electrode were studied and found to be reversible in 1 M potassium cyanide. The oxidation potential of the chromocyanide–chromicyanide couple was determined both polarographically and by classical means, and found to be -1.14 v. in 1 M potassium cyanide. The standard potential was estimated to be -1.28 v.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 10, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Osmotic Pressure and Viscosity Measurements with Cellulose Acetate Fractions[1]

BY A. BARTOVICS AND H. MARK

Flory,[2] Huggins[3] and Powell, Clark and Eyring[4] have recently very considerably extended our theoretical knowledge of dilute high polymer solutions, and developed equations for the dependence of osmotic pressure and specific viscosity of such solutions upon concentration of the solute. Fuoss and Mead[5a] and Flory[5b] have carried out osmotic pressure and viscosity measurements with fractionated polyvinyl chloride and polyisobutylene samples. It is the purpose of this paper to contribute some similar results obtained with cellulose acetate fractions.

Experimental

A. Material.—Fifteen fractions of cellulose acetate were studied; their preparation and characterization was described in a previous paper.[6] They were the final result of a threefold fractionated precipitation of an Eastman Kodak Co. Cellulose Acetate having 38.6% acetyl, 0.06% ash content and a melting point of 250°. All fractions used in this investigation had inside the limits of error almost the same melting point, acetyl and ash content; they differed only by their osmotic pressure and specific viscosity.

B. Viscosity Measurements.—The determinations were made in acetone with an ordinary Ostwald viscometer, which had a capillary tube about 10 cm. long and with a 0.4 mm. bore. Exactly 5 ml. of the liquid was introduced into the large bulb of the viscometer by means of a pipet. The apparatus was then suspended in a constant temperature bath (30 or 40 ± 0.1°). After the viscometer and contents had acquired the temperature of the bath, suction was applied at the capillary arm of the viscometer until the level of the liquid rose above the upper graduation mark. The liquid was then allowed to flow back through the capillary, and the time required for the surface of the liquid to pass from the upper to the lower mark was noted by means of a stop watch.

Within the concentration range used in these experiments, the densities of solvent and solution differed by less than 0.2% and can be neglected. The specific viscosity, η_{sp}, of a solution is therefore calculated directly from the time observations as follows

$$\eta_{sp} = \frac{t_s - t_0}{t_0} = \frac{t_s}{t_0} - 1 = \eta_r - 1$$

where t_s and t_0 are the times of flow of the solution and solvent, respectively, and η_r is the relative viscosity of the solution.

C. Osmotic Measurements.—Two methods were used. The static, as described by Herzog and Spurlin[7] and Meyer,[8] and the dynamic, which was introduced by van Campen[9] and Obogi and Broda[10] and recently very substantially improved by Fuoss and Mead.[5a] These authors describe the procedure in their paper so clearly and in such detail that it seems to be sufficient to refer to their article. The results of both methods agreed with exception of the lowest molecular weight fractions, where it was difficult to arrive at a satisfactory equilibrium with the static method. This seems to be due to the diffusion of the solute through the membrane. For these fractions the dynamic values were used. All osmotic measurements were carried out in acetone at 25°.

TABLE I

VALUES FOR M_2 AND $[\eta]$ FOR SEVERAL CELLULOSE ACETATE FRACTIONS

$k' = 0.70$; $\mu = 0.43$

Fraction	2	4	8	9	11	13	15
$M_2 \times 10^3$	126	92	63	52	45	31	25
$[\eta]$*	31.0	25.0	19.0	16.5	15.5	12.0	10.5

* The concentration c_v is expressed in volume fractions.

Results and Discussion

Figure 1 shows the specific viscosities of five selected fractions (2, 4, 8, 9 and 13) divided by the volume fraction of the solute plotted against this volume fraction. It can be seen that the three

---

[1] This paper is part of A. Bartovics' Doctor's thesis, Polytechnic Institute of Brooklyn, January, 1943. Its main content was presented at the A. C. S. meeting in Buffalo, New York, in September, 1942.

[2] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[3] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939); THIS JOURNAL, **64**, 1712, 2716 (1942).

[4] R. E. Powell, C. R. Clark and H. Eyring, *J. Chem. Phys.*, **9**, 268 (1941).

[5] (a) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943); (b) P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[6] A. M. Sookne, H. A. Rutherford, H. Mark and Milton Harris, *J. Research Natl. Bur. Standards*, **29**, 123 (1942).

[7] R. O. Herzog and H. M. Spurlin, *Z. physik. Chem.*, Bodenstein Festband, 239 (1931).

[8] K. H. Meyer, "Natural and Synthetic High Polymers," Interscience Publ. Co., New York, N. Y., 1942, p. 12.

[9] P. van Campen, *Rec. trav. chim.*, **50**, 915 (1931).

[10] R. Obogi and E. Broda, *Kolloid-Z.*, **69**, 172 (1934).

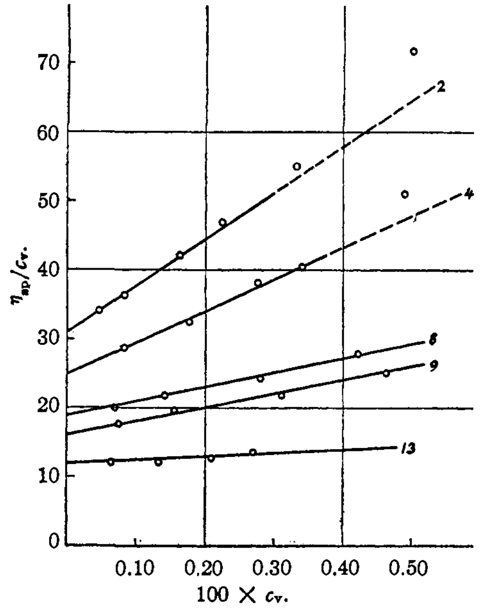

Fig. 1.—η_{sp}/c_v is plotted *versus* the volume fraction c_v of the solute.

lower fractions 8, 9 and 13 follow, up to 0.5 volume per cent., very closely the equation

$$\eta_{sp}/c_v = A + Bc_v \qquad (1)$$

while the last few points of fractions 2 and 4 indicate the interference of a third term on the right-hand side of (1). According to Huggins[3] one has to expect that at moderate concentrations of the solute, η_{sp}/c_v can be represented by

$$\frac{\eta_{sp}}{c_v} = \left(\frac{\eta_{sp}}{c_v}\right)_0 + k'\left(\frac{\eta_{sp}}{c_v}\right)_0^2 c_v = [\eta] + k'[\eta]^2 c_v \qquad (2)$$

The constant k' is characteristic for the system solvent–solute and should be the same for all fractions. It has been found that 24 experimental points of the graph can be represented with an average deviation of about 3 to 5% by taking $k' = 0.70$. The only exceptions are the last two points of fractions 2 and 4, which do not fall on the straight lines of the graph and therefore cannot comply with equation (2).

Schulz and Blaschke[11] have recently evaluated specific viscosity measurements of polymethyl methacrylates and arrived at a k'-value of 0.30. This constant describes, according to Huggins, in an empirical way the size, shape and cohesional properties of both solvent molecules and solute submolecules. The larger value of 0.70 as found for cellulose acetate as compared with 0.30 for polymethacrylate may be an expression of the comparatively greater stiffness of the cellulose derivative chains.

Figure 2 shows the osmotic pressures of five representative fractions divided by the weight concentration of the solute plotted against the weight concentration. It can be seen that all (20) points are arranged on straight lines within a concentration range up to 0.8 weight per cent. of solute.[12]

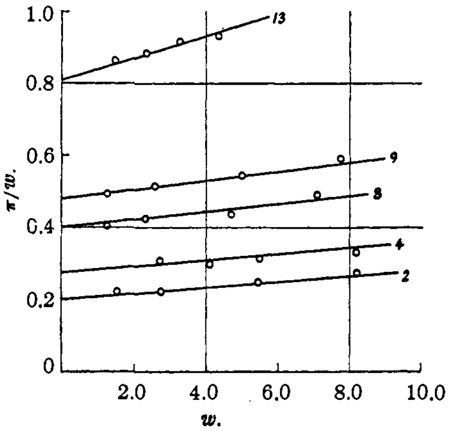

Fig. 2.—The reduced osmotic pressure π/ω is plotted against the weight concentration of the solute (w = grams of solute per kg. of solution).

It seems, therefore, that in the case of cellulose acetate fractions, the formulas of Flory[2] and Huggins[3] can be applied. According to their theory the reduced osmotic pressure π/c_2 can be expressed by

$$\pi/c_2 = \frac{RT}{M_2} + \frac{RT}{V_1 d_2^2}(1/2 - \mu)\, c_2 \qquad (3)$$

R = gas constant
T = absolute temperature
V_1 = molar volume of the solvent
d_2, M_2 = density and molecular weight of the solute
c_2 = concentration of the solute in g. of solute per cc. of solution.

μ is a constant characteristic for the system solvent–solute depending upon the heat and entropy of mixing. One should expect it to have the same value for all fractions. Figure 2 shows that this is not exactly true, but holds with a fair degree of accuracy. The fractions 2, 4, 8 and 9 have practically identical slopes. Only fraction 13 deviates and shows a steeper slope. We are, however, not quite certain whether this deviation does not fall inside the limits of error of our experiments.

(11) G. V. Schulz and F. Blaschke, *J. prakt. Chem.*, **158**, 130 (1941).

(12) Flory points out that this is not the case for polyisobutylene fractions. In an investigation of polystyrene fractions we have also found that the π/c_2 *versus* c_2-lines curve already at very low concentrations. This seems to be also compatible with the theory if one uses a better approximation (comp. M. L. Huggins, ref. 3).

In the sense of the theories, which lead to equations (2) and (3), it is to be expected that for a given fraction of cellulose acetate the magnitudes $[\eta]$, k' and μ should depend upon the nature of the solvent, while M_2 (the reciprocal intercept in Fig. 2) should not change with the solvent. This is because the first three quantities are characteristic for the average shape of the dissolved molecules which depends upon the solvent and for the interaction of the submolecules of the polymer with the solvent molecules; M_2, on the other hand, depends only upon the polymerization degree of the solute.

A sample of fraction 8 was therefore taken and its specific viscosity and osmotic pressure determined in a mixture of acetone and methanol, which contained somewhat less methanol as was necessary to produce a visible turbidity in the solution.

Figure 3a gives a plot of η_{sp}/c_v *versus* c_v for fraction 8 in acetone (curve 8) and in acetone–methanol (curve 8′). Both intercept and slope are decreased, showing that they both depend upon the interaction of solvent and solute. The straight line 8′ cannot be represented by $k' = 0.70$, showing that it does not fit into the pattern of Fig. 1, due to the fact that there is now a different specific interaction between solvent and solute. Figure 3a leads to a value of 0.60 for k'.

Figure 3b shows π/c_2 plotted against c_2 in acetone (curve 8) and in acetone–methanol (curve 8′) and makes it evident that the intercept (M_2) is unsensitive against the change of the solvent, while the slope is very noticeably affected.

Another experiment to check upon the significance of the quantities $[\eta]$, k', M_2 and μ was the following. A sample of fraction 9 was taken and by treatment with acetic anhydride in pyridine, its acetyl content was increased up to about 39.4%. According to the general experience, such an after-acetylation does not affect the polymerization degree of the material noticeably; it does, however, change its solubility characteristics. Viscosity and osmotic measurements of this material in acetone and their comparison with the original material leads to figures 4a and 4b. It can be seen that the increase of acetyl content leaves M_2 practically unaffected, but changes $[\eta]$, k' and μ in the sense that acetone proves to be a less good solvent for the higher acetylated acetate, just as acetone–methanol was a poorer solvent for the original material.

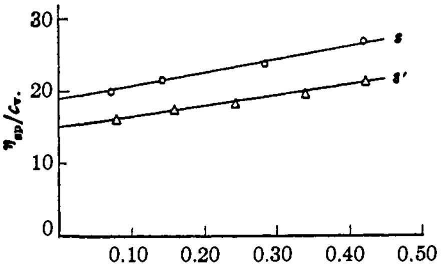

Fig. 3a.—Viscosity–concentration relationship of fraction 8 in acetone (8) and acetone–methanol (8′). In acetone $[\eta] = 19.0$, $k' = 0.70$; in acetone methanol $[\eta] = 15.0$, $k' = 0.60$.

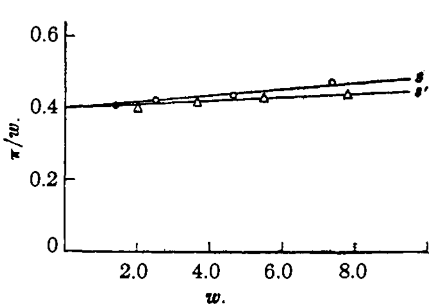

Fig. 3b.—Osmotic pressure–concentration relationship of fraction 8 in acetone (8) and acetone–methanol (8′): $\mu = 0.43$ in acetone; 0.46 in acetone-methanol.

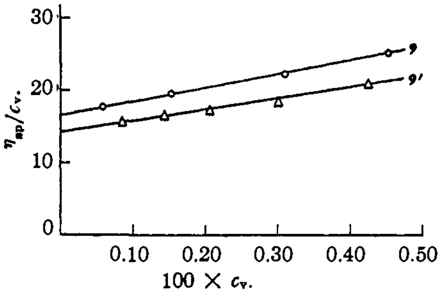

Fig. 4a.—Viscosity–concentration relationship of the original fraction 9 (acetyl content 38.6%) and an after-acetylated sample 9′ (acetyl content about 39.4%). For 9, $[\eta] = 16.5$, $k' = 0.70$; for 9′ $[\eta] = 14.5$, $k' = 0.60$.

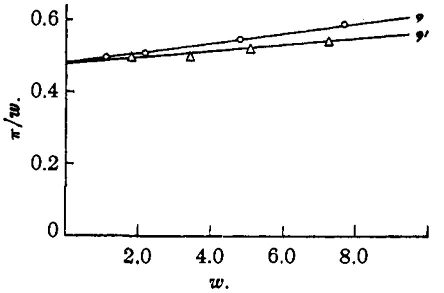

Fig. 4b.—Osmotic pressure–concentration relationship of the original fraction 9 (acetyl content 38.6%) and an after-acetylated sample 9′ (acetyl content about 39.4%). The μ-values are 0.43 and 0.45, respectively.

TABLE II

VALUES FOR K AND a, WHICH HAVE BEEN ESTABLISHED BY COMPARING OSMOTIC AND VISCOSITY MEASUREMENTS OF STRICTLY FRACTIONATED SAMPLES

Substance	Solvent	T in °C.	K	a	Authors	M_2-range
Polyhydroxyundecanoic acid	Chloroform	25	3.2×10^{-5}	1.0	*a*	Not very wide
Polystyrene	Benzene	..	3.6×10^{-5}	1.0	*b*	Not very wide
Polyvinyl chloride	Cyclohexane	25	7.0×10^{-5}	1.0	*c*	Fairly wide (28,000 to 102,000)
Polyisobutylene	Diisobutylene	20	3.60×10^{-4}	0.64	*d*	Very wide (8000 to 1,300,000)
Cellulose acetate	Acetone	25	1.04×10^{-2}	0.67	*e*	From 25,000 to 126,000

[a] W. O. Baker, C. S. Fuller and J. H. Heiss, Jr., THIS JOURNAL, **63**, 3316 (1941). [b] A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942). [c] D. J. Mead and R. M. Fuoss, THIS JOURNAL, **64**, 277 (1942). [d] P. J. Flory, *ibid.*, **65**, 372 (1943). [e] Present paper.

These facts seem to indicate that at least in the case of a straight chain polymer such as cellulose acetate, the formulas derived by Flory and Huggins reflect in a fair way the behavior of a high polymer in a dilute solution.

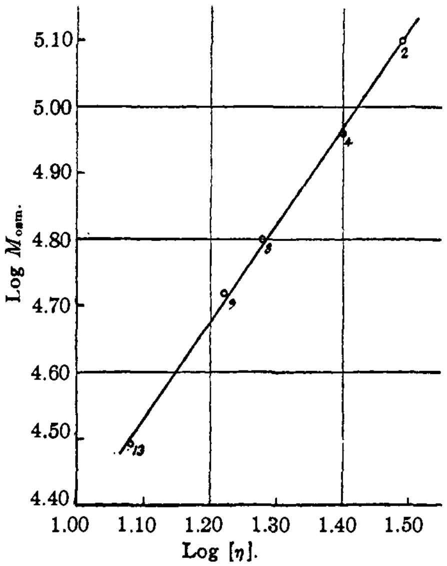

Fig. 5.—Log M_2 as obtained from the intercepts of Fig. 2 is plotted *versus* log [η] as obtained from the intercepts of Fig. 1.

It was next of interest to compare the intersects of Fig. 1 ([η]-values for the different fractions) with the corresponding reciprocal intersects of Fig. 2 (M_2-values for the different fractions). In the sense of the Staudinger rule the relationship between these two magnitudes should be expressed by a straight line, the slope of which gives the K_m-constant. It was, however, pointed out[13] that a relation of the somewhat more complicated form

$$[\eta] = KM^a \tag{4}$$

is theoretically better founded and seems to be necessary to cover satisfactorily the experimental findings in the range of high degrees of polymerization. Houwink,[14] has used a similar expression and Flory[15] in a very careful and thorough investigation of polyisobutylene fractions has shown that (4) establishes a satisfactory relationship between M_2 and [η] over a very wide range of both variables.

Figure 5 represents a plot of log M_2 *versus* log [η] and shows all points falling fairly on a straight line. From this and the figures of Table I, one derives for cellulose acetate fractions

$$K = 1.04 \times 10^{-2}$$
$$a = 0.67$$

Flory found for polyisobutylene $K = 3.60 \times 10^{-4}$ and $a = 0.64$; Houwink for different vinyl derivatives, $a = 0.6$.

If one wants to evaluate intrinsic viscosity measurements for molecular weight determinations of fractionated high polymers, in the range of higher polymerization degrees, it seems therefore to be recommended to use equation (4) instead of the Staudinger rule and to calibrate its two constants for each system solute–solvent by osmotic measurements.

Table II contains numerical values for these two constants as far as they have been established by comparative osmotic and viscosity measurements on strictly fractionated samples over a wide range of polymerization degrees. It may be added that equation (4) only holds in the domain of high molecular weights, while for molecular weights below 5000 a small additive term is necessary to reach agreement with the experiments.[16]

The authors wish to express their sincerest

---

(13) H. Mark, "Preparation and Properties of High Polymers": Lecture given in Zürich on January 8, 1937; "Der feste Korper," Leipzig, 1938, p. 103; R. Simha, *J. Appl. Phys.*, **13**, 147 (1942).

(14) R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940).

(15) P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

(16) Compare, *e. g.*, K. H. Meyer and A. Van der Wyck, *Helv. chim. acta*, **19**, 218 (1936); R. Fordyce and H. Hibbert, THIS JOURNAL, **61**, 1912 (1939); W. O. Baker, C. S. Fuller and J. H. Heiss, *ibid.*, **63**, 3316 (1941); G. V. Schulz and A. Dinglinger, *J. prakt. Chem.*, **158**, 136 (1941).

gratitude to Dr. Milton D. Harris and Mr. A. M. Sookne for supplying them with the cellulose acetate fractions and for kindly consulting them throughout this investigation.

Summary

1. The specific viscosities of cellulose acetate fractions were determined at various concentrations (up to 0.5 volume per cent. of the solute). The slopes of the η_{sp}/c_v *versus* c_v curves can be represented by a single constant $k' = 0.70$.

2. The osmotic pressures of the same fractions were measured at various concentrations (up to 0.8 weight per cent. of the solute). The slopes of the π/c_2 *versus* c_2 curves can, within reasonable limits, be represented by one single constant $\mu = 0.43$.

3. The $[\eta]$-values for all fractions can be expressed by M_2 according to equation $[\eta] = 1.04 \times 10^{-2} \times M_2 0.67$.

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y. RECEIVED JUNE 24, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Activity Coefficients of Lead Chloride Determined from E. m. f. and Solubility Data at 25° in Ethylene Glycol–Water Solutions

BY A. B. GARRETT, RUSKIN BRYANT AND GEORGE F. KIEFER

The dihydric character of ethylene glycol, together with the moderately low value of its dielectric constant and its total miscibility with water, make it an interesting solvent in which to study solvation effects and to measure certain thermodynamic properties of solutes.

The cell data are used in this paper to evaluate the reciprocal of the mean molality at ionic strength of zero, $(1/m_\pm)_{\mu=0}$, and the value of the activity coefficient, γ, to saturation; the solubility data are used to give a qualitative idea of the degree of dissociation and to evaluate γ above saturation.

Experimental

The experimental procedure is similar to that previously described.[1,2]

The cell Pb(Hg), $PbCl_2$, AgCl, Ag was used.[3]

All solutions were made on a weight basis. The work was done in an atmosphere of nitrogen. Conductivity water was used throughout the work. Three grades of ethylene glycol were used: namely, (a) Eastman Kodak Co. purest grade, (b) C. P. grade redistilled and (c) C. P. grade dried over sodium sulfate and redistilled; in each of the latter two cases, the center cut was used. The amalgam contained approximately 5% lead and was prepared thermally. The silver–silver chloride electrodes were prepared by the method previously described.[1] All chemicals were reagent quality or purified to that standard. The temperature was 25.00 ± 0.01°.

Data

The data are collected in Table I, and are shown in Figs. 1 and 2. The values of m_{PbCl_2} at saturation are those published earlier.[2] The

TABLE I

E. M. F. VALUES FOR THE CELL Pb-Hg/$PbCl_2$[H_2O-$C_2H_4(OH)_2$]/AgCl/Ag AND SOLUBILITY DATA FOR THE SYSTEM $PbCl_2$–ETHYLENE GLYCOL–H_2O–KCl

Solution concentrations given in % by wt. water-ethylene glycol; *D*, dielectric constant; $PbCl_2$ and KCl as moles in 1000 g. of solvent.

I. 78.25%–21.75%. $D = 72.2$			II. 57.43%–42.57%. $D = 65.8$		
$PbCl_2$	*E*. obs.	γ	$PbCl_2$	*E*. obs.	γ
0.003124	0.5573	0.737	0.00206	0.5695	0.751
.006248	.5351	.656	.00619	.5345	.620
.007727	.5287	.626	.00845	.5254	.576
.01225	.5151	.562	.01238	.5147	.519
.02450	.4959	.463	.02476	.4961	.420
.03821*	.4842†	.402	.02728	.4936	.407
*(satn.)	†(extrap.)		.04016*	.4842†	.356
			*(satn.)	†(extrap.)	
$PbCl_2$	KCl	γ	$PbCl_2$	KCl	γ
0.03187	0.0196	0.402	0.03440	0.0192	0.355
.02690	.0392	.395	.02882	.0382	.354
.01951	.0783	.377	.02158	.0765	.336
.01733	.0995	.359	.01456	.1534	.289
.01080	.1968	.304	.01288	.1922	.268
.00682	.4972	.201	.00700	.3868	.219
.00482	.8098	.165	.00400	.7837	.167
.00402	1.222	.134	.00345	1.194	.133
.00496	2.096	.087	.00395	2.054	.089
$(1/m_\pm)_{\mu = \text{satn.}} = 16.49$			$(1/m_\pm)_{\mu = \text{satn.}} = 15.69$		
$(1/m_\pm)_{\mu = 0} = 41.1$			$(1/m_\pm)_{\mu = 0} = 44.1$		

---

[1] Black and Garrett, THIS JOURNAL, 65, 862 (1943).

[2] Garrett, Noble, Bryant and Kiefer, *ibid.*, 65, 293 (1943).

[3] Carmody, *ibid.*, 51, 2905 (1929).