

of substituents about the double-bonded carbons ($R_2C=CHR$) is reflected in the strong 12.16μ band.³ The structure of the low boiling isomer is clearly indicated to be the unconjugated form, 4-methyl-4-penten-2-one, by the fact that the $C=O$ band appears at the normal unconjugated ketone position, 5.83μ , and that the strong band in the 10 to 15μ region occurs at 11.16μ , the position associated with the $R_2C=CH_2$ configuration.³ This result is in agreement with the Raman work of Dupont and Menut⁴ on a mixture of the isomers, the presence of a 1716 cm.^{-1} line associated with unconjugated $C=O$ indicating an unconjugated form.

In agreement with chemical evidence referred to in the preceding article, no appreciable concentration of enol form was present as indicated by the weakness of hydroxyl group absorption near 3.0μ .

The ultraviolet absorption spectra (2100 to 5000 Å.) independently lead to the same conclusion. The high-boiling isomer exhibits bands at 2310 and 3290 Å. (molar extinction coefficients 1.20×10^4 and 40.5 liters/mole cm. respectively; spectra of *i*-octane solutions). These bands are closely similar in position and intensity to those

(3) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

(4) G. Dupont and M. L. Menut, *Bull. soc. chim.*, **6**, 1215 (1939).

of other compounds containing the conjugated system $C=C-C=O$. The low-boiling isomer shows only the single band near 2900 Å. (molar extinction coefficient *ca.* 77 liters/mole cm., spectrum of *i*-octane solution) characteristic of simple unconjugated ketones.

The intensity of the 2310 Å. band made it a logical choice for quantitative analyses for the conjugated isomer, and it was so used in the work described in the preceding article.¹ The infrared spectra, which as obtained for this work were not suitable for use in precise quantitative analyses, were nevertheless used analytically to get approximate ratios of conjugated to unconjugated isomers, and to check for the presence of extraneous compounds (water, acetone, hydration products, etc.).

Summary

1. The infrared (2 to 15μ) and ultraviolet (5000 to 2100 Å.) absorption spectra of two isomers of mesityl oxide are reported.

2. The spectra of the high-boiling isomer show it to have the commonly accepted conjugated structure, 4-methyl-3-penten-2-one. Those of the low-boiling isomer clearly indicate it to be 4-methyl-4-penten-2-one.

EMERYVILLE, CALIF.

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

The Temperature Dependence of the Osmotic Pressure of Polyvinyl Chloride Solutions¹

BY PAUL DOTY² AND ELI MISHUCK³

Statistical thermodynamic theories^{4,5} of polymer solutions give for the free energy of dilution $\Delta\bar{F}_1$, the following expression

$$\Delta\bar{F}_1 = RT[\ln(1 - v_2) + v_2(1 - 1/x) + \mu v_2] \quad (1)$$

The volume fraction of polymer is denoted by v_2 and the ratio of the volume of the polymer molecule to the solvent molecule by x . The quantity μ is of critical importance. Huggins⁴ suggested that it be considered as the sum of a temperature independent term, β , corresponding to the entropy contribution and a temperature dependent term α/RT , corresponding to the heat contribution.

To a first approximation β is equal to the reciprocal of the coordination number of the hypo-

thetical lattice used in deriving equation (1). More detailed considerations,^{4,6,7} however, show that β depends in a complicated manner on the concentration of polymer segments in the immediate vicinity of a given polymer segment; this in turn depends on the flexibility of the polymer, the amount of branching and on the concentration. Estimates from experimental measurements on rubber-benzene⁸ and rubber-toluene⁹ and from the theory place the value of β in dilute solutions in the range 0.3 to 0.4 for non-polar polymers.

The quantity α is approximately equal to the heat of dilution, $\Delta\bar{H}_1$, divided by v_2^2 . (This approximation would be an exact equality if v_2 were independent of temperature.) For non-polar polymers in dilute solution the value of α should be in the range of 0 to about 100 cal./mole. For

(1) Presented at the Polymer Forum, 109th meeting of the American Chemical Society, Atlantic City, N. J., April 9, 1946.

(2) Present address: Department of Colloid Science, The University, Cambridge, England.

(3) Taken in part from a thesis presented in partial fulfillment for the degree of Master of Science, Polytechnic Institute of Brooklyn, June, 1946.

(4) Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); **44**, 431 (1943).

(5) Flory, *J. Chem. Phys.*, **9**, 666 (1941); **10**, 51 (1942).

(6) Flory, *ibid.*, **13**, 453 (1945). In this paper there is a review of all measurements which allow an estimation of the values of β and α in dilute solution.

(7) Zimm, *ibid.*, **14**, 164 (1946).

(8) Gee and Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

(9) Meyer, Wolf and Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).

polar polymers negative values should be possible when there is specific polymer-solvent interaction.

Because of the very small number of investigations of the value of β and α , and since no measurements have been made on polar polymers, the study reported below was undertaken. The temperature dependence of the osmotic pressure of dilute solutions of polyvinyl chloride in cyclohexanone, methyl ethyl ketone and dioxane was determined. These solvents were chosen because they cover the range from very good to very poor solvents. The solution of some technical difficulties permitted the measurements to be made over a temperature range of 0-80°.

Experimental Details

Osmometer.—The osmometer cell was made of stainless steel following in most respects the design of Fuoss and Mead.¹⁰ A diagram of the osmometer in the constant temperature bath is shown in Fig. 1. The only significant differences from the Fuoss and Mead design are the use of metal stand pipes and Wood's metal seals instead of glass-to-metal seals join the capillaries to the metal bushing.

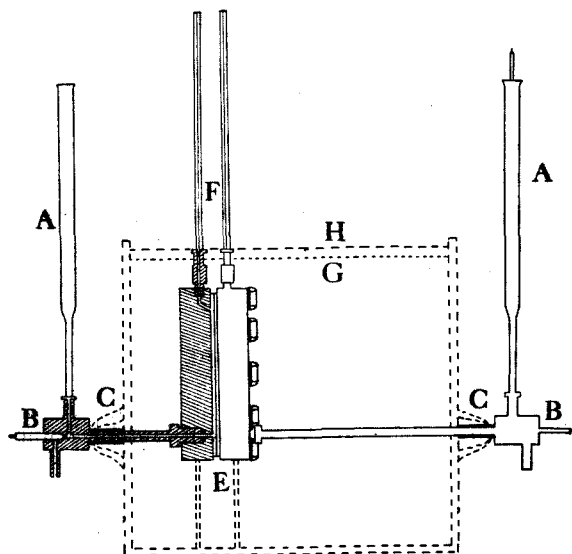


Fig. 1.—Diagram of osmometer in thermostat: A, side tube; B, drain valve; C, flange; D, osmometer cell; E, membrane; F, capillaries; G, water level; H, metal shield.

The osmometer is mounted as shown in a specially constructed, cylindrically shaped thermostat. The thermostat was constructed from copper pipe (10 inches in diameter) in two parts. The two parts join at the level of the connecting tubes of the osmometer by means of specially designed flanges which are bored horizontally to permit the passage of the connecting tubes. The flanges are held together by eight bolts which are evenly spaced around the thermostat. Rubber

tubing surrounds the connecting tubes where they pass through the flange and a thick rubber gasket, punched to accommodate the bolts, is fitted into the space between the two flanges. The exterior of the bath was covered with cork sheet for insulation.

A constant source of heat or cold was supplied by heating coils (with Variac) or copper tubes carrying cold water. One or two long, cylindrical 40-watt light bulbs furnished the heat for regulation and were controlled by a mercury-in-glass thermoregulator connected to an electronic relay. Observations showed that if the fluctuation of the meniscus in the capillary attached to the closed side of the osmometer (solution side) is to be less than 0.005 cm. the temperature of the enclosed liquid must be constant to within about 0.005°. Although the thermoregulator ordinarily did not regulate better than $\pm 0.02^\circ$ it was possible to achieve the desired regulation by making use of the large heat capacity of the osmometer cell. This heat capacity causes the temperature of the cell liquid to lag at least one minute behind the bath liquid temperature. Consequently, if the thermoregulator breaks the circuit several times per minute the temperature of the bath liquid at its upper and lower extremes is never transmitted to the liquid in the osmometer. By rapid stirring and by allowing the thermoregulator to vibrate slightly with the motor of the stirrer it was possible to increase the frequency of the heating periods and thus eliminate any observable fluctuation of the meniscus height (± 0.005 mm.).

It was also necessary to prevent water from condensing on the capillaries when the bath was operating at elevated temperatures. Placing a metal shield as shown in Fig. 1 and surrounding the lowest part of the capillaries with rubber tubing was sufficient to eliminate this cause of fluctuation in the meniscus height.

At temperatures above 65° the Wood's metal used to seal the capillaries to the metal bushings had to be replaced by porcelain cement (Sauer-eisen) which was found to be impervious to the solvents used. The diameter of the capillaries¹¹ was constant to within 1% and hence the capillary rise in each tube was the same within the precision of observation.

Almost all the measurements were obtained with the use of the same membrane over a period of about one year. This membrane was prepared by denitrating nitrocellulose in the manner described by Montonna and Jilk.¹² When it was desired to change from one solvent to another the osmometer was filled for several-hour periods with solvent mixtures increasing in concentration of the new solvent. Usually about five mixtures of different composition were used.

For future work at different temperatures a new osmometer has been designed in this Labo-

(11) Fischer and Porter Company, Hatboro, Pennsylvania.

(12) Montonna and Jilk, *J. Phys. Chem.*, **45**, 1374 (1941).

(10) Fuoss and Mead, *J. Phys. Chem.*, **47**, 59 (1943).

ratory. Its features include much greater ease of operation and thermostating and much smaller volume requirements.¹³

Manipulation.—Upon filling the osmometer the drain valves are opened for a few seconds to allow for the removal of any air that may be trapped in them. By means of a Y-tube air pressure (by mouth) is simultaneously exerted on the liquid in both capillaries. This is then repeated on the standpipes thus forcing liquid out of the capillaries. After several washes the meniscus difference usually becomes constant in about one hour. This difference (zero reading) should be less than 0.05 cm. and should remain constant when the osmometer is refilled with fresh solvent. If this situation does not obtain the membrane is discarded. The presence of air bubbles at elevated temperatures is particularly annoying. They could usually be eliminated by preheating the solvent and solution (with reflux condenser) thus removing the dissolved air.

After the zero reading is obtained, the osmometer is washed out with fresh solvent and solution on the solvent and solution sides respectively. Following a second filling the vertical valve is closed and an "expected value" of the osmotic pressure is found by observing the meniscus difference after it has become essentially constant. Usually this observation is repeated on a third filling and then the osmometer is filled for the actual observation of the osmotic pressure. The meniscus difference is at once adjusted, to the expected value and the time is noted. Measurements are recorded every five minutes for at least eighty minutes. In the more concentrated solutions the effect of diffusion often can be detected by the meniscus difference never becoming quite constant. A straight line is fitted through the points taken after thirty minutes and its intersection at zero time is recorded as the observed osmotic pressure after correction for the zero reading and the density of the solvent. The density of the solvent is taken at the temperature recorded by a thermometer in the vicinity of the capillaries; it is always near room temperature.

Materials.—The polymer used for most solutions was fraction 7 from a fractionation of a commercial polyvinyl chloride¹⁴ carried out by means of successive additions of *n*-butanol to about a one per cent. solution of the polymer in cyclohexanone by Jelling and Auerbach.¹⁵ After a refractionation twenty-three fractions were obtained, two of which were used in this investigation. Fraction 7 had an intrinsic viscosity of 1.27 in cyclohexanone, 0.92 in butanone, and 0.80 in dioxane at 26°. At 60° in cyclohexanone fraction 7 had an intrinsic viscosity of 1.05; that of fraction 12 was 0.97 and that of the unfractionated polymer was 0.88.

(13) General Gauge and Tool Company, 30 Irving Place, New York, N. Y.

(14) Geon 101, Goodrich Chemical Company, Cleveland, Ohio.

(15) V. Auerbach, Thesis, Polytechnic Institute of Brooklyn, 1945.

The *n*-butanone was of C.P. quality and had the correct refractive index. The dioxane was purified by refluxing with sodium for several hours followed by distillation. The cyclohexanone was that from a middle fraction of a distillation in an efficient still having a boiling point range of 0.5°.

Density Determinations.—In order to know precisely the concentration of the solutions at various temperatures the variation of density with temperature is required for all the solvents. The temperature coefficient of thermal expansion was determined for the solvents used by means of a calibrated volumetric flask with a graduated neck (100 ml.). Evaluation of the data obtained over a sixty degree temperature range gave for the increase in volume of one cc. of liquid per degree centigrade the following: cyclohexanone, 0.000857; butanone, 0.00125; dioxane, 0.00109. At 20° the following densities were used: cyclohexanone, 0.947; butanone, 0.805; dioxane, 1.033.

Results and Discussion

The results obtained are recorded in Figs. 2 to 6 inclusive. The osmotic pressure in grams per sq. cm. divided by the concentration in grams per 100 cc. of solution is plotted against concentration. In general each point has been checked or is the average of two independent determinations. The size of the circles indicating experimental points is an estimation of the probable experimental error as judged from the reproducibility of the measurement. The data at 68° in dioxane were the first taken at an elevated temperature and are

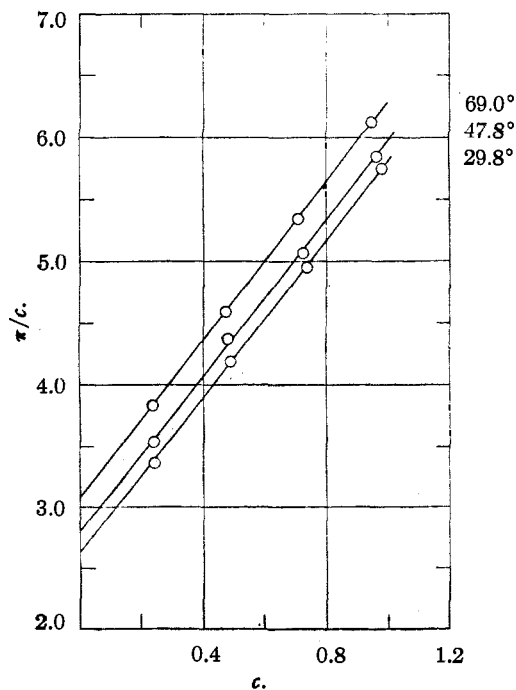


Fig. 2.—Osmotic pressure data for cyclohexanone, fraction 7.

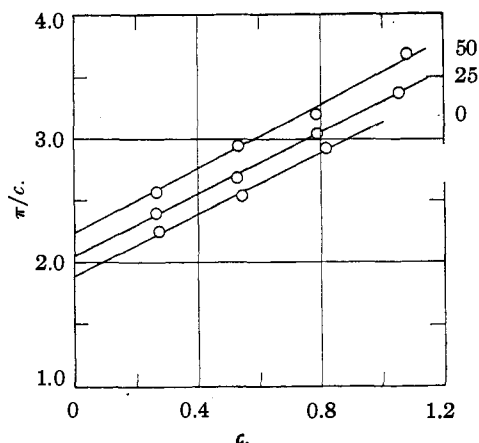


Fig. 3.—Osmotic pressure data for butanone-2, fraction 7.

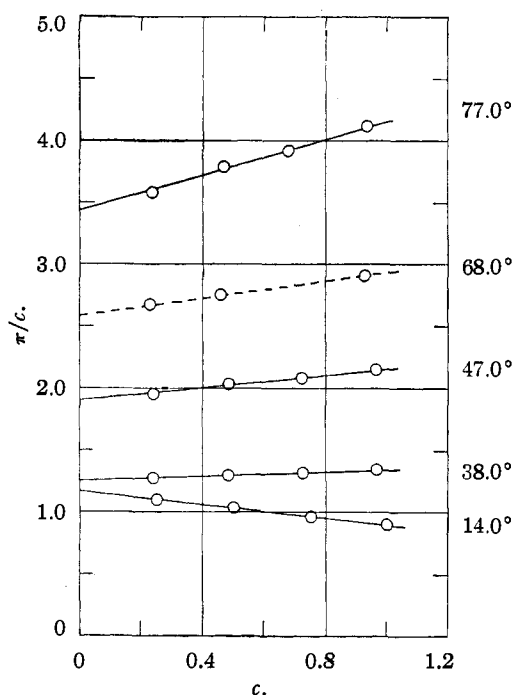


Fig. 4.—Osmotic pressure data for dioxane, fraction 7.

not precise enough for use in evaluating the heat of dilution.

Equation (1) after expansion can be written in terms of osmotic pressure and concentrations as follows, if higher terms are neglected. These higher terms are smaller than probable experimental error at concentrations less than 1%.

$$\frac{\pi}{c} = \frac{RT}{M} + \frac{RT}{100V_1\rho} \left(\frac{1}{2} - \mu \right) c \quad (2)$$

The density of the solute is denoted by ρ ; the molecular weight of the solute by M ; the molar volume of the solvent by V_1 . With the units of osmotic pressure and concentration used here the gas constant R has a value of 848. The slope determined from the graphs can be set equal to the coefficient of the concentration in the second term

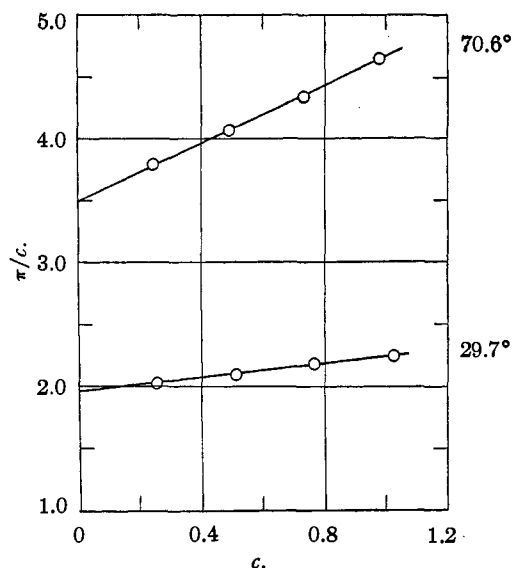


Fig. 5.—Osmotic pressure data for dioxane, fraction 12.

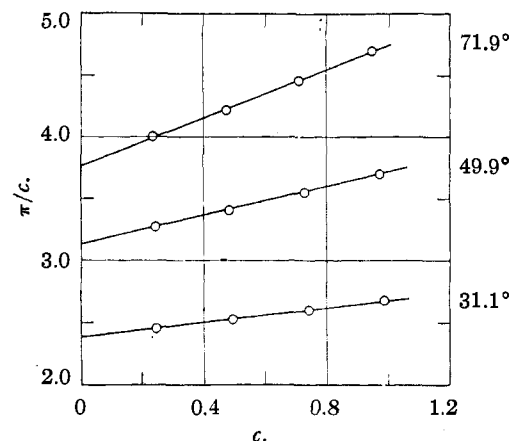


Fig. 6.—Osmotic pressure data for dioxane, unfractionated polymer.

TABLE I
THE VALUES OF μ AND MOLECULAR WEIGHT FOR POLY-VINYL CHLORIDE IN SOLUTION

System	Temp., °C.	μ	Mol. wt.
Fraction 7	29.8	0.240	99,000
Cyclohexanone	47.8	.252	98,500
	69.0	.264	93,500
Fraction 7	0.1	.402	122,000
Butanone-2	26.0	.409	121,000
	49.6	.413	122,000
Fraction 7	14.0	.518	210,000
Dioxane	38.0	.493	210,000
	47.0	.485	142,000
	68.0	.478	111,000
	77.0	.454	86,500
Fraction 12	29.7	.477	131,000
Dioxane	70.6	.427	84,000
Unfractionated	31.1	.482	107,000
Dioxane	49.9	.461	88,000
	71.9	.440	78,000

and the result solved for μ . Using a value of 1.41 for the density of polyvinyl chloride the value of μ was calculated for each series of concentrations measured. These values are listed in Table I. Most of these μ -values are plotted against the reciprocal of absolute temperature in Fig. 7.

Straight lines are obtained for each system verifying Huggins' division of μ into two terms: one independent of temperature and the other inversely proportional to temperature. The following expressions for μ result when β and α are determined from Fig. 7

Fraction 7, cyclohexanone	$\mu = 0.46 - 129/RT$
Fraction 7, butanone	$\mu = 0.47 - 36/RT$
Fraction 7, dioxane	$\mu = 0.16 + 203/RT$
Unfractionated, dioxane	$\mu = 0.12 + 213/RT$

It is estimated that the values of β are reliable to ± 0.02 and those of α to ± 10 cal./mole. However, the values of β and α for fraction 7 and the unfractionated polymer are considered to be significantly different even though the difference is slightly within the estimated probable error. Values of β and α are not recorded for fraction 12 since there are measurements at only two temperatures.

From the plots of osmotic pressure data shown in Figs. 2 to 6, the number average molecular weights have been calculated in accordance with equation (2). These values are listed in Table I. The variation of the molecular weight with solvent and temperature is quite new and unexpected. This phenomenon has been studied in detail by a number of different methods and has been proven to be due to association.¹⁶ The data on fraction 7 presented here are the same as quoted in this publication. The kind of association is shown to be static, not dynamic, and hence M does not vary with concentration. This fact is important here for otherwise the π/c plots would be strongly curved. Examination of Fig. 4 also shows that the variation of molecular weight does not affect the slope because the slopes at 47 and 77° can be predicted from the slopes at 14 and 38° where the molecular weight remains constant.

The values of β and α obtained for cyclohexanone and butanone solutions are not unreasonable. It is well known that cyclohexanone is one of the best solvents for polyvinyl chloride. This is reflected by the large negative value of α which is indicative of considerable solvation. The origin of this strong polymer-solvent attraction is the hydrogen bonding between the hydrogen on chlorine-bearing carbon atoms and the ketonic oxygen and the close similarity of the cohesive energy densities¹⁷ of the polymer and solvent. The value of α is considerably less in butanone solutions because the hydrogen bonding is less pronounced owing to the absence of a cyclic struc-

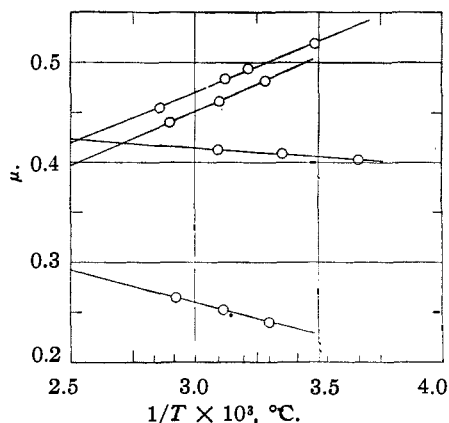


Fig. 7.—Plot of μ for polyvinyl chloride solutions against reciprocal of absolute temperature.

ture and because the cohesive energy densities differ more.

The values of β are much closer to 0.5 and hence the entropies of dilution are much less than in other systems where measurements or estimates have been made (see Reference 6 for review). However these lower entropies are perhaps understandable, for the number of possible configurations of the polyvinyl chloride chains may be greatly reduced due to several factors. First, the consideration of minimum energy will predict that the chlorine atoms will be found to alternate on opposite sides of the carbon chain, thus resulting in a stiffer more extended chain. Secondly, some polymer-polymer contacts may be rather durable if opposing dipoles are properly oriented reducing further the number of configurations available. Finally there may be a relatively large number of branches in these polyvinyl chloride molecules. In view of these possible deviations from a randomly-kinked structure it is not surprising to find exceptionally low values for the entropies of dilution.

The values of β and α for the dioxane solutions are most puzzling for there is no reason to expect the occurrence of large entropies of dilution (small β); cohesive energy densities considerations¹⁷ would predict only a small positive value of α . It is tempting to place the blame on the excessive association that exists in this case, but careful examination does not reveal any real support for this. For the present then we must admit that the actual complexities in this system have not been resolved by our thermodynamic approach and further experimental work is required to elucidate this seeming paradox. Consequently the usual interpretation of α and β should not be applied in this case without reservation.

The small differences noted between the β and α values for the different polyvinyl chloride samples must be due to an heterogeneity of structure or composition within the original polymer.

With the data now available it was thought to be of interest to determine approximately how the

(16) P. Doty, H. Wagner and S. Singer, *J. Phys. and Colloid Chem.*, **51**, 33 (1947). The data on Fraction 7 are quoted in this publication.

(17) P. Doty and B. Zimm, unpublished data.

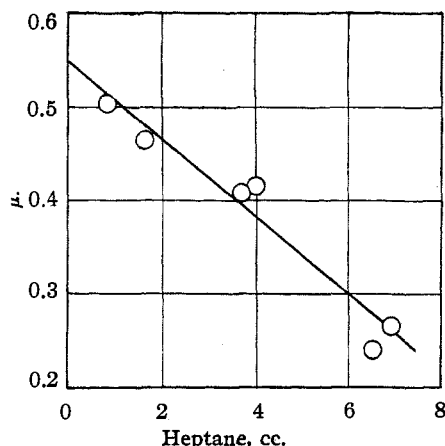


Fig. 8.—Plot of μ -values against amount of heptane to cause cloud point.

solubility of polyvinyl chloride varies in these three solvents. Solutions of fraction 7 in the three solvents were titrated to the cloud point (visual examination) at 24 and 61° with *n*-heptane. The only correlation obtained was between μ -values and the amount of heptane required for the cloud point. This is shown in Fig. 8, where μ is plotted against the cc. of *n*-heptane necessary to bring a definite opalescence to 5 cc. of 0.5% solution of fraction 7. The intersection of the plot at zero amount of *n*-heptane occurs at a μ -value of approximately 0.55. This is slightly greater than the critical value calculated from the theory^{4,5} but corresponds closely to the value

determined from swelling experiments.¹⁸ (This value of μ separates solvents from non-solvents for small concentrations of polymer.) Such a correlation is another illustration that in dilute solution μ -values are as practical as well as a thermodynamic measure of solvent ability.

Acknowledgment.—The authors wish to express their appreciation for the help of Dr. W. J. Badgley and Mrs. J. Bunker.

Summary

1. The thermostating of a Fuoss-Mead type osmometer is described in detail together with the technique of operation at various temperatures.
2. Osmotic pressure measurements at several concentrations of polyvinyl chloride solutions in cyclohexanone, butanone-2 and dioxane over a 0–77° temperature range are reported.
3. The μ -values and molecular weights are calculated from these measurements. The μ -values may be represented as follows for fraction 7: cyclohexanone, $\mu = 0.46 - 129/RT$; butanone, $\mu = 0.47 - 36/RT$; dioxane, $\mu = 0.16 + 203/RT$.
4. The molecular weight depends on the solvent and the temperature (because of association).
5. To a good approximation the amount of *n*-heptane required to cause opalescence in polyvinyl chloride solutions is linearly dependent on the value of μ .

(18) P. Doty and H. S. Zable, *J. Polymer Sci.*, **1**, 90 (1946).

CAMBRIDGE, ENGLAND RECEIVED SEPTEMBER 10, 1946

[COMMUNICATION NO. 1135 FROM THE KODAK RESEARCH LABORATORIES]

The Solubility of Cellulose in Mixtures of Nitrogen Tetroxide with Organic Compounds

BY W. F. FOWLER, JR., C. C. UNRUH, P. A. MCGEE AND W. O. KENYON

Only a few types of solvents for cellulose are known including aqueous salt solutions, certain inorganic acids, inorganic bases at low temperatures, quaternary nitrogen bases, and complexes of copper with ammonia or organic amines. The existing knowledge of this field is summarized in recent texts,^{1,2} which may be used as sources for references to experimental papers.

During a study of the oxidizing effect of oxides of nitrogen (NO_2 , N_2O_4) on carbohydrates,³ mixtures of the oxides with several classes of organic compounds were found to be solvents for cellulose.

(1) E. Heuser, "The Chemistry of Cellulose," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 136–164.

(2) H. M. Spurlin, "High Polymers," Vol. V in "Cellulose Derivatives," E. Ott, editor, Interscience Publishing Co., New York, N. Y., 1943.

(3) P. A. McGee, W. F. Fowler, Jr., E. W. Taylor, C. C. Unruh and W. O. Kenyon, *THIS JOURNAL*, **69**, 355–361 (1947). References to earlier papers of this series are given therein.

This paper is a preliminary qualitative description of such solvents.

Experimental

Materials.—Nitrogen tetroxide of commercial grade purified as previously described.³

Organic compounds employed in the solvent mixtures were either Eastman Kodak Co. White Label Grade or were prepared by the usual synthetic methods and purified to meet the accepted values of boiling point or melting point. Liquid substances were tested for moisture with a small amount of anhydrous copper sulfate. If moisture was present, it was removed by shaking the liquid over anhydrous magnesium sulfate.

Cotton linters of good commercial quality and having a cuprammonium hydroxide viscosity of seven seconds were employed. They were ground to 20-mesh, then dried at 105° to constant weight.

Substituted sulfonic esters were synthesized by refluxing one mole of the sulfonyl chloride, 1.25 moles of the phenol and two moles of pyridine for eighteen hours. The reaction mixture was washed consecutively with water, dilute aqueous hydrochloric acid, water, dilute aqueous