Ultracentrifugal Evaluation of Chemical Potentials for the System Poly(chloroprene)—Methyl Ethyl Ketone

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ABSTRACT: In accordance with Scholte, an attempt was made to determine the chemical potentials of components in the system poly(chloroprene) (PCP)—methyl ethyl ketone (MEK) by the sedimentation equilibrium method. The measurements were performed at 15, 25, and 35°C over the range of polymer concentrations up to about 70 wt%. From the data the Flory—Huggins interaction parameter was determined as a function of composition and temperature. The results were then used to compute Flory's enthalpy and entropy parameters (κ and ψ) at 25°C, the theta temperature for the system studied, over a wide range of compositions. It was found that the infinite-dilution values of these parameters are equal and unusually small, in conformity with the finding by Hanafusa, *et al.*, from light-scattering measurements. Finally, the results from equilibrium ultracentrifugation were checked by osmotic pressure data, though the comparison was limited to relatively low concentrations (<20 wt%).

KEY WORDS Poly(chloroprene) / Methyl ethyl ketone / Chemical potential / Sedimentation equilibrium / Osmotic pressure / Flory—Huggins interaction parameter / Flory's enthalpy and entropy parameters /

Basically, the thermodynamic behavior of a polymer solution can be evaluated if the chemical potential or activity of the solvent component is determined as a function of composition, pressure, and temperature. Conventional methods for this determination utilize osmotic pressure, vapor pressure, isothermal distillation, equilibrium sorption, and so forth. Each of them has the advantages characteristic of it, and experimentalists usually adopt a combination of them, depending on the system as well as the experimental conditions to be studied.

In the 1930s Pedersen¹ and Drucker² suggested that the sedimentation equilibrium method could be utilized as a technique for evaluating the chemical potential of the solvent component in binary solutions. Wales³ in 1951 applied for the first time this idea to methyl ethyl ketone solutions of polystyrene and poly(vinyl acetate), though the measurements were limited to a polymer concentration below about 20 wt%. After Wales, however, the Pedersen—Drucker approach was completely ignored until recently Scholte⁴ took it up for a study of polystyrene in toluene

and cyclohexane. He was able to determine the chemical potentials of the solvents up to a polymer concentration as high as about 80 wt% and found that the results agreed closely with those obtained by previous authors from other equilibrium measurements. One of the most important discoveries by Scholte was that, if use was made of the short-column method which is now usual in dilute solution studies by equilibrium ultracentrifugation, sedimentation equilibrium was attained in a reasonably short time of centrifugation even in highly concentrated solutions. However, as far as the authors are aware, no attempt to check Scholte's disclosure with other polymer—solvent systems is as yet reported in the literature.

This paper describes our attempt to determine the thermodynamic behavior of the system poly(chloroprene) (PCP)—methyl ethyl ketone (MEK) over a wide range of compositions comparable to Scholte's work mentioned above by the sedimentation equilibrium method. The system PCP—MEK was chosen because of its rather unique dilute solution behavior discovered by

Hanafusa, *et al.*,⁵ in that the temperature coefficient of the second virial coefficient in the region of at least 10°C above and below the theta temperature, which is located at 25°C, is essentially nil. According to the conventional Flory theory⁶ of polymer solutions, this fact implies that both enthalpy and entropy parameters, κ and ϕ , are unusually small and their ratio takes the value of unity at 25°C. A check of it by sedimentation equilibrium measurements (Hanafusa, *et al.*, used the light-scattering method) was one of the principal interests in the study reported below.

EXPERIMENTAL

Samples

One of the most serious drawbacks of the sedimentation equilibrium method for use in the determination of chemical potentials of solutions is that no unambiguous analysis of the experimental data can be made except when the solution is strictly binary, *i.e.*, it consists of a single solvent and a molecularly homogeneous solute. This requirement is not met with polymeric solutes which are always heterogeneous at least in molecular weight. In sedimentation equilibrium studies with such a solute we must tackle the fractionation effect. For this effect the chemical potentials determined at any position in the solution at sedimentation equilibrium do not correspond to the molecular weight distribution of the given sample used to make up the test solution. No general theory is yet available which allows these potentials to be corrected for the difference between the local molecular weight distribution and the true one of the sample. The only one now available to us is an approximate theory developed by Scholte⁴ on the assumption of certain particular expressions for the chemical potentials in quasi-binary solutions. Close examination of his derivation indicates that the proposed method is actually useful only for samples of sufficiently narrow molecular weight distribution. For this reason we undertook the present work with a polymer sample prepared by extensive fractionation.

A PCP sample ($\bar{M}_v = 1.4 \times 10^5$, 30 g) prepared at a low conversion ratio at the Aomi Plant of Denikagaku Kogyo Co., Japan, was first divided into three parts by fractional precipitation with

Table I. Molecular weight of PCP samples used

Sample code	$\bar{M}_w \times 10^{-4}$ ^a	$\bar{M}_n \times 10^{-4}$ ^b	$\bar{M}_w/\bar{M}_n$
F-5	11.2	10.4	1.08
F-6	13.9	13.1	1.06

^a Weight-average molecular weight determined from sedimentation equilibrium measurements with MEK of 25°C as solvent.

^b Number-average molecular weight determined from osmotic pressure measurements on a Mechrolab Model 502 high-speed membrane osmometer with MEK of 25°C as solvent.

benzene as solvent and methanol as precipitant. The middle portion ($\bar{M}_v = 1.2 \times 10^5$, 10 g) was then separated into 10 fractions by column elution with mixtures of benzene and isopropanol. Each of these fractions was purified by repeated precipitation from benzene solution into methanol, freeze-dried from a benzene solution containing 1-% phenyl- β -naphthylamine, and stored in a nitrogen-filled bottle at -20°C. Before use it was again precipitated many times from benzene solutions into methanol for a complete removal of the antioxidant and then freeze-dried.

Sedimentation equilibrium data were obtained with a middle fraction labeled F-5 as the sample. This fraction was almost exhausted after completion of the sedimentation experiments. Hence we used another fraction F-6, which had average molecular weights comparable to those of fraction F-5, for osmotic pressure measurements undertaken to check the results from sedimentation measurements. The necessary data for density and refractive index were obtained by using some of the other fractions and the unfractionated material. Table I gives the values of $\bar{M}_n$, $\bar{M}_w$, and their ratios for fractions F-5 and F-6. We may judge that these fractions were fairly homogeneous in molecular weight.

Refractive Index Measurement

The differences in refractive index, Δn , for the wavelength of 546 nm between solution and solvent at 15, 25, and 35°C were measured over the concentration range up to 55 wt%. For concentrations below 1.3 wt% use was made of a differential refractometer of the modified Schulz-Cantow type. The specific refractive index increments, dn/dc , at 15, 25, and 35°C estimated from these measurements were 0.151,

0.154, and 0.158 cm³/g, respectively. The value at 25°C lies between those reported by Hanafusa, *et al.*,⁵ (0.156 cm³/g) and Curchod and Ve⁷ (0.152 cm³/g). In the region of intermediate concentrations (1.3—ca. 25 wt%) we used a Bausch & Lomb precision sugar refractometer. For the more concentrated solutions the following indirect method was employed. First, the refractive index of a given solution was estimated approximately by extrapolating the data already obtained at lower concentrations. Then we selected a suitable liquid which had a refractive index close to the estimated value and determined the refractive index difference, Δn_1 , between this liquid and MEK by the Bausch & Lomb refractometer. Next, the refractive index difference, Δn_2 , between the given solution and the selected liquid was measured by using the differential refractometer mentioned above. Finally, the sum of Δn_1 and Δn_2 was taken as the desired value for Δn . All the test solutions were prepared gravimetrically in a stoppered flask.

Density Measurement

Solution densities at 15, 25, and 35°C were measured over the same concentration range as in the refractive index measurements. Use was made of a U-tube type pycnometer for concentrations below 25 wt% and a bulb-type pycnometer for the higher concentrations. The accuracies were $\pm 0.003\%$ with the former pycnometer and $\pm 0.03\%$ with the latter. The values obtained for pure MEK were in close agreement with the reported ones (at 25°C, 0.79946 g/cm³: 0.7994 g/cm³ by Hanafusa, *et al.*,⁵ 0.79945 g/cm³ by Weissberger⁸; at 15°C, 0.80999 g/cm³: 0.81000 g/cm³ by Weissberger⁸). All the test solutions were made up as in the refractive index measurements.

Sedimentation Equilibrium Measurement

A Beckman-Spinco Model E ultracentrifuge equipped with an electronic speed control unit was used. The schlieren optical system was used to photograph sedimentation patterns. Measurements were performed at 15, 25, and 35°C over the range of concentrations up to 70 wt%, using a Kel-F double-sector cell of 12 mm in depth and adjusting the length of solution column between 1.5 and 2.5 mm. Rotor speeds were chosen between 5,200 and 10,000 rev/min, depend-

ing on the initial concentration of the solution. In this range of speed, the schlieren patterns for the solvent were perfectly horizontal, indicating the absence of a compression effect.

For a given solution the experiment was commenced at 15°C. It was striking that the solutions at this temperature attained sedimentation equilibria after essentially constant periods of centrifugation (about 24 hr), regardless of their initial concentration. This fact made it possible to examine a number of solutions up to high concentrations. After the data at 15°C had been taken the temperature was raised to 25°C, leaving the rotor to run at the initially given speed. The solution attained a new equilibrium state after about 12 hr, again regardless of the initial concentration. The situation was entirely similar in the runs at 35°C that followed.

From the schlieren patterns photographed, the values of dn/dr (refractive index gradient) at the midpoint of the solution column were determined. The concentrations at the same point were also evaluated from the simultaneously taken interference patterns when the initial concentrations were lower than 2 wt% and from the schlieren patterns for the higher initial concentrations. In the latter it was assumed that both dn/dw (w is the weight fraction of the solute) and solution density do not vary appreciably with the radial distance.

The calibration constant needed to convert schlieren patterns to dn/dr was determined at three bar angles of 75, 80, and 85° with aqueous solutions of sucrose (for which dn/dc was taken to be 0.1431 cm³/g⁹) at 25°C. A Nikon Shadowgraph Model 6 was used to measure the vertical distances between equilibrium patterns for solution and solvent. As usual, the readings were taken at the mid-points of the shadow lines; the accuracy was ± 0.005 mm.

Test solutions of initial concentrations below 50 wt% were prepared gravimetrically in a stoppered flask, while those above this concentration were made up by placing weighed amounts of polymer and solvent in the ultracentrifuge cell, allowing the mixture to stand for about 36 hr and then warming at 35°C for 3 hr. None of them exhibited irregular schlieren patterns at sedimentation equilibrium, which ensured the molecular dispersion of the solute in them.

Osmotic Pressure Measurement

Osmotic pressures at 35°C were measured in the range up to 20 wt% by the use of a Knauer osmometer fitted with Sartorius Ultracellafilter membranes. Measurements at concentrations higher than 20 wt% were not feasible. The conditioning of the membranes was made by transferring them from isopropanol to MEK through a series of mixtures of increasing MEK contents.

RESULTS AND DISCUSSION

Determination of Chemical Potentials

Basic Relations. Let us consider a strictly binary solution (solvent 0+solute 1) which is at sedimentation equilibrium in an ultracentrifuge cell. If the weight fraction of the solute, w , is taken as the composition variable (for simplicity of the ensuing presentation we omit subscript 1 from w), the equilibrium condition for the solvent reads

$$M_0(1-\bar{v}_0\rho)\omega^2r=(\partial\mu_0/\partial w)_P(dw/dr) \quad (1)$$

Here M_0 , $\bar{v}_0$, and μ_0 are the molecular weight, partial specific volume, and chemical potential (per mol) of the solvent component, respectively, ρ is the density of the solution, and r is the radial distance measured from the center of rotation. Furthermore, the subscript P attached to the derivative $(\partial\mu_0/\partial w)$ denotes hydrostatic pressure. For the system considered we can derive the relation

$$1-\bar{v}_0\rho=-(w/\rho)(\partial\rho/\partial w)_P \quad (2)$$

Hence eq 1 may be written

$$-(\partial\mu_0/\partial w)_P=M_0X_1\omega^2r/(dw/dr) \quad (3)$$

with

$$X_1=(w/\rho)(\partial\rho/\partial w)_P \quad (4)$$

To proceed further we impose restrictions that, as in the present experiments, rotor speeds are so slow and solution columns are so short that no appreciable pressure gradient is set up between the meniscus and bottom of the cell. Then the pressure dependence of ρ , n , and activity coefficient of the solvent on the weight fraction basis may be ignored, and eq 3 can be rewritten

$$-(\partial\mu_0/\partial w)=M_0X_1X_2X_3^{-1}\omega^2r \quad (5)$$

where

$$X_2=\partial n/\partial w \quad (6)$$

$$X_3=dn/dr \quad (7)$$

The absence of subscript P to $(\partial\mu_0/\partial w)$ and $(\partial n/\partial w)$ is due to the above-mentioned neglect of the pressure dependence. For the same reason the subscript P in eq 4 may be dropped. Thus both X_1 and X_2 determined, respectively, from density and refractive index measurements at 1 atm may be substituted into eq 5. With these data and the values of w and X_3 obtained at a given radial position r in the solution at sedimentation equilibrium, we can calculate from eq 5 the value of $-\partial\mu_0/\partial w$ corresponding to a known w . This information can be increased by repeating similar determinations, either at other radial positions in the solution of a given initial concentration, or with experimental data obtained for other initial concentrations. Once $\partial\mu_0/\partial w$ is known as a function of w from a very low concentration upward, it is possible to compute by integration the difference in chemical potential, $\Delta\mu_0$, between the solvent at a given w and that at $w=0$. Also, with the aid of the Gibbs—Duhem relation and the known molecular weight for the solute component, we can calculate $\partial\mu_1/\partial w$ as a function of w , where μ_1 denotes the chemical potential (per mol) of the solute.

This is the Pedersen—Drucker approach as described by Scholte.⁴ In what follows, we illustrate it in terms of our experimental data on the system PCP—MEK. Before moving ahead it is to be remarked that, in the present work, X_3 and the corresponding w were measured only at the midpoint of the solution column for any initial concentration examined, differing from Scholte's work in which these data were taken at a number of radial positions when the solutions were dilute.

Data from Refractive Index Measurements. It was found that, as illustrated with the data at 25°C in Figure 1, the experimental values for Δn as a function of w at a given temperature were fitted quite closely by a polynomial cubic in w over the entire range of measurement. Differentiation of these equations for the three temperatures studied with respect to w yields

Figure 1. Refractive indices of PCP-MEK solutions at 25°C for light of wavelength 546 nm; w , the weight fraction of the polymer.

$$\partial n/\partial w = 0.122 + 0.080w + 0.075w^2 \quad (15^\circ\text{C})$$

$$\partial n/\partial w = 0.123 + 0.080w + 0.090w^2 \quad (25^\circ\text{C}) \quad (8)$$

$$\partial n/\partial w = 0.124 + 0.080w + 0.129w^2 \quad (35^\circ\text{C})$$

Data from Density Measurements. The following empirical equations were found to fit our density data quite closely:

$$\rho = 0.80999 + 0.2955w + 0.0890w^2 + 0.100w^3 \quad (15^\circ\text{C})$$

$$\rho = 0.79946 + 0.2985w + 0.0900w^2 + 0.105w^3 \quad (25^\circ\text{C})$$

$$\rho = 0.78902 + 0.2995w + 0.0952w^2 + 0.110w^3 \quad (35^\circ\text{C})$$

(9)

Figure 2 illustrates the "goodness of fit" with the data for 25°C. It should be noted that these empirical equations for Δn and ρ are not the results from least-squares fitting.

Scholte¹⁰ demonstrated that Heller's empirical extension¹¹ of the Lorentz-Lorenz equation to binary mixtures predicts the density data on the systems glycerol-water and polystyrene-toluene quite accurately from measurements of refractive index. We wish to check his finding in terms of our experimental data.

Heller's empirical equation for ρ is

$$\rho = (n^2 - 1)(n^2 + 2)^{-1} [R_0 + (R_1 - R_0)w]^{-1} \quad (10)$$

with

$$R_0 = (n_0^2 - 1)(n_0^2 + 2)^{-1} \rho_0^{-1} \quad (11)$$

$$R_1 = (n_1^2 - 1)(n_1^2 + 2)^{-1} \rho_1^{-1} \quad (12)$$

where n_i and ρ_i ($i=0, 1$) are the refractive index and density of component i in the pure state.

Figure 2. Densities ρ of PCP-MEK solutions at 25°C: solid line, calculated from eq 9; dashed line, calculated from refractive index data by using eq 10.

Figure 3. $\log(-\partial\mu_0/\partial w)$ vs. w for PCP-MEK solutions at 15, 25, and 35°C.

Chemical Potentials of Polymer Solutions
Table II. Ultracentrifugal data on the system PCP—MEK

Initial concn, wt%	T , °C	ω , rad/sec	Bar angle, deg	$\lambda \bar{M}_w^a$	dn/dr $\times 10^2$, cm ⁻¹	Midpoint concn, wt%	$-d\mu_0/dw$ $\times 10^{-7}$, erg/mol	$d\mu_1/dw$ $\times 10^{-12}$ erg/mol
0.3637	15	543	75	0.836	0.154	0.349	1.52	6.74
	25			0.827	0.151	0.348	1.60	7.09
	35			0.834	0.147	0.349	1.68	7.47
0.5539	25	546	75	0.821	0.233	0.536	1.61	4.65
2.368	15	543	85	0.907	0.976	2.27	1.58	1.06
	15		80	—	0.973	—	1.59	1.06
	15		75	—	0.954	—	1.62	1.08
	25		85	0.924	0.946	2.27	1.69	1.13
	25		80	—	0.912	—	1.75	1.17
	25		75	—	0.907	—	1.76	1.18
	35		80	0.916	0.880	2.28	1.86	1.24
	15		75	0.829	1.68	4.83	2.02	0.616
5.018	25	543	85	0.826	1.60	4.86	2.19	0.667
	25		80	—	1.55	—	2.26	0.688
	25		75	—	1.54	—	2.28	0.693
	35		85	0.833	1.47	4.87	2.45	0.745
	35		80	—	1.47	—	2.45	0.745
	15		85	0.609	2.28	7.62	2.80	0.527
7.762	25	584	85	0.618	2.05	7.63	3.22	0.605
	35			0.639	1.84	7.63	3.68	0.693
	15			1.24	2.12	11.3	4.64	0.560
11.44	25	584	85	1.22	1.96	11.4	5.18	0.625
	35			1.21	1.79	11.4	5.85	0.707
	15			0.817	1.71	15.0	8.01	0.700
15.05	25	584	85	0.829	1.57	—	8.96	0.787
	35			0.819	1.45	—	10.1	0.882
	15			0.470	1.40	20.3	14.1	0.861
20.34	15	584	85	—	1.44	—	13.8	0.837
	25		85	0.464	1.26	—	16.3	0.930
	35		85	0.466	1.16	—	18.4	1.12
25.44	15	584	85	0.633	0.967	—	27.3	1.24
	25			0.633	0.861	—	31.7	1.45
	35			0.627	0.800	—	35.8	1.63
29.2	15	584	85	0.554	0.726	—	43.9	1.65
	15	707	85	0.812	1.08	—	43.2	1.63
	25	707	85	0.813	0.997	—	48.6	1.83
	35	707	85	0.835	0.926	—	55.2	2.08
30.26	15	584	75	0.780	0.666	—	50.0	1.79
	15	584	80	—	0.667	—	49.9	1.79
	15	584	85	—	0.678	—	49.1	1.76
	15	707	85	1.14	1.02	—	47.9	1.71
	25	707	80	1.12	0.914	—	55.5	1.99
	25	707	85	—	0.935	—	54.3	1.94
	35	707	85	1.18	0.899	—	59.5	2.13
	15	707	85	0.599	0.755	—	79.2	2.32
34.63	25	707	85	0.620	0.649	—	96.0	2.81
	35			0.751	0.610	—	108	3.17
	15			0.722	0.488	—	153	3.55
40.07	25	707	80	0.732	0.480	—	162	3.77
	35			0.745	0.458	—	182	4.23
	15			0.441	0.391	—	224	4.39
44.26	15	707	80	—	0.404	—	217	4.25
	25		80	0.445	0.373	—	246	4.82
	35		80	0.459	0.367	—	270	5.29
	15		75	0.478	0.285	—	391	5.82
51.05	25	707	75	0.481	0.271	—	432	6.44
	35		80	0.487	0.265	—	483	7.19
62.46	15	1048	80	1.06	0.321	—	1100	10.2
	25		80	1.05	0.320	—	1170	10.9
	35		85	1.06	0.324	—	1280	12.0
68.59	15	1048	80	0.966	0.219	—	1920	13.7
	25			0.993	0.222	—	2020	14.4
	35			1.00	0.206	—	2440	17.4

^a λ : parameter defined by $(1 - \bar{v}_1 \rho)(r_2^2 - r_1^2)\omega^2/2RT$ with r_1 and r_2 being, respectively, the radial positions of the air—liquid meniscus and the cell bottom.

Our experimental values of n_0 and ρ_0 give 0.288 cm³/g for R_0 , while the corresponding value of R_1 is calculated to be 0.259 cm³/g from the literature data¹² for n_1 (1.55) and ρ_1 (1.23 g/cm³). With these values of R_0 and R_1 and our observed data for n at 25°C we have computed ρ from eq 10. The dashed line in Figure 2 depicts the calculated results. It is seen that Heller's equation predicts the observed densities with an accuracy better than 0.5%.

Chemical Potentials. Table II summarizes the complete numerical data obtained from sedimentation equilibrium experiments. It is to be remarked that the values of $\partial\mu_0/\partial w$ (and hence those of $\partial\mu_1/\partial w$) for fixed initial concentrations and temperatures were essentially independent of the rotor speed and the bar angle.

Figure 3 shows $\log(-\partial\mu_0/\partial w)$ plotted against w . The sigmoidal behavior of the indicated curves should be noted. Figure 4 displays plots of $-\Delta\mu_0$ vs. w derived from these curves. The necessary integration for w below 0.06 was carried out graphically on a $-\partial\mu_0/\partial w$ vs. w diagram, whereas for the higher concentrations the data for $\log(-\partial\mu_0/\partial w)$ at a given temperature were first fitted by a polynomial cubic in w with

the aid of the least-squares method and then the resulting expression for $-\partial\mu_0/\partial w$ was integrated numerically by Simpson's one-third rule.

Figure 5 shows plots of $\partial\mu_1/\partial w$ vs. w . In deriving these data by the Gibbs-Duhem relation, we used $\bar{M}_w$ for the molecular weight of the solute component. If the practical activity coefficient of the solute component on the weight fraction basis is denoted by β_1 , we have

$$\ln \beta_1 = -\frac{1}{RT} \int_0^w \left(\frac{\partial\mu_1}{\partial w} - \frac{RT}{w} \right) dw \quad (13)$$

In accordance with this relation we have computed $\ln \beta_1$ as a function of w by substituting the data in Figure 5; actually, the integration was carried out analytically after the values for the integrand were fitted by a cubic polynomial in w . The results obtained are shown as $\Delta\mu_1^\infty$ vs. w in Figure 6. Here $\Delta\mu_1^\infty$ represents $RT \ln \beta_1 w$, i.e., the difference in chemical potential between the solute at a given w and that at $w=0$.

Since the polymer sample used was not monodisperse, the chemical potential differences obtained above, denoted here by $(\Delta\mu_0)_{SE}$ and $(\Delta\mu_1^\infty)_{SE}$ for the convenience of the following

Figure 4. $-\Delta\mu_0$ vs. w for PCP-MEK solutions at the three temperatures indicated.

Figure 5. $\partial\mu_1/\partial w$ vs. w for PCP-MEK solutions at the three temperatures indicated.

Figure 6. $\Delta\mu_1^0$ vs. w for PCP-MEK solutions at the three temperatures indicated.

discussion, must suffer fractionation effects. Actually, they are certain average values over the molecular weight distributions of the solute at the midpoint of the solution column. As mentioned in the foregoing, there is available at present no rigorous theory which allows them to be corrected to the molecular weight distribution of the given sample, but an approximate method due to Scholte⁴ seems to be relevant under the conditions of the present experiments.

Scholte's theory assumes that $\Delta\mu_0$ of a quasi-binary solution may be described by a modified Flory-Huggins expression of the form

$$\Delta\mu_0 = RT[\ln(1-w) + (1 - M_0/\bar{M}_n)w + \chi_w w^2] \quad (14)$$

If this assumption is accepted, it can be shown that

$$(\Delta\mu_0)_{SE} = \Delta\mu_0 + RTM_0(\bar{M}_n^{-1} - \bar{M}_w^{-1})w \quad (15)$$

in the approximation that the weight-average molecular weight of the solute at the midpoint

of the solution column may be equated to that of the given sample before centrifugation. This approximation is sufficiently accurate if the sample is of narrow-distribution and the experiment is done with a low speed of rotation and a short solution column, as was the case with the present work.

Evaluation of Thermodynamic Parameters

For this purpose we adopt another modified Flory-Huggins expression for $\Delta\mu_0$, i.e.,

$$\Delta\mu_0 = RT[\ln(1-\phi) + (1 - \bar{P}_n^{-1})\phi + \chi_\phi \phi^2] \quad (16)$$

where $\bar{P}_n$ is the number-average degree of polymerization of the polymer solute, and ϕ is the base mole fraction of the polymer solute defined by¹³

$$\phi = \frac{w/m_1}{(1-w)/M_0 + w/m_1} \quad (17)$$

with m_1 being the molar weight of a repeat unit of the polymer molecule. Actually, eq 16 is the defining expression for the thermodynamic parameter χ_ϕ .

We have converted the data for $(\Delta\mu_0)_{SE}$ given in Figure 4 to $\Delta\mu_0$ by means of eq 15 and then computed χ_ϕ from eq 16. The results are shown in Figure 7. It appears that, at any of the

Figure 7. Concentration dependence of the interaction parameter χ_ϕ derived from ultracentrifugal data for PCP-MEK solutions at the three temperatures indicated.

Figure 8. Temperature dependence of χ_ϕ as function of ϕ .

Figure 9. Flory's enthalpy and entropy parameters, κ and ψ , for PCP-MEK solutions at 25°C.

three temperatures indicated, χ_ϕ tends to 0.5 at the limit of infinite dilution. However, this is not precisely the case. An enlarged graph reveals a slight decrease in the infinite-dilution value of χ_ϕ with the increase in temperature. Figure 8 depicts the temperature dependence of χ_ϕ for nonzero concentrations.

We may define Flory's enthalpy and entropy parameters,¹⁴ κ and ψ , in terms of χ_ϕ as

$$\kappa = -T(\partial\chi_\phi/\partial T), \quad \psi = 0.5 - \partial(T\chi_\phi)/\partial T \quad (18)$$

The values of these parameters at 25°C calculated from the curve in Figure 7 are plotted against ϕ in Figure 9. As indicated in the insert, both κ and ψ can be extrapolated to the same infinite-dilution value of 0.025 ± 0.005 . This limiting value of ψ compares favorably to the rough estimate of 0.05 made previously Hanafusa, *et al.*,⁵ from the measurements of the light-scattering second virial coefficient. It is smaller by one order of magnitude than the reported values for polystyrene-cyclohexane¹⁵ and poly-(isobutylene)-benzene.¹⁶ According to Flory's formalism,⁶ the agreement of the infinite-dilution values of κ and ψ for 25°C predicts that this temperature should be the theta point for the system PCP-MEK, and also the very small infinite-dilution ψ predicts that the temperature coefficient of the second virial coefficient in the vicinity of the theta point should be almost nil. In fact, these predictions are in excellent conformity to the previous observations by Hanafusa, *et al.*,⁵ who used light-scattering experiments.

Comparison with Osmotic Pressure Data

The results from osmotic pressure measurements at 35°C are shown in Figure 10, where $c(=\rho w)$ denotes the c -scale concentration of the solute component. According to thermodynamics, the osmotic pressure π is related to $\Delta\mu_0$ by the equation

$$\pi = -\Delta\mu_0/\bar{V}_0 \quad (19)$$

where $\bar{V}_0$ is the partial molar volume of the solvent and can be evaluated by substituting

Figure 10. Reduced osmotic pressure plotted against c -scale concentration for PCP fraction F-6 in MEK at 35°C.

Figure 11. Comparison of χ_ϕ values derived from osmotic pressure data (○) with those from sedimentation data (—).

the data for $\rho(w)$ into eq 2 ($\bar{V}_0 = M_0 \bar{v}_0$). With eq 16 and 19 we have computed χ_ϕ corresponding to the data points in Figure 10. Figure 11 shows the results together with the corresponding curve derived from the sedimentation equilibrium data. The agreement of the two sets of data is satisfactory.

It should be noted that we used different samples of PCP for these osmotic pressure and sedimentation equilibrium measurements (fraction F-6 for the former and fraction F-5 for the latter). Although recent work¹⁷ disclosed a significant molecular weight dependence of χ_ϕ in the region of low solute concentrations, this effect may be ignored in looking at Figure 11, because the two fractions had comparable average molecular weights (see Table I).

Finally, we calculate an apparent second virial coefficient A_2^* defined by

$$A_2^* = [-\Delta\mu_0/(RTc\bar{V}_0) - 1/\bar{M}_n]/c \quad (20)$$

from the $\Delta\mu_0$ data obtained at 35°C. The calculated results are shown in Figure 12, where the points are from osmotic pressure $\Delta\mu_0$ and the line from sedimentation equilibrium $\Delta\mu_0$. Noting that the ordinate intercept and initial slope of this type of plot yield the second virial coefficient A_2 and the third virial coefficient A_3 , respectively, we find that $A_2 = 1.5 \times 10^{-5} \text{ cm}^3 \text{ mol/g}^2$ and $A_3 \approx$

Figure 12. Apparent second virial coefficient A_2^* vs. c at 35°C: (○), from osmometry; (—), from equilibrium ultracentrifugation.

$6 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$ for the system PCP—MEK at 35°C. The corresponding plot obtained from the sedimentation equilibrium $\Delta\mu_0$ at 25°C gives zero A_2 and an A_3 of the same magnitude as above. This result does not agree with all the theoretical predictions¹⁸ made so far for A_3 , according to which A_3 should vanish at the theta temperature. In this connection we note that the osmotic pressure data by Flory and Daoust¹⁹ for benzene solutions of poly(isobutylene) at 24.5°C give $A_2 = 0$ and $A_3 \approx 3 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$.

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