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The Electroviscous Effect with Measurements on Sodium Polymethacrylate Solutions

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April 13, 1948

CERTAIN solutions of negative colloids, like agar,¹ gum arabic,² and starch,³ show a very high viscosity, which is lowered greatly by the addition of electrolyte. This was discovered by Kruyt and Bungenberg de Jong. The authors explained this phenomenon by assuming rigid particles, surrounded by a double layer which influences the viscosity, according to calculations by Smoluchowski. It has often been said, however, that the observed changes are much larger than can be accounted for by this theory. Therefore, an alternative explanation may be suggested.

If a long chain molecule is dissolved in a medium by which it is not repelled, it will extend through an average volume of solvent which depends on the length and on the structure of the chain. If a number of negative charges are attached to this chain at regular intervals, the different parts of the chain will repel each other and the molecule will expand through a larger volume of liquid. This amounts to a swelling of the colloid particles. If an electrolyte is now added to the solution of this polymer, each negative charge on the chain will surround itself by a positive ion sphere, which lowers the electrostatic repulsion. This causes the particles to shrink again, but in no case to quite the same size as the uncharged molecule would have.

From these considerations the following facts are to be expected, if we take into account the fact that in a colloidal solution containing a certain number of particles, the viscosity increases with the volume pervaded by each particle.

1. Addition of electrolytes to a solution of a (negative) linear polymer causes a rapid decrease of the viscosity in the concentration range where the "radius" of the ion sphere is of the same order of magnitude as the distance between the nearest charges on the chain which can move fairly independently.

2. The efficiency of different salts in lowering the

viscosity increases rapidly with the charge of the positive ions. The charge of the negative ions is without influence.

3. Even at high electrolyte concentrations the viscosity of the negative colloid is higher than that of the same polymer in the uncharged condition.

These conclusions are in general agreement with the observations of Kruyt, Bungenberg de Jong, and their collaborators. However, it seemed desirable to check them with a polymer, the linear character of which was beyond doubt. Aqueous solutions of polymethacrylic acid and its sodium salt behave entirely as predicted (Table I).

In normal colloids $\eta/\eta_{H_2O}-1$ is either approximately proportional to the concentration, or increases even more steeply. Table I shows that for sodium polymethacrylate the opposite is true, except at the very lowest concentrations. From our model this is easily understood. The increase of the number of Na^+ ions with increasing polymer concentration causes the colloid particles to shrink. In solutions of undissociated polymethacrylic acid, on the other hand, $\eta/\eta_{H_2O}-1$ was found proportional to the concentration with a very satisfactory accuracy. Addition of NaCl did not affect the viscosity of these solutions.

It may be pointed out that in Staudinger's laboratory Kern and others observed a similar behavior in the case of sodium polyacrylate.⁴ They found the behavior of polyacrylic acid itself entirely different from the results of our measurements on polymethacrylic acid.

I am deeply obliged to Mr. F. Langford, A.E.B., Plastics Division Research Manager, I.C.I., Welwyn Garden City, England.

¹ H. R. Kruyt and H. G. Bungenberg de Jong, *Zeits. f. physik. Chemie* **100**, 250 (1922).

² H. R. Kruyt and H. J. C. Tendeloo, *Koll. Beih.* **29**, 396 (1929).

³ H. G. Bungenberg de Jong, *Rec.* **43**, 189 (1924). Kindly provided by Mr. F. Langford, Plastics Division Research Manager, I.C.I., Welwyn Garden City, England.

⁴ H. Staudinger and H. W. Kohlschütter, *Ber.* **64**, 2091 (1931); H. Staudinger and E. Trommsdorff, *Lieb. Ann.* **502**, 201 (1933); W. Kern, *Zeits. f. physik. Chemie A.* **181**, 283 (1938).

A Note on Gaseous Thermal Diffusion: The Effect of a Third Component*

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IN his study of the kinetic theory of gases, Chapman¹ showed that a temperature gradient in a mixture of two gases results in establishment of a concentration gradient. His mathematical theory of thermal diffusion is based upon considerations of intermolecular force fields and upon relative molecular weights and diameters. More recently Gillespie² developed a simple theory of thermal diffusion based on elementary kinetic considerations. His treatment does not account for the dependence of the effect on the size of the molecules and their mutual forces, but is based solely on molecular weight which is the variable of major importance.

On the basis of his simplified treatment, Gillespie was able to show that in a mixture of any number of gases the

TABLE I. Viscosity of polymethacrylate and of polymethacrylic acid solutions (25°).

Polymethacrylic acid gram/liter	NaOH mole/liter	Added electrolyte mole/liter	η/η_{H_2O}
0.320	0	0	1.000
0.340	0.00328	0	1.43
0.340	0.00328	0.00691 NaCl	1.123
0.340	0.00328	0.0345 NaCl	1.069
0.340	0.00328	0.173 NaCl	1.051
0.340	0.00328	0.00169 $MgSO_4$	1.139
0.340	0.00164	0	1.362
0.340	0.00164	0.00691 NaCl	1.097
0.340	0.00082	0	1.060
9.18	0.0886	0	4.523
4.59	0.0443	0	3.230
1.53	0.0148	0	2.135
0.510	0.00492	0	1.550
0.170	0.00164	0	1.243
0.0567	0.000547	0	1.087
0.0189	0.000182	0	1.016

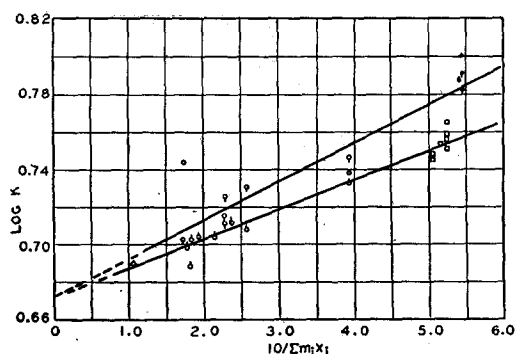


FIG. 1. Logarithm of the apparent equilibrium constant $p_{\text{H}_2\text{O}}/(p_{\text{H}_2} \times \% \text{O})$ as a function of reciprocal mean root-molecular weight of the gaseous mixture.

Added gas	None	Helium	Argon	Mercury
No preheat	●		○	(mean of 7)
Low preheat	●		○	
High preheat	●	□	○	△

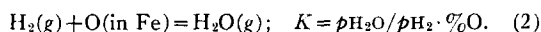
relative separation of two gases is given by the equation

$$d \ln(x_1/x_2)/d \ln T = (m_2 - m_1)/(2 \sum m_i x_i), \quad (1)$$

where x_1 and x_2 are the mole fractions of the two gases, m_1 and m_2 the square roots of their molecular weights, and the summation is over all species present. According to this equation, the relative separation of two gases by thermal diffusion is inversely proportional to the mean root-molecular weight of the mixture, and it was therefore suggested that thermal separation of isotopes might be aided by addition of a third gas of low molecular weight.

An opportunity recently presented itself for testing the validity of this equation with respect to the addition of an inert gas to a mixture of water vapor and hydrogen in a thermal gradient at high temperatures. In an experimental study of equilibrium in the reaction of hydrogen with oxygen dissolved in molten iron, a controlled mixture of hydrogen and water vapor impinges upon the surface of the molten metal which is heated and also stirred by high frequency induction. It was shown some years ago³ that under these conditions thermal diffusion occurs in the gas mixture near the hot metal surface, the result being a lower oxygen content of the metal than that which would correspond to equilibrium with the entrant gas. It was shown that strong preheating of the gas diminished the error due to thermal diffusion but whether or not the error was completely eliminated has remained undetermined. Equation (1) suggests the admixture of inert gas of high molecular weight as a means of minimizing thermal separation, and the results of such a study offer qualitative support for the validity of the equation.

It has been established⁴ that the activity of oxygen in the melt is proportional to its percent by weight. It is therefore permissible to use the percentage of oxygen in the equilibrium constant as follows.



Experiments were conducted at substantially constant steam-hydrogen ratios, the metal being held at 1563°C about twice as long as actually required to establish equilibrium. The oxygen content of the metal fell in the range 0.03–0.04 percent which is high enough for good analytical accuracy and low enough to avoid formation of a non-metallic phase.

The results are shown in Fig. 1 in which the logarithm of the apparent K is plotted against the reciprocal of the mean square root of the molecular weight of the gaseous mixture. The results fall into two groups with respect to intensity of preheating of the gas and include three early results without preheat. Previous results are confirmed in that preheating decreases the apparent value of K . Much more striking, however, is the effect of adding purified argon to the gas mixture. This decreased the apparent K by an amount proportional to the reciprocal of the mean root molecular weight. Addition of helium gave results approximately the same as those without admixture. In one series mercury vapor was added and here the apparent K was the lowest observed. Straight lines may be drawn through the two groups corresponding to the two degrees of preheat.

Each method of preheating was sufficiently reproducible to establish a constant temperature pattern within the apparatus. Thus $\int d \ln T$ of Eq. (1) was essentially constant for each condition. Figure 1 shows that under such circumstances $\int d \ln(x_{\text{H}_2\text{O}}/x_{\text{H}_2})$ is inversely proportional to $\sum m_i x_i$ as required by the equation. The constant of proportionality cannot be evaluated from the results but with this reservation these experiments confirm Gillespie's equations of thermal diffusion.

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¹ S. Chapman, Phil. Trans. (London) **A217**, 115 (1917).

² L. J. Gillespie, J. Chem. Phys. **7**, 438(1), 530 (1939).

³ J. Chipman and M. G. Fontana, J. Am. Chem. Soc. **56**, 2011 (1934).

⁴ M. G. Fontana and J. Chipman, Trans. Am. Soc. Metals **24**, 313 (1936).

Erratum: The C—H Bond Energy in Toluene and the Xylenes

[J. Chem. Phys. **16**, 128 (1948)]

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THE end of the sentence at the foot of p. 135 in the above letter should be amended as follows: Delete the word "xylene" and substitute "xylyl radical." The sentence should now read: ". . . hyperconjugation occurring for example in para xylyl radical as follows:

