BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 351—355 (1972)

On the Viscosities of Mixtures of Oligotrifluorochloroethylene and *n*-Heptadecane

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(Received June 18, 1971)

The viscosities, η_m, of mixtures of oligotrifluorochloroethylene and *n*-heptadecane were expressed as follows: $\eta_m=[(1-\Phi_R)-n(1-\Phi_R)]\eta_H+[\Phi_R+n(1-\Phi_R)]^2/[\Phi_R/\eta_R+n(1-\Phi_R)/\eta_H]$, where Φ_R is the volume fraction of the oligotrifluorochloroethylene in the mixture; η_R and η_H, the viscosities of oligotrifluorochloroethylene and *n*-heptadecane respectively, and n, a parameter. The two components were considered to be comparatively well compatible with each other, because the parameter, n, was small (here about 0.1). The free-volume fractions, f_T, of the mixed systems, as calculated from the WLF parameters, were larger than those calculated by assuming a simple additivity between those of the two components. This effect is considered to be caused by the mitigation of physical interactions among oligotrifluorochloroethylene molecules, which are dispersed by *n*-heptadecane as good compatibility is achieved between the two components.

The viscoelastic properties of a mixture of polymers depend on the ratio of the components and on their mixing state.[1] If two components are completely compatible with each other, the mixed system behaves, for example, like a random copolymer with only a glass-transition temperature which is a function of the monomer ratio.[2] Such a compatible system has been obtained, for example, by blending polyvinyl chloride and butadiene-acrylonitrile rubber within a certain volume fraction range of the components.[3] On the contrary, a mixed system of two incompatible or poorly compatible components, such as is observed in ordinary cases, gives properties consistent with those of the original components. If the two components are slightly compatible with each other, they partially dissolve one another according to the natures of the components and the manner of mixing.

In this work, the viscosities of mixtures of oligotrifluorochloroethylene and *n*-heptadecane were studied in connection with their compatibility and free-volume fractions.

Experimental

Materials. Daifloil No. 50, which was obtained from the Daikin Kogyo Company, was used as the sample of oligotrifluorochloroethylene. The oligotrifluorochloroethylene was fractionated by the manner described in our previous paper.[4] Fractionated oligotrifluorochloroethylene samples with the number-average molecular weights of 910, 950, and 1000, which were estimated by the cryoscopic method, were used as polymer components in the mixed systems. A guaranteed-grade *n*-heptadecane, which was obtained from the Kanto Kagaku Company, was used without further purification. The mixed samples of oligotrifluorochloroethylene and *n*-heptadecane were prepared in the following manner: the two components were mixed well together with benzene in various proportions, and then the benzene was removed by vacuum distillation from the mixture at temperatures from 30 to 50°C.

The volume fractions of oligotrifluorochloroethylene in the mixed samples are shown in Table 1.

Procedure. The viscosities and the densities of the liquid samples were measured with an Ubbelohde-type viscometer and a dilatometer respectively in the manner described in the previous paper.[4] The measurements were carried out in the temperature range from 30 to 70°C, with an accuracy of ±0.01°C, in a thermostated water bath.

Results and Discussion

The viscosities of oligotrifluorochloroethylene, *n*-heptadecane, and mixed samples are listed in Table 2-a and 2-b.

Mixing Model for Mixtures of Oligotrifluorochloroethylene and n*-Heptadecane.* The mixing states of oligotrifluorochloroethylene and *n*-heptadecane in the samples have been discussed, on the basis of the dependence of their viscosities on the volume fractions

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1) R. Buchdahl and L. E. Nielsen, *J. Polymer Sci.*, **15**, 1 (1955).

2) K. Fujino, K. Senshu, and H. Kawai, *J. Colloid Sci.*, **16**, 262 (1961).

3) M. Kawamata and Y. Inoue, *Kogyo Kagaku Zasshi*, **63**, 1831 (1960).

4) N. Yoshida, S. Hamada, and T. Shirai, This Bulletin, **42**, 3131 (1969).

Table 1. Volume fractions Φ_R of oligotrifluorochloroethylene in samples at 50°C

Sample	Φ_R	Sample	Φ_R	Sample	Φ_R
910−0.05[a]	0.0496	910−0.6	0.5992	950−0.8	0.7976
910−0.1	0.0971	910−0.7	0.7015	950−0.9	0.8994
910−0.2	0.1995	910−0.8	0.8000	1000−0.7	0.6985
910−0.25	0.2495	910−0.9	0.8945	1000−0.8	0.7997
910−0.4	0.3995	950−0.7	0.6991	1000−0.9	0.9011

a) The numerical symbol "910" denotes the number-average molecular weight of the oligotrifluorochloroethylene, while the numerical post-script "0.05" denotes the rough volume fraction of the oligotrifluorochloroethylene in the sample.

Table 2-a. Viscosities of liquid samples

Sample	Viscosities η_m, poise					
	30°C	35°C	40°C	45°C	50°C	55°C
n-$C_{17}H_{36}$[a]	0.03183	0.02848	0.02564	0.02320	0.02111	0.01930
910−0.05	0.03728	0.03295	0.02947	0.02665	0.02404	0.02215
910−0.1	0.04237	0.03747	0.03346	0.03016	0.02727	0.02481
910−0.2	0.06073	0.05283	0.04629	0.04083	0.03625	0.03237
910−0.25	0.07369	0.06329	0.05485	0.04815	0.04266	0.03781
910−0.4	0.1574	0.1292	0.1075	0.09057	0.07723	0.06660
910−0.6	0.5849	0.4414	0.3410	0.2692	0.2168	0.1778
910−0.7	1.323	0.9574	0.7109	0.5408	0.4206	0.3340
910−0.8	3.493	2.411	1.711	1.247	0.9305	0.7101
910−0.9	11·20	7.295	4.897	3.381	2.395	1.739
910−1.0[b]	64.97	38.63	23.79	15.13	9.920	6.688

a) n-heptadecane, alone.
b) oligotrifluorochloroethylene with the molecular weight of 910, alone.

Table 2-b. Viscosities of liquid samples

Sample	Viscosities η_m, poise				
	30°C	40°C	50°C	60°C	70°C
910−0.7	1.323	0.7109	0.4206		
910−0.8	3.493	1.711	0.9305		
910−0.9	11.20	4.897	2.395		
910−1.0	64.97	23.79	9.920		
950−0.7		0.8972	0.5174	0.3234	
950−0.8		2.288	1.207	0.6952	
950−0.9		7.880	3.698	1.928	
950−1.0		39.63	15.88	7.124	
1000−0.7		1.225	0.6742	0.4163	0.2835
1000−0.8		3.346	1.715	0.9579	0.5764
1000−0.9		12.32	5.605	2.800	1.518
1000−1.0		63.63	26.74	11.54	5.440

of oligotrifluorochloroethylene, by using the mixing theory proposed by Takayanagi.[5,6] As a consideration of the "R in H" type parallel-model as Fig. 1 shows, the viscosities, η_m, of mixtures of oligotrifluorochloroethylene and n-heptadecane can be expressed as follows:[5]

$$\eta_m = [(1-\Phi_R)-n(1-\Phi_R)]\eta_H+[\Phi_R+n(1-\Phi_R)]^2/[\Phi_R/\eta_R+n(1-\Phi_R)/\eta_H] \qquad (1)$$

where the subscripts R and H denote oligotrifluorochloroethylene and n-heptadecane respectively, and where n is a parameter which indicates the degree of contribution of the series element in the parallel-model. The values of the viscosities at 50°C, as calculated by Eq. (1), are shown by solid curves in Fig. 2. The observed values, which are shown by filled circles in Fig. 2, agree well with those calculated by assuming the "R in H" type parallel-model when is nearly equal to 0.1. These mixed systems were considered to be comparatively well compatible under suitable conditions because of the small value of n, *i.e.*, the smaller contribution of the series element.

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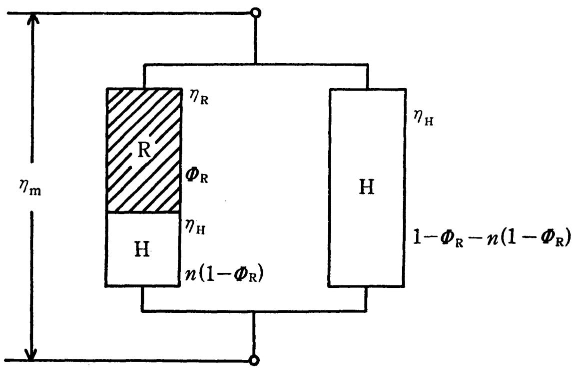
[5] M. Takayanagi, *Kobunshi*, **10**, 289 (1961).

[6] E. Shiraki and G. Okamoto, *Kogyo Kagaku Zasshi*, **65**, 148 (1962).



R: Oligotrifluorochloroethylene
H: *n*-Heptadecane

Fig. 1.

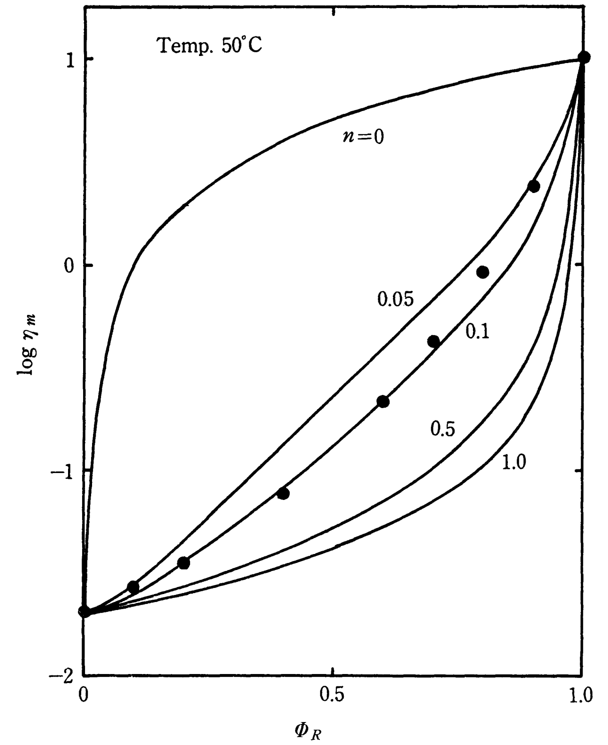


Fig. 2. Relationship between log η_m and Φ_R.

This conclusion was supported by the facts that it was difficult to separate the two components into two phases and that the η_m values did not change even when measured after 2 months, providing the conditions were suitable. A slight deviation of the observed values from the solid line (n is 0.1) in the volume fraction range larger than 0.7 is considered to be caused by the change in the degree of compatibility between the two components.

The η_m/η_H ratio of the viscosities of the mixture and *n*-heptadecane can be expressed by rewriting Eq. (1) as follows:

$$\eta_m/\eta_H = (1-\Phi_R) + [\Phi_R{}^2\eta_R + n\Phi_R(1-\Phi_R)(2\eta_R-\eta_H)]/[\Phi_R\eta_H + n(1-\Phi_R)\eta_R] \quad (2)$$

When the volume fraction, Φ_R, is small and when n is nearly equal to 0.1, η_m/η_H can be approximately expressed as follows:

$$\eta_m/\eta_H = 1+\Phi_R+\Phi_R{}^2/n(1-\Phi_R) \quad (3)$$

because $\eta_R \gg \eta_H$, and $n(1-\Phi_R) \gg \Phi_R\eta_H/\eta_R$. With the assumption of $n=\Phi_R f(\Phi_R)$, the following relationship is obtained:

$$\eta_m/\eta_H = 1 + \Phi_R + \Phi_R/(1-\Phi_R)f(\Phi_R) \simeq 1 + a\Phi_R + b\Phi_R{}^2 \quad (4)$$

where a and b are parameters. Figure 3 shows the relationship between $(\eta_m/\eta_H-1)/\Phi_R$ and Φ_R at 50°C and at volume fractions, Φ_R, smaller than 0.2. The linear relationship was found to be as follows: $(\eta_m/\eta_H-1)/\Phi_R=2.5+5.6\Phi_R$. Similar relations have been found for dilute solutions of polymers.[7–10)]

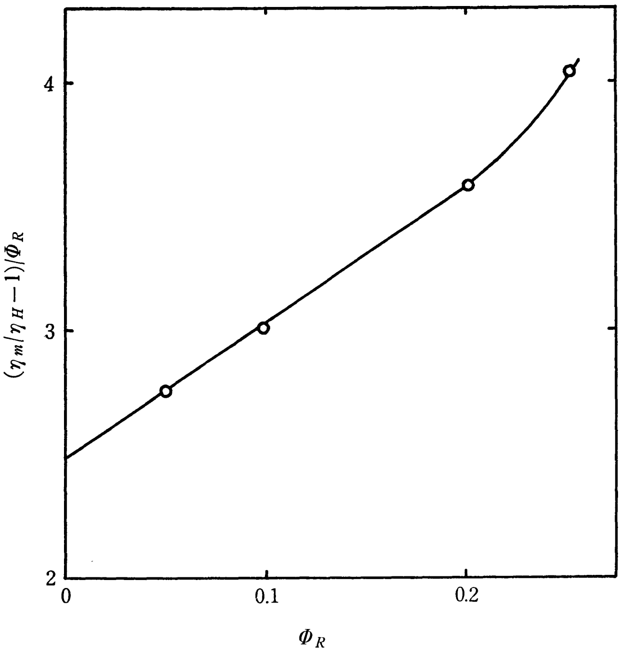


Fig. 3. Relationship between $(\eta_m/\eta_H-1)/\Phi_R$ and Φ_R at 50°C.

Temperature Dependence of Viscosities. Figure 4 shows the relationships between $(T-T_0)$ and $(T-T_0)/\log a_T$. The shift factor, a_T, which was expressed by $\eta\rho_0T_0/\eta_0\rho T$, was calculated on the basis of an arbitrary fixed temperature, T_0. The linear relationships made it clear that the temperature dependence of the viscosities of the mixed samples could be well explained by the WLF equation.[11)] The WLF parameter, $C_1{}^0$ and $C_2{}^0$, were estimated on the basis of T_0 from the linear relationships between $(T-T_0)$ and $(T-T_0)/\log a_T$ in Fig. 4.

The free-volume fraction, f_0, at T_0 and its thermal-expansion coefficient, α_f, were expressed by $1/2.303C_1{}^0$ and $1/2.303C_1{}^0C_2{}^0$ respectively. Table 3 shows the free-volume fractions, f_T, at 30°C and their thermal-expansion coefficients, α_f.

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7) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 266 (1936).
8) R. Simha, *J. Appl. Phys.*, **23**, 1020 (1952).
9) N. Saito, *J. Phys. Soc. Jap.*, **7**, 447 (1952).
10) M. Sugita, *ibid.*, **7**, 554 (1952).
11) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).

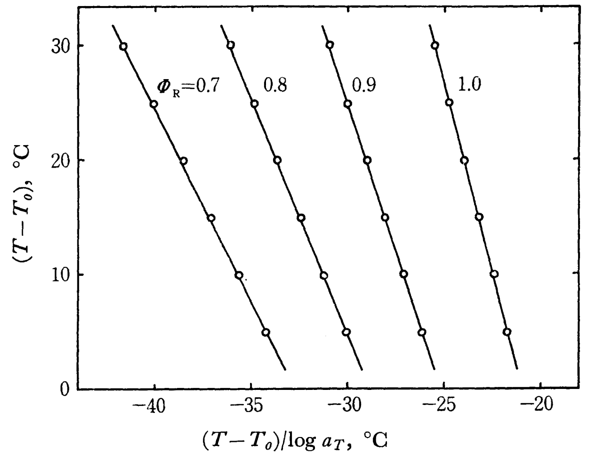

Fig. 4. Relationship between $(T-T_0)$ and $(T-T_0)/\log a_T$.

TABLE 3. VALUES OF f_T AT 30°C AND α_f

Sample	$f_T\times 10^2$	$\alpha_f\times 10^4$
n-$C_{17}H_{36}$	20.52	10.72
910−0.1	18.97	9.83
910−0.2	17.37	9.41
910−0.4	17.09	12.73
910−0.6	15.24	14.37
910−0.7	12.97	11.77
910−0.8	10.54	8.92
910−0.9	8.46	6.59
910−1.0	6.67	4.92
950−0.7	11.99	10.51
950−0.8	9.76	7.92
950−0.9	7.70	5.68
950−1.0	6.32	4.61
1000−0.7	10.93	9.09
1000−0.8	8.98	6.95
1000−0.9	7.14	5.07
1000−1.0	5.79	4.00

If physical interactions between n-heptadecane and oligotrifluorochloroethylene molecules or phases do not exist at all, the volume, V, and the free-volume, v_f, of the mixture may be given by simple additivity as follows:[12]

$$V = V_R + V_H \tag{5}$$

$$v_f = v_{f,R} + v_{f,H} \tag{6}$$

and

$$f = v_f/(V_R+V_H) = \Phi_R f_R + (1-\Phi_R)f_H \tag{7}$$

where V_R and V_H are the substantial volumes of oligotrifluorochloroethylene and n-heptadecane in the mixture, and where $v_{f,R}$ and $v_{f,H}$ are the respective free-volumes of the components. Therefore, the temperature dependence of the free-volume fraction, f_T, at T is expressed as follows when the physical interactions do not exist at all:

$$f_T = \Phi_R[f_{0,R}+\alpha_{f,R}(T-T_0)] + (1-\Phi_R) \times [f_{0,H}+\alpha_{f,H}(T-T_0)] \tag{8}$$

where $f_{0,R}$ and $f_{0,H}$ are the respective free-volume fractions of oligotrifluorochloroethylene and n-heptadecane at T_0, and $\alpha_{f,R}$ and $\alpha_{f,H}$, their respective thermal-expansion coefficients.

Figure 5 shows the dependence of the free-volume fractions, f_T, of the mixture at 30°C on the volume fractions of oligotrifluorochloroethylene with the molecular weight of 910. The broken line shows the relationship calculated by means of Eq. (7). The free-volume fractions, f_T, were larger than those obtained by assuming a simple additivity between the two components. Thus, some physical interactions between the two kinds of molecules or phases are considered to exist. In view of the physical interactions, the free-volume fraction, f_T, of a mixture is generally given by the following equation:

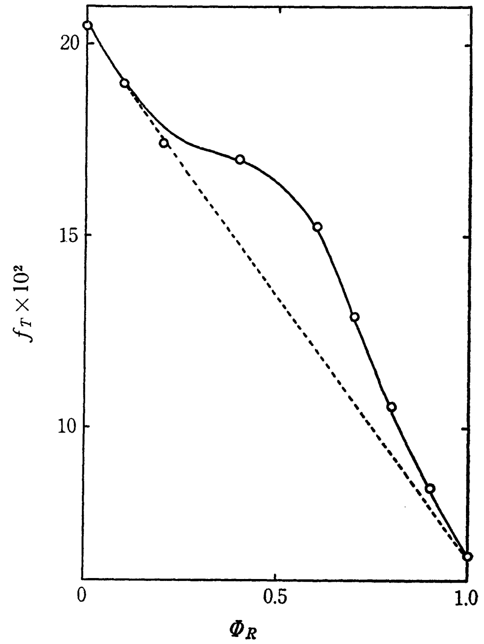

Fig. 5. Relationship between f_T and Φ_R at 30°C.

$$f_T = \Phi_R\beta_R(p,T,\Phi_R)f_{T,R} + (1-\Phi_R)\beta_H(p,T,\Phi_R)f_{T,H} \tag{9}$$

where the β's are interaction parameters, and p, the internal pressure induced by one phase on the other due to the difference between the thermal-expansion coefficients of the two phases. The free-volume fractions, f_T, varied abnormally at Φ_R values of about 0.2.

Molecular-weight Dependence of the Viscosities of the Mixture. Figure 6 shows the dependence of the viscosities of the mixtures on the molecular weights of oligotrifluorochloroethylene at 50°C. At molecular weights ranging from 910 to 1000, linear relationships were observed between $\log \eta_m$ and $\log M_n$. The slopes of the linear relationships were much larger than unity, and they decreased with a decrease in the volume fraction, Φ_R.

Figure 7 shows the dependence of the reciporcals of the free-volume fractions, $1/f_T$, on the molecular weights of the oligotrifluorochloroethylene in the mixtures. The reciprocals of the free-volume fractions,

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[12] T. Horino, Y. Ogawa, Y. Soen, and H. Kawai, *J. Appl. Polym. Sci.*, **9**, 2261 (1965).

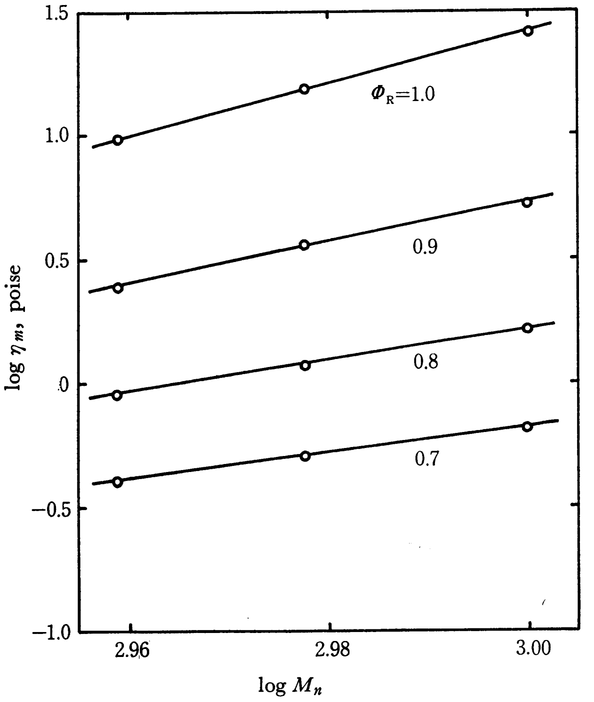

Fig. 6. Dependence of viscosity on molecular weight at 50°C.

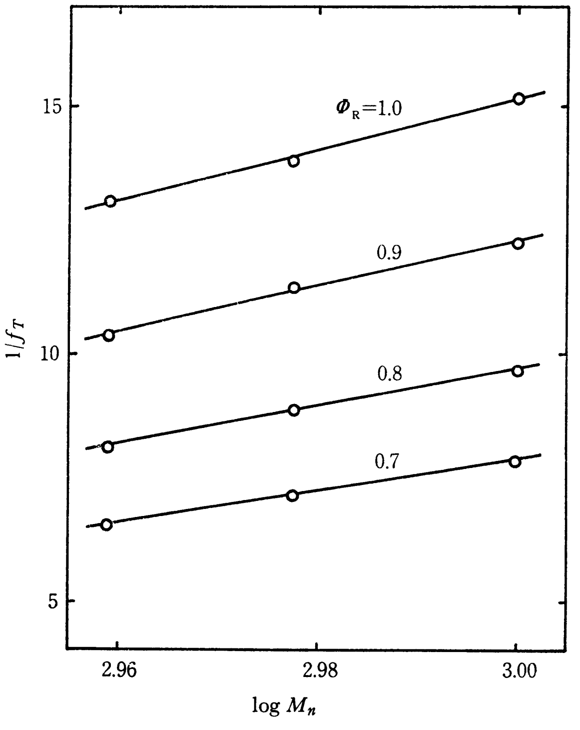

Fig. 7. Relationship between $1/f_T$ and $\log M_n$ at 50°C.

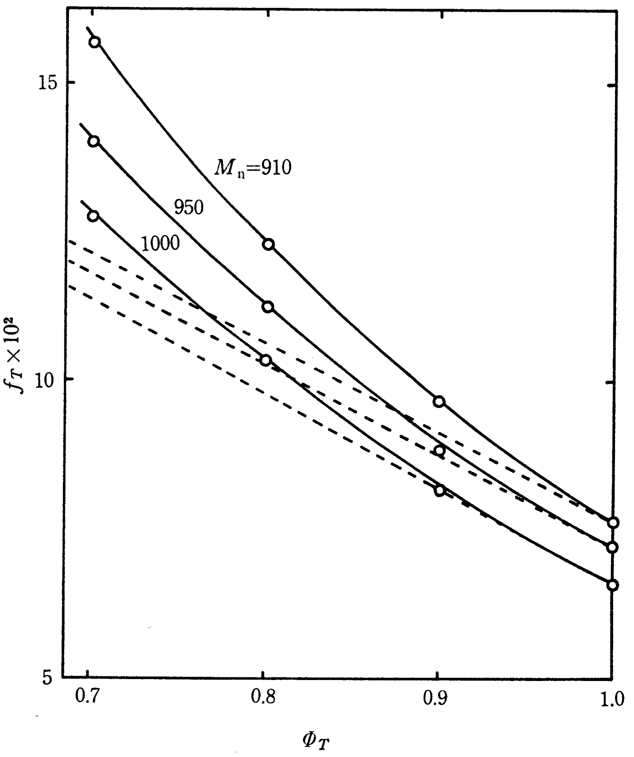

Fig. 8. Dependence of free volume fraction on Φ_T at 50°C.

$1/f_T$, varied linearly with $\log M_n$. The slopes of the linear relationships were much larger than unity, and they varied with the volume fractions, Φ_R, as did those of $\log \eta_m$-$\log M_n$ relationships.

Figure 8 shows a plot of the free-volume fraction, f_T, against the volume fraction, Φ_R, at 50°C. The broken lines shows the relationships calculated by Eq. (7). The estimated free-volume fractions, f_T, of the mixtures were larger than those calculated by Eq. (7), and the deviation from the calculated values increased with a decrease in the volume fraction, Φ_R, and with a decrease in the molecular weight. A negative effect on the physical interaction among oligotrifluorochloroethylene molecules is implied by the results, because the *n*-heptadecane molecules are considered to disperse among the oligotrifluorochloroethylene molecules and to obstruct the physical interaction among them. The viscosities of liquid oligotrifluorochloroethylene are larger than those of usual chain-polymers with the same chain-lengths.[4,13] Judging from the results shown in Fig. 8, strong interactions may be considered to exist. It has been suggested that these intermolecular actions are a result of the polarization of molecules induced by electronegative atoms or groups bound on the chain-skeletons.[3]

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[13] N. Yoshida and S. Hamada, This Bulletin, **45**, 88, (1972).