Solubility Criteria for a Thermally Stable Polymer Determined by Gas–Solid Chromatography

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Synopsis

The Gibbs energy of adsorption, the Flory-Huggins interaction parameter χ, and a specific interaction parameter Λ, based on hydrogen-bonding and charge-transfer complexing properties of solvents, are obtained by gas–solid chromatography for a type of polyquinoxaline denoted as PQF. Interactions between 40 organic solvents and PQF have been determined at 176.35° and 200.85°C. PQF is an aromatic, heterocyclic polymer which is at least partially soluble in several organic solvents. The parameters χ and Λ and the solubility parameters of solvents are proposed to be the determining factors for miscibility of a PQF–solvent pair.

INTRODUCTION

Polymers containing aromatic-heterocyclic structures have been objects of prime interest, since such polymers exhibit superior thermal stability.[1] Polybenzimidazoles, whch have totally aromatic structures with a pseudoaromatic ring, have shown excellent thermal stability.[2] Other types of polymers with aromatic structures having unusually good thermal stability are derived from the condensation of the quinoxaline unit or the tetraazaanthracene unit.[3,4] In this work a polyquinoxaline polymer, PQF (poly[3,9-diphenylfuro[2,3-*g*:4,5-*g'*-[diquinoxaline-2,10-diyl]-*p*-phenyl]enoxy-*p*-phenylene]), whose structure is shown below, has been the subject of study:
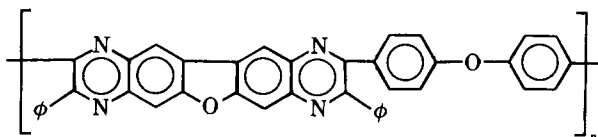
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PQF

In processing nonmelting polymers such as PQF, it is vital to find an appropriate solvent to dissolve the polymer of interest before processing. The study of thermodynamic properties of polymer–solvent systems provides assistance in finding appropriate solvents to dissolve the polymer of interest.

Gas chromatography (GC) has been recently replacing "static" methods for measuring the thermodynamic properties of various systems, especially polymer–solvent systems. This is because GC is a method by which data can be obtained quickly, and it does not involve the complications of most static methods.[5]

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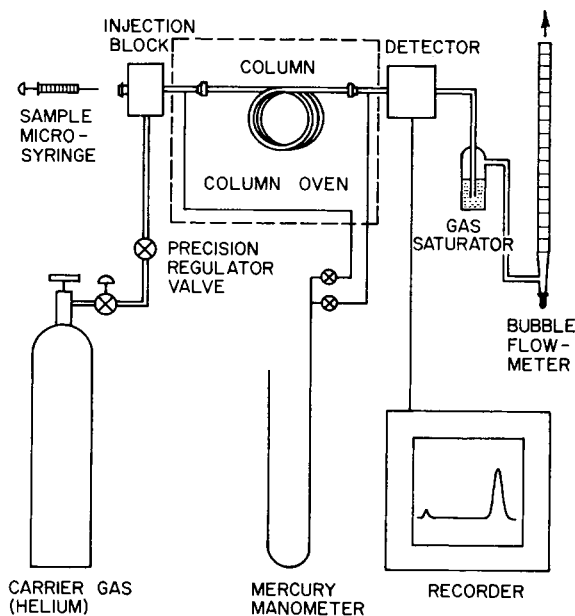
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Fig. 1. Gas-chromatographic apparatus.

Gas chromatographs have long been used analytically to measure gas and liquid compositions. The study of polymers by GC was restricted to the analysis of volatiles in polymers because of the low volatility of polymers. However, starting with the work of Smidsrød and Guillet,[6] polymers have been used as the stationary phase and their interactions with known solvents measured. This procedure is known as "inverse" gas chromatography. The name inverse gas chromatography has been used[7] to denote the use of gas chromatography to determine the properties of an unknown stationary phase with the aid of a known vaporizable solvent in the moving phase. This is the "inverse" of conventional GC used to determine the property of an unknown sample in the moving phase with a known stationary phase.

In gas–liquid chromatography (GLC) the stationary phase is liquid. On the other hand, in gas–solid chromatography (GSC) the stationary phase is solid. In our study, due to the extremely high glass transition temperature of PQF[8] (T_g = 405°C), GSC was necessarily used to study the interactions of PQF with various solvents.

EVALUATION OF THERMODYNAMIC FUNCTIONS FROM GC

Retention Volume

The specific retention volume (V_g^0), corrected to a reference temperature of 0°C, is obtained from the relation[9]

$$V_g^0 = Q(t_g - t_r) \frac{T_0}{T_r} \left(\frac{1}{m_2}\right) f_p \tag{1}$$

where f_p is the pressure drop correction, Q is the outlet carrier gas flow rate measured at room temperature, T_0 is 273.15 K, T_r is room temperature, t_g is the

TABLE I
Specific Retention Volumes[a] and ΔG_{ads} Values at 176.35° and 200.85°C

	176.35°C		200.85°C	
Solvent	V_g^0, ml/g	ΔG_{ads}, kJ/g-mole	V_g^0, ml/g	ΔG_{ads}, kJ/g-mole
1. Acetaldehyde	3.75	−18.35	2.77	−20.55
2. Acetic acid	26.88	−9.84	14.89	−12.70
3. N-Acetyl-2-aminoethanol	2.72	−16.37	1.33	−20.10
4. 2-Aminoethanol	64.45	−6.50	28.66	−10.05
5. Benzene	34.79	−7.89	18.21	−10.87
6. Bromobenzene	207.76	1.40	105.65	−1.19
7. 1-Bromobutane	51.48	−4.33	23.50	−7.65
8. 2-Bromobutane	31.24	−6.19	14.10	−9.66
9. 1-Butanol	35.87	−7.97	17.31	−11.28
10. Butanone	17.07	−10.85	10.10	−13.52
11. Chlorobenzene	125.19	−1.74	59.27	−4.78
12. o-Chlorophenol	—	—	247.30	1.38
13. Cyclohexane	8.09	−13.06	7.04	−14.32
14. 1,2-Dichloroethane	35.44	−6.94	16.15	−10.41
15. Dichloromethane	8.60	−12.80	4.49	−16.06
16. Diethyl ether	7.47	−13.83	2.01	−19.77
17. N,N-Dimethylethanamide	148.04	−2.07	72.77	−4.98
18. N,N-Dimethylmethanamide	92.99	−4.46	40.94	−7.94
19. Dipropyl ether	28.38	−7.64	11.75	−11.54
20. Ethanenitrile	8.90	−15.40	5.01	−18.50
21. Ethanol	5.38	−16.84	4.61	−18.37
22. Ethyl ethanoate	19.66	−9.57	10.34	−12.62
23. Furan	7.63	−14.08	3.43	−18.00
24. Heptane	22.84	−8.53	12.90	−11.25
25. Hexane	9.81	−12.25	5.51	−15.20
26. Methanamide	57.58	−8.07	25.19	−11.76
27. Methanol	5.03	−18.44	2.20	−22.69
28. Nitromethane	12.65	−12.59	7.79	−15.20
29. Nonane	110.07	−1.73	35.98	−6.23
30. Octane	47.18	−5.33	22.50	−8.54
31. Propanone	6.83	−15.08	5.99	−16.43
32. Propenenitrile	13.27	−12.95	7.38	−15.95
33. Tetrachloromethane	10.39	−9.87	5.95	−12.60
34. Tetrahydrofuran	24.29	−9.54	11.09	−13.14
35. Toluene	82.40	−4.05	34.64	−7.68
36. Trichloromethane	24.73	−7.58	10.85	−11.24
37. 2,2,2-Trifluoroethanol	5.62	−13.79	5.02	−14.97
38. Water	2.10	−23.88	2.09	−25.20
39. 2-Methylpentane	7.86	−13.08	6.91	−14.30
40. 2-Methylhexane	17.90	−9.44	8.29	−12.99

[a] Standard deviation of V_g^0 is ±1%.

retention time of evaporated solvent measured to peak maximum, t_r is the retention time of air measured to peak maximum, and m_2 is the mass of polymer in the column. The pressure correction factor f_p is given by[10]

$$f_p = \frac{3}{2}\left(\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}\right) \qquad (2)$$

where P_i is inlet pressure and P_0 is outlet pressure; P_0 is assumed to be atmospheric pressure in this work.

TABLE II
Values of $\alpha_1,$[19] $\mu_1,$[20] and δ_1[21,22,23] for Solvents at 25°C[a]

Solvent no.[d]	$\alpha_1, 10^{-24}$ cm^3	$\mu_1, 10^{-30}$	δ_1 (cal/cm^3)$^{1/2}$
1	4.49	9.07	9.87
2	5.12	5.80	13.01
3	10.22	14.18	14.78
4	6.49	7.57	15.52
5	10.40	0	9.16
6	13.49	5.67	9.87
7	11.25	6.94	8.65[c]
8	11.25	7.44	8.42[c]
9	8.76	5.57	11.60
10	8.24	9.24	9.45
11	12.34	5.70	9.67
12	12.96	4.54	14.24[c]
13	10.71	0	0
14	8.34	5.00	9.91[c]
15	6.42	5.14	9.88
16	8.80	3.84	7.53
17	9.57	12.79	9.13[c]
18	7.84	11.34	9.52[c]
19	12.57	4.34	7.58[c]
20	4.40	13.21	12.11
21	5.07	5.67	12.78
22	8.83	5.93	8.91
23	7.60	2.30	9.4
24	13.71	0	0
25	11.85	0	0
26	3.96	10.84	19.2
27	3.25	5.67	14.50
28	4.95	11.91	12.90
29	17.42	0	7.64
30	15.54	0	7.54
31	6.43	9.61	9.62
32	6.19	12.77	10.56
33	8.34	5.00	9.91[c]
34	7.97[b]	5.84	9.1
35	12.34	1.23	8.93
36	8.32	3.40	9.16
37	4.80	6.77	11.89[c]
38	1.59	8.34	23.53
39	11.86	0	7.05
40	13.69	0	7.23

[a] Solubility parameter of PQF is estimated[18] to be 14.23 (cal/cm^3)$^{1/2}$.
[b] Estimated from group contribution values of Bondi.[24]
[c] Estimated from group contribution values of Fedors.[18]
[d] See Table I for key.

Molar Gibbs Energy of Adsorption

In computing the molar Gibbs energy of adsorption (ΔG_{ads}), we use two different standard states: one for the gas phase and one for the polymer phase. The standard state for the gas phase is taken to be pure solvent as an ideal gas at 1 atm and column temperature. The standard state for the polymer phase is taken to be solvent obeying Henry's law at column conditions. Although some adsorption isotherms do not obey Henry's law, at infinitesimal concentrations
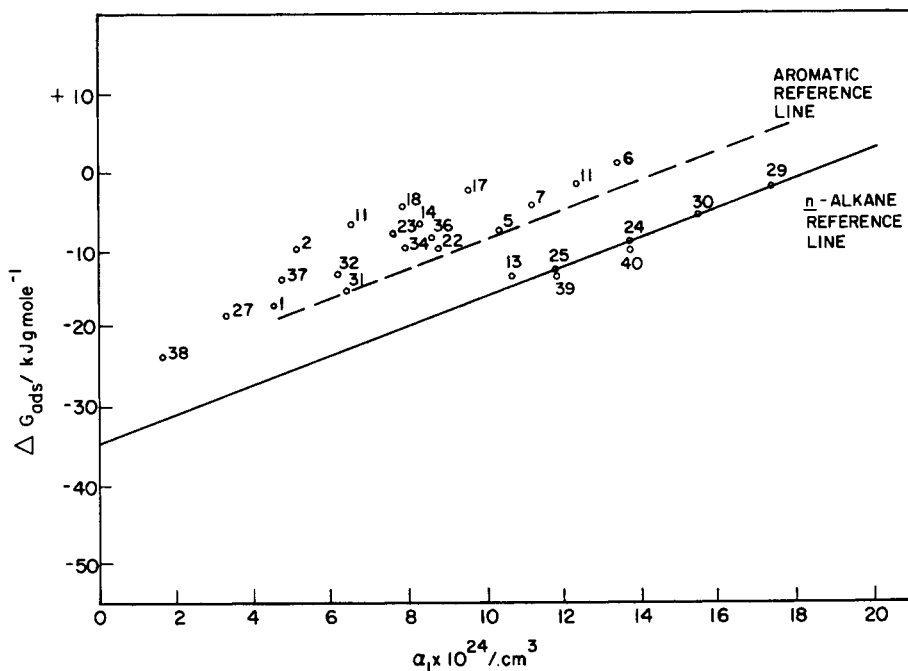
Fig. 2. ΔG_{ads} vs α_1 at 176.35°C for solvents. See Table I for key to solvent numbers.

of solute, as used in this work, the straight-line approximation of Henry's law is not a drastic assumption. The use of a Henry's law standard state, although a hypothetical standard state for solvents which are only adsorbed, permits treatment of adsorption and absorption data in a consistent way. The term ΔG_{ads} is related to V_g^0 by[11]

$$\Delta G_{ads} = RT \ln \left(\frac{M_1 V_g^0}{RT_0/1 \text{ atm}} \right) \tag{3}$$

where M_1 is the molecular weight of the solvent and R is the universal gas constant with its pressure dimension in atmospheres.

Correlation of Gibbs Energy of Adsorption

The value of ΔG_{ads} derived experimentally is related to solvent polarizability α_1, solvent dipole moment μ_1, and a specific interaction parameter Λ, which represents gas–solid interactions due to hydrogen bonding, charge-transfer complexing, and so on. The equation used to relate ΔG_{ads} to α_1, μ_1, and Λ is[11]

$$\Delta G_{ads} = a_1 \alpha_1 + b_1 \mu_1 + \Lambda \tag{4}$$

where a_1 and b_1 are statistically determined coefficients.

The Flory-Huggins Interaction Parameter

The Flory-Huggins interaction parameter χ is a measure of the strength of interaction between polymer and solvent. The parameter χ can be computed from experimental GC data and measurable quantities from the relation[9]

$$\chi = \ln \left(\frac{273.15 R v_{2sp}}{V_g^0 P_1^s v_1} \right) - \left(1 - \frac{v_1}{v_2} \right) - \left(\frac{P_1^s}{RT} \right) (B_{11} - v_1) \tag{5}$$
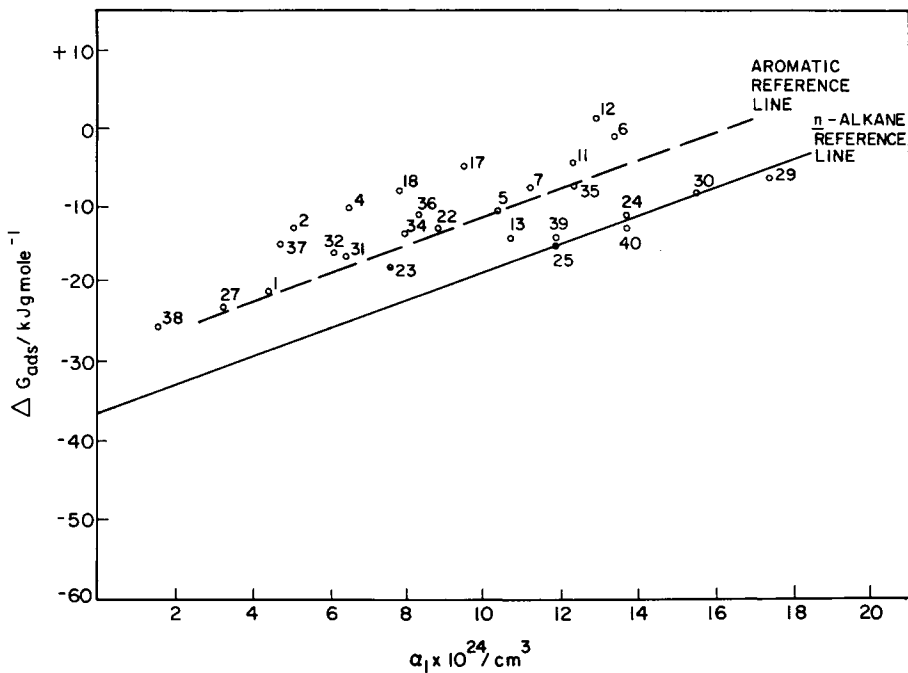
Fig. 3. ΔG_{ads} vs α_1 at 200.85°C for solvents.
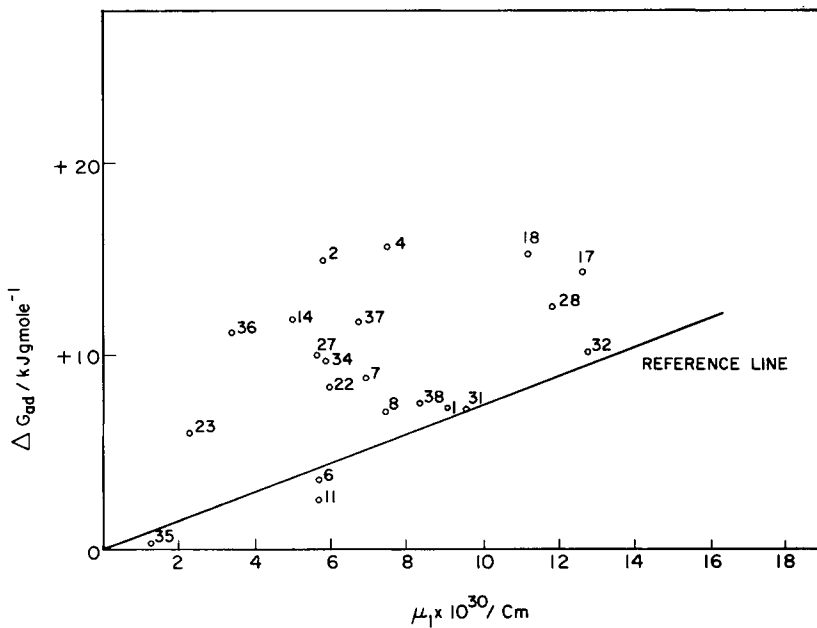
Fig. 4. ΔG_{ad} vs μ_1 at 176.35°C for solvents.

where B_{11} is the pure solvent second virial coefficient, P_1^s is the saturated vapor pressure of solvent, v_1 and v_2 are the liquid molar volumes of solvent and polymer, respectively, at column temperature T, and v_{2sp} is the specific volume of polymer.

The parameter χ represents the energetic interactions in a polymer solution. However, χ determined by GSC could be interpreted to represent the molecular interactions between the solid polymer and gaseous solvent. Although the calculation of χ from eq. (5) by using liquid molar volumes for a gas–solid system could lead to some ambiguity in the values of χ, the interpretation of χ as representing molecular gas–solid interactions would be justified. The χ's calculated by eq. (5) for a gas–solid system should be used to compare the results for different solvents rather than interpreting single values of χ. In this work we observed that solvents have much larger negative values of χ than nonsolvents. Another possible interpretation of χ for a gas–solid system could be made if polymer solution occurs locally as a solvent pulse passes through the column, lowering T_g of the mixture below operating temperature. In that case, χ would have the same meaning as for a polymer solution.

Experiments were carried out with methanol and trichloromethane to detect any change in the slope of $\ln V_g^0$ versus $1/T$ over a wide temperature range. The experiments failed to show a change in slope of $\ln V_g^0$ versus $1/T$. If a change in the slope had been observed, then one would conclude that lowering of T_g is taking place locally, and thus local solution exists.[12]

EXPERIMENTAL

A Carle AG 311 GC with a thermal conductivity detector was used in this study. A Fisher Recordall Series 5000 recorder was used to record the response from the detector. An Instrulab digital thermometer with a precision of $\pm 0.01°C$ was used to read the oven temperature. The inlet pressure to the column was mea-
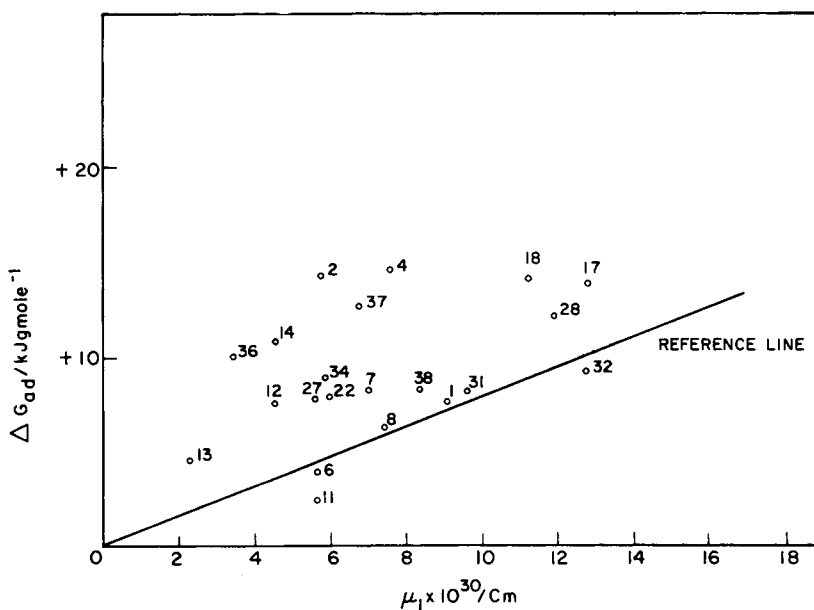

Fig. 5. ΔG_{ad} vs μ_1 at 200.85° for solvents.

DINÇER AND BONNER

TABLE III
Values of Λ and χ at 176.35° and 200.85°C

Solvent no.[a]	176.35°C		200.85°C	
	Λ, kJ/g-mole	χ	Λ, kJ/g-mole	χ
1	0.84	−0.41	0.55	—
2	10.62	−0.29	9.85	−0.27
3	−11.80	2.18	−13.40	2.18
4	10.05	0.14	8.63	0.19
5	0	−1.63	0	−1.40
6	−0.77	−1.95	−0.39	−1.82
7	3.75	−1.92	2.91	−1.58
8	1.51	−1.63	0.49	−1.26
9	5.81	−1.17	4.87	−1.00
10	1.16	−0.96	0.67	−0.88
11	−1.77	−1.87	−1.92	−1.62
12	—	—	4.02	−2.26
13	1.23	−0.24	2.69	−0.51
14	8.06	−1.51	6.94	−1.15
15	5.71	−0.88	4.66	−0.63
16	1.18	−1.27	−2.33	—
17	4.78	−1.10	4.00	−0.98
18	6.72	−0.78	5.31	−0.52
19	−0.11	−1.67	−1.32	−1.24
20	0.85	0.42	−0.50	0.55
21	3.81	0.14	4.37	−0.22
22	3.81	−1.27	3.11	−1.06
23	4.34	−1.07	2.82	−0.68
24	0	−1.23	0	−1.11
25	0	−0.91	0	−0.75
26	10.79	2.03	8.91	2.12
27	5.63	0.27	3.35	0.57
28	3.60	0.29	2.83	0.29
29	0	−1.80	0	−1.23
30	0	−1.45	0	−1.21
31	0.29	−0.33	0.98	−0.63
32	0.27	−0.41	−0.85	−0.27
33	5.31	−0.52	5.26	−0.38
34	5.53	−1.39	4.22	−1.01
35	−0.73	−1.95	−1.30	−1.54
36	8.66	−1.65	7.41	−1.23
37	3.24	0	7.39	−0.41
38	1.31	3.72	1.74	3.27
39	0	−0.85	0	−1.14
40	0	−1.16	0	−0.82

[a] See Table I for key.

sured by a Seegers pressure gauge, 0–30 psi, which had a precision of ±0.1 psi. Helium was used as the carrier gas, and it was purified by molecular sieves before it entered the column. The flow rate of the carrier gas was measured using a soap-bubble flowmeter. The flow rate of the gas through the GC was controlled by flow controllers installed in the chromatograph. Atmospheric pressure was measured barometrically. The gas-chromatographic apparatus is shown schematically in Figure 1.

The column, a 2-ft-long, $\frac{1}{8}$-in.-o.d. steel tube, was filled with 0.0473 g PQF coated on Fluoropak-80 support with a loading weight of 2.97% (polymer/

TABLE IV
Values of δ for Solvents at 176.35° and 200.85°C

Solvent no.[a]	δ (cal/cm³)$^{1/2}$	
	176.35°C	200.85°C
1	8.3	—
2	12.1	11.9
3	9.3	9.2
4	13.0	12.9
5	7.8	7.7
6	7.9	7.8
7	7.1	6.9
8	6.8	6.7
9	9.2	9.0
10	8.1	7.8
11	8.1	8.0
12	—	11.5
13	7.1	6.9
14	8.4	8.2
15	8.4	8.0
16	6.2	—
17	9.3	9.2
18	9.9	9.8
19	6.5	6.3
20	11.0	10.7
21	11.2	10.8
22	7.6	7.4
23	7.9	7.3
24	6.3	6.1
25	6.2	5.9
26	16.7	16.6
27	13.9	13.3
28	11.5	11.3
29	6.4	6.3
30	6.3	6.2
31	8.6	8.3
32	9.6	9.2
33	7.5	7.3
34	8.4	8.2
35	7.6	7.5
36	7.9	7.6
37	10.0	9.5
38	22.5	22.2
39	5.9	5.6
40	6.1	5.9

[a] See Table I for key.

(polymer + support)). PQF was supplied by Dr. T. E. Helminiak of the Air Force Materials Laboratory.

Trichloromethane is the only solvent which has a low boiling point and can dissolve PQF at least partially. Trichloromethane was therefore used to dissolve PQF. Because of partial dissolution, PQF was dissolved in a small amount of trichloromethane, then Fluoropak was added, and the mixture was heated at 50°C on a hot plate and Fluoropak was coated with PQF as PQF left the solution. The resulting coated support was dried in an oven at 50°C for two days. The column was then filled uniformly with the PQF-coated Fluoropak support. Silane-treated glass wool was used to plug the ends of the column.

A flow rate of approximately 4 ml/min of carrier gas at room temperature was maintained through the column. Since there was not much difference between the retention volume obtained by extrapolation to zero flow rate and the retention volume at 4 ml/min or lower flow rates, the flow rate of 4 ml/min was taken to approximate the zero flow rate conditions. The flow rate of approximately 4 ml/min was selected because better control of flow rate was obtained than for lower flow rates.

A Hamilton 1-μl syringe was used to inject the solvent through a silicone rubber septum at the injection port. All solvents used were reagent grade with 99+% purity. Initially, the syringe was flushed many times with the solvent. Then, 0.1 μl liquid solvent was withdrawn into the syringe. All liquid solvent was then flushed out. Approximately 0.1 μl of the traces of the solvent was injected into the chromatograph and the response recorded. Further 0.1-μl injections of the traces were made until the peak height of the eluted solvent could not be observed on the recorder. Retention time was measured as the time from the injection to the time corresponding to the intersection point of the tangents drawn on each side of the solvent peak. The technique of drawing tangents to the peaks was adopted due to asymmetry of the peaks. Retention times were then plotted against peak height, and the retention times corresponding to zero peak height were obtained by extrapolation. Air was used as the reference gas, and 0.5 μl was injected in order to obtain an easily detectable peak.

RESULTS

The experimental retention volumes for 40 solvents, covering a wide range of polarizabilities, dipole moments, and solubility parameters with PQF-coated Fluoropak, are shown in Table I. The experiments were carried out at 176.35° and 200.85°C. The ΔG_{ads} values calculated from eq. (3) are also given in Table I.

The values of α_1 and μ_1 used in fitting ΔG_{ads} according to eq. (4) are shown in Table II. The α_1 and μ_1 values are for 25°C. Since the temperature dependence of α_1 and μ_1 is sometimes not very well known, the values of α_1 and μ_1 were assumed constant with temperature. In order to fit ΔG_{ads} according to eq. (4), first reference lines for n-alkanes, 2-methyl alkanes, and aromatics (ΔG_{ads} as a function of α_1) were established in Figures 2 and 3.* The reference line for n-alkanes was obtained by applying a least-squares fit to the n-hexane, n-heptane, n-octane, and n-nonane points and was found to be, with the standard deviation s, as indicated:

$$\Delta G_{ads}\ (176.35°C) = 1.88 \times 10^{24}\alpha_1 - 34.43 \quad \text{kJ/g-mole} \tag{6}$$
$$s = 0.71 \quad \text{kJ/g-mole}$$

$$\Delta G_{ads}\ (200.85°C) = 1.81 \times 10^{24}\alpha_1 - 36.40 \quad \text{kJ/g-mole} \tag{7}$$
$$s = 0.10 \quad \text{kJ/g-mole}$$

The reference line for aromatics was approximated by passing a line through the benzene point parallel to the n-alkane line. The reference lines for the two temperatures were found to be

$$\Delta G_{ads}\ (176.35°C) = 1.88 \times 10^{24}\alpha_1 - 27.44 \quad \text{kJ/g-mole} \tag{8}$$

$$\Delta G_{ads}\ (200.85°C) = 1.81 \times 10^{24}\alpha_1 - 29.69 \quad \text{kJ/g-mole} \tag{9}$$

* Not all data given in Table I are shown in Figures 2 and 3 owing to near overlap of a few points.

The appropriate reference line for solvents such as N,N-dimethylethanamide and N,N-dimethylmethanamide is that of the 2-methyl alkanes. However, as can be seen in Figures 2 and 3, there is an insignificant difference between the 2-methyl alkane data and the normal alkane data. We therefore used the n-alkane reference line for all compounds except aromatic compounds.

We denoted the difference between ΔG_{ads} predicted by eqs. (6), (7), (8), and (9) and the experimental values of ΔG_{ads} as ΔG_{ad}. Values of ΔG_{ad} were plotted against μ_1 (see Figs. 4 and 5). A reference line for ΔG_{ad} was established by applying a least-squares fit to the ΔG_{ad} versus μ_1 values of the solvents which do not form hydrogen bonds and do not have charge transfer characteristics (chlorobenzene, bromobenzene, acrylonitrile, etc.). The reference lines found were (with the standard deviations as indicated)

$$\Delta G_{ad} \, (176.35°C) = 0.75 \times 10^{30}\mu_1 \quad \text{kJ/g-mole} \tag{10}$$
$$s = 1.54 \quad \text{kJ/g-mole}^{-1}$$

$$\Delta G_{ad} \, (200.85°C) = 0.79 \times 10^{30}\mu_1 \quad \text{kJ/g-mole} \tag{11}$$
$$s = 1.51 \quad \text{kJ/g-mole}$$

Finally, ΔG_{ad} values of solvents with the reference line values of eqs. (10) or (11) subtracted yielded the specific interaction parameters Λ given in Table III.

The χ parameters calculated from eq. (5) are shown in Table III. In eq. (5), B_{11} values were estimated from correlations of Tsonopoulos.[15,16] Saturation vapor pressures P_1^s were obtained from the Frost-Kalkwarf-Thodos correlation,[14] and solvent molar volumes v_1 were estimated from a corresponding-states method.[14]

Solubility parameters δ_1 for solvents were estimated at column temperature from an expression given by Hildebrand[17] and are shown in Table IV. The polymer solubility parameter was estimated to be 14.23 $(cal/cm^3)^{1/2}$ using the method of Fedors.[18]

From bench scale studies we find that, of the solvents studied, the only solvent that dissolves PQF completely at room temperature is o-chlorophenol. Its χ value at 200.85°C is quite negative, its specific interaction parameter at 200.85°C is highly positive, and its solubility parameter is quite close to that of PQF at 25°C. Trichloromethane, which partially dissolves PQF, has a highly negative χ and a highly positive Λ at both temperatures studied, but its solubility parameter is much smaller than that of PQF at 25°C. On the other hand, methanol and 2-aminoethanol have solubility parameters close to that of PQF at 25°C, their specific interaction parameter Λ with PQF at the temperatures studied is highly positive, but their χ values at the temperatures studied are positive. Bench-scale tests showed that methanol and 2-aminoethanol do not dissolve PQF.

The χ parameter of a polymer in a solvent is usually an indication of whether a solvent can dissolve a polymer or not. However, in this work polymer is studied at temperatures less than its T_g, and the χ parameters could be interpreted as the adsorption interaction parameter of the solid polymer surface and the solvent. Considering the above discussion on the χ parameters of o-chlorophenol, trichloromethane, methanol, and 2-aminoethanol and their ability to dissolve PQF, the negative values of χ could be interpreted as a sign of favorable interaction and the positive values as a sign of unfavorable interaction between the polymer

surface and the gaseous solvent. On the other hand, as stated earlier, assumption of local bulk absorption of solvent in polymer could lead to the interpretation of the χ parameter as a polymer solution interaction parameter.

CONCLUSIONS

From this study we conclude tentatively that a solvent can dissolve the thermally stable polymer PQF if GSC study indicates a highly positive Λ, a highly negative χ, and polymer and solvent solubility parameters are similar at 25°C. These criteria are met by o-chlorophenol at 200.85°C. We find that o-chlorophenol is a solvent for PQF. The first and third conditions are met for methanol and 2-aminoethanol but their χ values are positive, and therefore these solvents do not dissolve PQF. On the other hand, trichloromethane, which partially dissolves PQF, meets the first two conditions but fails in the third. Its ability to dissolve PQF, at least partially, can be attributed to its penetration of the highly rigid aromatic structure of PQF because of its capacity to act as a Lewis acid in the proper surroundings.

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