

CONTINUOUS THERMODYNAMIC CALCULATION OF SOL-GEL PHASE EQUILIBRIA FOR POLYDISPERSE PETROLEUM RESINS

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Abstract—We present a continuous thermodynamic framework which utilizes the Flory-Huggins theory for calculating sol-gel phase equilibrium properties of polydisperse petroleum resins. The sample resins are separated into sol and gel phases by n-hexane at 10-30°C for 5-12 hours. The molecular weight distributions for feed resin and subsequently separated sol and gel phases are determined by gel-permeation chromatograph and they are correlated by the gamma distribution function. The equilibrium distribution coefficients between sol and gel phases are modeled by the modified Flory-Huggins equation in which the mole fractions are replaced by a continuous distribution variable index. We found that the Flory-Huggins model with the continuous thermodynamic framework fits the measured sol-gel phase equilibrium data well for a wide range of separation conditions.

INTRODUCTION

Petroleum resins comprise a class of synthetic polymeric hydrocarbons derived from a variable mixture of unsaturated monomers obtained as volatile by-products, mainly C₅ or C₉ fractions in the cracking of natural gas or petroleum naphthas. The petroleum resins are usually produced by the cationic Friedel-Craft polymerization reaction. Worldwide, the production capacity of the petroleum resins is now more than 1,000,000 tonnes/year and they have rapidly become the resin of potential choice in various areas such as paints, printing inks, rubber compounds and adhesives. Still the petroleum resins can be regarded as new materials since they are capable of wide development and refinement with close tailoring of properties to meet the need of any new application. Accordingly, a certain fraction of well purified petroleum resins is demanded for various specific uses [1, 2]. Thus, one frequently needs to purify the resins with a certain range of distribution of the molecular weights.

Currently various phase separation techniques such as successive solution fractionation and successive

precipitation fractionation are used in industry for purifying the petroleum resins [3]. To fractionate a petroleum resin, the synthetic virgin resin is usually dissolved into a solvent and split it successively into polymer-rich phase and polymer-lean phase called as gel and sol phase, respectively. Thus, one needs a reliable method of calculating sol-gel phase equilibrium properties for a rational design of such purification processes. However, an intrinsic polydisperse nature of the resins makes it difficult to utilize classical thermodynamic methods for various phase equilibrium calculations. Thus, we present here a continuous thermodynamic framework which is particularly useful for describing thermodynamic properties of mixtures containing very many components such as the polydisperse petroleum resins.

Thermodynamic properties of a mixture which contains many components can alternatively be treated by the recently developed continuous thermodynamic method. Solutions of polydisperse polymers, petroleum fractions, and coal-derived fluids are typical examples of such continuous mixtures. The composition of such mixtures are not described by conventional discrete concentration variables such as mole fraction for the components but by the continuous distribution

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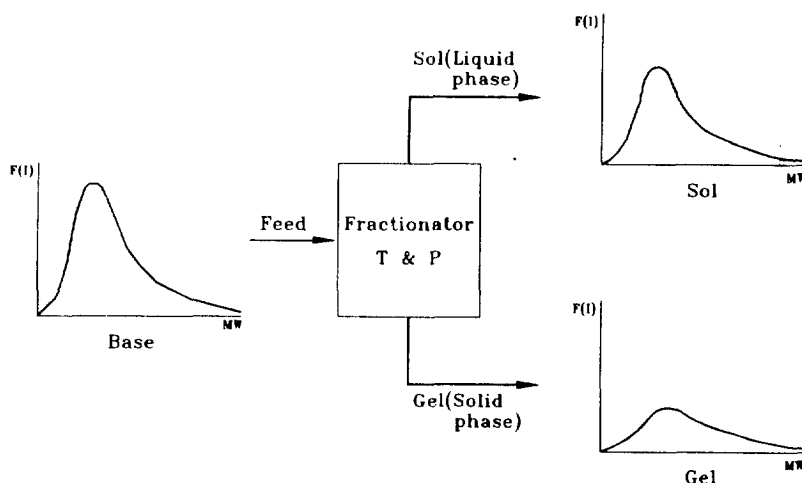


Fig. 1. Schematic diagram of sol-gel fractionation process for a continuous mixture.

function whose continuous variables are some appropriate characterizing quantities such as molecular weight, effective carbon number, degree of polymerization or normal boiling point [3-7]. The concept of thermodynamic modelling which incorporated with a continuous distribution function is not new, however, a general procedure for calculating phase equilibria of such mixtures using continuous thermodynamic framework with any one of well-defined thermodynamic models such as equations of state has been recently reformulated by several investigators [3-14].

In this article, by adopting Flory-Huggins model which is combined with a continuous distribution function, we presented an extended use of the continuous thermodynamic framework to calculate the phase equilibrium properties of the polydisperse petroleum resins. To illustrate the method, we performed an experiment on the sol-gel phase splitting of the petroleum resin. The feed resin used here are the commercial-grade products purchased from Nippon Chemical Co. (Neopolymer N120H), Japan. The approximate molecular weights dispersed from monomer of polystyrene derivatives to 6000 and its average softening point is about 120°C. The distribution of molecular weights for feed, sol and gel phases at various separation conditions are determined by a gel-permeation chromatography. The feed resin has a distribution of molecular weights with gamma functional statistical mean and variance 2.13×10^3 and 2.08×10^4 , respectively. We modeled the distribution of molecular weights by gamma distribution function and they are incorporated into the Flory-Huggins equation. This modified Flory-Huggins model is used to correlate the

experimental phase equilibrium data of the resins.

PHASE EQUILIBRIA OF POLYDISPERSE POLYMERS BY FLORY-HUGGINS MODEL

Fig. 1 schematically illustrates a typical fractionation process for polydisperse petroleum resins. If a feed is separated into sol and gel phases and they are thermodynamically in equilibrium at constant temperature and pressure and furthermore if the feed, sol and gel phase polydisperse polymers can sufficiently be characterized by a single distribution variable such as molecular weight distribution index I , the equilibrium relation in terms of chemical potentials in sol(′) and gel(′′) phases for all values of I can be defined by

$$\mu'(I) = \mu''(I) \quad (1)$$

For liquid-liquid equilibria of a polydisperse polymer, it is useful to express the Gibbs free energy for phase ' as a function of molar probability distribution function, $F'(I)$. Then one can calculate the chemical potential by the well-known thermodynamic relation

$$\mu'(I) = \left[\frac{\delta G'}{\delta n' F'(I^+)} \right]_{T, P, I^+ \neq I} \quad (2)$$

where n' is the total number of moles of a continuous mixture. The chemical potential for a solvent is found from the conventional relation: $(\partial G' / \partial n_1')$. Among various models for Gibbs energy, we suppose that the Gibbs energy of a polydisperse polymer (2) in a solvent (1) can appropriately be described by the modified Flory-Huggins theory with the continuous concentration variable by

$$\begin{aligned}
G' = & RTn_1' \ln \phi_1' + RT \int_I n_2' F'(I) \ln \phi'(I) dI \\
& + \chi RT \phi_1' \int_I \phi'(I) dI (n_1' + \int_I n_2' F'(I) m(I) dI) \\
& + n_1' g_1'' + \int_I n_2' F'(I) g_2'' dI
\end{aligned} \quad (3)$$

As shown in Fig. 1, the sol and gel phases are related to the feed through material balances. If we assume that the composition of the polydisperse polymer in each phase is represented as a function of molecular weight by the gamma function, then, this assumption enables us to solve analytically the equilibrium equation and to relate distribution function parameters in the sol phase to those in the gel phase. However, it is not readily possible to solve material balances exactly, given the condition that the distribution of polymer is described by the same type of distribution function in each phase. Therefore, to avoid numerical solution of the material balance equation, we use an approximate method of solution which is based upon statistical moments of the material balance equation [8, 9, 15, 16]. The method of moments is an approximation because it introduces error into the material balances. However, in some but not all cases, this error is not significant [9]. Thus, we write a material balance for the solvent (1)-polydisperse polymer (2) system in terms of the volume fraction ϕ and a parameter ξ which is the ratio of the volume of the sol phase to that of the feed. The excess volume is zero in the Flory-Huggins theory and accordingly we write the material balance by

$$\phi_1^F = \xi \phi_1' + (1 - \xi) \phi_1'' \quad (4)$$

For the polymer at every value of molecular weight I , we write

$$\phi^F(I) = \xi \phi'(I) + (1 - \xi) \phi''(I) \quad (5)$$

Also, the expression for the volume distribution of polymer is related to the mass distribution function $F(I)$ by

$$\phi(I) = \frac{n_2 \theta_N \frac{F(I)}{I} m(I)}{n_1 + n_2 \theta_N \int_I \frac{F(I)}{I} m(I) dI} \quad (6)$$

where θ_N is the number average molecular weight, and $m(I)$ is the molar volume ratio of polymer to solvent and is assumed to be a linear function of molecular weight written by

$$m(I) = \frac{v_2 I}{v_1} \quad (7)$$

where v_2 is the specific volume of polymer and v_1 is the molar volume of solvent.

Based on Eq. (6), the volume fractions of the solvent and polydisperse polymer are given by

$$\phi_1 = \frac{n_1}{n_1 + n_2 \theta_N \int_I \frac{F(I)}{I} m(I) dI} \quad (8)$$

$$\phi_2 = \int_I \phi(I) dI \quad (9)$$

If we multiply Eq. (6) by I and integrate over the range of I the first order statistical moment can be expressed

$$\phi_2^F \alpha_F \beta_F = \xi \phi_2' \alpha' \beta' + (1 - \xi) \phi_2'' \alpha'' \beta'' \quad (10)$$

Also, by multiplying Eq. (6) by I^2 and integrating, we can derive the second order statistical moment by

$$\begin{aligned}
\phi_2^F \alpha^F (\alpha^F + 1) (\beta^F)^2 = & \xi \phi_2' \alpha' (\alpha' + 1) (\beta')^2 \\
& + \xi \phi_2'' \alpha'' (\alpha'' + 1) (\beta'')^2
\end{aligned} \quad (11)$$

As discussed in the later section, since the shift parameters γ are the same all the phases, we can relate α and β in the three phases through Eqs. (10) and (11).

Finally the chemical potential given by Eq. (2) is expressed by continuous thermodynamic analogue of the discrete form of Flory-Huggins equation for ' phase

$$\begin{aligned}
\frac{\mu'(I) - \mu'(I)^\circ}{RT} = & \ln \left[\frac{n_2' \theta_N' \left(\frac{V_2}{V_1} \right) F'(I)}{n_1' + n_2' \theta_N' \left(\frac{V_2}{V_1} \right)} \right] + [1 - m(I)] \\
& + \left[1 - \frac{V_1}{V_2 \theta_N'} \right] m(I) \left[\frac{n_2' \theta_N' \left(\frac{V_2}{V_1} \right) F'(I)}{n_1' + n_2' \theta_N' \left(\frac{V_2}{V_1} \right)} \right] dI \\
& + \chi m(I) \left[\frac{n_1'}{n_1' + n_2' \theta_N' \left(\frac{V_2}{V_1} \right)} \right]^2
\end{aligned} \quad (12)$$

Otherwise it can be expressed as

$$\begin{aligned}
\frac{\mu'(I) - \mu'(I)^\circ}{RT} = & \ln \phi'(I) + [1 - m(I)] \\
& + \left[1 - \frac{V_1}{V_2 \theta_N'} \right] m(I) \phi_2' + \chi m(I) \phi_1'^2
\end{aligned} \quad (13)$$

where χ is the Flory-Huggins parameter and $\mu'(I)^\circ$ is the chemical potential of the reference state. In the previous equations, most of variables are constant except of $F(I)$ and index variable I . We now can calculate the molecular weight distributions of the resin in sol

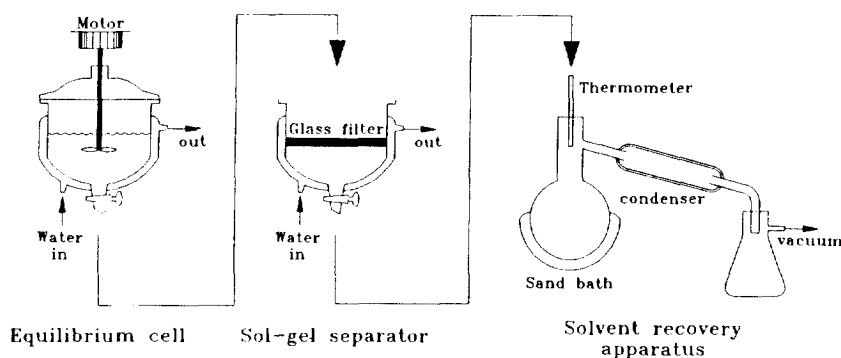


Fig. 2. Experimental apparatus of sol-gel separation.

and gel phases and the equilibrium distribution coefficient $K(I)$ expressed by

$$\ln K(I) = \ln \left[\frac{F^{Sol}(I)}{F^{Gel}(I)} \right] = A \cdot I + B \quad (14)$$

where the thermodynamic relation of the ratio of equilibrium distribution function F in sol and gel phases can be obtained from Flory-Huggins equation and the terms in the ratio of F is arranged by A is slope for index I and B is intercept as Eq. (14). The rearranged slope A and intercept B in Eq. (14) are given by

$$A = \frac{V_2}{V_1} \left(\chi [(\phi_1')^2 - (\phi_1'')^2] + \left(1 - \frac{V_1}{V_2 \theta_N} \right) \phi_2' - \left(1 - \frac{V_1}{V_2 \theta_N} \right) \phi_2'' \right) \quad (15)$$

and

$$B = \ln \phi_2' - \ln \phi_2'' \quad (16)$$

The terms in A and B from Flory-Huggins equation are independent to the index, I and, accordingly, the equilibrium distribution coefficient $\ln K$ is assumed to be linear with respect to I in Eq. (14). The parameters A and B are obtainable based on the distributions of molecular weights of the petroleum resins. Thus, by specifying feed composition and pure component volumes, the coefficient A in Eq. (15) for Flory-Huggins parameter, χ can be regressed from the experimental equilibrium data and subsequently we can calculate the compositions and relative amounts of the sol and gel phases.

COACERVATIVE SOL-GEL PHASE SEPARATION

The schematic diagram of the equilibrium cell is

Table 1. The amount of resins separated into sol and gel phases by percent at various temperatures

Phase	Separation temperatures, C		
	10	20	30
Sol %	76.5	78.2	82.1
Gel %	23.5	21.8	17.9

shown in Fig. 2. The equilibrium cell equipped with stirrer is made as the jacket type and the cell inside is coated with Teflon. The temperature is controlled by the Haake heating and cooling controller and the temperature is maintained within $\pm 0.5^\circ\text{C}$. The separated sol and gel phases are recovered in the separator with the compartmented glass filter aid.

The petroleum resin is dissolved with n -hexane by slowly stirring at 40°C . The amount of the resin in one batch was 52.63 grams and the weight fraction after dissolution is completed was 5 percent with respect to that of n -hexane. It usually takes about twelve hours to reach the sol-gel phase equilibrium conditions. The equilibrium temperatures are varied from 10 to 30°C at atmospheric pressure. After separating the sol and gel phases, the residual n -hexane solvent in each phase is recovered by the vacuum distillation apparatus. With this experiment, the amount of resin separated in sol and gel phases by percent is summarized in Table 1. This flashed rescue. The distributions of the molecular weights for the sol and gel phases are determined by the gel-permeation chromatography.

MOLECULAR WEIGHT DISTRIBUTIONS BY GEL-PERMEATION CHROMATOGRAPH

The gel-permeation chromatography can be used to fractionate polymers and analyse the molecular weight distribution of polydisperse polymers for labo-

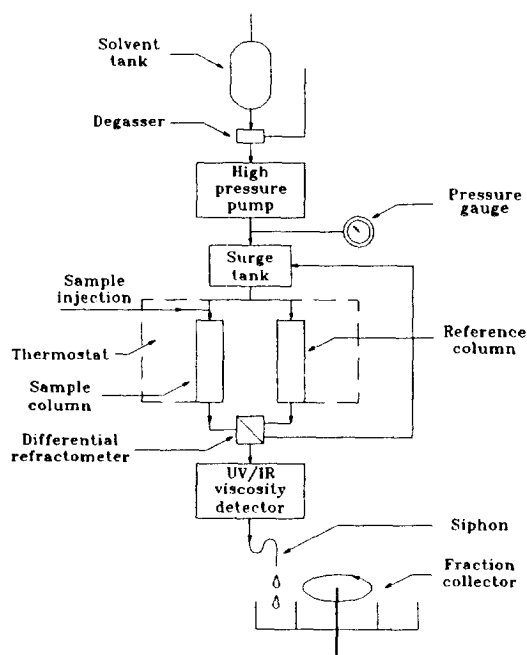


Fig. 3. Schematic representation of a gel permeation chromatograph.

ratory scale. However, we only used the chromatography to determine the distribution of molecular weights of the sol and gel phase resins. Fig. 3 shows the schematic flowsheet of the gel permeation chromatography used in the present study. The type of the liquid chromatography is Waters Association model number 410 of R.I. type with ultra styragel column and Waters 510 liquid pump. One of the representative chromatographic curves are shown in Fig. 4. The representative experimental GPC data are shown in Table 2. The molecular weight distribution from the curve is calcu-

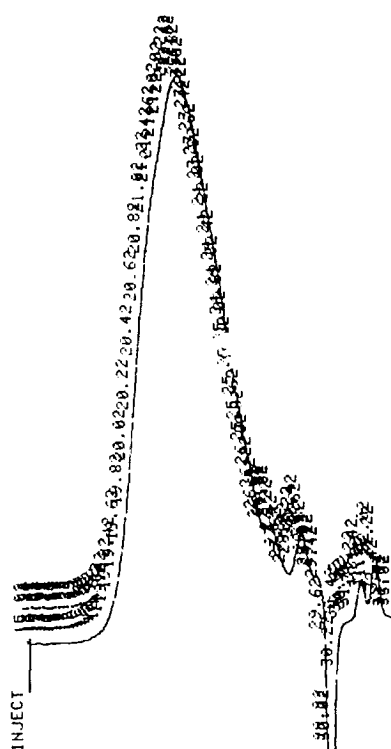


Fig. 4. A typical gel permeation chromatographic chart for feed petroleum resin.

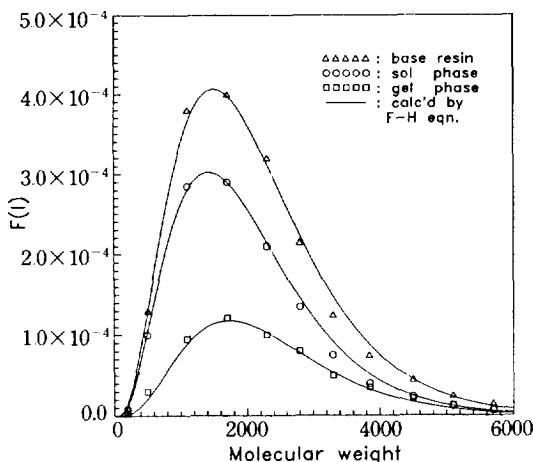
lated based on the flow rate and the retention time as the usual case of liquid chromatographic analysis. The tail part of the low molecular weight region of the chromatographic curve as shown in Fig. 4 was identified as the residual solvent fraction and we neglect these portions when we fit the chromatographic curves by the distribution function. The information of the distributions of molecular weights for feed, sol

Table 2. Normalized experimental GPC data of petroleum resin for feed, sol and gel phases

Mol. wt.	Feed	T=10°C		T=20°C		T=30°C	
		sol	gel	sol	gel	sol	gel
200	9.989×10^{-4}	8.012×10^{-6}	2.004×10^{-4}	7.964×10^{-6}	2.035×10^{-6}	8.021×10^{-6}	1.978×10^{-6}
500	1.301×10^{-4}	1.037×10^{-4}	3.013×10^{-5}	1.018×10^{-4}	2.812×10^{-5}	9.779×10^{-5}	3.220×10^{-5}
1100	3.813×10^{-4}	2.851×10^{-4}	9.501×10^{-5}	2.901×10^{-4}	9.000×10^{-5}	2.859×10^{-4}	9.410×10^{-5}
1700	4.006×10^{-4}	2.903×10^{-4}	1.210×10^{-4}	2.950×10^{-4}	1.050×10^{-4}	3.019×10^{-4}	9.809×10^{-5}
2300	3.211×10^{-4}	2.112×10^{-4}	1.007×10^{-4}	2.201×10^{-4}	9.999×10^{-5}	2.279×10^{-4}	9.209×10^{-5}
2800	2.151×10^{-4}	1.350×10^{-4}	8.021×10^{-5}	1.450×10^{-4}	6.999×10^{-5}	1.499×10^{-4}	6.509×10^{-5}
3300	1.253×10^{-4}	7.531×10^{-4}	5.005×10^{-5}	8.015×10^{-4}	4.500×10^{-5}	8.662×10^{-5}	3.837×10^{-5}
3850	7.516×10^{-4}	4.006×10^{-4}	3.500×10^{-5}	4.542×10^{-5}	2.960×10^{-5}	4.899×10^{-5}	2.601×10^{-5}
4500	4.499×10^{-4}	2.388×10^{-5}	2.171×10^{-5}	2.542×10^{-5}	1.957×10^{-5}	2.824×10^{-5}	1.675×10^{-5}
5100	2.501×10^{-4}	1.182×10^{-5}	1.317×10^{-5}	1.317×10^{-5}	1.183×10^{-5}	1.449×10^{-5}	1.051×10^{-5}
5700	1.489×10^{-4}	6.428×10^{-6}	8.571×10^{-6}	7.322×10^{-6}	7.677×10^{-6}	8.249×10^{-6}	6.751×10^{-6}

Table 3. Parameters in the gamma distribution function for the molecular weights of petroleum resins

Phase	Temperature(°C)	α	β	γ
Base	10	3.25	630.2	80.0
Sol	10	3.27	590.0	80.0
Gel		3.80	592.1	80.0
Sol	20	3.30	600.0	80.0
Gel		4.12	550.0	80.0
Sol	30	3.50	605.0	80.0
Gel		5.10	410.0	80.0

**Fig. 5. Molecular weight distributions for base and sol-gel phase resins fractionated at 10°C.**

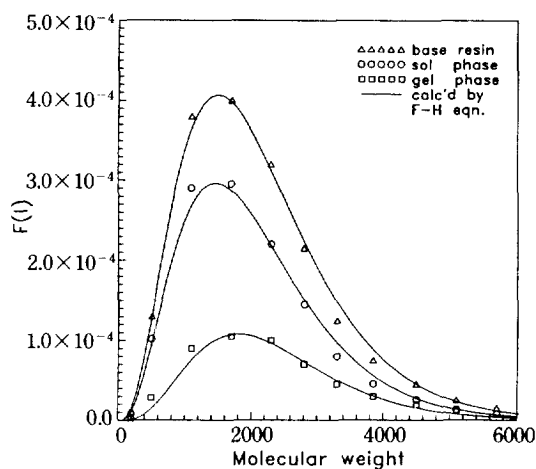
and gel phases are used as the continuous distribution index for the gamma distribution function. The gamma function is

$$F(I) = \frac{(1-\gamma)}{\beta \Gamma(\alpha)} \exp\left[\frac{-(1-\gamma)}{\alpha}\right] \quad (17)$$

where α , β and γ are adjustable parameters. The mean is $\alpha\beta + \gamma$ and the variance is $\alpha\beta^2$, respectively. The shift parameter, γ , indicates the origin of the gamma function $F(I)$; the shift parameters for the feed, sol, and gel phases have the same value as discussed in the previous section. In Table 3, the optimum values of these parameters are summarized for the feed, sol and gel phase petroleum resins obtained from the experimental gel-permeation data.

RESULTS AND DISCUSSION

The molecular weight distribution is taken as an index variable I of the gamma distribution function, $F(I)$ and this function is used as the continuous concen-

**Fig. 6. Molecular weight distributions for base and sol-gel phase resins fractionated at 20°C.**

tration variable in the Flory-Huggins equation instead of discrete mole fraction. In Fig. 5, the experimental data of the molecular weight distributions of feed, sol and gel phases at 10°C are shown together with the approximated gamma distribution curves. The calculated characteristic parameters, α , β , and γ in the gamma distribution curves for each phase are based on the method of moment to the representative gel-permeation chromatographic data points. The optimum values of the parameters are summarized in Table 3. As one can see in Fig. 5, the gamma distribution function with the optimum values of the parameters correlate quite well the experimental polydisperse distributions of the molecular weights obtained at 10°C. Similarly, the experimental molecular weight distributions of the sol and gel phases at 20 and 30°C, respectively can be fitted very well with the gamma distribution function as shown in Fig. 6 and 7. The approximated optimum values of the parameters of the gamma distribution function are also shown in Table 3.

Finally, the experimental and the calculated sol and gel phases equilibrium distribution ratios, $K(I)$ s, at 10, 20, and 30°C based on the Flory-Huggins equation are shown in Fig. 8. In calculating the distribution ratios, the material balances of Eq. (10) and (11) are solved simultaneously during the moment analysis. The calculated coefficients A and B in Eq. (15) and Eq. (16) are summarized in Table 4 where the volume parameters for resins and solvent used in the calculation are summarized in Table 5. The specific volume of the resins represents a hypothetical one which corresponds to volume of a repeating unit of the resins and this hypothetical value is obtained by dividing the spe-

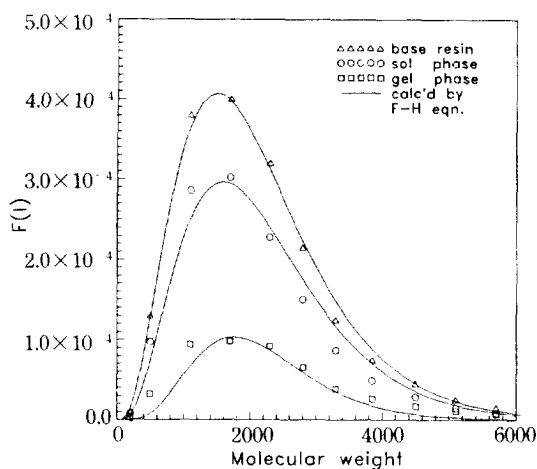


Fig. 7. Molecular weight distributions for base and sol-gel phase resins fractionated at 30°C.

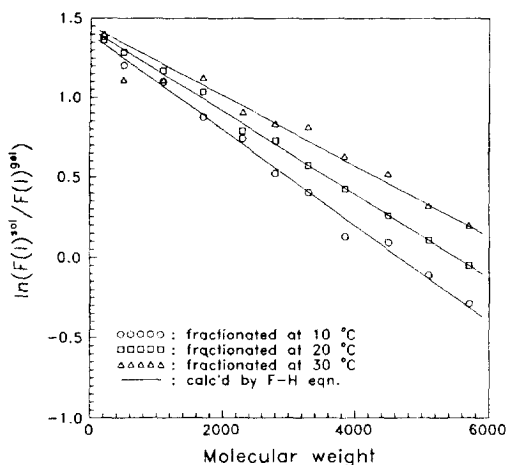


Fig. 8. Sol-gel phase distribution ratio of fractionated petroleum resin.

Table 4. Sol-gel phase equilibrium distribution ratio*

Temperature(°C)	A × 10 ⁴	B
10	-2.997	1.3974
20	-2.595	1.4321
30	-2.203	1.4520

*The coefficients A and B are defined by Eq. (15) and Eq. (16), respectively.

Table 5. Volume parameter of resin and solvent

Component	Volume	Mwt.
n-hexane	108.039 cm ³ /mol	84.162
Polystyrene(amorphous)	0.95238* cm ³ /g	104.152

*specific volume

cific gravity of amorphous polystyrene by the molecular weight of a repeating unit of the polystyrene. Finally, the calculated distributions for both phases at different temperatures are in very good agreement with experiment.

CONCLUSION

In this work, we illustrated the continuous thermodynamic method of calculating the phase equilibria of the polydisperse polymers. As an example, we considered a solution of polydisperse petroleum resins in n-hexane. To model the distribution of molecular weights and a sol-gel phase equilibrium calculation, we used the gamma function and the Flory-Huggins model. However, in principle, any desired distribution function may be used for one or more variables. Also, any other appropriate molecular thermodynamic model may be used. The continuous thermodynamic framework presented here provides a potentially useful tool in designing chemical processes dealing with polydisperse systems as well as some fluid mixtures containing very many components.

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NOMENCLATURE

- A, B : coefficients in phase equilibrium distribution ratio of Eq. (14)
- F(I) : continuous distribution function
- G : Gibbs free energy [cal/mol]
- g° : molar Gibbs energy of the reference state
- I : variable index
- K(I) : sol-gel phase equilibrium distribution ratio
- m(I) : molar volume ratio of polymer to solvent
- n : discrete number of moles [mol]
- P : pressure [atm]
- R : gas constant [atm lit/mol°K]
- T : temperature [°C]
- v : molar volume [cm³/mol]

Greek Letters

- α, β, γ : characteristic parameters in Γ-function
- χ : Flory-Huggins residual parameter
- φ : volume fraction
- ξ : ratio of sol to the feed
- φ(I) : volume distribution of polymer

θ_v : the number-average molecular weight
 μ : chemical potential
 Γ : gamma function

Superscripts

F : base of feed of polymer
 ' : sol phase
 " : gel phase

Subscripts

$^{\circ}$: reference state
 1 : solvent
 2 : polymer

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