is exhibited to a greater or less degree by all gels in the process of aging.(5) In "false gels", of course, the syneresis is evident to a greater degree. The liquid which is extruded is not simply the pure dispersion medium but rather is a dilute solution of all the constituents present in the gel. Therefore, it may be looked upon as a dilute colloidal sol derived from a concentrated colloid system.

The fact that syneresis occurs on aging indicates very definitely that gels do not remain in an equilibrium state; accordingly, they are not amenable to physico-chemical treatment which presupposes the existence of a state of equilibrium. This fact has often been overlooked; the fact that the gels are dynamic and not static colloid systems. Attempts to deal with them as though all constituents were in complete equilibrium are likely to lead to erroneous conclusions.(5)

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(5) Gortner, R. A. Selected Topics in Colloid Chemistry. Ithaca, New York. Cornell University Press. (1937). 67.

(5) Gortner, R. A. Ibid. 69.

The tabulated results indicate which alcohols tend to give gels upon the addition of a saturated solution of these quasi-inorganic salts. Calcium acetate and sodium benzoate consistently act as the best gelling agent.

C. Baskerville in his patent made a complete departure from the ordinary method of hardening fuels and used this quasi inorganic substance, calcium acetate, as his hardening agent.(2)

Thorne and Smith took up this incentive and contributed a detailed investigation of this reaction.(20)(21) They observed that the amount of calcium acetate which was needed to make the gel depended on the amount of water in the alcohol. Ten cubic centimeters of 98 per cent alcohol required .01 cubic centimeters of saturated calcium acetate solution. This gel formed was stable for five days. Analysis of this gel showed that it contained 0.024 grams of calcium acetate in eight grams of gel (.3 per cent dry substance). If an alcohol purer than 98 per cent was employed then their analysis indicated that the gel contained a smaller amount of dry substance. After four or five days this gel became very soft. A white gelatinous mass of water-free calcium acetate appeared and the liquid was extruded. (

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(2) Baskerville, C. U.S. Pat. 1,208,265. (1916).

(20) Thorne & Smith. *Kolloid Z.* *48*. (1929). 113.

(21) Thorne & Smith. *Kolloid Z.* *54*. (1931). 181.

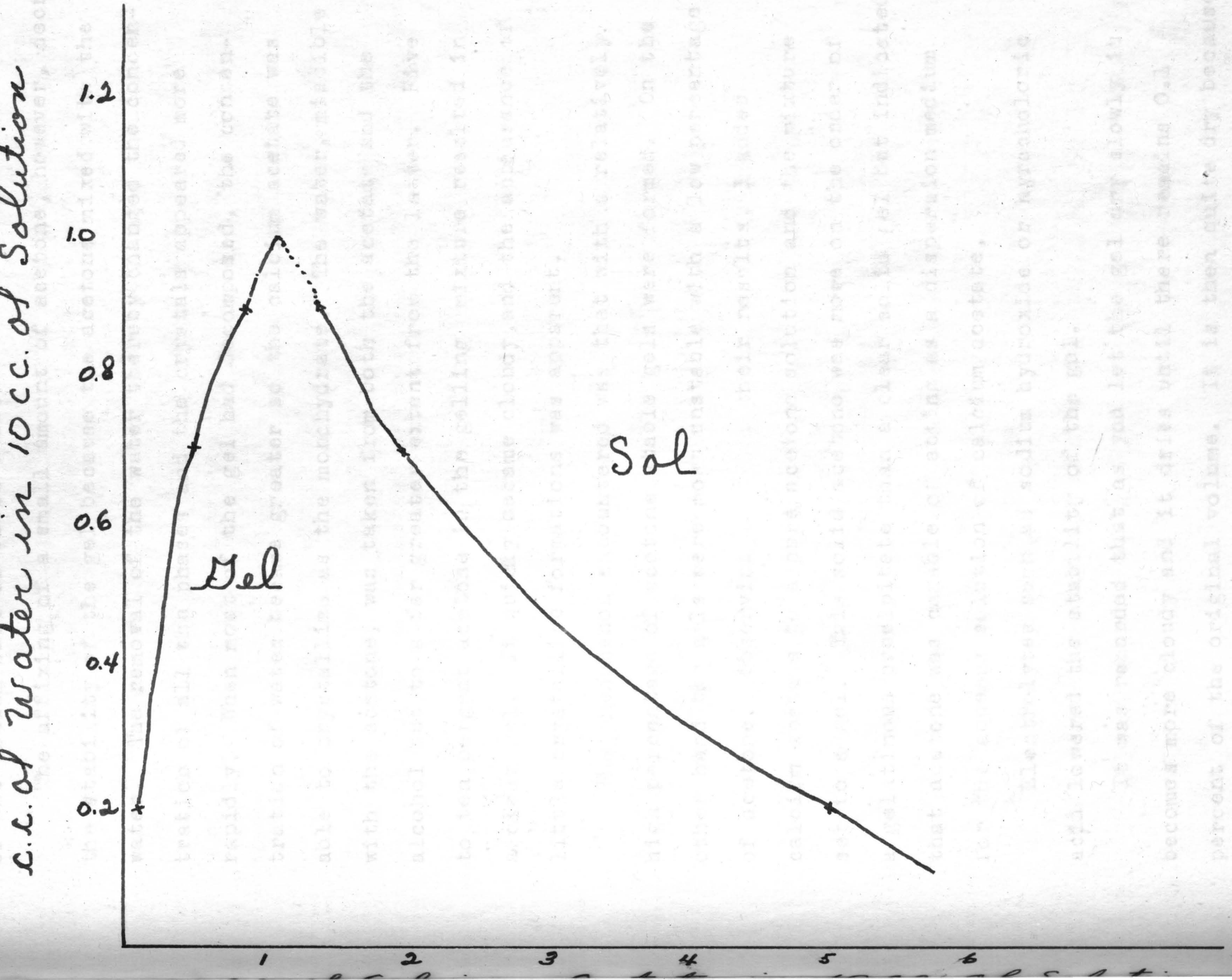
As indicated graphically 0.7 cubic centimeter of water in ten cubic centimeters of the alcohol and water solution required .5 cubic centimeters of calcium acetate, and 0.9 cubic centimeters of water in ten cubic centimeters of solution required .8 cubic centimeters of calcium acetate. Experimentally they reached a borderline for the calcium acetate addition after which they could not produce gelation. They surmised that the less water in the alcohol, the more opportunity there was for gelling and a greater space or period was indicated on the graph. The maximum amount of water permissible for forming the gel was one cubic centimeter of water in a ten cubic centimeter mixture of the alcohol and water.

These gels were reported stable for five days. Small nodules formed in the gel as it started to decompose. As they grew they sank to the bottom of the test tube and the liquid rose to the top. In the process of growth these nodules changed from amphorous to crystalline substances. They were more or less crystalline according to the amount of water present in the gel. They developed from all sides finely shaped crystals. Within two days the gel had either completely or partially broken up.

The conclusion drawn was that the making of the gel prevented crystals of calcium acetate from forming and that the whole reaction seemed to be one of delayed crystallization due to the adsorption of the alcohol by the minute crystals of calcium acetate.

DEPENDENCE OF CALCIUM ACETATE REQUIREMENT UPON THE AMOUNT OF WATER PRESENT IN THE ALCOHOL

GRAPH I.



(20) Thorne & Smith. Kolloid Z. 48. (1929). 115.

The alcohol remained solid for one month on the addition of the sodium salt of oleic acid.

The affixing of a small amount of acetone, however, decreased the stability of the gel because the acetone mixed with the water. The removal of the water thereby changed the concentration of all the phases and the crystals appeared more rapidly. When most of the gel had decomposed, the concentration of water became greater so the calcium acetate was able to crystallize as the monohydrate. The water, miscible with the acetone, was taken from both the acetate and the alcohol but to a far greater extent from the latter. Five to ten percent acetone in the gelling mixture resulted in a clear gel. It quickly became cloudy, and the appearance of little crystalline formations was apparent.

The phenomenon encountered was that with a relatively high percentage of acetone stable gels were formed. On the other hand the gels were most unstable with a low percentage of acetone. Observing these or their results, I added calcium acetate to a pure acetone solution and the mixture set to a gel. This solid acetone was more on the order of a gelatinous precipitate than a clear solid gel but indicated that acetone was capable of acting as a dispersion medium for the aqueous solution of calcium acetate.

Electrolytes such as sodium hydroxide or hyrocholoric acid lowered the stability of the gel.

It was recorded that as you let the gel dry slowly it becomes more cloudy and it dries until there remains 0.1 percent of the original volume. It is then quite dry because most of the liquid has evaporated. Finally after four to six weeks the white mass disappears suddenly. It dissolves in the small amount of water which still remains. The way to visualize the situation is that a small amount of alcohol and water are there. At the moment when the last amount of alcohol evaporates then the calcium acetate dissolves in the water.

Thorne and Smith also initiated the study of methanol gels. These differ from the aqueous gels in that methyl alcohol instead of water is used as a solvent for the gelling agent. Their experimental results indicated that there was no change in the time required for formation of the gel if methyl alcohol was used as the solvent for the calcium acetate. Also, hot solutions gave as well formed gels as cold solutions. Therefore, the gel formation is independent of temperature.

Below are listed numerically the explanation and cause of this gel formation as tabulated by Thorne and Smith. (21)

1. The getting of gels is based on the dehydration power of alcohol; that is, alcohol removes the water from calcium acetate. It takes away the solvent, water, and therefore, it causes fusing together of calcium acetate particles.
2. When the dehydration preceeds too rapidly a gelatinous precipitate is formed with a weak structure. During a slow dehydration a certain structure of the gel has been formed; therefore, a true gel is formed.

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(21) Thorne & Smith. Kolloid Z. 54. (1931). 189-90.

3. A very fast dehydration could be accomplished by the use of acetone or pyridine. The former is the better dehydrating agent.
4. A proof that dehydration takes place is given by employing organic liquids which had no affinity for water. These liquids do not have any effect on the gel formation.
5. The adding of an electrolyte with an acetate ion, for example, sodium acetate or magnesium acetate, causes a formation of a gel in the same way as an organic dehydrating agent. This is explained by the forced reversing of the dissociation of the acetate ion. The result is that the association of the calcium acetate proceeds faster.

   The dissociation probably increases with the addition of an electrolyte which reacts chemically with the calcium acetate. This type of electrolyte inhibits the gel formation. Therefore, the inorganic dehydrating agents give only inconsistent results.
6. The calcium acetate forms two different kinds of crystals during the change of the system; hair-like crystals of anhydrous salt and needles of the monohydrate.

Henstock, in his investigation, proclaims that the ultimate seat of gel formation is the salt solution which he investigated by means of adsorption experiments. He examined aqueous solutions of many salts of various metals and ammonia with a large number of different organic acids with a view of testing their capabilities of colloidal precipitation by these methods. To date he has recorded only three which appear to possess this property: calcium acetate sodium benzoate, and potassium ethyl sulphate. (11)

In a discussion of the causes of gel formation, he states that he is led to the conclusion that this formation is not dependent upon a large number of molecules of solvent taken up by anion of a salt. The sulphonates of the benzene series have this property to a high degree in aqueous solution and, therefore, should readily form gels. It has been found that none are produced by the sodium, potassium or calcium salts of benzene and other aromatic sulfonic acids in either aqueous or methanol solution. Therefore, his conclusion appears valid.

On the other hand, he concludes that gel formation seems to depend on: (11)

1. A cation having a large volume, but an element of small atomic weight.
2. An anion of fairly low molecular weight and low oxygen content, especially among carboxylic acids.
3. A fairly concentrated solution.
4. A dispersion medium or precipitant in which the salt is insoluble, but which is miscible with the solvent in all proportions.
5. To a less extent on the crystalline or amorphous nature of the salt.

For Henstock these causes did not go to the heart of the problem since he states that none, except perhaps number four, is applicable in all cases. This number four will subsequently be indicated as weak as a result of employing higher chain alcohols as a dispersion medium.

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(11) Henstock, H. J. Am. Chem. Soc. 61. (1939). 673.

(11) Henstock, H. J. Ibid. 671.

These are but slightly miscible with water.

Henstock holds to his conviction that gel formation must be closely connected with some inherent property of the salts themselves, but only when in solution in a suitable solvent coupled with a suitable dispersion medium. The salt solutions are not, strictly speaking, sols capable of forming gels on standing, cooling or other appropriate treatment, until the dispersion medium is added to them. When this has been done, the gels form so rapidly that detailed investigation of the true sols is not practicable. The most important part of these true sols, according to Henstock, is the methanol solutions which he investigated thoroughly.(11)In this paper, the main emphasis is on the gel formation with aqueous salt solutions.

With a preview in mind of the work done, the attention is focused on the results here obtained. These previously discussed men had used ethyl alcohol as a disperdion medium for gelling the solution of calcium acetate. To propyl alcohol and isopropyl alcohol were added various metalic acetates and sodiumbenzoate in definite proportions. The results are clearly given in the table. Each alcohol√in turn was treated similarly and either positive or negative gelation was indicated. In most cases the solutions were described either by indicating the phases present or the appearance of the mixture.

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(11) Henstock, H. J. Am. Chem. Soc. 61. (1939). 671.

The gels formed by the sodium benzoate solution are of the same general type as those yielded by calcium acetate, but they differ in many respects such as elasticity, transparency, speed of formation and permanency. The ratio of salt solution for these sodium benzoate gels is smaller in requirement than the calcium acetate gels. Sometimes these ratios were difficult to obtain. Isobutyl alcohol, N amyl alcohol, isoamyl alcohol, and hexyl alcohol required but one drop of sodium benzoate solution to set a six to nine millimeter volume of alcohol to a gel.

Henstock recorded that ethanol and the series of saturated alcohols up to N butanol formed fairly solid white opaque gels with six volumes of precipitant to one volume of saturated salt solution.(10)This was verified by the results here obtained. No globules appear, but the whole forms a solid mass, with some of the solid salt dispersed through it, the moment the precipitant is added. On heating to about 50°C they dissolve but unlike those of calcium acetate they will partly reform on cooling and standing for some hours. They are, therefore, partially elastic gels.

Sodium benzoate is soluble in the lower members of the series of saturated aliphatic alcohols; nevertheless, these liquids act as a dispersion medium because of the large quantity of solid present in a saturated aqueous solution. Also, the series of alcohols above and including N butyl

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(10) Henstock, H. Trans. Faraday Society. 30. (1934). 561.

alcohol, except tertiary butyl alcohol, are but slightly miscible with water (refer table II). Yet, secondary butyl, tertiary butyl, isobutyl, amyl, secondary amyl, isoamyl and hexyl alcohol, all act as dispersion mediums for this saturated aqueous solution of sodium benzoate and form solid white gels. This is an exception to Henstock's fourth cause which he held as the only one apparently without exception.

Henstock reported that no other benzoate produced an aqueous gel. He suggested, therefore, that this property of the sodium salt might be used for the identification of the benzoate ion. (10)

A problem was encountered with 1,1,1, trichloro 2 methyl propanol 2($C_4H_7OCl_3$), commonly termed chloretone. It is a solid alcohol and in order to test it as a dispersion medium, it was necessary to use a solvent. It is soluble in methanol. The solution was prepared and calcium acetate was added. No gel formed. A goodly amount of acetone was added, and the mixture set to a solid, clear gel. Syneresis occured almost immediately, therefore, the gel was unstable.

There was some doubt as to whether the acetone acted as a catalyst to the gel formation or whether the acetone, which by itself forms a gel with the salt solution, was the main bulk and structure of the gel.

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(10) Henstock, H. *Trans. Faraday Soc. 30*. (1934). 561.

From observation I would judge that it was more on the order of an acetone gel: (1) because the gel did not form when a few drops of acetone were added but formed on the addition of a considerable amount of acetone, and (2) because the gel was more on the order of a gelatinous precipitate. To the methanol solution of chloretone, sodium benzoate was added but no gel formed.

A solid gel was formed when two alcohols were mixed and used as a dispersion medium. Nine volumes of tertiary butyl alcohol, which itself gives a solid gel, was mixed with one volume of isobutyl alcohol which alone gives a gelatinous precipitate. Also, one volume of tertiary butyl alcohol to two volumes of isobutyl alcohol yields a solid gel on the addition of a saturated solution of calcium acetate.

It is my opinion that these ratios should not be taken too literaly. Many factors enter in, as discussed under hysteresis. There is quite probably a range, although it may not be wide, in which a certain gel can be formed. In these determinations it is quite probable that I recorded the minimum for I was adding the salt solution to the alcohol and recorded the minimum requirement of salt solution for the gel.

VI SUMMARY AND CONCLUSION

The term "solidified alcohol" can be applied to the following on the addition of a saturated solution of calcium acetate.

1. N propyl alcohol
2. Isopropyl alcohol
3. N butyl alcohol
4. Secondary butyl alcohol
5. Tertiary butyl alcohol
6. Allyl alcohol
7. One volume tertiary butyl alcohol and two volumes of isobutyl alcohol.
8. One volume of isobutyl alcohol and nine volumes of tertiary butyl alcohol.
9. Chloretone (methanol solvent), acetone added (discussion indicates could be called "solid acetone")

These alcohols formed solid gels on the addition of a saturated solution of sodium benzoate:

1) Isopropyl alcohol
2) Secondary butyl alcohol
3) Tertiary butyl alcohol
4) Isobutyl alcohol
5) N amyl alcohol
6) Secondary amyl alcohol
7) Isoamyl alcohol
8) Hexyl alcohol

Propyl alcohol gave a borderline gelatinous precipitate-gel.

None of these acetates -- sodium, methyl, zinc, barium, aluminum, or chromium-- formed gels with the various alcohols employed.

Those liquids which formed the gels were usually miscible with water. A few exceptions were encountered when the higher chain alcohol, only slightly soluble in water, formed gels with sodium benzoate solutions. The salt should, as a rule, be almost insoluble in the alcohol or dispersion medium to form the gel; but this, also, has found exception in the case of sodium benzoate for it is soluble in the lower members of the series of saturated alcohols.

Particles, and sometimes crystalline forms of these salts, were observed to precipitate on addition to the indicated alcohol:

Sat. aq. sol. salt	alcohol
barium acetate	N propyl
barium acetate	isopropyl
aluminum acetate	N butyl
barium acetate	secondary butyl
barium acetate	tertiary butyl
chromium acetate	secondary amyl
aluminum acetate	isobutyl
aluminum acetate	N amyl
aluminum acetate	isoamyl
sodium benzoate	octyl
calcium acetate	benzyl

This precipitate would be commonplace for solvent extraction with alcohol is a known method of "salting out". The colloidal gel formation is not the common occurance but the exception.

The cause of gel formation put forth by Thorne and Smith was the dehydration action of the alcohols. Henstock attributed the seat of gel formation to some inherent property of the salts themselves. These theories remain to be disproved or proved conclusively.

VII SUGGESTION FOR FURTHER STUDY

Only a few of the possible alcohols were treated here as dispersion mediums. Many others, both unsaturated aliphatic and aromatic, should prove interesting. It is not absolutely necessary that these alcohols be miscible with water. The unsaturated alcohol, allyl alcohol, formed a gel with calcium acetate solution. Therefore, other unsaturated alcohols might give some positive information on gel formation.

Metallic salts, which are soluble in methyl alcohol, could be tested as gelling agents for various alcohols. Chloretone in methanol solvent could be treated for gelation with a methanol solution of calcium acetate.

The effect of acetone on these various alcohols in forming solid gels should cultivate some interest.

There is one phase of this gel formation that perhaps may hold the answer to the cause of this sudden gel of rigid structure. Von Weimarn introduced certain statements which have been confirmed as quite generally valid. He emphasized the effect of the concentration of the solutions on the formation of the colloidal systems. (23)

> When the reacting solutions are very dilute, the resulting solid precipitates in a definitely crystalline form. At low concentrations the velocity of formation of nuclei is small, and the few nuclei which do form grow so slowly

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(23) Weiser, H. B. A Textbook of Colloid Chemistry. New York. John Wiley & Son. (1949). 140.

> at the cost of the solute present in weakly supersaturated solution that large crystals result. Conversely, when the reacting solutions are very concentrated, jellies are formed consisting of drops of the liquid surrounded by the solid. The rate of formation of nuclei is extremely high at the high concentration, so that at any point where the two solutions touch there is formed immediately a network of nuclei which do not have time to crystallize further and so yield a solid film. Subsequently, the nuclei grow into crystals as the interacting substances diffuse through the film.

Von Weimarn illustrated the great influence of concentration on the form of a precipitate from his comprehensive studies of the inorganic salt, barium sulfate.(23)The influence of concentration on the form of precipitate by quasi-organic salts such as calcium acetate, sodium benzoate or potassium ethyl subhate should provide an ample topic for research and give results which might help to determine the cause or series of influences which bring about this gel formation.

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(23) Weiser, H. B. *A Textbook of Colloid Chemistry.* New York. John Wiley & Son. (1949). 137.

VIIIANNOTATED BIBLIOGRAPHY

(1) Alexander, J. (ed) *Colloid Chemistry*. New York. Chemical Catalog Company. 1932.

A summary of developments of solid alcohols to date of publication.

(2) Baskerville, C. U. S. Pat. 1,208,265. 1916.

Use of a quasi inorganic substance as the hardening agent in a solid alcohol. A saturated aqueous solution of calcium acetate used.

(3) Fallnicht, R. English Pat. 15,030.1899.

A patent covering the production of soap in alcohol when warm and the setting of the cooling solution.

(4) Fisher, H. L. U.S. Pat. 1,389,638. 1921.

A patent on the use of methyl and ethyl alcohol with 4% water plus caustic soda and stearic acid which gave a solid alcohol which could be extinguished and relit until completely consumed.

(5) Gortner, R. A. *Selected Topics in Colloid Chemistry*. Ithaca, New York. Cornell University Press. 1937.

A brief treatment of the properties of gells including syneresis and hysteresis.

(6) Graham, T. "Properties of Silicic Acid". *J. Chem. Soc.* *Vol. 17*. pp. 318. (1864).

A paper dealing with the properties of silicic acid and comments on analogies to physiological processes.

(7) Hartman, R. J. *Colloid Chemistry*. New York. Riverside Cambridge Press. 1939.

A section on solid alcohols and their composition, also, called "false gels."

(8) Hempel, H. "Solid Fuel Preparation". *Seifensieder Ztg.* *Vol. 31*. p. 33. (1904).

Preparation of hardening material for solid alcohols employing coconut oil and sodium laurate.

*

(9) Henstock, H. "Calcium Acetate Gels". Trans. Faraday Society. Vol. 29. p. 1101. (1933.)

Gels formed by the addition of various liquids to a solution of calcium acetate in methyl alcohol.

(10) Henstock, H. "Sodium Benzoate Gels". Trans Faraday Society. Vol. 30. p. 560. (1934).

Preparation of alcogels using sodium benzoate as a gelling agent.

(11) Henstock, H. "An Investigation into the Causes of Gel Formation by Some Organic Salts in Methanol Solution". J. Am. Chem. Soc. Vol. 61. pp. 670-3. (1939).

On the causes of gel formation by organic salts in methyl alcohol solution.

(12) Hirsch, R. & Witt, O. N. "Preparation of a Solid Fuel from Alcohol". Chem. Ind. Vol. 18. P. 475. (1895).

A resume of researches which led up to first attempts to produce a solid methylated spirit.

(13) Kolliger, A. "Die Händedesenfeklion mit Alkoholseifenpasta" Chem. Ztg. Vol. 45.. p. 649. (1921).

A resume of the work done upon the germicidal properties of alcohol and the use of alcohol soaps.

(14) Laing, M. E. "The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol." Trans. Chem. Soc. (London) Vol. 113. P. 435. (1918).

An investigation tending to show that soap exists as a simple unpolymerized electrolyte in true solution in alcohol.

(15) Mark, H. S. & Esseln, G. U. S. Pat. 1,545,595. 1925.

Patent covering a solid alcohol containing a saponaceous base, a combustible alcoholic solvent and a volatile, combustible liquid or mixture of liquids which gave a fuel which would burn quietly and not liquify.

(16) Moore, F. J. History of Chemistry. New York. McGraw - Hill Book Co., Inc. 1939.

A discussion of the motives which lead men to pursue science.

(17) Patrick, W. A. "The Nature of Soap in Alcohol". J. Phys. Chem. Vol. 29. p. 1004. (1925.)

An investigation of soap as a simple unpolymerized electrolyte in true solution in alcohol.

(18) Raynaud, E. U. S. Pat. 879,193. 1903.

Use of sodium silicate as the fixing material in conjunction with soap in solid alcohols. The first time a purely inorganic material was used in the preparation of a solid fuel.

(19) Strobl, A. U. S. Pat. 1,277,149. 1918.

Patent on the use of methyl alcohol, alone or with denatured alcohol to lesson the sooty flame of solid alcohols.

(20) Thorne & Smith. "Ueber Kalziumazetatgele I". Kolloid Z. Vol. 48. P. 113. (1929).

An investigation of the results of using calcium acetate in solid alcohols.

(21) Thorne & Smith. "Ueber Kalziumazetatgele II". Kolloid Z. Vol. 54. P. 181. (1931).

The effect on stability of the use ofcalcium acetate in solid alcohols, also its effect on ionization.

(22) Weeks, C. English Pat. 251,948. 1927.

A patent for the use of an alcohol base to improve face cream.

(23) Weeser, H. B. A Textbook of Colloid Chemistry. New York. John Wiley & Son. 1949.

Von Weimarn statements on the effect of the concentration of the solutions on the formation of the colloidal systems.

* (24) Hempel, H. D. R. P. 152,682. 1898.

A patent for use of saponified animal tallow and stearic acid plus 80% alcohol in production of solid alcohol.

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