PHYSICS AND CHEMISTRY OF HYDROCARBON GELS

ON March 24, a Royal Society Discussion was held on the subject of the physics and chemistry of hydrocarbon gels. Interest in these systems arose in the first instance from the desire to extend the range of flame throwers in which hitherto ordinary liquid hydrocarbons had been used. It was evident at a very early stage in the investigation that a possible improvement in range could be effected if the fuel could be made thixotropic in character, or at any rate if its intrinsic viscosity could be varied over wide ranges on changing the rate of shear. Further investigation revealed the fact that another physical property or combination of properties embraced under the term 'stringiness' or 'extensibility' had also to be taken into consideration.

Since gels are two-phase systems, inquiry centred around the preparation of suitable hydrocarbon gels. The gel-forming polymeric network could be introduced into the hydrocarbon by swelling and dispersion, or could be formed *in situ* as a result of suitable chemical reaction. Of the former, the early rubber–petrol systems were soon replaced by *iso*-butylmethacrylate or by cellulose acetate in a suitable fuel solvent, whereas the aluminium soaps of fatty acids were found to be most suitable among the latter class.

A linear polymer will dissolve in a hydrocarbon if the free energy of solution ΔF is negative. A high heat of solution ΔH may counterbalance the large (for polymers) entropy ΔS of solution. If $\Delta F = \Delta H - T \Delta S$ is positive, complete solution does not occur, but there results a swollen gel in equilibrium with almost pure solvent.

The degree of swelling of the gel phase is determined by a solvent-polymer interaction term μ. For linear polymers, μ can be defined by

$$\Delta F = RT \log (1 - \nu) + \nu \left(1 - \frac{1}{n}\right) + \mu \nu^2,$$

where ν is the volume fraction of the polymer and n the ratio of solute/solvent molecular weight.

For a cross-linked polymer, the free-energy term must include not only the change due to dilution, but also the elastically stored free energy in the swollen network; expressions for this term, both for equilibrium strain-free and strained conditions, were described by Dr. L. R. G. Treloar.

This elastic energy may be stored as orientation entropy in the flexible chains, as potential energy in bent or stretched valency bonds or as a twist against the hindered potential opposing free rotation about the C—C axis. In the case of an isolated long-chain molecule, Kuhn showed that the force per unit extension would be inversely proportional to the number of bonds for orientation entropy and inversely proportional to the square of the number for twisting against hindered rotation.

The molecular spring in a gel is the average strand between two junction points in the framework, and the number of junction points as well as the number of strands is evidently proportional to the square of the volume concentration. The average length of a strand is, conversely, proportional to the concentration; consequently, the rigidity of the network should be proportional to the square of the volume concentration for the energy stored in the chain entropy, and to the cube of the concentration for twisting against hindered rotation. Data on the rigidity of gels as a function of the concentration of gelling polymer are scanty; but, such as they are, they suggest that twisting of the chains against hindered rotation rather than bond extension or chain entropy is the main factor involved.

It is evident that to obtain a fuller understanding of this partition of polymer between swollen gel and dilute solutions as separate phases, a close examination of the phase behaviour of polymer and solvent is desirable. Dr. A. E. Alexander gave an account of the examination of the swelling and solubility of cellulose acetate in benzene–xylenol mixtures. He has found that the solubility of the acetate in benzene–xylenol mixtures is greatly influenced by the degree of acetylation. By comparing the solubilities and swelling powers of the separated fractions in benzene–xylenol mixtures of different compositions, it has been shown that preferential adsorption of the xylenol takes place from these mixtures, and from the two sets of experiments phase diagrams have been constructed which when superimposed on one another reproduce the data obtained with the original material.

The rather complex rheological properties of these 'thickened' hydrocarbon systems were the subject of several communications, including those of Dr. A. H. Nissan, Dr. K. Weissenberg and Mr. R. S. Rivlin.

While the majority of these polymer-containing hydrocarbon systems are thixotropic in character and thus can store potential or elastic energy when distorted, they all exhibit the property of anomalous viscosity or non-Newtonian flow; indeed, the intrinsic viscosity may vary as much as a millionfold when the rate of shear is changed.

The point of thixotropic breakdown is now generally associated with a balance being achieved between the rate of cross-linking or bond formation and bond breaking, and it is evident that if these can be regarded as independent rate processes, the anomaly in the viscosity shear curves can readily be interpreted. Attempts have also been made to apply the considerations advanced by Eyring to these systems; but the physical interpretation of the actual mechanics of the processes involved on this basis is by no means clear. One of the most interesting conclusions arrived at from theoretical argument is the fact that to describe the flow properties of these solutions, two, and not one, physical parameters are required. If viscosity be chosen as one of them, the other is a normal stress coefficient. In a steady state of flow the normal stress coefficient may not vanish and will give rise to many of the effects which these anomalous liquids exhibit.

A great deal of attention has been devoted to the aluminium soaps as gelling agents for hydrocarbon fuels, and communications on this subject were made by Dr. A. E. Alexander, Dr. G. A. Parry and Dr. J. H. Schulman. Aluminium exhibits six-fold co-ordination and is amphoteric in its salts. The simplest compounds may be regarded as derivatives of $[Al(OH)_6{}''']\overset{+}{H}_3$ (aluminic acid) and $[(H_2O)_6 \rightarrow \overset{+++}{Al}]\,Cl_3$ respectively. Salts of the type $[(H_2O)_5\ Al\ \overset{++}{R}]\ \bar{R}_2$ can evidently be prepared.

Bjerrum and Stiasny were the first to examine the condensation of these substances by the elimination

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of water by processes they termed 'olation' and 'oxolation', and condensation polymers up to the tetramer can readily be identified.

For the purposes of gelation, the anhydrous aluminium soaps are most readily prepared by reaction of the aluminium alkoxides formed by direct interaction of the metal with the alcohol and fatty acids in an organic solvent, although similar results can be obtained from freshly precipitated aluminium hydroxide and the free fatty acids, or by ordinary metathesis between an alkali metal soap and an aluminium salt.

There still appears to be a certain amount of doubt in respect to the nature of the soaps of aluminium. The existence of di-acid soaps, $Al(OH)L_2$ and $Al(OR)L_2$, where L is the acid radical, is well established both by Karl Fischer's method for water determination and also calorimetrically from the heats of neutralization. Neither the tri- nor mono-soap appears to be readily prepared, at least from aqueous solutions, the product consisting mainly of the di-soap with adsorbed free fatty acid or hydrated alumina.

The complexes formed in strong solutions can be broken down by means of peptizing agents. Their mode of action can be ascribed to the breaking of the aluminium oxygen co-ordinate links by preferential co-ordination with the peptizer, and thus a large variety of compounds, such as water, amines, pyridine, alcohols, and, after that, phenols and fatty acids, can serve as peptizers.

ERIC K. RIDEAL

VARIABLE AND CONSTANT COMPONENTS OF CHROMOSOMES

By DR. A. E. MIRSKY and HANS RIS
Rockefeller Institute for Medical Research, New York

A STUDY of isolated chromosomes has shown that they contain desoxyribonucleic acid, histone and another protein of an entirely different character from a histone[1]. This protein remains as a microscopic fibre after extraction of desoxyribonucleic acid and histone from the chromosome. The coiled thread that is left after removing desoxyribonucleic acid and histone is called a 'residual chromosome', and the protein of the thread is referred to as the 'residual protein' of the chromosome. Some ribonucleic acid is combined with residual protein. The thread of residual protein is the basis for the thread-like structure of the chromosome. In the isolated chromosomes that were first prepared, those of nucleated erythrocytes of the carp and of calf thymus, the residual protein represented only 4 and 8·5 per cent respectively of the dried mass of the total chromosome, the remainder of the lipid-extracted chromosome being almost entirely nucleohistone.

Isolated chromosomes have now been prepared from beef liver, kidney and pancreas. For this purpose it was necessary to add several steps to the original procedure, for otherwise the chromosomes obtained were contaminated with considerable quantities of non-chromosomal material. In a suspension of isolated chromosomes, morphologically different individuals can be identified, and the same chromosomes are found in preparations from thymus, liver, kidney and pancreas of the same organism. This recognition of chromosome individuality in preparations of isolated chromosomes from different tissues is especially striking when the chromosome is the one to which a nucleolus is attached.

Fractionation of liver, kidney and pancreas chromosomes shows (figures given in Table 1) that their composition differs markedly from that of erythrocyte and thymus chromosomes, in that the former contain less nucleic acid and far more residual protein.

The composition of a chromosome appears to be related to the nucleo-cytoplasmic ratio of the cell in which it is located. Thymus lymphocytes have only a scanty cytoplasm compared with the abundant cytoplasm present in most cells of the liver, kidney and pancreas. We find that the nucleus represents 60 per cent of the mass of thymus cells and only 10–18 per cent of the mass of cells of the liver, kidney and pancreas. Chromosomes of nucleated erythrocytes, as seen in Table 1, have a composition that would be expected if they were in a cell with scanty cytoplasm. They have, in fact, a large cytoplasm, but one that is relatively inert metabolically. This shows that what is significant in the relationship between nucleo-cytoplasmic ratio and chromosome composition is the metabolic activity of the cytoplasm, as well as its bulk. Further evidence may be cited relating chromosome composition to nucleo-cytoplasmic ratio of the cell. The lymphocytes in the lymph nodes of beef contain far more cytoplasm than do the lymphocytes of calf thymus; and, in accordance with the rule that has just been mentioned, the nuclear substance of lymph node lymphocytes has a much lower percentage of desoxyribonucleic acid. The nucleo-cytoplasmic ratio of liver cells changes considerably when an animal fasts. In fasting, there is a decrease in the ratio of cytoplasm to nucleus. In these circumstances we would expect to find the percentage of desoxyribonucleic acid in the nuclear substance of liver cells to increase during fasting—and analysis does, indeed, show this.

Table 1

Chromosomes of:	Desoxyribonucleic acid (per cent)	Residual protein (per cent)
Carp erythrocyte	41	4
Calf thymus	39	8·5
Calf liver	26	39
Calf kidney	28	33
Beef pancreas	28	29

From the data given in Table 1 it cannot be said whether the differences in percentage composition of chromosomes of different cells of the same organism are due to variations in the quantity of nucleic acid or in the quantity of residual protein present in a given chromosome. When cytologists observe differences in staining of chromosomes, they frequently conclude that more or less chromatin is present in the chromosomes. The material in the chromosome that stains (chromatin) is desoxyribonucleic acid, and in the cytological literature there are many statements, based on staining, concerning an alleged increase or decrease in quantity of desoxyribonucleic acid in chromosomes. What is actually being observed is a change in percentage composition. An apparent decrease in quantity of nucleic acid (chromatin) may be simply a decrease in the percentage of nucleic acid due to an increase in quantity of residual protein in the chromosome, the actual quantity of nucleic acid in the chromosome possibly remaining constant.

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