

# Theta-Cosolvent Solutions for Poly(vinyl Chloride) by Cloud Point and Osmotic Pressure Measurements

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## Synopsis

The possibility of utilizing cloud point titrations for obtaining theta-cosolvent compositions for PVC solutions was examined for a range of THF-nonsolvent systems. Hansen's<sup>1-3</sup> "radii of solubility spheres" were calculated for the various solvents and cosolvent solutions and compared with the observed solubility behavior. The application of theta-cosolvent solutions for simplifying the determination of the number-average molecular weight was also examined.

## INTRODUCTION

There are distinct advantages in measuring certain polymer solution properties in theta solvents. "One point" osmotic pressure determinations, utilizing only one polymer concentration, would be most desirable to speed up the determination of polymer number average molecular weights, for example. The solution of a polymer sample directly in a theta solvent might be expected to be difficult because, by its very definition, a theta solvent is a poor one. The use of cosolvent solutions, on the other hand, appears entirely practical when one of the solvents is a good solvent for the particular polymer and the other is essentially a nonsolvent. Then the polymer may be readily dissolved in the good solvent, and the nonsolvent may be added in sufficient quantity to produce a theta-cosolvent solution. Such a procedure would require the knowledge of the theta-cosolvent composition for the particular polymer.

One method of finding possible theta-cosolvent mixtures is that of turbidity or cloud point titrations.<sup>4</sup> This procedure involves the preparation of polymer solutions of different concentrations and titration with a nonsolvent until the first sign of cloudiness. The procedure recommended was the extrapolation on a log-log graph of the cloud point concentrations for a number of different polymer concentrations to that corresponding to 100% polymer. This procedure is suitable when the cosolvents are composed of a nonsolvent added to a polymer dissolved in a good solvent. It has also been reported by Sarkar and Palit<sup>5</sup> that theta-cosolvent compositions for polystyrene and poly(methyl methacrylate) were obtained using a combination of two nonsolvents.

The general topic of polymer solubility is complex, especially for polymers that are polar and that have a tendency to form hydrogen bonds in solution. The complexity arises because of the difficulty in defining various types of molecular interactions which occur in polymer solutions, including possible association or

aggregate formation. The use of two-component cosolvent solutions adds yet another dimension to the possible complexity. The work of Banks and Prausnitz,<sup>6</sup> Hansen,<sup>1,2</sup> and Hansen and Skaarup<sup>3</sup> has done much to establish a rational approach to miscibility limits for polymers. Dividing the polymer and solvent solubility parameters into three components,  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$ , to account for dispersion, polar, and hydrogen-bonding interactions, respectively, Hansen was able to construct three-dimensional "solubility spheres" for different polymer-solvent systems. The radius of each solubility sphere within which the solubility characteristics could be defined was determined from

$$\gamma = (4\Delta\delta_d^2 + \Delta\delta_p^2 + \Delta\delta_h^2)^{1/2} \quad (1)$$

$$\Delta\delta_i = \delta_{i,\text{polymer}} - \delta_{i,\text{solvent}} \quad (2)$$

The model utilized a unit length for  $\delta_d$  which was twice that of the other two solubility parameter components. The three solubility parameter components were related to the Hildebrand and Scott<sup>7,8</sup> solubility parameter  $\delta$  for both polymer and solvent:

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (3)$$

When applied to cosolvent systems, the component solubility parameters were weighted according to the volume fraction of the constituent components. The original procedure for evaluating the component parts of the solubility parameters was an extensive trial-and-error one based on experiments with many polymer-solvent systems. Tables have been assembled<sup>1</sup> and subsequently revised<sup>3</sup> for values of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  for a considerable number of solvents. An attempt has been made by Chen<sup>9</sup> to describe polymer-diluent systems according to a "solubility circle" using two,  $x_h$  and  $\delta_h$ , instead of three parameters, the first concerned with the combined effects of molecular dispersion and polarity and the second, as before, with hydrogen bonding. More recently, Koenhen and Smolders<sup>10</sup> attempted to correlate the solubility parameter vectors with associated properties of solvents such as surface tension, dipole moment, and refractive index for application to those for polymers.

The concentration dependence of the osmotic pressure for polymer solutions is normally written as

$$\pi = \frac{RT}{M_n} C_2 + A_2 C_2^2 + A_3 C_2^3 + \dots \quad (4)$$

In a theta solvent and at low polymer concentrations, the osmotic pressure is essentially independent of polymer concentration; and hence  $A_2$ , the second virial coefficient, becomes negligible. Equation (4) is considered to apply equally well for cosolvent solutions.<sup>4</sup> It is usually found that  $A_2$  is relatively large and positive in good solvents, and small or even negative in poor solvents or cosolvent solutions.

## EXPERIMENTAL

Commercial polymers produced by a suspension polymerization process by Imperial Oil Enterprises, Esso grades 353, 363, and 373, were used in the cloud point and osmometry experiments. Three additional samples of different mo-

lecular weights, designated PV-2, PV-3, and PV-4, were supplied by the Pressure Chemical Company. The THF solvent was obtained from the Fisher Scientific Company and used as received. Previous work with this solvent<sup>11</sup> had indicated that the specified levels of impurities, chiefly 0.02 wt % water, were not exceeded and the effects of which were therefore considered negligible for this work. The nonsolvents ethylene glycol (reagent grade), methanol (99.9 mole % specified), and heptane (99.5% min. specified) were also purchased from Fisher Scientific. Absolute ethanol was obtained from the Liquor Control Board of Ontario. Distilled water was also used as nonsolvent.

In preparation for the cloud point experiments, a maximum concentration in THF solvent corresponding to about 20 g/l. of each polymer was initially prepared. These solutions were subsequently diluted to various concentrations down to about 1 g/l. In the cloud point determination, a 20-ml aliquot of each solution was very slowly titrated dropwise with nonsolvent supplied from a 10-ml microburet graduated in 0.02 ml. For this purpose, a flask was arranged with a magnetic stirrer, and light was located behind the stirred flask so that the visual cloud point could be clearly observed with the addition of one or two drops of nonsolvent. The experiments were performed at room temperature ( $22^{\circ} \pm 2^{\circ}\text{C}$ ) and were readily reproduced.

A Hewlett-Packard Model 501 automatic osmometer equipped with a Schleicher and Schuell Type 08 (fine) membrane was used for the osmotic pressure determinations. For measurements with cosolvent solutions, the membranes were initially preconditioned to THF solvent and then to the particular cosolvent solution prior to installation in the osmometer. The reference chamber and reservoir of the osmometer were also filled with the appropriate cosolvent. Polymer solutions for osmotic pressure determinations were prepared by dissolving approximately 1 g polymer in THF in a 100-ml volumetric flask. Solution was enhanced by heating and stirring. After the solution was cooled and made up to exactly 100 ml, aliquots were further diluted. In the preparation of cosolvent solutions, only 10-ml portions were further treated since only 2-3 ml were required in the osmometer. The cosolvent was titrated dropwise into the stirred THF solution to the prescribed volume, and care was taken to ensure that any slight polymer precipitate which occasionally formed was redissolved in the cosolvent solution. Due account was taken in the osmotic pressure determinations for the reduced polymer concentration and actual density of the cosolvent solution. Duplicate analyses were usually reproduced to within  $\pm 2\%$ . The sample preparation procedure and osmotic pressure measurement together required less than 2 hr. Certain samples, however, were purposefully aged or ultrasonically treated to study these particular effects on polymer gel structure.

A PVC sample of Esso 363 of approximately 25 g was dissolved in THF and fractionated into eight fractions by a nonsolvent precipitation method. Of possible nonsolvents, water was considered the most effective based on preliminary experiments. Preliminary experiments also established suitable volumes of nonsolvent required to produce appropriate quantities of polymer in each fraction. The initial polymer concentration chosen, apparatus, and method of fractionation were largely as described by Pezzin et al.<sup>12</sup> The fractionation apparatus consisted of a 3-liter jacketed glass vessel supplied with a magnetic stirrer and thermostatically controlled circulating water system. After an initial

addition of nonsolvent, the volume of which was determined by preliminary experiments, distilled water was added slowly at a rate of 0.5 ml/min using a Harvard apparatus syringe pump and a 100-ml syringe. The initial solution contained 25 g polymer dissolved to produce 2000 ml solution to which 200 ml water was slowly added.

Subsequent additions of nonsolvent were by syringe pump until a sufficient quantity of precipitate was produced. The solution and precipitate were then heated to 40°C and stirred until the polymer redissolved. The solution was then allowed to cool slowly and then to stand without stirring for 24 hr during which a coacervate or precipitate was formed at the bottom of the vessel. The supernatant solution was removed by syphoning while the polymer fraction was dissolved in THF. The dissolved fraction was reprecipitated in flocculant form with an excess of methanol, filtered, washed with hot distilled water, and finally with methanol. Successive fractions were similarly separated. The fractions were analyzed by osmometry in both THF and THF-methanol cosolvent solutions.

## RESULTS AND DISCUSSION

### Cloud Points

The cosolvent concentrations for THF-nonsolvent mixtures at the cloud point are listed in Table I and graphically shown in Figure 1 as a function of the final diluted polymer concentration. True mass fractions of components were used with consideration for the densities of solvents and polymer. For the sake of simplicity, however, it was assumed that there was no volume change on mixing. As suggested by Elias,<sup>13,14</sup> the cloud point concentrations were found to be a linear function of polymer concentration on a logarithmic plot. Further, it was suggested by Elias that extrapolation of the cloud point concentrations to a composition of 100% polymer would yield the theta-cosolvent composition. For the THF-highly polar cosolvent system, in addition to the reference point corresponding to the pure polymer, a second one can be defined. It is that corresponding to the solubility limit for PVC in the major solvent component, THF. At this point no nonsolvent is required to cause precipitation.

Hence, as with certain other phase diagrams, there appear to be two useful reference points for the type of polymer-cosolvent systems involving limited polymer solubility with the major solvent component. It is estimated that the solubility limit for Esso 363 is approximately 30 wt % polymer at 20°C. The solute-free nonsolvent concentration for methanol and heptane estimated from Figure 1 for a polymer solubility of 30 g/l. corresponds to 40 vol-% and 39 vol-%, respectively, which can be favorably compared with experimentally determined theta-cosolvent concentrations of 42 vol-% and 43 vol-%. The latter were determined from osmotic pressure measurements. On the other hand, the equivalent theta-cosolvent compositions for methanol and heptane calculated for the polymer composition of 100% would be 30 vol-% and 29 vol-%, respectively, significantly lower than those experimentally determined.

It was possible to observe the effect of polymer molecular weight on the cloud point concentration for THF-methanol cosolvent solutions. For the polymers PV-2 and PV-4, with respectively lower and higher molecular weights than Esso

TABLE I  
Nonsolvent Concentrations at Cloud Point for PVC Polymers, ESSO 363, PV-2, and PV-4<sup>a</sup>

Nonsolvent	Polymer	Polymer concn., g/l.	X <sub>2</sub>	X <sub>3</sub>	Polymer concn., g/l.	X <sub>2</sub>	X <sub>3</sub>	Polymer concn., g/l.	X <sub>2</sub>	X <sub>3</sub>
Water	Esso 363	0.71	0.157	0.00067	1.41	0.149	0.0014	2.82	0.145	0.0027
Ethylene glycol	Esso 363	5.64	0.145	0.0055	11.3	0.145	0.0109	22.6	0.125	0.0222
		2.81	0.303	0.0022	5.64	0.286	0.0046	11.3	0.283	0.0092
Ethanol	Esso 363	22.6	0.277	0.0184	5.63	0.475	0.0033	11.3	0.457	0.0069
		2.81	0.513	0.0016	5.63	0.475	0.0033	11.3	0.457	0.0069
Methanol	Esso 363	22.5	0.417	0.0148	3.98	0.439	0.0025	7.96	0.409	0.0053
		1.99	0.442	0.0013	3.98	0.439	0.0025	7.96	0.409	0.0053
Methanol	PV-2	15.9	0.391	0.0109	3.81	0.416	0.0024	7.63	0.390	0.0050
		1.91	0.465	0.0012	3.81	0.416	0.0024	7.63	0.390	0.0050
Methanol	PV-4	15.3	0.390	0.0105	3.51	0.419	0.0023	7.03	0.408	0.0047
		1.76	0.454	0.0011	3.51	0.419	0.0023	7.03	0.408	0.0047
Heptane	Esso 363	14.1	0.377	0.0099	8.5	0.367	0.0061	12.8	0.357	0.0093
		4.3	0.375	0.0031	8.5	0.367	0.0061	12.8	0.357	0.0093
Methanol-water (75:25 vol-%)	Esso 363	17.1	0.347	0.0126	21.4	0.337	0.0160	11.3	0.241	0.0097
		2.81	0.251	0.0024	5.63	0.250	0.0048	11.3	0.241	0.0097
Ethanol-water (83:17 vol-%)	Esso 363	22.5	0.238	0.0193	5.63	0.250	0.0048	11.3	0.241	0.0097
		2.81	0.330	0.0021	5.63	0.317	0.0044	11.3	0.303	0.0088
		22.5	0.302	0.0177	5.63	0.317	0.0044	11.3	0.303	0.0088

<sup>a</sup> X<sub>2</sub> = Nonsolvent mass fraction at cloud point; X<sub>3</sub> = polymer mass fraction at cloud point.

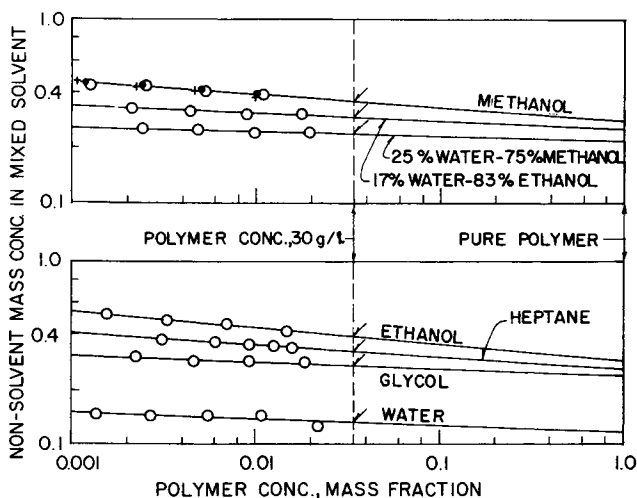


Fig. 1. Cloud points obtained on addition of various nonsolvents to PVC-THF solutions: (O) Esso 363; (+) PV4; (●) PV2.

363, it appears significant that the precipitation points are nearly independent of the polymer molecular weight. The effect of the polymer molecular weight on the theta condition has previously been considered scarcely detectable.<sup>4</sup> It would appear that the nature of the polymer-cosolvent interaction affects the polymer solubility characteristics much more than a variation in polymer molecular weight.

### Hansen "Solubility Spheres"

The solvent power of several solvents for PVC has been investigated by Moore and Hutchinson<sup>15</sup> who found that the solvent power depended somewhat on the criterion used to measure it. They listed an order of solvent power for the solvents based on osmotic pressure and swelling measurements. Their data, along with the cloud point determinations performed in this work, provided a means for testing the applicability of the Hansen solubility parameters to PVC-solvent systems. It is apparent from eq. (1) that the choice of actual values for the solubility parameter vectors would very much influence the size of the solubility sphere. Whereas the overall cohesive energy density is relatively well defined for most solvents because it is based on readily measurable properties, the allocation of solubility parameter vectors to polar and hydrogen bonding interactions is much more arbitrary. For polymers, all three solubility parameter vectors can be evaluated only indirectly. Hansen's original solubility parameter vectors<sup>1</sup> were evaluated by the application of a homomorph concept jointly with essentially a trial-and-error adjustment of parameters to satisfy observed polymer solubility behavior. Based on additional data for the solubilities of relatively low molecular weight solutes such as dyes, nonionic emulsifiers, binders, and pigments, Hansen and co-worker revised the values for the solubility parameter vectors for solvents.<sup>2,3</sup> The suggestion was that deviations from the original published values were generally insignificant.

The two sources of solvent solubility parameter vectors (1 and 3) were compared by calculating radii of solubility spheres for PVC,  $\gamma_1$  and  $\gamma_2$ , as shown in Table II. Three solubility regions may be found in Table II: soluble region ( $\gamma_1 < 2.0$ ), limiting solubility or cloud point ( $2.0 < \gamma_1 < 2.6$ ), and insoluble region ( $\gamma_1 > 2.6$ ). It is apparent that the numerical values for  $\gamma_1$  and  $\gamma_2$  are significantly different for three of the solvents, morpholine, nitrobenzene, and acetone, which, if the  $\gamma_2$  values were used, would incorrectly describe the observed solubility behavior by comparison with solubilities in other solvents or cosolvent mixtures. On the other hand, only THF-methanol cosolvent and dioxane fall somewhat outside the observed limits of the three solubility regions as defined by the other 16 solvents. The solubility and reversible gel formation of PVC in dioxane solvent has been investigated in detail by Haas and MacDonald.<sup>16</sup> It may be considered that the strong propensity for PVC to form three-dimensional structures in dioxane is not fully reflected in the values for the solubility parameter vectors. The calculated  $\gamma_1$  suggests that PVC might have been soluble in dioxane. Hansen<sup>2</sup> indicated that deviations for  $\gamma$  might be outside the region  $\gamma \pm 0.5$  in about 2.5% of the systems. Such expected inconsistencies may explain the slightly high value for  $\gamma_1$  for the THF-methanol cosolvent.

The overall assessment of the use of solubility parameter vectors for PVC solutions would be that they describe the observed behavior very well indeed. It may also be considered that the parameters based on experiments performed with resins and polymers appear to describe solubilities for PVC more consistently than those partially based on the solubility behavior of low molecular weight solutes. Whether this is more generally applicable to other polymer solutions is yet to be evaluated. It may be eventually shown that two values for solubility parameter vectors may be required depending on whether the solute is a high molecular weight polymer or a low molecular weight nonionic solute. Such an approach appears credible since it is known that solubility is at least to some extent a function of solute molecular weight. It is also significant that the cloud point experiments with cosolvent solutions correspond to a relatively narrow range for the radii of solubility spheres, largely substantiating the application of solubility parameter vectors for predicting solubilities in cosolvent solutions. Such a conclusion was also reached by Nunn<sup>17</sup> in dealing with a potential solvent system for a particular epoxy resin, "Epikote 1001," although one anomaly was described. It was found that acetone appeared to be incorrectly placed by comparison with the solvent power of other solvents. It is noted, however, that by the use of Hansen's original solubility parameter vectors,<sup>1</sup> the anomaly disappears.

The solubility parameter vectors for PVC as estimated by Koenhen and Smolders<sup>10</sup> may be compared with those of Hansen<sup>1</sup>:  $\delta_D = 4.9$  (3.5),  $\delta_H = 1.5$  (3.5), the values in parentheses being those of Hansen. The former values were used to estimate the radii of solubility spheres,  $\gamma_3$  and  $\gamma_4$ , based on the two different sources for *solvent* solubility parameter vectors<sup>1,3</sup> the results of which are listed in Table II. It is evident from Table II that anomalies can be found in the order of placement of several solvents. These anomalies incorrectly suggest that nitrobenzene is a very good solvent for PVC and that acetone and dioxane are also good solvents. It must be concluded that some further modification to the predictive methods for polymer solubility parameter vectors is required.

TABLE II  
Radii of "Solubility Spheres" for PVC in Different Solvent and Cosolvent Solutions<sup>a</sup>

Solvent	Composition	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$	Solubility	Reference
THF	—	0.28	0.82	3.19	3.69	Highly Sol.	15
Cyclohexanone	—	0.99	1.52	2.62	1.62	Highly Sol.	15
Morpholine	—	1.46	2.56	3.35	3.91	Sol.	15
Nitrobenzene	—	2.17	3.04	1.55	1.63	Sol.	15
Heptane/THF	0.38/0.62	2.04	2.10	3.81	4.20	Cloud pt.	this work
Water/THF	0.12/0.88	2.09	1.95	4.72	4.63	Cloud pt.	this work
Glycol/THF	0.23/0.77	2.24	2.60	4.74	5.21	Cloud pt.	this work
Ethanol/THF	0.42/0.58	2.62	2.78	5.32	5.30	Cloud pt.	this work
Methanol/THF	0.39/0.61	3.13	3.23	5.66	5.77	Cloud pt.	this work
Water/Ethanol/THF	0.05/0.25/0.70	2.49	2.52	5.14	5.16	Cloud pt.	this work
Water/Methanol/THF	0.06/0.18/0.76	2.52	2.57	5.11	5.12	Cloud pt.	this work
Dioxane	—	1.83	3.46	1.48	4.45	Swollen by 15 solvent	this work
Acetone	—	2.91	2.48	3.28	3.67	Swollen by 15 solvent	this work
Heptane	—	5.12	5.12	6.08	6.08	Insol.	this work
Ethanol	—	6.28	6.12	8.73	8.52	Insol.	this work
Methanol	—	8.09	7.96	10.3	10.1	Insol.	this work
Glycol	—	9.85	9.39	9.85	11.4	Insol.	this work
Water	—	18.1	18.2	20.1	19.5	Insol.	this work

<sup>a</sup> Source of solubility parameters:  $\gamma_1$ : Solvent (ref. 1), Solute (ref. 1);  $\gamma_2$ : Solvent (ref. 3), Solute (ref. 1);  $\gamma_3$ : Solvent (ref. 10);  $\gamma_4$ : Solvent (ref. 3); Solute (ref. 10).



TABLE III  
 $M_n$  Values for PVC Solutions in THF as a Function of Age and Treatment

Polymer	Age	$M_n$	Age	$M_n$	$A_2 \times 10^{6a}$	Treatment	New $M_n$	New $A_2 \times 10^6$
Esso 363	<2 hr	40,000	36 days	42,400	5.97	ultrasonic	39,000	5.02
Esso 363 (reprecip.)	<2 hr	49,600	<1 hr	49,600	4.67	—	—	—
Esso 373	<2 hr	79,800	3 days	83,800	5.02	—	—	—
PV 2	<2 hr	25,600	36 days	28,300	4.50	—	—	—
PV 3	<2 hr	41,000	36 days	54,100	4.33	ultrasonic	39,500	3.89

<sup>a</sup> Units of  $A_2$ :  $\text{erg-cm}^3/\text{g}$ .

TABLE IV  
 $M_n$  Values with THF and Heptane-THF and Methanol-THF Cosolvent Solutions

Polymer	$M_n$ in THF	35 vol-% Heptane			43 vol-% Heptane			42 vol-% Methanol		
		Age	$M_n$	$A_2 \times 10^{6a}$	Age	$M_n$	$A_2 \times 10^{6a}$	Age	$M_n$	$A_2 \times 10^{6a}$
Esso 353	35,100	<2 hr	56,500	0.16	<2 hr.	50,800	0.08	<2 hr	34,900	0.25
Esso 363	40,600	<2 hr	45,900	0.24	1 day ultrason.	66,800 53,600	-0.08 0.23	—	—	—
Esso 373	79,800	<2 hr	84,100	1.35	—	—	—	<2 hr	82,700	0.17
PV-2	25,600	<2 hr	32,200	0.48	—	—	—	—	—	—
PV-3	41,000	<2 hr	63,600	1.12	—	—	—	—	—	—
PV-4	54,000	<2 hr	62,900	0.40	1 day	105,000	0.39	<2 hr	53,000	-0.50

<sup>a</sup> Units of  $A_2$ :  $\text{erg}\cdot\text{cm}^3/\text{g}$ .

TABLE V  
 $M_n$  Values for Fractionated Esso 363 in THF and 42% Methanol-THF Cosolvent Solutions

Sample	$M_n$ in THF	$A_2 \times 10^{6a}$	$M_n$ in meth.-THF	$A_2 \times 10^{6a}$	$\Delta\%$	$M_n$ "one point"	$\Delta\%$
Fraction 1	102,200	3.54	109,100	0.38	6.8	111,400	9.0
2	97,500	3.72	98,700	0.35	1.2	99,400	1.9
3	80,200	3.81	—	—	—	—	—
4	76,900	3.46	76,200	0.09	0.9	78,200	1.7
5	63,500	3.54	—	—	—	—	—
6	59,400	3.89	60,100	0.52	1.2	60,800	2.4
7	38,600	4.50	37,000	0.43	4.1	38,000	1.6
8	18,900	4.84	18,700	-0.61	1.1	19,700	4.2
Total (reprecip.)	49,600	4.41	50,100	0.78	1.0	50,500	1.8
Average	—	3.97	—	0.28	2.3	—	3.2

<sup>a</sup> Units of  $A_2$ :  $\text{erg}\cdot\text{cm}^3/\text{g}$ .

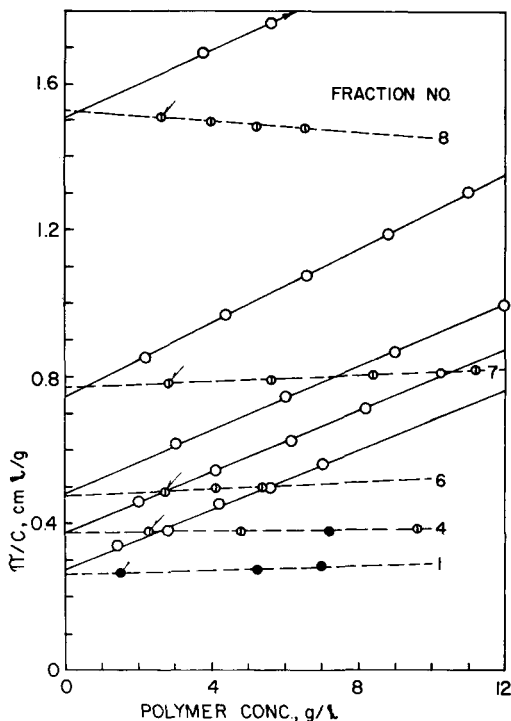


Fig. 2. Osmotic pressures of fractionated Esso 363 in (O) THF and (●) methanol-THF cosolvent solutions.

### Theta Cosolvent by Osmometry

PVC is known to form molecular aggregates in THF, particularly in aged solutions, which can be dispersed by ultrasonic radiation as described by Rudin and Benschop-Hendrychova.<sup>18</sup> Table III lists the apparent number-average molecular weights as determined from osmotic pressure measurements for several PVC samples dissolved in THF showing the effect of aging as well as ultrasonic treatment. As indicated by Rudin and Benschop-Hendrychova,  $M_n$  values can be seen to be somewhat larger for solutions aged up to 36 days at room temperature, although  $M_w$  values would probably have been more affected by aggregate formation. Whether or not ultrasonic radiation caused a further breakdown of the polymer itself is open to question, but it would appear that the molecular aggregates were fully dispersed by it, even after the prolonged aging period.

The results of osmotic pressure measurements in two concentrations of heptane-THF cosolvent and methanol-THF cosolvent are listed in Table IV. These measurements were performed in an attempt to find a suitable theta cosolvent for PVC. The apparent  $M_n$  in heptane-THF cosolvent is extremely high even although the solution preparation period was relatively short, suggesting a very high degree of aggregation. Furthermore, neither heating to boiling nor ultrasonic radiation just prior to measurement appeared to be able to disperse the relatively stable microgel, in both cases making little difference to the apparent  $M_n$ . Hence, one may conclude that although heptane-THF solutions produce very low second virial coefficients, they are nonetheless unsuitable as theta cosolvents because of the extensive microgel formation that rapidly forms in them.

The particular osmometer used was designed for a rapid response to changes in polymer concentration; measurements could normally be completed within 30 min. For heptane-THF cosolvent solutions, however, considerably longer periods of time (up to 3 hr) were required to reach a pseudosteady-state condition. At first, it was considered that the membrane characteristics were changing in the presence of the heptane-containing solution. Even after exposure to the heptane-THF solution for several days, the membrane produced osmotic pressure readings which still required excessively long periods of time. Consequently, it was considered that the polymer-solvent characteristics were changing with time or that the polymer was agglomerating while in the osmometer. This explanation would also appear to account for some lack of reproducibility in results when using heptane-THF solutions.

By contrast,  $M_n$  determinations in 42 vol-% methanol-THF cosolvent solutions were very similar (within 4%) to those in THF solutions, with no evidence of aggregate formation during the normal solution preparation and measurement period. In addition, the second virial coefficients were small, indicating that the particular cosolvent concentration indeed constituted a theta-cosolvent solution for PVC. To determine conclusively whether methanol-THF was suitable as a theta cosolvent even for PVC of various molecular weights,  $M_n$  measurements were made in both THF and methanol-THF solutions for several fractions of Esso 363 PVC.

The  $M_n$  values, second virial coefficients, and percentage differences in  $M_n$  from those in THF are listed in Table V. The actual osmotic pressures for those determinations are graphically shown in Figure 2. The intercepts for the reduced osmotic pressures are almost identical, but the slopes or second virial coefficients are much lower for the cosolvent solution. For this comparison, the hydraulic head measurements in the cosolvent solutions were converted to equivalent THF ones so that comparable reduced osmotic pressures were obtained. It is noted also that "single point" osmotic pressures could have been used in determining  $M_n$  with success, provided that they were obtained at the lowest polymer concentration of 1-3 g/l. The average deviation for the "one point" osmometry of 3.2% may be compared with that of 2.3% based on the reduced osmotic pressures extrapolated to infinite dilution as shown in Table V. Such deviations approach the limit of accuracy for osmotic pressure measurements themselves.

Trials with other theta-cosolvent combinations indicated that ethanol-THF and water-methanol-THF would also produce theta cosolvents which would produce a minimum of agglomeration with dissolved PVC. As a result of these experiments, it may be concluded that possible theta cosolvents based on solvent-nonsolvent combinations may be selected by cloud point titrations. For the purpose of utilizing theta cosolvents for measuring polymer solution properties, however, it is necessary to ensure that polymer agglomeration or microgel formation does not interfere with the measurements.

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