Solvent Volatilities from Polymer Solutions by Gas–Liquid Chromatography

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Inverse gas chromatography was used to study polymer/solvent interactions at infinite dilution. Consideration was given to the effect of solute sample size, gas flow rate, and the chemical nature of the substrate. Experimental results are presented for a wide variety of organic solvents, both polar and nonpolar, with polybutadiene (353–373 K) and polyisoprene (328 K). Weight fraction activity coefficients, Flory–Huggins χ parameters, and heats of solution have been calculated from measurements of the retention volumes. The same general solubility behavior was observed with both polyisoprene and polybutadiene.

Introduction

This investigation was prompted by the general lack of reported vapor–liquid equilibrium data for polymer/solvent systems. The objective was to obtain experimental data on the behavior of polymeric materials and volatile solvents in order to eventually develop methods to correlate and predict this behavior. In order to determine the thermodynamic quantities needed for our analysis, we used inverse gas chromatography, which has long been recognized as a convenient and fast method to obtain infinite dilution solvent volatilities from concentrated polymer solutions.

Experimental Section

Apparatus. The gas chromatograph used was a Varian Model 3400 chromatograph equipped with an autosampler. The carrier gas in all experiments was helium. To maintain constant carrier-gas flow rates, the pressure upstream of the column was regulated by a factory-calibrated digital flow controller. The system was modified by installing a pressure transducer to measure the inlet and outlet pressures of the column with an accuracy of 0.1%. Samples were injected into the carrier gas with a Hamilton 1-μL syringe or the autosampler. The output from the thermal conductivity detector was fed to the printer/plotter built into the gas chromatograph and to a Varian DS-654 data system for further analysis of the chromatogram. After passing through the detector, the carrier gas was saturated with water to eliminate any uncertainty caused by partial saturation from the soap solution in the bubble flow meter.

Materials. The solutes were of reagent-grade materials supplied by Thomas Scientific Co. and were used without any further purification. All polymers were used as received from the suppliers. Detailed characterization of these polymers is given in Table I.

Column Preparation. The columns were prepared by first dissolving a weighed sample of polymer in a suitable solvent and then stirring the solution with a weighed amount of substrate in a Pyrex pan. The mixture was allowed to dry while being stirred continuously to ensure a uniform mixture. Once all the solvent was evaporated, the coated support was packed into $^1/_8$-in.- or $^1/_4$-in.-o.d. stainless steel silanized tubing, with use of a water aspirator at the detector end of the column and a vibrator to gently tap it. To check the percent loading of the coated material, a sample of the batch was put through a Soxhlet extraction. The principle behind this method is to extract the polymer by leaching the substrate with a refluxing organic solvent. The extracted sample was dried in a vacuum oven, and the polymer content was determined. This method has an accuracy of 1–2%. The characteristics of the chromatographic columns used in this study are summarized in Table II.

Solid Supports. Two substrates were used in this study: Chromosorb W-HP (80/100 mesh), a diatomaceous earth material in origin, made by Supelco; Fluoropack-80 (40/60 mesh), a powdered Teflon derived from poly(tetrafluoroethylene), obtained from Alltech Associates. Newman and Prausnitz (*1*, *2*) have indicated that for polar solvents Chromosorb columns often give highly asymmetric peaks and a dependence of retention time on sample size. On the other hand, Fluoropack support produces nearly symmetric peaks and eliminates the dependence of retention time on sample size for polar solvents. For nonpolar solvents, however, it was shown (*3–5*) that surface adsorption was greater on Fluoropack than on Chromosorb materials; therefore, there was a larger dependence of retention volume on polymer loading for nonpolar solvents when Fluoropack support was used.

An independent experiment was undertaken to investigate the adsorption of different types of solutes by Fluoropack-80 and Chromosorb W-HP. This study was done by measuring specific retention volumes, defined later, of the different solutes injected into two different columns: one packed with uncoated Fluoropack-80 and the other packed with uncoated Chromosorb W-HP. The results, as shown in Table III, indicate that surface adsorption of nonpolar solvents by the Fluoropack product was almost 10 times greater than adsorption by the Chromosorb material. For most of the polar solvents, however, Fluoropack-80 gives superior peak symmetry, no dependence of retention time on sample size, and less surface adsorption. On the basis of these findings, both Chromosorb W-HP columns and Fluoropack-80 columns were prepared coated with polybutadiene (PBD) or polyisoprene (PIP). The percent loadings were chosen in the range of 10–13% by weight in order to eliminate any surface effects.

Procedure. After a preconditioned column was placed in the chromatographic oven, the temperatures of the injector block and the detector cell were set about 30 K above the oven temperature to avoid condensation in the detector assembly that could lead to chemical contamination. Solute sample size was kept as small as possible, consistent with obtaining a measurable peak. Nonpolar solvents were injected as liquid samples in the columns containing polymer-coated Chromosorb W-HP, and polar solvents were injected in the columns containing polymer-coated Fluoropack-80. Following this procedure, we found that there was no dependence of retention time on sample size below 0.1 μL. Usually, about 0.3 μL of air was injected along with the liquid sample as the inert component in order to obtain the adjusted retention time. To ensure that the measured retention volumes are those at equilibrium, the helium flow rate was varied during each temperature study. In this work, the retention volumes were found to be independent of carrier-gas flow rate for both polar and nonpolar solvents. After the solutes were studied at one temperature, the pressure drop across the column was measured and the oven set to the next temperature.

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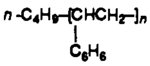
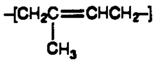
Table I. Description of Polymers

polymer	source	characterization[a]	molecular structure	notes
polystyrene (PS)	Pressure Chemical Co.	M_n = 86 700 (GPC) $M_w/M_n \leq 1.04$ (GPC)	 $n\text{-}C_4H_9\text{-}[CH(C_6H_6)CH_2\text{-}]_nH$	very stable powder form
polybutadiene (PBD)	Pressure Chemical Co.	M_n = 22 600 (MO) M_w/M_n = 1.06 (GPC)	$-[CH_2CH{=}CHCH_2-]_n$	trans-1,4, 52 mol % cis-1,4, 40 mol % vinyl 1,2, 8 mol %
polyisoprene (PIP)	Good Year Chemicals	M_n = 10 800 (MO) M_w/M_n = 1.11 (GPC)	 $-[CH_2C(CH_3){=}CHCH_2-]_n$	trans-1,4, 18 mol % cis-1,4, 76 mol % 3,4, 6 mol %

[a] Abbreviations: GPC = gel permeation chromatography; MO = membrane osmometry.

Table II. Details of Chromatographic Columns

polymer	column no. (o.d., in.)	solvent	support	% loading	W_2,[a] g
polystyrene	3C ($^1/_8$)	chloroform	Chromosorb W-HP (80–100 mesh)	8.85	0.1459
	4 ($^1/_8$)	chloroform	Chromosorb W-HP (80–100 mesh)	11.70	0.2283
	5C ($^1/_8$)	chloroform	Chromosorb W-HP (80/100 mesh)	4.95	0.0896
	6A ($^1/_8$)	chloroform	Chromosorb W-HP (80/100 mesh)	14.96	0.2975
polyisoprene	8 ($^1/_8$)	toluene	Chromosorb W-HP (80/100 mesh)	10.14	0.1738
	9 ($^1/_8$)	toluene	Fluoropack-80 (40/60 mesh)	10.06	0.5068
polybutadiene	11 ($^1/_8$)	benzene	Chromosorb W-HP (80/100 mesh)	11.83	0.2133
	12 ($^1/_4$)	benzene	Fluoropack-80 (40/60 mesh)	12.62	0.9424

[a] Weight of polymer in the column.

Table III. Support Contribution to Bulk Retention

solutes	specific retention volume,[a] cm^3/g of support: Fluoropack-80	Chromosorb W-HP
Nonpolar Solvents		
cyclohexane	0.220	0.033
benzene	0.260	0.028
toluene	0.407	0.045
n-dodecane	2.29	0.213
hexane	0.187	0.021
1,2-dichloroethane	0.213	0.033
chloroform	0.224	0.033
ethylbenzene	0.557	0.045
xylenes	0.619	0.070
methylene chloride	0.142	0.014
carbon tetrachloride	0.325	0.014
tetradecane	5.96	0.569
n-butylbenzene	1.167	0.100
Polar Solvents		
acetone	0.104	0.219[b]
acetic acid	0.175[c]	0.946[c]
methanol	0.067	2.04[c]
isopropanol	0.083	0.092
cyclohexanone	0.587	0.397[c]
N,*N*-dimethylformamide	0.421	1.07[c]
tetrahydrofuran	0.189	0.118[b]
acetonitrile	0.094	1.49[c]
ethyl acetate	0.169	0.163[b]
methyl ethyl ketone	0.173	0.153
methyl isobutyl ketone	0.270	0.125
aniline	0.702	0.352[b]
benzyl alcohol	0.882	0.829[c]
butyl alcohol	0.150	0.187[b]
benzaldehyde	0.988	0.397
ethylene glycol	0.209[d]	1.46[c]

[a] Obtained at 413 K. [b] Dependence on sample size observed. [c] Tailing and dependence on sample size observed. [d] Tailing observed.

Test of the Apparatus

The apparatus was tested by measuring infinite dilution volatilities of cyclohexane, benzene, toluene, cyclohexanone, and dimethylformamide (*N*,*N*-DMF) from polystyrene (PS) coated on Chromosorb W-HP at 423 and 448 K. In this test, the contribution of support adsorption was isolated from bulk sorption by varying the polymer loading on four columns, keeping the amount of solid support constant. As shown in Table IV, cyclohexane, benzene, and toluene showed no significant variation of the specific retention volume with polymer loading. Figure 1 illustrates this result at 448 K. For these solvents, the specific retention volumes were determined by averaging the values for all the columns. On the other hand, the polar solvents—cyclohexanone and *N*,*N*-DMF—exhibited an effect of coverage, as indicated in Table IV. It was found that the functional behavior of V_g with respect to $1/W_2$ could be represented by the following empirical equation

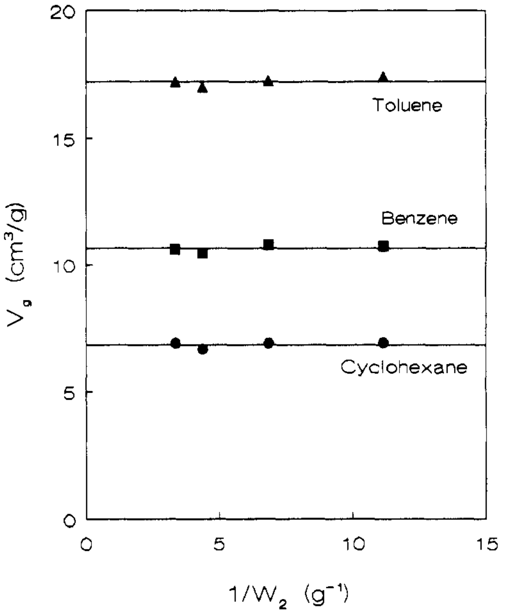


Figure 1. Loading effect on V_g for nonpolar solvents at 448 K.

$$\ln V_g = a + b(1/W_2)^2 \qquad (1)$$

where *a* and *b* are constants characteristic of each polymer/solvent pair. Figure 2 affirms the linear dependence of the logarithm of V_g with $(1/W_2)^2$ for the PS/*N*,*N*-DMF system at 448 K. Equivalently, good results were obtained for the PS/cyclohexanone system and at all temperatures investigated. The values of V_g at infinite loading shown in Table IV for the

Table IV. Polystyrene/Solvent Interaction Data[a]

	cyclohexane		benzene		toluene		cyclohexanone		*N,N*-DMF	
% loading	423 K	448 K	423 K	448 K	423 K	448 K	423 K	448 K	423 K	448 K
Specific Retention Volume V_g, cm^3/g										
14.96%	8.51	6.91	15.3	10.6	26.3	17.2	70.6	41.4	61.3	33.4
11.70%	8.24	6.68	15.0	10.5	26.2	16.9	70.9	41.6	60.7	34.2
8.85%	8.66	6.92	15.5	10.8	27.0	17.3	72.1	42.6	65.1	39.3
4.95%	8.46	6.94	15.5	10.7	26.7	17.4	75.0	44.5	82.1	60.8
Largest % Difference in V_g for Nonpolar Solvents										
	4.89	3.68	3.15	2.92	3.08	2.44				
Infinite Loading V_g, cm^3/g										
	8.47	6.86	15.3	10.6	26.5	17.2	70.2	41.1	58.3	31.0
Solvent Properties[b]										
vapor pressure, atm	5.49	8.73	5.74	9.25	2.73	4.65	0.862	1.60	0.930	1.66
molecular weight	84.2	84.2	78.1	78.1	92.1	92.1	98.1	98.1	73.1	73.1
molar volume, cm^3/g-mol	130	137	106	112	125	130	119	123	89.3	92.5
second virial coeff, cm^3/g-mol	−654	−562	−605	−529	−959	−822	−1388	−1189	−1314	−1113
density, cm^3/g	0.645	0.613	0.731	0.696	0.737	0.707	0.825	0.799	0.819	0.790
polystyrene density, cm^3/g	0.997	0.982	0.997	0.982	0.997	0.982	0.997	0.982	0.997	0.982
Other Parameters										
Ω_1^∞	10.1	8.61	5.69	5.62	5.67	5.63	6.07	6.05	9.11	10.3
χ	0.880	0.684	0.429	0.383	0.434	0.401	0.616	0.594	1.01	1.12

[a] Polymer: PS (M_w = 90 100, M_n = 86 700). Support: Chromosorb W-HP (80/100 mesh). [b] Solvent property data are taken from Daubert and Danner (*11*).

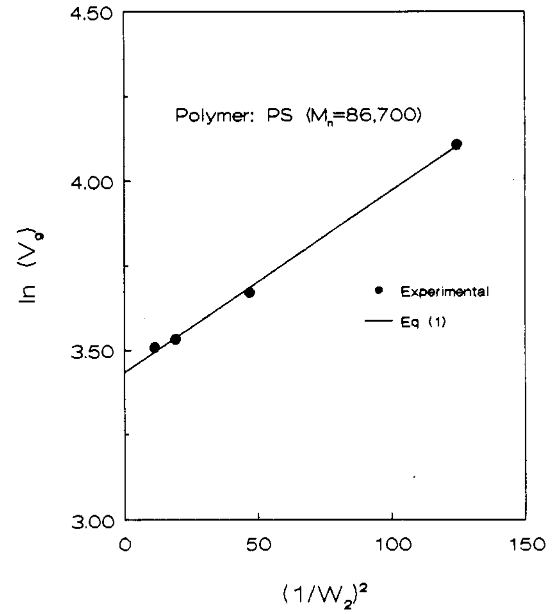


Figure 2. Loading effect on V_g for PS/*N,N*-DMF at 448 K.

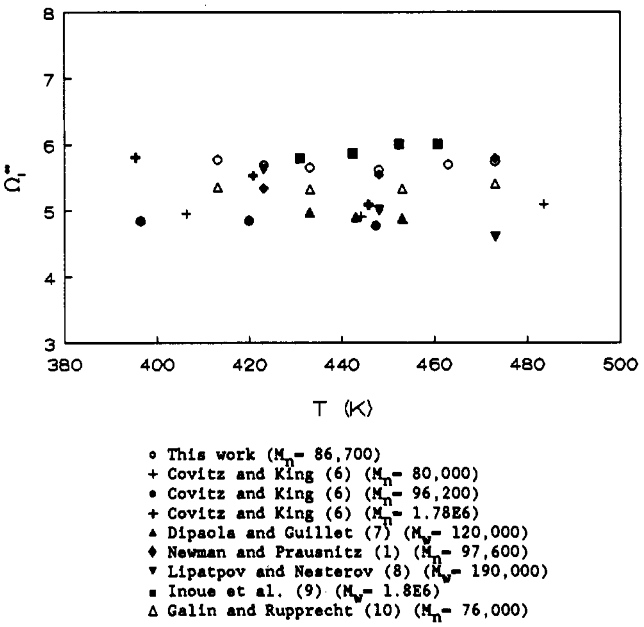


Figure 3. Temperature dependence of Ω_1^∞ for PS/benzene.

PS/polar solvent systems were obtained by taking the exponential of the intercept of ln V_g versus $(1/W_2)^2$. Table IV also gives the weight fraction activity coefficients and the Flory–Huggins χ parameters, defined later, for the polystyrene/solvent systems tested. There are serious problems with the infinite dilution weight fraction activity coefficients, Ω_1^∞, found in the literature. A typical example of such data is given in Figure 3, which shows the data for the infinite dilution weight fraction activity coefficients of benzene in polystyrene as a function of temperature. There is clearly a lot of scatter in these data. Our data are in the center of the data and are in good agreement with those reported by Newman and Prausnitz (*1*) and Galin and Rupprecht (*10*). Similar results were obtained for toluene, cyclohexane, and cyclohexanone. For the case of *N,N*-DMF, however, significant differences in the retention volumes were observed. This discrepancy is probably due to the different extrapolation procedures. On the basis of the good agreement for the other four solvents, we concluded that the apparatus was operating properly and that our data reduction methods are sound.

Data Reduction

Weight Fraction Activity Coefficient. At equilibrium, the fugacity of the solvent in the vapor phase equals that of the solvent in the liquid phase (1 = solvent, 2 = polymer, 3 = helium)

$$\phi_1 P_1 = \gamma_1 x_1 f_1^\circ \tag{2}$$

With a reference pressure of zero, the fugacity of the pure solvent at the system temperature may be written as

$$f_1^\circ = \phi_1^s P_1^s \exp \int_{P_1^s}^{0} \frac{V_1}{RT}\, dP = P_1^s \exp\left[\frac{P_1^s(B_{11} - V_1)}{RT}\right] \tag{3}$$

At infinite dilution ($y_1 \rightarrow 0$), the vapor-phase fugacity coefficient reduces to

$$\phi_1 = 1 \tag{4}$$

Therefore, the mole fraction activity coefficient at infinite dilution is

$$\gamma_1^\infty = \left(\frac{P_1}{x_1}\right)^\infty \frac{1}{P_1^s} \exp\left[-\frac{P_1^s(B_{11} - V_1)}{RT}\right] \tag{5}$$

It can be shown that, at infinite dilution, the solvent volatility is related to the experimental retention volume by the simple equation

$$\left(\frac{P_1}{x_1}\right)^\infty = \frac{RT}{V_g M_2} \tag{6}$$

Substitution of eq 6 into eq 5 gives

$$\gamma_1^\infty = \frac{RT}{V_g P_1^s M_2} \exp\left[-\frac{P_1^s(B_{11} - V_1)}{RT}\right] \tag{7}$$

Since, at infinite dilution,

$$\Omega_1^\infty = \gamma_1^\infty \frac{M_2}{M_1} \tag{8}$$

The weight fraction activity coefficient may be written as

$$\Omega_1^\infty = \frac{RT}{V_g P_1^s M_1} \exp\left[-\frac{P_1^s(B_{11} - V_1)}{RT}\right] \tag{9}$$

The physical properties of the solvent, P_1^s, M_1, B_{11}, and V_1, were obtained from Daubert and Danner (*11*). The specific retention volume is given by

$$V_g = Q(t_g - t_r)\frac{f_p}{W_2} \tag{10}$$

where f_p is a correction term for the pressure gradient across the column as given by (*12*)

$$f_p = \frac{3}{2}\frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]} \tag{11}$$

In this work, the maximum percent error obtained for V_g was approximately 5%. Using the errors introduced by the solvent properties and carrying out a propagation of error analysis on Ω_1^∞ gave a maximum percent error of almost 8%.

***Flory-Huggins* χ *Parameter*.** The Flory-Huggins χ theory of polymer solutions (using volume fractions) gives the activity of the solvent as

$$\ln a_1 = \ln \Phi_1 + \left(1 - \frac{1}{r}\right)\Phi_2 + \chi\Phi_2^2 \tag{12}$$

where Φ_1 is the volume fraction. At infinite dilution, $\Phi_1 \rightarrow 0$, and the Flory-Huggins parameter becomes

$$\chi = \ln \Omega_1^\infty - \left(1 - \frac{1}{r}\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) \tag{13}$$

with

$$r = \frac{(\bar{M}_2)_n \rho_1}{M_1 \rho_2} \tag{14}$$

Substituting eq 14 into eq 13 gives

$$\chi = \ln\left[\frac{RT}{V_g P_1^s V_1 \rho_2}\right] - \left[1 - \frac{\rho_2 V_1}{(\bar{M}_2)_n}\right] - \frac{P_1^s}{RT}(B_{11} - V_1) \tag{15}$$

Table V. Values of the Coefficients in Equation 16 for the Densities

polymer	*A*	*B*	*C*
polystyrene[a]	1.0865	-6.19×10^{-4}	1.36×10^{-7}
polybutadiene[b]	0.869	3.5×10^{-4}	-5.0×10^{-6}

[a] From Höcker et al. (*14*). [b] From Barlow (*15*).

The χ parameter was used in this study as a measure of the strength of interaction between polymers and solvents. The polyisoprene density was obtained from Wood and Martin (*13*). For polystyrene and polybutadiene, the densities were obtained from the empirical equation

$$\rho = A + Bt + Ct^2 \tag{16}$$

where t is in °C. Coefficients A, B, and C are shown in Table V.

***Heat of Solution*.** The heat of solution, ΔH_s, is determined from GLC by using the approximate relation

$$\Delta H_s = -R\left(\frac{d \ln V_g^0}{d(1/T)}\right) \tag{17}$$

where

$$V_g^0 = V_g(273.2/T) \tag{18}$$

Results and Discussion

***Polybutadiene*.** Experimental retention volumes for 25 solvents at three different temperatures (353, 363, and 373 K) are shown in Table VI. This table also includes the corresponding weight fraction activity coefficients, the Flory-Huggins χ parameters, and the heats of solution.

From stability analysis as applied to the Flory-Huggins equation, complete polymer solubility exists only when χ is less than 0.5. Even though the Flory-Huggins theory has the major disadvantage of assuming that χ is independent of concentration, the above criterion could be used at least qualitatively to interpret the compatibility between the polymers and solvents. If the χ parameters in Table VI are examined, *p*-xylene appears to have the minimum value for χ at the three different temperatures. Hence, *p*-xylene is predicted to be the most suitable solvent for polybutadiene. The results in Table VI indicate that Ω_1^∞ is very weakly dependent on temperature except for the alcohols (methanol, isopropyl alcohol, butyl alcohol, and benzyl alcohol). The nonpolar solvents, in general, have better solubility characteristics with polybutadiene than the polar solvents. The χ parameters tabulated show that benzene, toluene, ethylbenzene, and *n*-butylbenzene have relatively favorable interactions with polybutadiene. On the other hand, as the relatively high χ parameters indicate, hydrogen-bonding solvents, such as alcohols, and polar solvents, such as acetonitrile and dimethylformamide, exhibit very poor solubility characteristics. Tetrahydrofuran, contrary to all the other polar solvents, can penetrate the polymer matrix and dissolves polybutadiene with a solvency power comparable to that of benzene and cyclohexane. The heats of solution obtained for polybutadiene in this work are reported over a temperature range of 80–100 °C. Lau et al. (*16*) reported a constant Flory-Huggins χ parameter of 0.21 for the PBD/cyclohexane system, and 0.23 for the PBD/benzene system. These values are in good agreement with our results, as shown in Table VI.

***Polyisoprene*.** The experimental results for the polyisoprene/solvent systems reported at 328 K are given in Table VII. By carrying out the same solvency power analysis used for polybutadiene, the same solubility behavior was also observed with polyisoprene except that now carbon tetrachloride is the most suitable solvent for polyisoprene with a χ value of 0.094. The analogy in the solubility behavior found between PBD and PIP could be attributed to their similarities in molecular

Table VI. Polybutadiene/Solvent Interaction Data

	V_g, cm^3/g			Ω_1^∞			χ			$-\Delta H_s$, kcal/mol
solutes	353 K	363 K	373 K	353 K	363 K	373 K	353 K	363 K	373 K	353–373 K
cyclohexane[a]	88.4	68.4	53.7	4.12	4.13	4.16	0.240	0.234	0.233	7.25
benzene[a]	106	80.6	63.5	3.62	3.67	3.65	0.233	0.238	0.226	7.45
toluene[a]	248	182	136	3.37	3.40	3.42	0.158	0.158	0.159	8.50
hexane[a]	40.9	31.8	25.5	6.28	6.20	6.36	0.482	0.458	0.473	6.89
ethylbenzene[a]	499	358	259	3.33	3.31	3.35	0.151	0.140	0.145	9.29
chloroform[a]	74.5	57.3	45.5	1.92	1.96	1.98	0.121	0.135	0.135	7.16
carbon tetrachloride[a]	101	77.3	61.0	1.75	1.79	1.81	0.101	0.118	0.117	7.41
p-xylene[a]	571	406	291	3.13	3.14	3.19	0.081	0.079	0.089	9.53
methylene chloride[a]	34.0	27.1	22.3	3.09	3.11	3.08	0.464	0.459	0.439	6.23
1,2-dichloroethane[a]	92.9	71.1	55.9	3.62	3.59	3.53	0.586	0.570	0.547	7.37
n-butylbenzene[a]	2193	1420	957	3.18	3.23	3.25	0.101	0.113	0.115	11.57
methyl isobutyl ketone[a]	138	101	76.6	6.81	6.84	6.75	0.774	0.770	0.749	8.49
cyclohexanone	604	432	314	5.63	5.49	5.37	0.765	0.734	0.710	9.27
N,*N*-dimethylformamide	255	187	137	16.3	15.4	15.2	1.83	1.77	1.75	8.89
tetrahydrofuran	74.6	57.4	44.9	3.63	3.68	3.74	0.238	0.243	0.250	7.37
acetone	24.1	18.7	15.4	10.5	10.6	10.3	1.17	1.17	1.13	6.63
acetonitrile	34.5	27.0	20.4	23.3	22.8	23.6	1.96	1.93	1.96	7.58
methanol	30.4	19.5	14.5	17.3	19.8	20.1	1.69	1.81	1.82	10.4
isopropyl alcohol	22.6	17.6	14.6	24.3	22.0	19.1	2.02	1.91	1.76	6.38
butyl alcohol	90.9	66.7	51.5	20.2	18.2	16.1	1.88	1.77	1.64	8.16
benzyl alcohol	2465	1622	1107	16.9	14.8	13.0	1.97	1.84	1.71	11.2
ethyl acetate	52.7	39.9	31.2	5.98	6.00	5.97	0.745	0.738	0.723	7.58
methyl ethyl ketone	48.3	37.5	29.8	8.53	8.41	8.25	0.987	0.961	0.932	7.05
benzaldehyde	1201	826	584	6.80	6.52	6.26	1.05	1.01	0.970	10.2
aniline	1492	1011	712	9.02	8.37	7.75	1.31	1.24	1.16	10.4

[a] On Chromosorb W-HP (80/100 mesh).

Table VII. Polyisoprene/Solvent Interaction Data at 328 K

	V_g, cm^3/g				
solutes	this work	Tewari and Shreiber	% deviation	Ω_1^∞	χ
cyclohexane[a]	175			4.29	0.265
cyclohexane	177			4.29	0.254
benzene[a]	186	184	1.4	4.37	0.402
toluene[a]	496	486	2.0	3.98	0.305
hexane[a]	80.6	79.1	1.9	6.31	0.482
ethyl benzene[a]	1122	1108	1.2	3.87	0.281
chloroform[a]	134			2.11	0.200
carbon tetrachloride[a]	206			1.77	0.094
p-xylene[a]	1295	1226	5.3	3.61	0.230
methylene chloride[a]	51.7			3.82	0.669
1,2-dichloroethane[a]	174			4.22	0.722
cyclohexanone	1303			7.32	1.00
N,*N*-dimethylformamide	495			24.9	2.23
dioxane	263			6.03	0.891
tetrahydrofuran	127			4.35	0.402
acetone	29.2			17.3	1.66
acetonitrile	24.8			68.6	3.03
acetic acid	125			37.9	2.74
ethylene glycol	281			1145	6.23
methanol	12.1			105	3.47
isopropyl alcohol	29.9			50.4	2.73
butyl alcohol	166			36.2	2.44
benzyl alcohol	5604			35.8	2.69
ethyl acetate	93.6			7.41	0.949
methyl ethyl ketone	78.0			11.4	1.27
methyl isobutyl ketone	285			8.19	0.943
benzaldehyde	2933			8.99	1.31
aniline	3087			16.7	1.91

[a] On Chromosorb W-HP (80/100 mesh).

structure. The specific retention volumes of several solvents in polyisoprene reported by Tewari and Shreiber (*17*) are also shown in Table VII. As indicated by the percent deviations, our results compare favorably with those reported by Tewari and Shreiber.

In conclusion, infinite dilution gas–liquid chromatography provides a convenient and rapid way to obtain solvent volatilities from concentrated polymer solutions. When the experimental results are expressed in the form of Flory–Huggins interaction parameters, their magnitudes allow a reasonable ranking of the solvents according to their power of solvency. The results of these studies indicated very similar solubility characteristics between polybutadiene and polyisoprene.

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sions and for the generous supply of substrate and other chromatographic items.

Glossary

a_1	activity of solvent in polymer solution
B_{11}	second virial coefficient of pure solvent, cm^3/(g-mol)
f_1°	fugacity of pure solvent at system T and reference pressure, atm
f_p	pressure correction term
ΔH_s	heat of solution, kcal/mol
M_i	molecular weight of component i
M_n	number average molecular weight
M_w	weight average molecular weight
P_1	partial pressure of the solvent, atm
P_1^s	saturation vapor pressure of the solvent, atm
P_i	column inlet pressure, psig
P_o	column outlet pressure, psig
Q	flow rate at column outlet pressure and temperature, cm^3/min
R	universal gas constant, 82.056 cm^3 atm/(g-mol K)
r	ratio of molecular volumes of polymer to solvent
T	system temperature, K
t	system temperature, °C
t_g	residence time of the solvent, min
t_r	residence time of air, min
V_1	molar volume of liquid solvent at saturation, cm^3/g-mol
V_g	specific retention volume, cm^3/g
V_g^0	specific retention volume corrected to 0 °C, cm^3/g
W_2	weight of polymer in column, g
x_1	liquid mole fraction of solvent
y_1	vapor mole fraction of solvent
γ_1	mole fraction activity coefficient of solvent
γ_1^∞	mole fraction activity coefficient of solvent at infinite dilution
ρ_i	mass density of component i, g/cm^3
ϕ_1	vapor-phase fugacity coefficient of solvent
ϕ_1^s	fugacity coefficient of solvent at saturation pressure
Φ_i	volume fraction of component i
χ	Flory–Huggins parameter
Ω_1^∞	weight fraction activity coefficient of solvent at infinite dilution

Registry No. PS, 9003-53-6; PBD, 9003-17-2; PIP, 9003-31-0; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; hexane, 110-54-3; ethylbenzene, 100-41-4; chloroform, 67-66-3; carbon tetrachloride, 56-23-5; *p*-xylene, 106-42-3; methylene chloride, 75-09-2; 1,2-dichloroethane, 107-06-2; *n*-butylbenzene, 104-51-8; methyl isobutyl ketone, 108-10-1; cyclohxanone, 108-94-1; *N*,*N*-dimethylformamide, 68-12-2; tetrahydrofuran, 109-99-9; acetone, 67-64-1; acetonitrile, 75-05-8; methanol, 67-56-1; isopropyl alcohol, 67-63-0; butyl alcohol, 71-36-3; benzyl alcohol, 100-51-6; ethyl acetate, 141-78-6; methyl ethyl ketone, 78-93-3; benzaldehyde, 100-52-7; aniline, 62-53-3; acetic acid, 64-19-7; ethylene glycol, 107-21-1.

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Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile

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Dielectric constants, densities, viscosities, and refractive indices for the propylene carbonate + acetonitrile system were determined over the entire composition range of the system and at various temperatures, ranging from 25 to 45 °C. Excess dielectric constants, excess volumes, excess viscosities, and excess Gibbs energies of activation of the viscous flow, as well as Kirkwood correlation factors, have been calculated and studied. Their behavior strongly suggests the existence of intermolecular interactions.

Introduction

Several previous papers (*1*, *2*) from our laboratory have been concerned with the physical and thermodynamic properties of binary liquid systems of technological interest. Here we report excess properties of the propylene carbonate (PC) + acetonitrile (AN) system. Although both components of the system have a wide range of technological applications, namely, in battery systems and plating techniques (*3*, *4*), it appears that their binary system has not been studied. We thus carried out measurements on the dielectric constants, viscosities, densities, and refractive indices over the entire mole fraction range of the system at 25, 30, 35, 40, and 45 °C. By means of the experimental results, the relevant excess functions as well as the Kirkwood correlation factor (g_k) have been evaluated since their study may lead to conclusions concerning the deviation of the system from an ideal mixture behavior.

Experimental Section

Propylene carbonate (Merck zur synthese 99%) was dried over 4A molecular sieves and fractionally distilled under vacu-

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