

Volatility of Solvents from Polysulfone Melt

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Synopsis

The equilibrium volatilities and solvent-polymer interaction indices are measured for 23 solvents in molten polysulfone. On the basis of the results, the solvents are ranked in the order of their effectiveness: phenol, pyridine, N-methylpyrrolidone, dimethylacetamide, methylene chloride, cyclohexanone, chlorobenzene, dimethylformamide, fluorobenzene, diglyme, toluene, xylene, chloroform, sulfolane, methyl ethyl ketone, acetonitrile, methanol, ethanol, carbon tetrachloride, dimethyl sulfoxide, decane, octane, and heptane. In determining the solvency power, the basic interpretative concept is that a large value of the Flory-Huggins interaction parameter indicates an unfavorable interaction, a low positive value indicates slightly favorable interaction, and a negative value indicates a rather strong specific interaction. Two other interaction indices, namely, the exchange energy parameter of Flory, X_{12} , and χ^* , the Flory-Huggins interaction parameter based on an hypothetical characteristic state, do not yield the same order as listed above. The data presented permits calculation of Henry's law constant and equilibrium volatilities at the temperature range of 250–300°C, a processing range for polysulfone.

INTRODUCTION

Recently, gas-liquid chromatography (GLC) has received general recognition as an effective simple technique for rapid measurement of polymer-solvent interaction, and solvent activity coefficient in molten homopolymers.^{1,2} Its advantages over all other methods are (i) simplicity, speed, and accuracy with which a large number of systems can be investigated; (ii) the wide range of temperatures accessible; and (iii) an ability to fix the solute and/or solvent weight, thereby fixing the solution concentration each time an experiment is run.

The technique has also been used to determine polymer miscibility,³ glass transition phenomena and the glassy state, crystallinity, adsorption isotherms, heats of adsorption, surface area, interfacial phenomena, diffusion coefficients, complex equilibria in solution, as well as curing processes in nonvolatile thermosetting systems.⁴ In this paper, the chromatographic procedure is used to study the solvent volatilities and solvent-polymer interactions between molten polysulfone and 23 solvents. We shall adopt the nomenclature of Guillet who coined^{1,5} the phrase "inverse gas chromatography." He considers the procedure as a "molecular probe" experiment where the vaporizable molecules are designated "probe molecules."

EXPERIMENTAL

Apparatus

A Micro-Tek 2500R gas chromatograph equipped with thermal-conductivity detector was used for this study. Temperatures of the injection block, column outlet block, and detector cell were monitored by pyrometer, but the column

temperature was doubly checked with a Digitec Model 551-4 plug-in platinum resistance thermometer. The average error in column temperature is $\pm 0.5^\circ\text{C}$. The flow rate of the helium carrier gas, controlled by a Micro-Tek regulator valve, is measured by a soap bubble flowmeter. Column pressure was measured differentially against the atmospheric outlet pressure with a U-tube manometer filled with mercury. The elution profiles were recorded by a Honeywell Electronik 19 chart recorder.

Column Preparation

The polysulfone was coated onto Fluoropak-80, 60–80 mesh, by dissolution in methylene chloride and slow evaporation in a Breeze-Away Packing Dryer (Chemical Research Services, Inc.), which is essentially a fluidized bed. The coated support was packed by a gentle tapping procedure into a 5 ft, 0.25 in. O.D. stainless steel silanized tubing, the ends of which were loosely plugged with glass wool. The tubing was then coiled to fit the oven chamber. After each experiment, the weight of polymer used was determined by one-week extraction with refluxing solvent in a Soxhlet extractor equipped with a ceramic thimble. The weight of polysulfone used in this study was 1.4729 g at a polymer/support ratio of ~ 0.1 .

TABLE I
Thermodynamic Quantities of Interaction in Molten Polysulfone^a

Solvent	Ω^∞	Ω^∞ $B_{11} = 0$	χ	χ^*	X_{12} , cal/cc	$-B_{11}$, cc/mole
Methanol	10.7	6.44	0.851	1.09	21.6	188.0
Ethanol	9.29	5.12	0.717	0.891	8.35	255.0
Phenol	3.24	2.84	0.051	0.201	-9.04	1090.0
Diglyme	7.65	6.17	0.698	0.897	-3.0	1060.0
Methyl ethyl ketone	8.79	6.25	0.665	0.875	-4.66	320.0
Cyclohexanone	6.57	5.56	0.556	0.71	-3.24	842.0
Dimethyl sulfoxide	7.31	6.21	0.811	0.954	1.53	1800.0
Sulfolane	5.34	5.16	0.657	0.737	3.77	3270.0
Dimethylformamide	7.66	5.97	0.631	0.782	10.8	1190.0
Dimethylacetamide	6.34	5.03	0.507	0.663	-3.21	1230.0
N-Methylpyrrolidone	5.09	4.42	0.392	0.504	-0.446	1960.0
Pyridine	5.08	4.25	0.336	0.493	-5.88	393.0
Acetonitrile	11.3	8.39	0.896	1.12	5.67	355.0
Chloroform	4.65	3.18	0.602	0.801	7.36	329.0
Methylene chloride	3.54	2.36	0.261	0.479	-13.1	182.0
Carbon tetrachloride	4.98	3.507	0.787	0.984	-2.20	407.0
Chlorobenzene	4.61	4.02	0.344	0.497	-3.86	427.0
Fluorobenzene	6.06	4.50	0.544	0.731	-3.56	336.0
Xylene	7.99	6.49	0.616	0.768	1.48	767.0
Toluene	7.61	5.87	0.604	0.781	-3.54	567.0
Decane	21.2	17.40	1.43	1.59	6.06	1510.0
Octane	23.5	17.37	1.51	1.70	3.48	869.0
Heptane	23.0	15.75	1.46	1.67	3.27	642.0

^a $T = 250^\circ\text{C}$.

Stationary Phase and Probe Molecules

Polysulfone used was P-1700 (Union Carbide Corporation), reduced viscosity = 0.48, 0.2 g/100 ml chloroform at 25°C, $\bar{M}_n \sim 400,000$. The probe molecules were reagent grades and were used without further purification.

Measured retention time is made up of four contributions: from polymer sorption, from support sorption (nonexistent in most practical operations), from gas–solid interfacial adsorption, and from gas–liquid interfacial adsorption. Only the contribution due to polymer sorption is important; all others are essentially eliminated by use of high polymer loading and very small solute sample size. Summers et al.⁶ have shown that accurate results are obtained at a polymer–support ratio of >6.5%, and Prausnitz et al.⁷ found that the situation is all the more improved by use of a nonpolar support such as Fluoropak-80 made from poly(tetrafluoroethylene). Alternatively, complete elimination of surface adsorption terms would entail obtaining retention data on a series of columns having different loadings each with a varying amount of solute sample followed by an extrapolation procedure to extract the infinite dilution bulk sorption. The former approach was adopted in this work. Five flow rates were employed at each temperature, and triplicate runs were made at each flow rate. To ensure operation at equilibrium, the retention–volume data were extrapolated to zero flow rate. These were used for subsequent calculations. During operation, checks on the dependence of peak maximum on probe sample size showed no perceptible variation over the range of 0.001–0.1 μ l; elution profiles are very nearly

TABLE II
Thermodynamic Quantities of Interaction in Molten Polysulfone^a

Solvent	Ω^∞	Ω^∞ $B_{11} = 0$	χ	χ^*	X_{12} , cal/cc	$-B_{11}$, cc/mole
Methanol	8.48	4.32	0.61	0.856	12.6	124.0
Ethanol	8.42	3.28	0.613	0.793	5.69	198.0
Phenol	3.07	2.47	-0.010	0.146	-11.7	790.0
Diglyme	5.95	4.15	0.44	0.645	-6.98	842
Methyl ethyl ketone	8.0	5.306	0.564	0.781	-7.86	198.0
Cyclohexanone	5.03	3.93	0.283	0.443	-8.65	602.0
Dimethyl sulfoxide	6.81	5.31	0.735	0.883	-0.921	1270.0
Sulfolane	4.76	4.44	0.539	0.623	1.70	2460.0
Dimethylformamide	5.76	4.20	0.340	0.496	5.17	756.0
Dimethylacetamide	4.57	3.23	0.173	0.335	-10.2	798.0
N-Methylpyrrolidone	3.90	3.13	0.123	0.239	-5.53	1370.0
Pyridine	4.11	3.17	0.118	0.281	-11.7	313.0
Acetonitrile	8.54	7.89	0.606	0.846	-4.56	6.42
Chloroform	4.29	2.48	0.516	0.721	5.98	299.0
Methylene chloride	3.45	1.90	0.229	0.454	-16.1	175.0
Carbon tetrachloride	4.40	2.73	0.658	0.861	-5.44	329.0
Chlorobenzene	4.37	3.47	0.286	0.445	-5.85	397.0
Fluorobenzene	5.22	3.20	0.388	0.581	-7.39	325.0
Xylene	7.25	5.27	0.514	0.672	-0.194	614.0
Toluene	6.65	4.57	0.464	0.648	-6.83	455.0
Decane	18.6	13.2	1.27	1.44	4.96	1160
Octane	21.8	13.95	1.43	1.62	2.46	678.0
Heptane	21.6	12.74	1.39	1.61	2.26	503.0

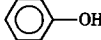
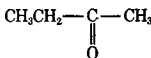

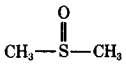

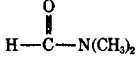
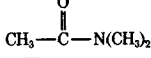
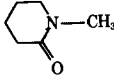



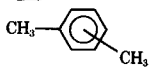
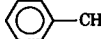
^a $T = 300^\circ\text{C}$.

symmetric over the range. Hence, all tests were performed with sample sizes of about 0.01 μ l.

Data Reduction

The use of inverse gas chromatography in measuring polymer-solvent interaction has been adequately described,^{1,6,7} and no further description will be given here. However, in calculating the various quantities, virial coefficients were obtained from the correlation of O'Connell and Pransmitz⁸ with the critical

TABLE III
Molecular Weights and Antoine Constants for Solvents Used

Solvent	M_w	A	B	C	Chemical formula
Methanol	32.04	8.07246	1574.99	238.86	CH ₃ OH
Ethanol	46.1	8.21337	1652.05	231.48	CH ₃ CH ₂ OH
Phenol	94.11	7.21399	1567.7	180.0	
Diglyme	134.17	7.29774	1621.642	208.22	CH ₃ O-(CH ₂ CH ₂ O) ₂ CH ₃
Methyl ethyl ketone	72.1	7.22182	1343.98	230.0	
Cyclohexanone	98.15	7.06136	1483.3	199.0	
Dimethyl sulfoxide	78.13	7.11859	1633.02	194.7	
Sulfolane	120.17	7.03494	1962.02	184.85	
Dimethylformamide	73.094	6.99608	1437.84	199.83	
Dimethylacetamide	87.12	7.76228	1889.10	221.0	
N-Methylpyrrolidone	99.12	7.21517	1745.1	200.62	
Pyridine	79.1	6.98825	1344.2	212.0	
Acetonitrile	41.05	7.07354	1279.2	224.0	CH ₃ CN
Chloroform	119.4	6.90328	1163.0	227.0	CHCl ₃
Methylene chloride	84.94	7.07138	1134.6	231.0	CH ₂ Cl ₂
Carbon tetrachloride	153.8	6.9339	1242.43	230.0	CCl ₄
Chlorobenzene	112.557	6.94504	1413.12	216.0	
Fluorobenzene	96.1	7.18703	1381.828	235.563	
Xylene	116.17	7.00908	1462.266	215.105	
Toluene	92.14	6.95464	1344.8	219.482	
Decane	142.276	6.95367	1501.268	194.48	CH ₃ -(CH ₂) ₈ -CH ₃
Octane	114.2	6.92377	1355.126	209.517	CH ₃ -(CH ₂) ₆ -CH ₃
Heptane	100.2	6.9024	1268.115	216.9	CH ₃ -(CH ₂) ₅ -CH ₃

constants (Table V) obtained from Dreisbach⁹ or internal sources or various group contribution format.¹⁰ Antoine constants, solute densities, and other physicochemical constants were obtained from Timmermans¹¹ or internal sources or group contribution format.¹⁰ The hard-core characteristic volume V^* , pressure p^* , and temperature T^* of Flory's equation of state were either obtained from the literature^{6,12} or calculated from internal experimental data. The solute thermal expansion coefficients α were similarly obtained. The acentric factors ω_H were obtained from the literature or estimated from the defining equation.¹⁰ The dipole moments μ were obtained from various chemical handbooks, whereas the association constants η of O'Connell-Pransnitz were taken from their paper.⁸

The temperature dependences of the specific volume of the probe molecules and of the polysulfone were calculated from the Flory¹³ equation of state at $P = 0$:

$$\tilde{v} = v/v^* = [1.0 + (\alpha T/3)(1 + \alpha T)]^3$$

For polysulfone, the thermal expansion coefficient α_1 in the melt was calculated via the Simha-Boyer correlation¹⁴,

$$(\alpha_1 - \alpha_g)T_g = 0.113$$

where α_g , the coefficient at the glassy state, was measured with a Thermomechanical Analyzer. The volume at T_g was obtained by integrating $\alpha_g V dT$ using the density value at room temperature as a reference. Its T_g is 185 °C, V^* is 0.7094, and α_1 equals $(4.14 \times 10^{-4})(T^{-1})$.

TABLE IV
Characteristic Parameters and Other Data for the Solvents Used

Solvent	P^* , atm	V^* , cc/g	T^* , °K	μ , Debye	η	ω_H
Methanol	5039.0	0.9416	4225.0	1.70	1.21	0.105
Ethanol	5400.0	0.9955	4845.0	1.69	1.0	0.152
Phenol	5641.0	0.6944	5205.0	1.45	1.0	0.279
Diglyme	3784.0	0.8179	4612.0	1.97	0.55	0.441
Methyl ethyl ketone	5655.0	0.9580	4590.0	2.70	0.30	0.187
Cyclohexanone	5878.0	0.8461	5162.0	2.99	0.50	0.244
Dimethyl sulfoxide	9127.0	0.7365	5336.0	4.30	0.30	0.201
Sulfolane	8792.0	0.6688	6534.0	4.81	0.30	0.275
Dimethylformamide	6403.0	0.917	7452.0	3.82	0.58	0.293
Dimethylacetamide	5932.0	0.8552	5134.0	3.72	0.62	0.352
N-Methylpyrrolidone	5763.0	0.8046	5853.0	4.09	0.50	0.302
Pyridine	6366.0	0.8129	5124.0	2.20	0.20	0.215
Acetonitrile	6797.0	0.9583	4283.0	3.94	0.0	0.152
Chloroform	3168.0	0.546	5280.0	1.02	0.28	0.187
Methylene chloride	6356.0	0.5732	4419.0	1.60	0.0	0.105
Carbon tetrachloride	5586.0	0.4870	4700.0	0.0	0.0	0.202
Chlorobenzene	5833.0	0.734	5550.0	1.69	0.0	0.233
Fluorobenzene	5027.0	0.7636	4742.0	1.58	0.0	0.233
Xylene	5050.0	0.971	6198.0	0.62	0.0	0.311
Toluene	5606.0	0.9115	5025.0	0.0	0.0	0.279
Decane	3597.0	1.136	5846.0	0.0	0.0	0.586
Octane	4330.0	1.1204	4850.0	0.0	0.0	0.408
Heptane	4317.0	1.1334	4641.0	0.0	0.0	0.352

RESULTS AND DISCUSSION

The various thermodynamic quantities of interaction for polysulfone at 250 and 300°C are represented in Tables I and II, respectively, where Ω^∞ is the infinite dilution weight fraction activity coefficient, B_{11} is the second virial coefficient where subscript 1 refers to the probe and 2 to the polymer, χ is the Flory-Huggins interaction parameter,¹⁵ χ^* is its counterpart based¹³ on the conditions of an hypothetical liquid at 0°K, and X_{12} is the exchange energy parameter of the Flory equation of state.¹³

The relative magnitude of the various interaction indices can be interpreted³ in terms of polar, complexing, and noncomplexing contributions based on the relative magnitude of the dipole moments, polarizabilities, and hydrogen bonding capabilities of the various probes. In general, the specific interactions of a probe with a stationary phase can be considered to consist of: π electron interactions, n -electron interactions, dipolar interactions, and proton donor-acceptor interactions. In the case at hand, it would be too speculative to attempt to analyze each case in as much as thermodynamic methods—of which GC is one—yield a weighted average of a wide range of “many-body” interactions.

For these reasons, we content ourselves with merely using the Flory-Huggins interaction parameter as a measure of solvency power. The deduction, therefore, is that, in the following order, these probes possess rather high affinity for polysulfone: phenol, pyridine, N-methylpyrrolidone, dimethylacetamide, methylene chloride, cyclohexanone, chlorobenzene, dimethylformamide, and fluorobenzene. Moderate interactions are exhibited by diglyme, toluene, xylene,

TABLE V
Critical Constants and Thermal Expansion Data for the Solvents Used^a

Solvent	T_c , °C	P_c , atm	V_c , l./mole	V_{20} , cc/g	$\alpha_{20} \times 10^3$, °K ⁻¹
Methanol	240.0	81.5	0.113	1.262	1.5155
Ethanol	243.0	63.0	0.167	1.2650	1.13
Phenol	421.2	60.5	0.264	0.8634	0.9956
Diglyme	334.2	28.18	0.430	1.0581	1.2542
Methyl ethyl ketone	262.5	41.0	0.265	1.2405	1.326
Cyclohexanone	356.0	38.0	0.312	1.0546	1.0108
Dimethyl sulfoxide	453.1	55.7	0.216	0.9093	0.9529
Sulfolane	576.4	65.4	0.285	0.787	0.685
Dimethylformamide	366.0	43.65	0.265	1.0535	0.9956
Dimethylacetamide	364.0	38.7	0.307	1.0677	1.0208
N-Methylpyrrolidone	439.8	37.17	0.355	0.9699	0.8145
Pyridine	347.0	55.6	0.253	1.0154	1.024
Acetonitrile	274.7	47.7	0.173	1.2767	1.469
Chloroform	263.4	54.0	0.222	0.6701	1.254
Methylene chloride	237.0	60.0	0.193	0.7538	1.3715
Carbon tetrachloride	282.2	45.0	0.276	0.626	1.243
Chlorobenzene	359.2	44.64	0.308	0.9043	1.0063/1.0101
Fluorobenzene	286.65	44.62	0.271	0.978	1.186
Xylene	346.0	36.0	0.370	1.1553	1.0037
Toluene	320.8	41.6	0.318	1.1515	1.132
Decane	346.0	20.80	0.602	1.3698	1.0497
Octane	296.2	24.64	0.486	1.4217	1.192
Heptane	267.2	27.1	0.416	1.4607	1.289

^a V_{20} is the specific volume at 20°C; α_{20} is the thermal expansion coefficient at 20°C.

chloroform, sulfolane, methyl ethyl ketone, acetonitrile, methanol, ethanol, carbon tetrachloride, and dimethyl sulfoxide; while the rest, namely, decane, octane, and heptane possess less-than-favorable affinity for polysulfone. It should be recognized, though, that this division is not clear-cut. Some systems are within 5%–10% of each other, and this is also the estimated range of the error. The division should, therefore, be considered as an attempt at using the calculated Flory-Huggins interaction parameter as a scale of relative solvent strength. When either χ^* or X_{12} is used as the measure of solvency power, completely different ranking is obtained. This discrepancy may reflect the fact that each quantity refers to different states of interaction and/or that the theory is inadequate. A different quantitative analysis will be published at a later time.¹⁶

Henry's law constant and, therefore, the volatilities can be calculated from Tables I and II in combination with Tables III, IV, and V. At infinite dilution, the Henry's law constant is

$$H = \Omega^\infty P^s$$

and the corresponding vapor pressure is

$$P = w_1 H$$

where w_1 is the weight fraction of the probe and its saturated vapor pressure is given by the Antoine equation

$$\log_{10} P^s = A - B/(C + t^\circ C)$$

where A , B , and C , the Antoine constants,¹⁰ appear in Table III. When the polymer concentration is low, the Flory-Huggins expression¹ is more reliable:

$$\ln P_1/P_1^s = \ln \psi_1 + (1 - V_1/M_2 V_2)\psi_2 + \chi\psi^2 + P_1^2(B_{11} - V_1)RT - P_1 B_{11}/RT$$

where $\psi_1 = w_1 V_1/(w_1 V_1 + w_2 V_2)$, $\psi_2 = 1 - \psi_1$, V_1 is the molar volume of the probe molecule in the pure liquid state, and R is the gas constant.

CONCLUSIONS

Inverse gas chromatography was used to study equilibrium volatilities and solvent-polymer interaction of 23 solvents with molten polysulfone. The three measures of interaction investigated do not give identical ranking of the potency of the solvents. This may reflect some inadequacy in the assumptions leading to the development of these quantities, or it may merely reflect the fact that each quantity does refer to different states of interaction. The Flory-Huggins interaction parameter allows a reasonable ranking of the solvents.

From the data presented, Henry's law constant and equilibrium volatilities could be calculated between 250 and 300°C, a processing range of polysulfone.

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