RES. LAB. REPRINT 1879

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SCHENECTADY, NEW YORK

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[Reprinted from the Journal of the American Chemical Society, 74, 68 (1952).]

[Contribution From The Research Laboratory, General Electric Company]

The Solubility of Polytrifluorochloroethylene

By H. Tracy Hall

A physico-chemical study of the solubility of the semi-crystalline polymer of trifluorochloroethylene has been made. Curves are given from which it is possible to determine whether a particular liquid will be a solvent and if so the solution temperature. The information necessary for the utilization of these cures is (a) the solubility parameter of the liquid at 25º, (b) the molar volume of the liquid at 25º and (c) the coefficient of cubical expansion of the liquid. Several thermo-dynamic constants have been determined from solubility and crystal melting temperature data for this polymer among which are the heat of fusion of the crystallites (18.1 cal./g.), the solubility parameter of the amorphous polymer ($\delta_P^T = 8.05e^{-0.000925T}$ where T is in ºC.), and the interaction parameter, *m*, for various polymer-solvent systems. For this particular polymer the interaction parameter m_s is given by the expression $m_s = V_{r.u.}/V_0^{T_s}$ where $V_{r.u.}$ is the volume of the repeating unit in the amorphous polymer and $V_0^{T_s}$ is the molar volume of the solvent at the solution temperature T_s.

This report presents the results of a physico-chemical study of the solubility behavior of the semi-crystalline polymer trifluorochloroethylene in normal solvents. The principal problems considered are as follows: (1) the prediction of solution temperature when certain fundamental data are known, (2) the lowest solution temperature to be expected, and (3) the determination of thermodynamic quantities for the polymer-solvent systems.

Because the temperature of solution for this polymer is much higher than that previously encountered is studies of polymer solubility it was found necessary to introduce the temperature dependence of solubility parameters and molar volumes. This has not been done before.

Satisfactory interpretation of the solubility of non-polar polymers in non-polar solvents has been made with the use of the equation[1]

$$\mu = \mu_s + \mu_H^T = \mu_s + V_0^T(\delta_0^T - \delta_P^T)^2/RT \qquad (1)$$

where μ is a free energy parameter expressing the interaction of the polymer and solvent as the sum of a temperature independent entropy term μ_s and a temperature dependent heat term μ_H^T. V_0^T is the molar volume of the solvent, δ_0^T the solubility parameter of the polymer all at the temp. T, ºK. R is the molar gas constant. δ_0^T, δ_P^T and V_0^T are all functions of temperature while μ_s is essentially independent of the temperature. The change of solution parameter with temperature for the amorphous polymer can be expressed by the relationship

$$\delta_P^T = \delta_P^0 \exp\{-[(n + 1)/2]\ \alpha_p{}^T\} \qquad (2)$$

where δ_P^T is the solubility parameter of the polymer at the temperature T, ºC., δ_P^0 is the solubility parameter of the polymer at 0ºC., α_p is the cubical coefficient of expansion of the amorphous polymer and n = 1.5 δ_0^T for the solvents considered here was calculated from heat of vaporization and density data available from the "International Critical Tables."

Experimental

The polymer used in this investigation was made by the M. W. Kellogg Company and designated as Kel-F #240. Before use it was micropulverized is a colloid mill. After this treatment the particle size was 1 to 10 microns. Three cc. of solvent plus 0.150 g. of this micropulverized polymer was placed in a heavy-walled glass tube, cooled in liquid air and sealed off with a torch. The tube was heated with shaking in a silicone oil-bath, the temperature of which was raised about one degree per minute. The polymer solvent mixture appears milky in the tube as it is shaken in the bath. Suddenly, however, when the proper temperature is reached, the fine polymer particles stick together and form a viscous ball. This phenomenon is easy to observe and occurs sharply. This is the

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[1] See "Solubility of Non-Electrolytes," Hildebrand and Scott, Ed. 3, Reinhold Publishing Corp., New York, N. Y., 1950.

temperature at which the crystallites melt. (As mentioned, this polymer is partially crystalline and hence contains both amorphous and crystalline regions.) On further heating a temperature is reached at which the ball of polymer is completely dissolved.

The following table gives the crystallite melting temperature T_m, the solution temperature T_s and the solubility parameters and molar volumes of the solvents at these temperatures where data were available for calculating the latter.

TABLE I

Solvent	T_m, °C	T_s, °C	$\delta_0^{T_m}$	$V_0^{T_m}$	$\delta_0^{T_s}$	$V_0^{T_s}$	δ_0^{298}	V_0^{298}
Cyclohexane	145	>235	6.32	130.0	. . .	. . .	8.20	109
Methylchloroform	120	120	7.05	114.0	7.05	114.0	8.50	100
Carbon tetrachloride	114	114	7.35	109.5	7.35	109.5	8.60	97
p-Xylene	133	140	7.71	135.0	7.62	136.0	8.75	124
Toluene	128	142	7.62	122.0	7.46	124.0	8.90	107
Benzene	118	200	7.78	101.2	6.27	118.3	9.15	89
Mesitylene	127	140	. . .	. . .	. . .	. . .	8.80	140
$SnCl_4$	158	>158	. . .	. . .	. . .	. . .	8.70	118
$TiCl_4$	. . .	>165	. . .	. . .	. . .	. . .	9.00	111
$GeCl_4$	143	>180	. . .	. . .	. . .	. . .	8.10	115
BCl_3	>92	>92	. . .	. . .	. . .	. . .	. . .	. . .
Cyclohexene	138	>150	. . .	. . .	. . .	. . .	8.58	. . .
None	208[2]							

Derivations from the Data.—The data from Table I when used with (1) and (2) above, and (3) and (4) below are sufficient to determine the heat of fusion per gram of crystalline polymer (for melting the crystallites) h_f, the solubility parameter of the polymer at 0°, δ_P^0, the interaction parameter μ_s and μ_H^T and the volume of the solvent and polymer present in the swollen gel at the crystal melting temperature. Note that solvent in these experiments is always present in excess of that imbibed at the crystal melting temperature T_m.

TABLE II

Thermodynamic Data for Polymer in Various Solvents

For $n = 1.5$: $\delta_P^0 = 8.05$, $hf = 18.1$ cal./g., $\delta_P^T = 8.05 \exp^{(-9.25 \times 10^{-4} T)}$ (T_m, °C)

Substance	m_s	n_2	$V_0^{T_s}$	$m_s V_0$	$m_s^2 V_0^T$	m^{T_m}	$\delta_P^{T_s}$	$\delta_0^{T_s}$
p-Xylene	0.450	0.030	136.0	61.2	27.6	0.510	7.07	7.62
Toluene	0.476	0.034	124.0	59.1	28.0	0.511	7.06	7.46
Benzene	0.478	0.051	118.3	56.6	27.0	0.517	6.69	6.27
Methylchloroform	0.497	$\rightarrow 0$	114.0	56.6	28.2	0.500	7.20	7.05
Carbon tetrachloride	0.499	$\rightarrow 0$	109.5	54.7	27.3	0.500	7.25	7.35

When the molecular weight is large, as it is in the case under consideration

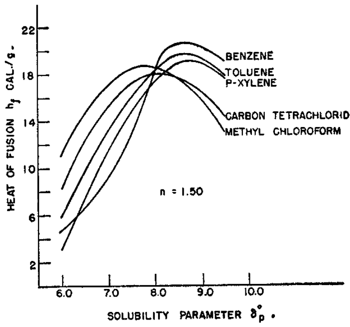

Fig. 1.—Plot of heat of fusion h_f *vs.* assumed value of solubility parameter δ_p^0 for $n = 1.50$.

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[2] Unpublished data of F. P. Price of this Laboratory.

$$\ln(1 - n_2) + n_2 + m(n_2)^2 = 0 \qquad (3)$$[3]

The quantity n_2 is the volume fraction of polymer in the solvent-swollen polymer (at the crystal melting temperature for this work).

Equation (4) below, is obtained by rearrangement of and substitution in (33) of Flory's[4] paper "Thermodynamics of Crystallization in High Polymers. IV." The substitutions are: $Z/Z_s = V/V_0$, $h_f = h_u X/M$, $V = M/\rho X$ where the symbols have the meaning given in Flory's paper.

$$h_f = [Rn_1/V_0^{T_m} - (n_1)^2(\delta_0^{T_m} - \delta_p^{T_m})^2/T_m]1/\rho(1/T_m - 1/T_m^0) \qquad (4)$$

h_f = heat of fusion/g. of crystalline polymer (to melt crystallites)

ρ = density of the polymer = 2.0 for this case

n_1 = $(1 - n_2)$ = volume fraction of solvent in swollen polymer at the melting temperature

T_m^0 = melting temperature of crystallites in the absence of any solvent

$\delta_0^{T_m}$ = solubility parameter of the solvent at the crystallite melting temperature

$\delta_p^{T_m}$ = solubility parameter of the polymer at the crystallite melting temperature.

A direct algebraic solution of (1) through (4) is not possible. Consequently, the following approach was used:

(a) values of δ_P^0 of 6.0, 6.5, 7.0 . . . 10.0 were substituted in (2) (first with n = 1, then with n = 1.5 and finally with n = 2). The temperature used was the solution temperature of the polymer in the particular solvent being considered. The cubical coefficient of expansion α_p of the amorphous polymer has the value 7.4×10^{-4}.

(b) At the solution temperature $\mu = 0.5$. Equation (1) was then solved for μ_s for each assumed δ_P^0 and n. Note that μ_s is temperature independent.

(c) When μ_s was known (in terms of assumed δ_P^0 and n) for each polymer solvent system, m^{T_m} at the crystallite melting temperature T_m was obtained by again applying (1) with data at T_m.

(d) A graph of m^{T_m} *vs.* n_2 was constructed by using (3). From this graph n_2 was obtained corresponding to the above values of m^{T_m}.

(e) When n_2 was known, n_1 was known since $n_1 + n_2 = 1$. All the data needed to solve (4) (at assumed δ_p's and n's) were now available. Equation (4) was solved for h_f for each assumed δ_P^0 and n. A plot of h_f vs. δ_p at fixed $n = 1.5$ is shown in Fig. 1.

The average crossover point in Fig. 1 gives the correct value of δ_P^0 for the assumed *n*. Expressed simply as average ± average deviation from the mean $\delta_P^0 = 8.05 \pm 0.08$ and $h_f = 18.1 \pm 0.3$ for $n = 1.5$. Similar plots to that of Fig. 1 for $n = 1.0$ give $\delta_P^0 = 7.95 \pm 0.09$ and $h_f = 18.1 \pm 0.4$. For $n = 2.0$, $\delta_p = 8.23 \pm 0.09$ and $h_f = 18.2 \pm 0.5$. Changing *n* within these reasonable limits does not have too great an effect on δ_p and h_f. For further discussion it will be assumed that *n* has the usual value of 1.50 that holds for liquids.

Table II gives data derived by using $n = 1.5$.

Note from the table that μ_s increases regularly as decreases. The product $\mu_s V_0^{T_s}$ is nearly a constant with a value of 57.6 ± 1.8 expressed as average ± average deviation from the mean. More nearly constant is the product $m_s^2 V_0^{T_s}$. Expressed as average ± average deviation, $\mu_s^2 * V_0^{T_s} = 27.6 \pm 0.4$ for the five polymer-solvent systems of Table II. It is of interest to note that the molar volume of the repeating unit in the amorphous polymer is 58.2 cc. Thus μ_s approximately equals the ratio of repeating unit volume to solvent molecule volume at the solution temperature. A better relationship is

$$\mu_s = 0.688\,(V_{r.u}/V_0^{T_s})\,½ = 5.26/(V_0^{T_s})\,½ \qquad (5)$$

where $V_{r.u}$ = molar volume of the repeating unit in the amorphous polymer.

Assuming that this relationship hold for other non-polar solvents, the solution temperature of this polymer is included in the expression

$$0.5 = 5.26/\{V_0^{298}\,[1 + \alpha_0\,(T_s - 298)]\}\,½ + V_0^{298}\,[1 + \alpha_0\,(T_s - 298)]\,[\delta_0^{298}\,(\exp - \alpha_0 k_0\,(T_s - 298)) - 8.05\,(\exp - 9.25 \times 10^{-4}\,(T_s - 273))]^2/RT. \qquad (6)$$

Where T_s is in degrees Kelvin, α_0 = coefficient of cubical expansion of the solvent, V_0^{298} = molar volume of the solvent at 298°K. and $k_0 = (n + 1)/2$ where n is characteristic of the solvent and is approximately equal to 1.50. Equation (6) is obtained by utilizing the above expression for μ_s and substituting $\delta_P^T = 8.05\,(\exp - 9.25 \times 10^{-4}\,(T - 273))$, $\delta_0^T = \delta_0^{298}\,(\exp - \alpha_0 k_0\,(T - 298))$ and $V_0^T = V_0^{298}\,[1 + \alpha_0\,(T - 298)]$ in (1). Equation (6) has been solved for δ_0^{298} as a function of T_s for $\alpha_0 = 0.0010$ and various values of V_0^{298}. the results are displayed in Fig. 2. If the polymer

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[3] Reference 1, Ch. XX, Eq. (44).

[4] P. J. Flory, J. Chem. Phys., 17, 223 (1949).

were completely amorphous the solution temperature as a function of δ_0^{298} at fixed α_0 and V_0^{298} would follow both the solid and dashed parts of the curves. However, the solution temperature must equal or be greater than the melting temperature so the melting temperature curves must be obtained. The melting temperature as a function of δ_0^{298} or fixed α_0 and V_0^{298} is shown as the shallow curve connecting the limbs of the corresponding solution curve above the dashed portions in Fig. 2.

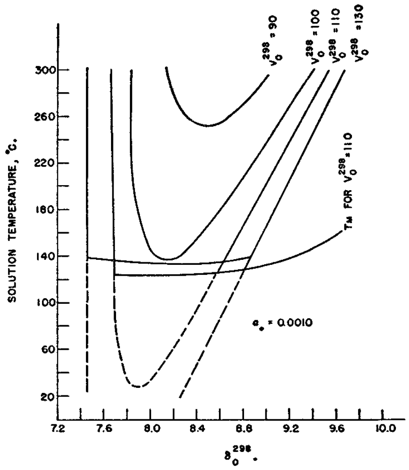

Fig. 2.—Solution temperature of polytrifluorochloroethylene as a function of the solubility parameter and molar volume of the solvent when the cubical coefficient of expansion for the solvent is 0.0010.

To obtain T_m the follow equations must be simultaneously satisfied along with (3), (5) and (6)

$$\delta_0^{298} = \{ \pm [(m^{T_m} - \mu_s)RT_m/V_0^{T_m}]\ \tfrac{1}{2} + \delta_p^{T_m}\}/b \qquad (7)$$

$$\delta_0^{298} = (\pm \{[Rn_1/ - \rho h_f\,(1/T_m - 1/T_m)]\ T_m/n_1^2\}\ \tfrac{1}{2} + \delta_p^{T_m})/b \qquad (8)$$

where $b = (\exp - \alpha_0 k_0\,(T_m - 298))$ and $V_0^{T_m}$ and $\delta_p^{T_m}$ have the temperature dependence shown previously. Equations (7) and (8) are obtained from equations (1) and (4).

When $T_s = T_m$, $n_1 \rightarrow 1$, $m^{T_m} = 0.5$ and the terms raised to the one-half power in (7) and (8) can be equated. This gives a quadratic in T_m that is readily solvable in terms of V_0 and α_0. This determines the intersection of T_s and T_m curves on the Fig. 2 plot.

When T_m is greater than the corresponding minimum in the T_s curve in Fig. 2 the minimum value of T_m is found by equating the term raised to the one-half power in (8) to zero. At this minimum $T_s = T_m$ and hence $n_1 = 1$. The above procedure by giving the intersections of the T_m and T_s curves as well as the minimum is sufficient to define the T_m curve where it falls within the limbs of the T_s curve. To establish the T_m curve outside this region is much more difficult. The author has carried out the computations only for the case of $\alpha_0 = 0.0010$ and $V_0^{298} = 110$ as shown in Fig. 2. The following procedure was used:

(1) A value of T_s was picked. This fixes δ_0^{298} and μ_s. For example, if $\alpha_0 = 0.0010$, $V_0^{298} = 110$ and $T_s = 180$, $\delta_0^{298} = 8.87$ (from Fig. 2), $V_0^{T_s} = 127$ and $\mu_s = 0.466$ from (5). (2) Equation (3) is solved for m^{T_m} and substituted in (7). (3) Equation (7) is equated to (8) and the resultant expression solved for T_m. This gives a quadratic in T_m as a function of n_1 when α_0 and V_0^{298} are fixed. (4) Various values of n_1 are substituted in this equation and the corresponding T_m found. (5) The above n_1 and corresponding T_m are now substituted in equation (8) and (8) is solved for . (6) The δ_0^{298} obtained is plotted *vs.* T_m and the

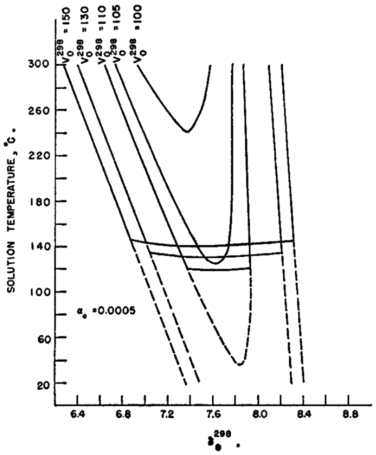

Fig. 3.—Solution temperature of polytrifluorochloroethylene as a function of the solubility parameter and molar volume of the solvent when the cubical coefficient of expansion for the solvent is 0.0005.

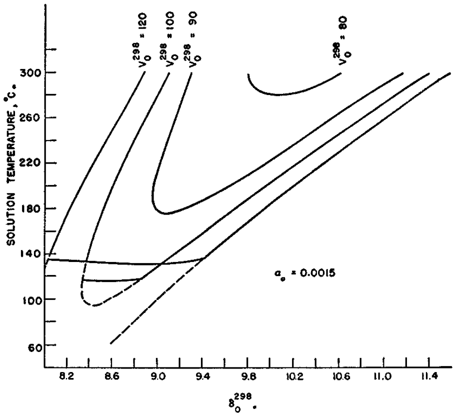

Fig. 4.—Solution temperature of polytrifluorochloroethylene as a function of the solubility parameter and molar volume of the solvent when the cubical coefficient of expansion for the solvent is 0.0015.

correct T_m corresponding to the δ_0^{298} of step (1) above obtained from the graph.

Figure 3 gives the solubility curves for $\alpha_0 = 0.0005$ and Fig. 4 for $\alpha_0 = 0.0015$.

The Minimum Solution Temperature.—Figures 2, 3 and 4 show that as V_0 gets smaller the minimum in T_s rises and the minimum in T_m decreases. Since crystals must melt before solution can take place the lowest solution temperature obtainable will occur when $T_m^{min} = T_s^{min}$. This value is obtained by eliminating $(\delta_0^T - \delta^T)^2$ from (1) and (4). The resultant equation is

$$T_m = T_s = h_f/\rho\ (h_{f\rho}/RT_m + 5.26/(V_0^{T_s})\ ½ + 0.5/V_0^{T_s}) \quad (9)$$

According to this equation T_s decreases as $V_0^{T_s}$ decreases. However $\delta_0^{T_s}$ is fixed and must have a real value when this equation is satisfied. This puts a lower limit on $V_0^{T_s}$ that is not obvious from the above equation. If various $V_0^{T_s}$ are placed in (9) and corresponding T_s obtained these may then be substituted in (7) and T_s as a function of $\delta_0^{T_s}$ obtained. This plot shows that T_s^{min} = 115° when $\delta_0^{T_s} = 7.24$ and $V_0^{T_s} = 110$ cc. Thus the lowest solution temperature attainable is 115° and the solvent that dissolves the polymer at this temperature will have a molar volume of 110 cc. and a solubility parameter of 7.24 and 115°. Carbon tetrachloride comes very close to satisfying these requirements. Figure 5 is a plot of T_s^{min} *vs.* $\delta_0^{T_s}$ for the condition that $T_s^{min} = T_m^{min}$. The corresponding $V_0^{T_s}$ is also given. The plot shows that T_s changes slowly near $\delta_0^{T_s} = 7.24$ so that there is some latitude in obtaining a solvent with the proper characteristics to give the lowest solution temperature. Note that 115° is the lowest solution temperature that can be expected for *non-polar* solvents. It is entirely possible that highly *polar* solvents exist that would interact strongly with the polymer and cause solution to occur at temperatures lower than 115°. Indeed, this research indicates that any attempt to find solvents that will dissolve polytrifluorochloroethylene of this molecular weight at lower temperatures should be directed toward finding solvents with specific interactions for the polymer.

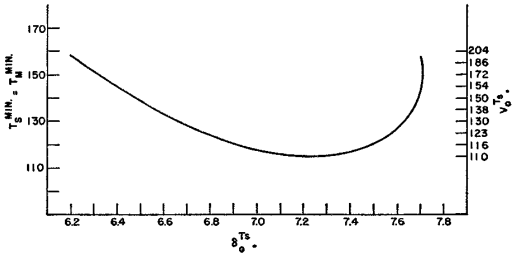

Fig. 5.—Minimum solution temperature and corresponding molar volume as a function of the solubility parameter of the solvent at the solution temperature for the condition that $T_s^{min} = T_m^{min}$.

Supercooling.—It should be mentioned that once the polymer is in solution it will supercool. Solvents that dissolve the polymer near the minimum solution temperature of 115° will supercool to approximately 90°. Solvents with higher solution temperatures supercool only a few degrees.

Conclusion.—The information as to whether or not a non-polar liquid will dissolve polytrifluorochloroethylene such as Kel-F #240 and the temperature of solution can be obtained from Figs. 2, 3 and 4 if the solubility parameter and molar volume of the solvent are known at 25° and if the coefficient of expansion of the solvent is known. Solubility parameters are not generally available but can be estimated by use of the Hildebrand rule.

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RECEIVED JUNE 6, 1951