pendent of molecular weight even at still higher concentration. Both F and χ are monotonically decreasing functions of concentration up to at least 7 vol %. These observations are not a result of a possible improper treatment of polydispersity; polydispersity has hardly any effect on the evaluation of F in this region of concentrations. While the spread of both F and χ values for all our samples at higher concentrations is not very large (about 0.015), it seems to be, nevertheless, experimentally well established.

These experimental facts suggest that the accepted theory of function g, as formulated by Koningsveld et al.,[2] may need some modification. Specifically, the term g_c should be reformulated to allow for its dependence on molecular weight and for its decrease with increasing concentration. The excess term g_e may require modification too; the rate of decrease of F with concentration in the *low* concentration region does not seem to depend on molecular weight as much as required by the theory.

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Thermodynamic Analysis of an Ethylene and Vinyl Acetate Copolymer with Various Solvents by Gas Chromatography

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ABSTRACT: We have obtained infinite-dilution properties of an ethylene–vinyl acetate copolymer containing 29 wt % vinyl acetate with 43 volatile solvents at 150.46 and 160.53 °C. We have calculated heats of solution, infinite-dilution activity coefficients, Flory–Huggins interaction parameters, and molar Gibbs energies of absorption for the 43 solvents at essentially infinite dilution of solvent from raw data obtained by gas–liquid chromatography. The heats of solution are resolved into their dispersion component, permanent dipole interaction component, and specific interaction component using a simple, general method. We show that information obtained from decomposition of the heats of solution can be used, in much the same way as Hansen's three-dimensional solubility parameter method, to explain otherwise anomalous interactions of solvents with a polar polymer. Additionally, an important conclusion is drawn regarding sample sizes and flow rates required to obtain reliable thermodynamic information from gas–liquid chromatography using polar solvents.

Although some data are available in the literature, thermodynamic interactions between polar polymers and solvents have not been studied in great detail for cases in which the polymer/solvent mixture is almost pure polymer. The purpose of this work is to show how the interactions between small amounts of solvents and a polar polymer can be determined experimentally and how the data can be resolved into the contributions of dispersion forces, polar forces, and specific interactions using a general method of analysis not linked to any specific theoretical method. The analysis we use provides an alternative to the semiquantitative Hansen three-dimensional solubility parameter approach for solutions of polar polymers.

The polymer we have chosen to use is a slightly polar polymer: ethylene–vinyl acetate copolymer (EVA). EVA is a simple, random copolymer with a glass-transition temperature well below room temperature. The vinyl acetate moiety in the polymer backbone provides the possibility of relatively strong specific interactions with certain solvents and polar interactions with other solvents. Also, the melting point of EVA is sufficiently low that it is not difficult to work with the molten polymer.

In order to determine the thermodynamic quantities needed for our analysis, we used gas–liquid chromatography (GLC). GLC has long been recognized[1,2] as an attractive alternative and rapid method to obtain thermodynamic properties.[3]

Experimental Section

Equipment. 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 ±0.01 °C was used to read the oven temperature. The inlet pressure to the column was measured by a Seegers 0–30 psi pressure gauge which had a precision of ±0.1 psi. Helium was used as the carrier gas, and it passed through a gas purifier containing molecular sieves before it entered the chromatograph. The flow rate of the carrier gas was measured using a 1.2-cm i.d. soap-film flow meter. The flow rate of gas through the GC was controlled by flow controllers installed in the chromatograph.

Column Preparation. The column, a $\frac{1}{8}$-in. o.d. stainless steel tube, was filled with 0.2876 g of EVA copolymer coated on 80–100 mesh Fluoropak-80 (a powdered Teflon) with a loading (weight of polymer per weight of polymer and support × 100) of 14.75%. Fluoropak-80 is a suitable support for polar-solute measurements since it gives nearly symmetric retention curves indicating minimal substrate adsorptive capacity.[4,5]

The EVA copolymer, 29% by weight vinyl acetate, was supplied by Dr. Samil Beret of Union Carbide Corp. The sample designation was DX-31034. DX-31034 is a random copolymer of ethylene and vinyl acetate produced by free-radical polymerization in a tubular reactor at high pressure. The number average molecular weight is 43200 g/g

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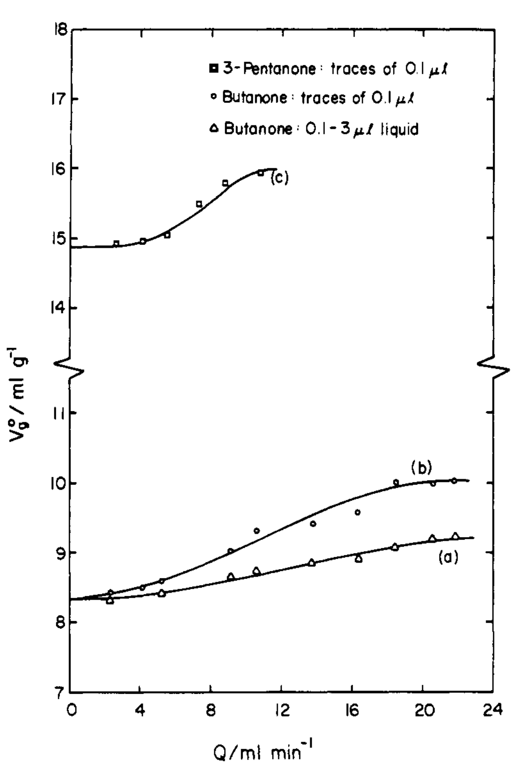

Figure 1. Flow rate and sample size effect on specific retention volume at 150.46 °C.

mol, the melt index is 15 dg min^{-1}, and the density is 0.9513 g cm^{-3}. The melting point of the EVA sample is below 100 °C.

Polymer was dissolved in *m*-xylene and filtered hot to remove undissolved material. Then it was dried and weighed. Columns were prepared by dissolving a weighed amount of polymer in 100 mL of *m*-xylene at 100 °C. After the polymer was completely dissolved, a weighed amount of Fluoropak-80 was stirred into the solution. The mixture was stirred gently until most of the solvent evaporated. Then the resulting coated support was dried in an oven at 90 °C for 3 days. The column was filled uniformly with the EVA-coated Fluoropak support. Silane-treated glass wool was used to plug the ends of the column. The amount of polymer inside each column was known within ±0.001 g.

Flow Rate. A flow rate of approximately 4 mL min^{-1} of carrier gas was maintained through the column. The flow rate of 4 mL min^{-1} was taken to approximate "0" flow rate, because control at lower flow rates was not good.

Injection Technique. 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 purity greater than 99%.

The following injection technique was adopted in order to insure the injection of "0" sample size. Initially, the syringe was flushed many times with the solvent. Then all liquid solvent was 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 distance from the injection point to the peak height divided by the chart speed. The peaks were quite symmetrical for polar or nonpolar solutes, justifying the use of Fluoropak-80 support.

Experiments were carried out with 2-butanone and 3-pentanone to detect the effect of flow rate and sample size on the retention volume data. Figure 1 illustrates these experiments.

Physical Properties. A computer program has been developed to compute retention volume, Gibbs energy of solution, and weight fraction infinite dilution activity coefficient from raw experimental data and also to estimate physical properties such as B_{11},[16,17] v_1,[18] $p_1{}^{s}$,[18] δ_1,[18,19] and critical properties.[18] The values of B_{11}, v_1, and $p_1{}^{s}$ used in eq 5 and 6 for 150.46 and 160.53 °C are shown in Table IV.

Data Analysis

Molar Gibbs Energy of Solution. The molar Gibbs energy of absorption, ΔG_{abs}, is based on the standard state for the solvent in the gas phase being pure solvent behaving as an ideal gas at 1 atm of pressure and column temperature and on the standard state for the solvent in the liquid polymer phase following Henry's law. The molar Gibbs energy of absorption is defined as:

$$\Delta G_{\text{abs}} = \mu_1{}^{0\text{g}} - \mu_1{}^{0\text{l}} \tag{1}$$

where $\mu_1{}^{0\text{g}}$ and $\mu_1{}^{0\text{l}}$ are the standard-state chemical potentials for the solvent in the gaseous and liquid phases. Based on definitions of $\mu_1{}^{0\text{g}}$ and $\mu_1{}^{0\text{l}}$, ΔG_{abs} can be related to measurable quantities by:[7]

$$\Delta G_{\text{abs}} = RT \ln (M_1 V_{\text{g}}{}^0/RT_0) \tag{2}$$

where M_1 is the molecular weight of solvent, $V_{\text{g}}{}^0$ is specific retention volume corrected to 0 °C, obtained in the usual way,[5] and R is the universal gas constant given in units of atmosphere for pressure.

Weight Fraction Infinite Dilution Activity Coefficient. The weight fraction infinite dilution activity coefficient, $\Omega_1{}^{\infty}$, is given by the relation:[4]

$$\ln \Omega_1{}^{\infty} = \ln \left(\frac{a_1}{w_1}\right)^{\infty} = \ln \left(\frac{273.15R}{P_1{}^{s} V_{\text{g}} M_1}\right) - \frac{P_1{}^{s}}{RT}(B_{11} - v_1) \tag{3}$$

where a_1 and w_1 are activity and weight fraction of solvent respectively, $p_1{}^{s}$ is vapor pressure of solvent at column temperature T, M_1 is the molecular weight of solvent, and B_{11} and v_1 are the second virial coefficient and molar volume of the pure solvent at column temperature, respectively. The activity coefficient, $\Omega_1{}^{\infty}$, a fundamental thermodynamic quantity, provides a useful function for relating thermodynamic behavior to intermolecular forces. It can also be related to the solvent volatility at finite solvent concentrations.[5]

The Flory–Huggins Interaction Parameter. The Flory–Huggins interaction parameter (χ) is a measure of the strength of interaction between polymer and solvent. The χ parameter can be determined from experimental GLC data by the relation:[4]

$$\chi = \ln \left(\frac{273.15Rv_{2\text{sp}}}{V_{\text{g}}{}^0 P_1{}^{s} v_1}\right) - \left(1 - \frac{v_1}{\overline{M}_{\text{n}} v_{2\text{sp}}}\right) - \frac{P_1{}^{s}}{RT}(B_{11} - v_1) \tag{4}$$

where v_2 is the liquid polymer molar volume, $v_{2\text{sp}}$ is the specific volume of polymer, and $\overline{M}_{\text{n}}$ is the number average molecular weight. If χ is less than 0.5, favorable interactions result between the solvent and polymer, and the solvent dissolves the polymer.[8]

Heat of Solution and Its Correlation. From GLC, we determine heat of solution (ΔH_{s}) using the approximate relation:[4]

$$\Delta H_{\text{s}}/RT^2 = \text{d} \ln V_{\text{g}}{}^0/\text{d}T \tag{5}$$

Interactions between nonpolar and polar molecules are mainly due to induced dipole moments which arise from the short-lived perturbations of electron positions during collision or near collision. The interactions between polar molecules are mainly due to (i) permanent dipole moments; (ii) quadrupoles and higher multipole moments; and (iii) hydrogen bonding, charge-transfer complexing, and the like. Interactions due to the latter types of forces are referred to as "specific interactions" in this work. Bearing these in mind, $-\Delta H_{\text{s}}$ can be represented in general as a function of polarizability (α_1), dipole moment (μ_1) of solvent, and specific interactions between solvent and polymer (X) using the relation:[4]

$$-\Delta H_{\text{s}} = f(\alpha_1,\mu_1) + X \tag{6}$$

The solvent dipole moment, μ_1, should not be confused with solvent chemical potential.

Table I
Thermodynamic Quantities Determined from GLC at 150.46 °C

Solvent	$V_g{}^0$ [a] mL g^{-1}	$-\Delta G_{abs}$, kJ g mol^{-1}	$\Omega_1{}^\infty$	χ
1. Acetaldehyde	2.79	16.47	5.53	0.155
2. Acetic acid	17.53	10.78	8.19	1.116
3. Benzene	15.64	10.25	3.55	−0.023
4. 1-Bromobutane	21.03	7.23	2.39	−0.163
5. 2-Bromobutane	16.47	8.09	2.42	−0.174
6. 1-Butanol	15.63	10.44	7.55	0.650
7. 2-Butanol	10.23	11.93	6.92	0.505
8. Butanone	8.54	12.67	6.72	0.554
9. Chlorobenzene	51.25	4.78	2.53	−0.062
10. Cyclohexane	13.15	10.60	4.22	0.070
11. 1,2-Dichloroethane	16.72	9.18	2.74	0.058
12. Dichloromethane	7.36	12.61	2.74	0.024
13. Diethyl ether	4.33	14.97	5.29	0.049
14. Dioxane	18.43	9.24	4.05	0.454
15. Dipropyl ether	11.06	10.53	4.86	0.174
16. Ethanenitrile	5.95	15.93	18.91	1.647
17. Ethanol	4.33	16.62	14.05	1.279
18. Ethyl ethanoate	7.75	12.30	5.70	0.481
19. Formic acid	16.95	11.82	6.76	1.076
20. Furan	5.21	14.60	3.95	0.070
21. Heptane	11.98	10.31	5.74	0.245
22. Hexane	6.75	12.86	6.34	0.253
23. Methanol	2.95	19.27	19.42	1.692
24. Methylcyclohexane	18.20	8.91	4.11	0.061
25. Nitroethane	15.57	10.41	7.67	0.995
26. Nitromethane	10.07	12.67	10.49	1.407
27. 1-Nitropropane	18.52	9.19	8.36	1.031
28. 2-Nitropropane	18.38	9.22	6.52	0.770
29. Octane	21.41	7.81	5.27	0.228
30. 1-Octene	20.99	7.94	4.90	0.173
31. Pentane	3.84	15.48	41.47	2.396
32. 3-Pentanone	14.94	10.07	5.42	0.357
33. Propanenitrile	9.00	13.43	13.03	1.255
34. 2-Propanol	5.10	15.12	10.61	0.933
35. Propanone	4.51	15.66	9.41	0.879
36. Propenenitrile	6.81	14.54	11.08	1.085
37. Propyl ethanoate	13.35	9.87	5.05	0.375
38. Tetrachloromethane	14.12	8.22	1.90	−0.039
39. Tetrahydrofuran	10.63	11.89	4.23	0.246
40. Trichloromethane	13.26	9.33	1.79	−0.246
41. 2,2,2-Trifluoroethanol	6.31	12.58	4.78	0.789
42. Water	3.41	20.79	121.01	4.095
43. *m*-Xylene	50.84	5.02	3.26	−0.023

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

Results and Discussion

Retention Volume. Experimental retention volumes for 43 solvents with EVA copolymer containing 29% by weight vinyl acetate are shown in Tables I and II at 150.46 and 160.53 °C. We observed that retention volumes were a function of both sample size and flow rate. In Figure 1, curve (a) represents experimental retention volumes for butanone in the flow rate range of 2.7–21.5 mL/min with 0.1–3-μL *liquid* sample injection. Curve (b) represents experimental retention volumes for butanone in the same flow rate range but with 0.1-μL *trace* injections, which was the technique used in this work. Curve (c) represents retention volume for 3-pentanone in the flow rate range of 2.5–10.8 mL/min with 0.1-μL trace injections.

Liu and Prausnitz[9] have used EVA copolymer with three different weight percents of vinyl acetate to measure weight fraction Henry's constants by GC with solutes such as propanone, butanone, and 2-propanol at 150 °C. In order to compare results, we plotted the Henry's constants of Liu and Prausnitz[9] against weight percent vinyl acetate in EVA copolymer and found the Henry's constants corresponding to 29% by weight vinyl acetate graphically. We then calculated the specific retention volumes corrected to 0°C. When we compared the specific retention volumes of Liu and Prausnitz with ours, we observed that the retention volumes of Liu and Prausnitz[9] are slightly larger than ours (propanone, 2.5%; butanone, 3.5%; 2-propanol, 8.1%). Since our experimental precision in $V_g{}^0$ is ±1% the differences cited are probably significant.

In order to compare flow rates on the same basis, one can assume that comparable results would be obtained if the Reynolds numbers are the same in the two types of columns. If the void fractions of packing in the columns are also equivalent (since we used nearly identical substrates), the internal diameter of the Liu and Prausnitz[9] column should be approximately four times larger than ours to give an identical Reynolds number. The actual ratio of internal diameters is 10/3 (5/16 in. vs. 3/32 in.). Thus the Liu and Prausnitz[9] data (from 10–24 mL/min) correspond to Reynolds numbers slightly larger than those encountered in our column at 4 mL/min. This would have some influence on the results since the results are flow-rate dependent at Reynolds numbers larger than those we used (see Figure 1).

Table II
Thermodynamic Quantities Determined by GLC at 160.53 °C

Solvent	V_g^0,[a] mL g^{-1}	$-\Delta G_{abs}$, kJ g mol^{-1}	Ω_1^∞	χ
1. Acetaldehyde	4.09	17.40	5.63	0.119
2. Acetic acid	14.87	11.63	7.47	1.006
3. Benzene	12.72	11.24	3.63	−0.020
4. 1-Bromobutane	16.44	8.29	2.48	−0.141
5. 2-Bromobutane	13.21	9.08	2.49	−0.163
6. 1-Butanol	12.29	11.56	7.41	0.611
7. 2-Butanol	8.55	12.86	6.54	0.424
8. Butanone	7.14	13.61	6.69	0.524
9. Chlorobenzene	39.13	5.87	2.63	−0.037
10. Cyclohexane	10.84	11.55	4.30	0.067
11. 1,2-Dichloroethane	12.69	10.40	2.99	0.124
12. Dichloromethane	6.35	13.44	2.73	−0.009
13. Diethyl ether	3.45	16.14	5.79	0.090
14. Dioxane	14.88	10.24	4.09	0.445
15. Dipropyl ether	8.80	11.60	5.06	0.192
16. Ethanenitrile	4.95	16.97	18.91	1.625
17. Ethanol	3.75	17.56	12.97	1.170
18. Ethyl ethanoate	6.15	13.43	6.00	0.505
19. Formic acid	13.85	12.84	6.44	1.008
20. Furan	4.50	15.48	3.95	0.036
21. Heptane	9.74	11.30	5.84	0.239
22. Hexane	5.73	13.76	6.33	0.221
23. Methanol	2.68	20.07	17.35	1.550
24. Methylcyclohexane	14.88	9.85	4.15	0.053
25. Nitroethane	12.48	11.46	7.59	0.966
26. Nitromethane	8.19	13.71	10.42	1.383
27. 1-Nitropropane	14.89	10.20	8.17	0.992
28. 2-Nitropropane	14.52	10.29	6.54	0.753
29. Octane	16.60	8.91	5.45	0.242
30. 1-Octene	16.45	9.01	5.03	0.180
31. Pentane	3.43	16.25	37.64	2.283
32. 3-Pentanone	11.78	11.16	5.60	0.369
33. Propanenitrile	7.39	14.46	13.00	1.232
34. 2-Propanol	4.54	15.90	9.60	0.807
35. Propanone	3.80	16.67	9.43	0.851
36. Propenenitrile	5.56	15.62	11.28	1.077
37. Propyl ethanoate	10.62	10.92	5.19	0.381
38. Tetrachloromethane	11.59	9.13	1.94	−0.041
39. Tetrahydrofuran	8.68	12.90	4.34	0.247
40. Trichloromethane	10.88	10.27	1.84	−0.241
41. 2,2,2-Trifluoroethanol	5.03	13.69	4.89	0.780
42. Water	2.83	21.95	118.41	4.060
43. *m*-Xylene	37.93	6.19	3.46	0.020

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

Another source of difference between our results and those of Liu and Prausnitz is that we purified our polymer sample to remove high molecular weight gel and additives, while Liu and Prausnitz[9] used their sample as received.

Heat of Solution. The values of $-\Delta H_s$ computed from eq 5 in the temperature range 150.5–160.5 °C are shown in Table III. The values of α_1[10] and μ_1[11] used in correlating $-\Delta H_s$ are also shown in Table III. These values are for 25 °C and they are used without temperature correction at the temperatures of this study.

To correlate $-\Delta H_s$ according to eq 6, we first plotted $-\Delta H_s$ values of solvents against the polarizabilities of solvents as shown in Figure 2. We established two reference curves: one for *n*-alkanes and another for aromatics. The *n*-alkane reference curve was forced through the origin, and the points for pentane, hexane, heptane, and octane were found to form a quadratic curve:

$$-\Delta H_s = 0.597\alpha_1 + 0.123\alpha_1^2 \text{ kJ g mol}^{-1} \qquad (7)$$

In eq 6, $\alpha_1 \times 10^{24}$ from Table III should be used for α_1. The reference curve for aromatics was established using the points of benzene and *m*-xylene and was forced through the origin. The aromatic reference curve was also found to be quadratic:

$$-\Delta H_s = 2.409\alpha_1 + 0.056\alpha_1^2 \text{ kJ g mol}^{-1} \qquad (8)$$

Here again, $\alpha_1 \times 10^{24}$ from Table III should be used for α_1.

The difference between experimental $-\Delta H_s$ values and those predicted by the reference curve at the same polarizability was denoted by ΔH_{ad}. The ΔH_{ad} values are measures of the strength of interaction due to the permanent electrical forces in the polar molecules and also due to specific interactions. ΔH_{ad} has been shown to be quantitatively equivalent to the enthalpy of "hydrogen bonding".[4]

The solid line in Figure 3 is the least-squares fit (forced through the origin) of data for solvents which, because of their chemical structures, should not have specific interactions with EVA copolymer. These solvents are indicated by the symbol "×" in Figure 3. The relation found for ΔH_{ad} as a linear function of μ_1 was:

$$\Delta H_{ad} = 1.78 \times 10^{24}\mu_1 \text{ kJ g mol}^{-1} \qquad (9)$$

The slight scatter around the line is probably due to the ex-

Table III
Polarizabilities,[a] Dipole Moments,[a] Solubility Parameters[a] of Pure Solvents, and Heats of Solution[b] and Specific Interaction Parameters[b] of Solvent–EVA Pairs

Solvent	$\alpha_1 \times 10^{24}$, cm^3	$\mu_1 \times 10^{30}$, C m	δ_1,[c] (cal cm$^{-3})^{1/2}$	$-\Delta H_s$(exptl), kJ g mol^{-1}	X, kJ g mol^{-1}
1. Acetaldehyde	4.60	9.07	9.87	23.08	1.59
2. Acetic acid	5.12	5.80	13.01	24.91	8.31
3. Benzene	10.40	0	9.16	31.12	
4. 1-Bromobutane	11.25	6.94	8.65[e]	37.10	
5. 2-Bromobutane	11.25	7.44	8.42[e]	33.76	
6. 1-Butanol	8.76	5.57	11.60	36.23	11.65
7. 2-Butanol	8.66	5.47	11.08	26.99	2.86
8. Butanone	8.24	9.24	9.45	27.27	
9. Chlorobenzene	12.34	5.70	9.67	41.02	
10. Cyclohexane	10.71	0	8.19	26.03	
11. 1,2-Dichloroethane	8.34	5.00	9.91[e]	41.30	18.87
12. Dichloromethane	6.58	5.14	9.21	22.64	4.24
13. Diethyl ether	8.92	3.84	7.53	34.21	12.26
14. Dioxane	8.56	1.40	10.13	33.08	16.47
15. Dipropyl ether	12.57	4.34	7.58	34.44	
16. Ethanenitrile	4.40	13.21	12.11	28.21	
17. Ethanol	5.07	5.67	12.78	21.32	5.04
18. Ethyl ethanoate	8.83	5.93	8.91	35.34	9.92
19. Formic acid	3.37	5.07	12.10	30.09	17.66
20. Furan	7.60	2.30	8.97	21.97	6.24
21. Heptane	13.71	0	7.50	31.79	
22. Hexane	11.85	0	7.27	24.63	
23. Methanol	3.25	5.67	14.50	14.48	1.15
24. Methylcyclohexane	12.88	0	7.92	30.94	
25. Nitroethane	6.74	11.81	11.24	32.98	
26. Nitromethane	4.95	11.91	12.90	31.78	
27. 1-Nitropropane	8.48	11.97	10.80	33.52	
28. 2-Nitropropane	8.56	12.44	10.58	35.36	
29. Octane	15.54	0	7.54	38.49	
30. 1-Octene	15.36	1.13	7.60	37.04	
31. Pentane	9.63	0	7.02	16.92	
32. 3-Pentanone	9.91	9.11	8.14	36.17	
33. Propanenitrile	6.26	13.44	10.73	30.06	
34. 2-Propanol	6.94	5.34	11.58	17.65	
35. Propanone	6.43	9.61	9.62	25.48	
36. Propenenitrile	6.19	12.77	10.56	30.46	
37. Propyl ethanoate	10.67	6.00	8.72	35.46	
38. Tetrachloromethane	10.24	0	8.55	29.65	
39. Tetrahydrofuran	7.97[d]	5.84	9.12	29.94	6.97
40. Trichloromethane	8.48	3.40	9.16	29.83	9.87
41. 2,2,2-Trifluoroethanol	4.80	6.77	11.13	35.11	17.36
42. Water	1.45	8.34	23.30	28.00	12.03
43. *m*-Xylene	13.91	1.17	8.88	44.36	

[a] At 25 °C. [b] In the temperature range of 150.48–160.53 °C. [c] Solubility parameter of EVA copolymer is estimated to be 8.95 (cal/cm$^{-3})^{1/2}$.[13,15] [d] Estimated from group contribution values of Bondi.[12] [e] Estimated from group contribution values of Fedors.[13]

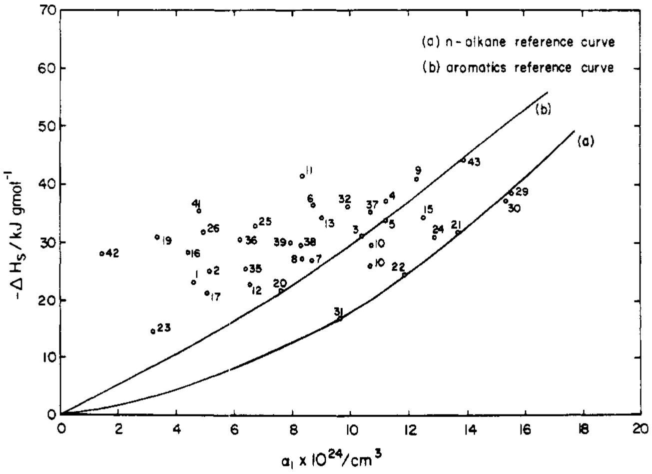

Figure 2. Heat of solution as a function of polarizability for solvents in EVA copolymer in the temperature range of 150.46–160.53 °C.

clusion of higher multipole moments and also the choice of the proper values of dipole moments.

Solvents whose points are well above the solid line in Figure 3 exhibit specific interactions with EVA such as hydrogen bonding and charge-transfer complexing. The vertical distances above the reference line are measures of the magnitudes of such interactions and are shown in Table III under the column labeled "X". Combining all these results we obtained a model for $-\Delta H_s$:

$$-\Delta H_s = 0.597\alpha_1 + 0.123\alpha_1^2 + 1.78\mu_1 + X \text{ kJ g mol}^{-1} \quad (10)$$

for alkanes. For aromatics, the following result was obtained:

$$-\Delta H_s = 2.409\alpha_1 + 0.056\alpha_1^2 + 1.78\mu_1 + X \text{ kJ g mol}^{-1} \quad (11)$$

In eq 10 and 11, $\alpha_1 \times 10^{24}$ and $\mu_1 \times 10^{30}$ should be used from Table III in place of α_1 and μ_1, respectively.

As seen in Table III, alcohols, acids, ethers, and chlorinated hydrocarbons have quite positive specific interaction (X)

Table IV
Physical Properties of Solvents

	t = 150.46 °C			t = 160.53 °C		
Solvent	B_{11}, cm^3 g mol^{-1}	v_1, cm^3 g mol^{-1}	p_1^s, mmHg	B_{11}, cm^3 g mol^{-1}	v_1, cm^3 g mol^{-1}	p_1^s, mmHg
1. Acetaldehyde	360	80.9	20816	336	57.1	24671
2. Acetic acid	672	62.4	2093	609	52.7	2734
3. Benzene	611	110.0	4436	579	91.3	5423
4. 1-Bromobutane	767	149.3	2722	725	126.4	3403
5. 2-Bromobutane	696	153.0	3492	659	128.9	4306
6. 1-Butanol	871	113.2	2108	812	93.4	2777
7. 2-Butanol	576	120.1	3566	537	97.2	4598
8. Butanone	747	108.0	4803	698	110.6	5904
9. Chlorobenzene	1090	117.3	1237	1024	119.0	1573
10. Cyclohexane	705	128.5	4157	670	131.1	5046
11. 1,2-Dichloroethane	627	99.2	4218	594	101.2	5188
12. Dichloromethane	366	88.0	12299	348	90.7	14680
13. Diethyl ether	455	144.8	13701	430	152.3	16364
14. Dioxane	698	87.9	2804	660	89.5	3503
15. Dipropyl ether	888	161.9	3578	839	165.8	4403
16. Ethanenitrile	1098	57.9	4484	1003	59.2	5500
17. Ethanol	422	69.8	6906	388	71.8	8846
18. Ethyl ethanoate	693	120.5	5121	652	123.6	6276
19. Formic acid	474	41.1	3454	430	41.9	4488
20. Furan	330	97.2	15651	312	100.7	18718
21. Heptane	1042	174.7	2815	985	178.8	3472
22. Hexane	751	164.8	5602	710	169.8	6786
23. Methanol	339	44.3	10858	309	45.7	13662
24. Methylcyclohexane	923	147.2	2574	875	150.0	3165
25. Nitroethane	1081	82.5	2082	995	84.0	2663
26. Nitromethane	1056	60.7	2999	964	61.8	3773
27. 1-Nitropropane	1316	102.9	1327	1217	104.6	1709
28. 2-Nitropropane	1236	104.5	1744	1140	106.3	2233
29. Octane	1400	186.2	1440	1319	189.8	1824
30. 1-Octene	1315	179.6	1617	1240	183.2	2041
31. Pentane	1123	105.6	1599	1069	107.4	1992
32. 3-Pentanone	985	126.8	2737	921	129.4	3422
33. Propanenitrile	1161	79.2	3041	1068	80.9	3780
34. 2-Propanol	451	97.1	5926	420	99.8	7518
35. Propanone	556	88.0	8495	519	90.6	10341
36. Propenenitrile	925	77.0	5173	849	78.9	6373
37. Propyl ethanoate	943	137.5	2771	887	140.4	3453
38. Tetrachloromethane	621	118.0	4701	589	120.5	5727
39. Tetrahydrofuran	579	92.4	6145	545	94.7	7490
40. Trichloromethane	489	105.9	7046	589	108.4	5727
41. 2,2,2-Trifluroethanol	551	84.2	6619	517	87.0	8336
42. Water	1460	14.0	2663	1251	14.2	3293
43. *m*-Xylene	1237	137.5	1019	1168	139.6	1303

values. This indicates that there are specific interactions such as hydrogen bonding and charge-transfer complexing between these compounds and the EVA copolymer. However, as will be explained later, strong specific interactions do not always indicate the solvent can dissolve the polymer.

Solubility Considerations. The values of ΔG_{abs}, Ω_1^∞, and χ calculated from eq 2, 3, and 4, respectively, are shown in Tables I and II for the temperatures 150.46 and 160.53 °C. Negative or near-zero values of χ for solvents such as benzene, 1-bromobutane, 2-bromobutane, chlorobenzene, cyclohexane, 1,2-dichloroethane, dichloromethane, diethyl ether, furan, methylcyclohexane, tetrachloromethane, trichloromethane, and *m*-xylene indicate favorable interaction between the EVA copolymer and the solvents. These solvents are potential solvents for EVA copolymer. The solubility parameters (δ_1)[13-15] of the above solvents are quite close to that of EVA copolymer.[13,15] The closer the solubility parameters of the solvent and the polymer are, the lower the χ parameter is. Solubility parameter theory cannot, of course, account for negative χ values.

The chlorinated hydrocarbons trichloromethane, dichloromethane, and 1,2-dichloroethane and the cyclic ethers furan and tetrahydrofuran, which have solubility parameters quite close to that of EVA copolymer, have χ values much lower than 0.5. These solvents at the same time have appreciable specific interactions (X) with the polymer. The specific interactions of these solvents aid the solvents to penetrate the polymer matrix and thus dissolve the polymer.

On the other hand, the alcohols, methanol, ethanol, 1-butanol, 2,2,2-trifluoroethanol, and acids such as formic acid and acetic acid have solubility parameters quite different from that of EVA copolymer. Thus their χ values are greater than 0.5. But from Table III we see that they have quite positive specific interaction values (X) indicating there are interactions between these compounds and the polymer. However, the specific interactions between these compounds and the polymer in solution are not enough to overcome unfavorable dispersion force differences between the solvents and EVA. Thus these compounds cannot penetrate easily into the EVA copolymer matrix to dissolve it.

On the other hand, aromatics such as benzene, chlorobenzene, and *m*-xylene have solubility parameters quite similar to that of the EVA copolymer, and their χ values are much lower than 0.5. Benzene and *m*-xylene have zero ΔH_{ad} values

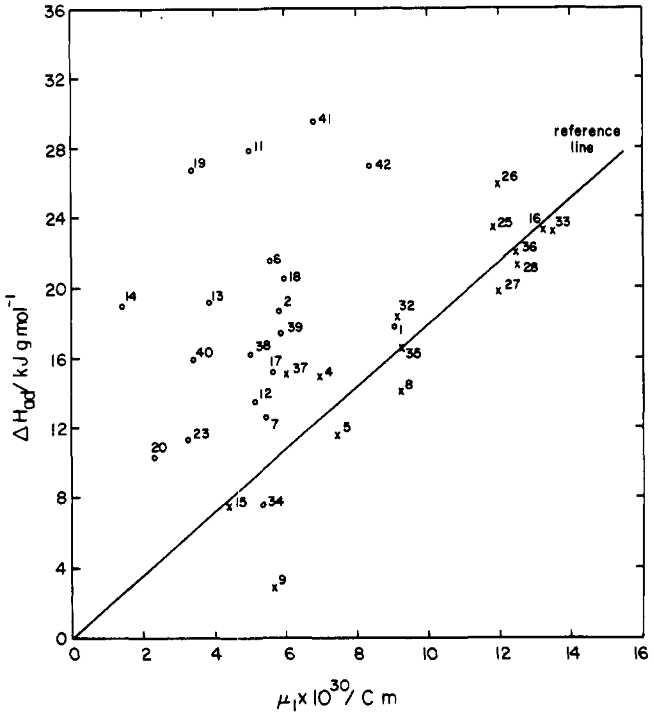

Figure 3. ΔH_{ad} values for solvents in EVA copolymer in the temperature range of 150.46–160.53 °C vs. their dipole moments.

because they are nonpolar, and chlorobenzene has a slightly positive ΔH_{ad} value. All three of these compounds have no specific interactions at all with the polymer, but they dissolve the EVA copolymer.

These results indicate that specific interactions between the solvents and the EVA copolymer are helpful in understanding solvent–polymer interactions better, but they are not sufficient to explain the dissolution of the polymer in a solvent.

Conclusion

Interactions of solvents with EVA copolymer have been described by the correlations between heats of solution at infinite dilution of binary systems and the molecular parameters of the polymer and solvents. It was possible to isolate the contributions of solute polarizability, dipole moment, and other solute–polymer interactions contributing to the heat of solution. Solution characteristics such as ΔG_{abs}, ΔH_{abs}, X, χ, and Ω_1^∞ were obtained in order to understand solvent–polymer interactions more fully. In EVA copolymer solutions, the values of X, i.e., the specific interactions, are not sufficient to determine if a solvent is a good solvent. However, X values provide insight into molecular interactions between polymer and solvent. Hence by comparing values of χ, δ_1, and X for different solvents one can understand better solvent–polymer interactions.

An important conclusion regarding the practice of obtaining thermodynamic data from gas–liquid chromatography has also been reached in this study. At least in the case of polar solvents, it is clear from our work that reliable data can only be obtained if very small sample sizes are used for injection and if the carrier gas flow rate (or Reynolds number) is sufficiently small that the data are not influenced by flow rate. The sample size and flow rate required are much smaller than had previously been demonstrated.

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