Thermodynamics

Thermodynamics of Polymer Systems
5. Sorption and Mixing Properties of Selected Solutes and Solubility Parameters of Atactic Poly(Styrene) by Gas Chromatography

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SUMMARY

Gas chromatography has been employed to determine partial molar free energies of sorption, $\Delta G_1{}^S$, as well as partial molar free energies of mixing, $\Delta G_1{}^\infty$, of atactic poly(styrene) with linear and branched alkanes (C_6–C_9), alkenes (C_8), cyclohexane and alkylbenzenes (Ph–H to PhC_6H_{13}) within the temperature range from 403 to 463 K. The influence of nature and constitution of the solute molecule on sorption and mixing properties in poly(styrene) are discussed in terms of the competing group contributions of the components. Knowledge of this influence may be transduced to understand polymer-polymer compatibility. The cohesive energy density concept has been used to calculate the infinite dilution solubility parameter for the polymer, with the aid of $\Delta G_1{}^\infty$. From the high temperature range the HILDEBRAND parameter δ_2 was extrapolated to 298 K. The value obtained, 9.14, indicates that gas chromatography is an promising alternative to the conventional methods for determination of the solubility parameter for polymers.

INTRODUCTION

Realistic ideas about the competing contributions of dispersive and specific inter- actions between the components of a mixture keep a key position in understanding of solution properties as well as of polymer miscibility. An usefull tool to predict solubility and solvent sensitivity of polymers represents the cohesive energy density concept based on regular solutions. The cohesive energy density of the material equals the potential energy of the volume unit numerically. For volatile substances[1] it may be determined from the heat of vaporization

$$\delta \equiv (\Delta E^V / V)^{1/2} = (\Delta H^V - RT)/V \qquad , \qquad (1)$$

where ΔE^V is the energy and ΔH^V the enthalpy of vaporization, V the molar volume. Thus the energy of mixing derived from the solubility theory is

$$\Delta E^m = V^m \phi_1 \phi_2 \, (\delta_1 - \delta_2)^2 \qquad , \qquad (2)$$

with ϕ_i the volume fraction of component i and V^m the average molar volume based on mole fractions. In this way solubility parameters δ_i may be used to estimate solution properties. Vice versa known mixing energies and δ for one component of the mixture make available the solution parameter of the other component.

Polymeric materials exhibit neglegible vapor pressures, however, and their molar volumes are not well defined usually. Consequently, solubility parameters for polymers are determined in an indirect way. Two experimental approaches are

quoted most oftenly in literature:

- Searching for the solvent in which the crosslinked polymer exhibits maximum swelling. The parameters determined by this way are dependent upon the cross-linked densitiy, however.

- The STAUDINGER index of the polymer is measured in a series of solvents. It is assumed to be identical with that of the solvent which yields the maximum value of the STAUDINGER index.

Within their theoretical limitations these methods are useful, although they are relatively tedious and time consuming.

Gas chromatography offers an effective alternative to those methods, as demonstrated by DiPaola-Baranyi and Guillet [2] for poly(styrene) and poly(methylmethacrylate) and by DiPaola-Baranyi, Guillet, Klein and Jeberien [3] for poly(vinylacetate).

The present work continuous our studies on the influence of the nature and constitution of the solute molecule on mixing and sorption properties of poly(styrene) [4] and additionally establishes the results of determination of the solubility parameter of poly(styrene) by gas chromatography.

EXPERIMENTAL PART

Materials. Low polydispersity atactic linear poly(styrene), PS, $M_w = 53700$, $M_w/M_n = 1.06$, was a Pressure Chemical product. The probe solutes, linear and branched alkanes ($C_6 - C_9$), alkenes (C_8) and alkylbenzenes (Ph-H to Ph-C_6H_{13}), were reagent grade and used without further purification (Fluka and Roth).

The polymer has been deposited onto Chromosorb A (Supelco, mesh size 45/60 specific surface 2.7 m^2g^{-1}) from toluene solution. The polymer weight in the column was .1194 g. Column preparation, instrumentation and measurement procedure are described elsewere [4].

DATA REDUCTION

Specific retention volumes, V_g^o, were calculated according

$$V_g^o = t_R (273,2 \, F/T_F \, w_2)^{3/2} \{ (p_i/p_o)^2 - 1\}\{(p_i/p_o)^3 - 1\}^{-1} \{1-(p_{H_2O}/p_a)\} \quad . \quad (3)$$

where t_R is the retention time of w_2 grams polymer, F the carrier gas flow rate at 298 K and athmospheric pressure p_a, and p_i and p_o the inlet and outlet pressure respectively. Solute vapor pressures have been computed from the ANTOINE equation with the constants A, B, C taken from the standard sources [5-7]. Second virial coefficients, B_{11}, were computed from the corresponding states equation proposed by McGlashan and Potter [8].

From the specific retention volumes the partial molar free energies of sorption were calculated according to the equation

$$\Delta G_1{}^s = RT \ln (V_g^o M_1 / 273 \, R) \quad . \quad (4)$$

where M_1 is the molar mass of the solute and R the universal gas constant (1 atm K^{-1} mol^{-1}). Consequently the heat of sorption is

$$\Delta H_1{}^s = R \, \partial \ln V_g^o / \partial \, (1/T) \quad . \quad (5)$$

The weight fraction activity coefficients at infinite dilution of the probe solute, Ω_1^∞, were calculated from V_g^o [9]

$$\ln \Omega_1^\infty = \ln (273 \, R \, v_2^{sp} / V_g^o \, p_1^o \, V_1) - 1 - p_1^o (B_{11} - V_1) / RT \quad . \quad (6)$$

From Ω_1^∞ the partial molar free energy of mixing, ΔG_1^∞, and the partial molar heat of mixing, ΔH_1^∞ were calculated

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \qquad (7)$$

and

$$\Delta H_1^\infty = R \, \partial \ln \Omega_1^\infty / \partial(1/T) \qquad (8)$$

RESULTS AND DISCUSSION

RETENTION VOLUMES AND SORPTION FUNCTIONS

Retention measurements have been carried out at 10° intervalls from 403 to 463 K. (The results of these measurements are presented as specific retention volumes for the entire temperature range – in a table which may be forewarded by the author). The retention volumes generally reveal a decrease of V_g^0 with rising temperature, as expected for an exothermic sorption process. At a given temperature V_g^0 increases in the series, alkane < alkene << alkylbenzene, as a consequence of the contribution of the double bond and especially the phenyl group to the interaction with the PS sites in the stationary phase.

Inside a homologous series an incremental rise of $\ln V_g^0$ with the carbon number was observed. It is worthwile to note that branching of the solute molecule in the hydrocarbon backbone effects a significant reduction of V_g^0. Comparing the V_g^0 of n-octane with 2-methylheptane and 2,2,4-trimethylpentane, resp. it can be seen that the number of branches in the solute molecule is determinant for lowering the V_g^0 on the PS sites (Fig. 1). Further the comparision of hexane with 2-methyl-pentane and 3-methyl-pentane indicates that branch points near the end of the solute molecule are more effective in lowering the specific retention volume (Fig. 2).
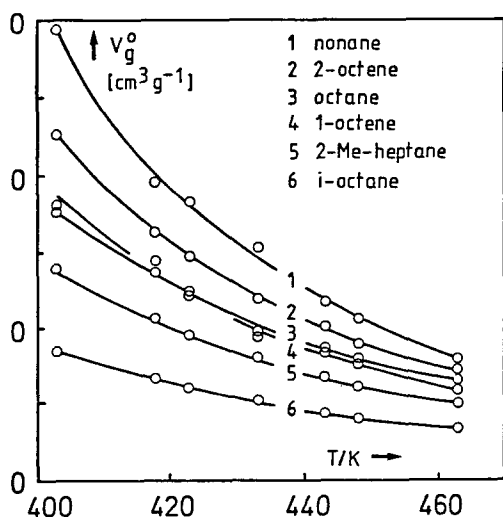

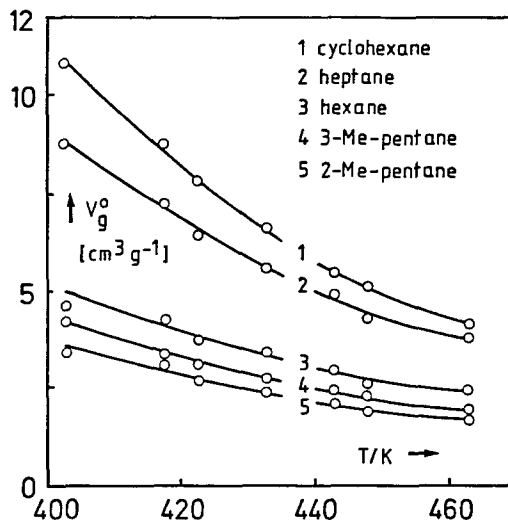Fig. 1. T-dependence of V_g^0 for isomeric octanes, octenes and nonane

Fig. 2. T-dependence of V_g^0 for isomeric hexanes, cyclohexane and heptane

The directly derived thermodynamic function is the partial molar free energy of sorption, ΔG_1^S, calculated according to eq 4.

At a given temperature the $\Delta G_1{}^S$ values can be presented for the n-alkanes and n-alkylbenzenes as linear functions of the carbon number of the molecule and of the alkyl chain, resp. (see. Table). The slope of these lines is interpreted as an incremental contribution to $G_1{}^S$ of the dispersive interactions of the methylene groups and the PS sites. A comparision between alkanes and alkylbenzenes indicates, within the experimental error that the $-CH_2$-contribution is (2.2 kJ mol^{-1}), not depending whether these groups belong to pure alkanes or to an alkyl chain of an alkylbenzene. The more negative slopes at lower temperatures (Table 1) indicate the exothermic sorption effect of the methylene groups once again. The contribution of the phenyl groups to the sorption process on the PS sites may be estimated easily from the intercepts in the $\Delta G_1{}^S$ versus nC plot for both solutes series. With increasing temperature $\Delta G_1{}^S(Ph)$ decreases from 19 kJ mol^{-1} at 423 K to 16 kJ mol^{-1} at 463 K. This value indicates that the main contribution to the sorption process of the alkylbenzenes in PS is due to the interactions between the phenyl groups of the solute and the polystyrene. The $V_g{}^o$ lowering effect of side methyl groups is transduced to $\Delta G_1{}^S$ through an endothermic contribution (see Figure 3).

Table 1: Intercept (a) and slope (b) of the linear dependence $\Delta G_1{}^S$ versus the carbon number at selected T

Alkanes	a	b
403 K	28.7	−2.57
433	30.0	−2.38
463	31.4	−2.22
Alkylbenzenes		
413 K	10.1	−2.15
433	12.0	−2.09
463	14.7	−2.00
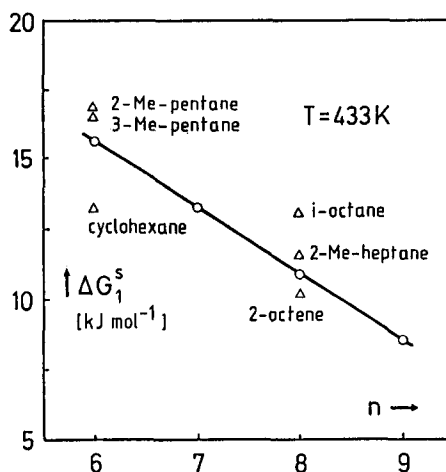
Fig. 3. Influence of solute constitution on $\Delta G_1{}^S$ (kJ mol^{-1})

Once again, this effect is more pronounced if the methyl group is placed near the solute chain end. Compared with hexane, $\Delta G_1{}^S$ increases about 2 kJ mol^{-1} for 2-methylpentane and 1,5 kJ mol^{-1} for 3-methylpentane. The effect due to the side methyl group lowers with the solute chain length: The soprtion process of 2-methyl-heptane is 0,5 kJ mol^{-1} more endothermic than of n-octane. The effect of the number of methyl side groups is evidenced by comparision of n-octane and 2,2,4-trimethyl-pentane in PS. Thus, we conclude that methyl groups establish smaller dispersive interactions with PS sites than methylene groups do. Neglecting an influence of conformation the lower $\Delta G_1{}^S$ value of cyclohexane faced to hexane may support partly this affirmation.

Keeping in mind that the energy of like contact interactions in the pure solute is related to the boiling temperature, further interpretation of the sorption process is possible. A plot of $\Delta G_1{}^S$ vs boiling points reveal a distinct linear dependence for the alkanes as well as for the alkylbenzenes. The vertical shift between the two linear graphs (constant energy of like contact interactions) illustrates the contribution from dipol and from induced dipol forces generated by unlike contacts between the phenyl groups in alkylbenzenes with those in the PS sites.
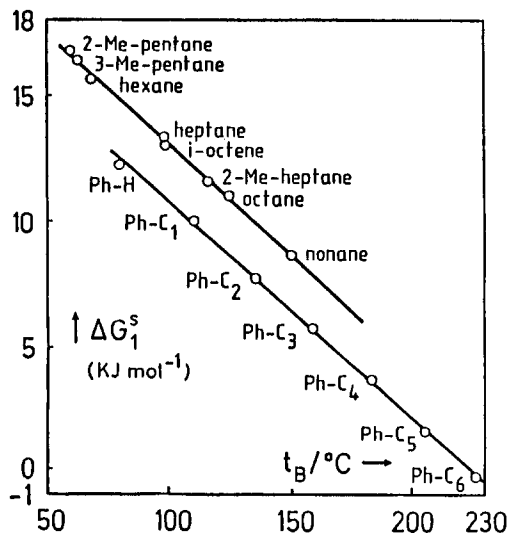
Fig. 4. Correlation of ΔG_1^S (433 K) with the boiling temperatures of selected solutes
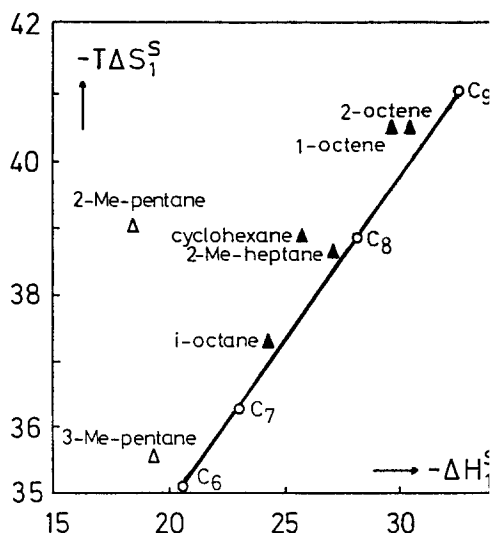
Figure 5. Correlation of $-T \Delta S_1^S$ and $-\Delta H_1^S$ for selected alkanes at 433 K

The enthalphy and entropy of sorption were calculated from the retention data for a more distinct examination. As it can be seen from Figure 5 the overall sorption process of n-alkanes is governed by large sorption entropies. On the other hand, with increasing carbon number of the n-alkanes, the enthalpy of sorption indicates a pronounced trend to rise towards exothermic values, whereas the entropy of sorption changes only slightly. It may be noted that the influence of branching of the solute molecule is caused mainly from the enthalpy of sorption as discussed above. We cannot explain, however, why the entropy of sorption of the branched hexanes is more negative than that of the linear isomer, whereas for the branched octanes the revers applies. On the other hand cyclohexane and the two isomeric octenes show significantly higher exothermic enthalpies of sorption than hexane and octane, respectively. At the same time the entropy of sorption of these solutes is not changed in the same manner. This offers an explanation for the enhanced sorption qualities of those solutes when compared with the respective alkanes.

ACTIVITY COEFFICIENTS AND MIXING FUNCTIONS

The weight fraction activity coefficients were computed according to eq. 6. Even for carefully obtained retention data the activity coefficients scatter at high temperatures as a consequence of: (i) the relative uncertainity of p_1^0, v_2^{sp} at elevated temperatures (ii) the small retention times of low boiling solutes and (iii) the extremly temperature sensitive correction term for nonideal behavior of the solute vapor. For exact values, the correction term in eq 6. cannot be ignored. The order of magnitude and the temperature dependence of the correction term is shown for the alkylbenzenes in Fig. 6.

The activity coefficient Ω_1^∞, and the related thermodynamic mixing functions, i. e. ΔG_1^∞, prove to be more sensitive to changes in the structure of the solute molecules than the sorption functions (see Table 2). Large endothermic ΔG_1^∞ of the linear and branched alkanes illustrate nonsolvent characteristics typically.

The "regularities" as discussed for the sorption process, with respect to the influences of chain extend and branching, are reflected also.

<u>Table 2:</u> Partial molar free energies of mixing ΔG_1^{∞} (kJ mol^{-1}) of the solutes studied in molten atactic PS at selected temperatures

T / K	403	433	463		413	433	463
n-hexane	8.43	8.63	8.79	benzene	5.38	5.68	6.12
n-heptane	8.19	8.38	8.63	toluene	5.43	5.88	6.18
n-octane	7.84	8.04	8.34	ethylbenzene	5.53	5.80	6.24
n-nonane	7.69	8.03	8.28	propylbenzenes	5.62	5.88	6.31
cyclohexane	6.67	6.93	7.46	butylbenzene	5.73	5.96	6.31
2-methylpentane	9.15	9.22	9.66	pentylbenzenes	5.85	6.08	6.42
3-methylpentane	8.72	9.03	9.38	hexylbenzene	6.05	6.26	6.56
2-methylheptane	8.24	8.18	8.47	1-octene	7.52a	7.86	8.10
2.2.4-trimethyl-pentane	8.24	8.47	8.84	2-octene	7.07a	7.46	7.82

a measured at 403 K

Thus, ΔG_1^{∞} decreases with the chain length of the n-alkane molecule. Branching produces an pronounced endothermic contribution to ΔG_1^{∞}, which depends on (i) the position of the branch (ii) the chain length of the solute molecule and (iii) the number ob branch points.
Cyclohexane and the isomeric octenes contrast with the alkanes by showing significantly lower ΔG_1^{∞} values, indicating solvent qualities better than the alkanes. For alkylbenzenes the ΔG_1^{∞} are markedly low an indication for solute – polymer miscibility. The ΔG_1^{∞} data which slightly increase with the alkylchain length, prove that the dispersive type interactions of $-CH_2-$ groups induce lower miscibility with PS. Therefore the two-component type alkylbenzenes offer the possibility to "tailor" ΔG_1^{∞} values, which range from benzene to a polymethylenic chain. The ΔG_1^{∞} prove that all solutes exhibit endothermic heats of dilution in PS, exept benzene, toluene and ethylbenzene (Figure 7). It is noteworthy that toluene has the most pronounced exothermic heat of dilution (-0,8 kJ mol^{-1}). Propylbenzene acts nearly athermic within the temperature range studied.
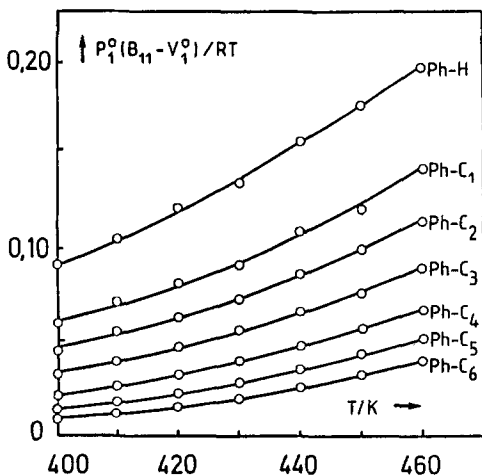

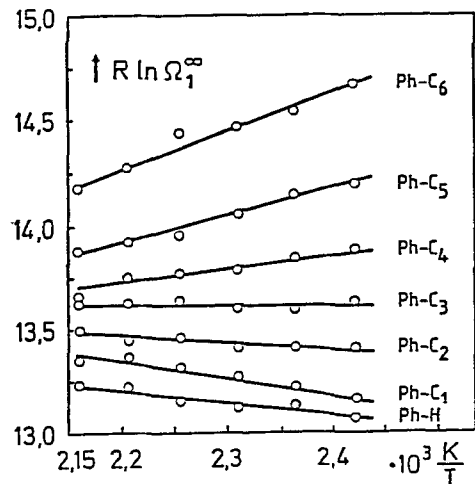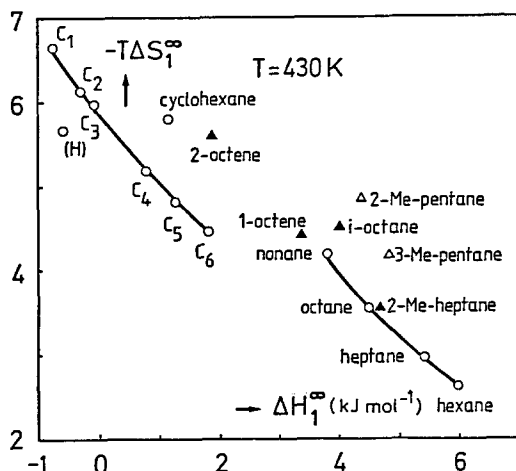Fig. 6. T-dependence of the correction term computed for alkylbenzenes

Fig. 7. T-dependence of $R\ln\Omega_1^{\infty}$ for alkylbenzenes

With the chain extent of alkylbenzenes the enthalpy of dilution yields positive values, i. e. 1.8 kJ mol^{-1} for hexylbenzene. They are significantly lower, however, than those of n-alkanes. It is noteworthy that in contrast the n-alkanes show better mixing qualities at increasing chain length. Branching lowers the ΔH_1^{∞}

values slightly. As demonstrated in Fig. 8 the $-T\Delta S_1^\infty$ term of the branched alkanes is higher than the enthalphy of dilution. Compared with the alkanes the $-T\Delta S_1^\infty$ term of the alkylbenzenes indicates more ordered states for the solvated solute molecule. Oncemore cyclohexane and the two isomeric octenes behave intermediary.

Fig. 8. $-T\Delta S_1^\infty$ vs. enthalpy of mixing ΔH_1^∞

SOLUBILITY PARAMETER FOR POLY(STYRENE)

Following the cohesive energy density concept the energy of mixing is defined for constant volume. In contrast the heat of mixing is derived commonly at constant pressure, with the consequence that the data differ from those at constant volume. As pointed out by Patterson[10] it is suitable therefore to connect ΔG_1^∞ with the solubility parameter. Thus for conditions of ideal "infinite dilution" chromatography, the equation for ΔG_1^∞, may be connected with the square of the solubility parameter difference

$$\Delta G_1^\infty = V_1 (\delta_1 - \delta_2)^2 \tag{9}$$

Table 3: δ_2-parameter for atactic poly(styrene) at different temperatures

T / K	423	443	463
intercept	8.0	7.73	7.45
slope	7.4	7.10	6.78
average	7.7	7.41	7.12

Transforming this equation one derives the solubility parameter δ_2 (PS) from the slope and from the intercept.

The solubility parameter for the solutes were calculated with eq. 1. The corresponding enthalphies of evaporation of the solutes where computed from vapour pressure data taken from various sources[6,7]. Figure 9 shows the plot for atactic poly(styrene) for all solutes studies at 423 K. Similar plots where drawn for all temperatures studied. This method of presenting data enables to visualize solute probes of different thermodynamic interaction on the same plot: benzene and toluene, where dipol and induced dipol forces effect the interactions, as well as nonsolvents like alkanes, where dispersive forces act exchangely. The solubility parameters are presented in Table 3 for some temperatures. An extrapolation of the data to the temperature region around 298 K can be effected without substantial loss of accuracy, as indicated by the correlation coefficients r. Intercepts and slopes follow a polynomial temperature dependence

intercept: $\delta_2 = 11.368 - 2.675 \cdot 10^3 T - 2.50 \cdot 10^{-5} T^2$ $r = 1.000$

slope: $\delta_2 = 9.060 + 6.650 \cdot 10^{-3} T - 2.50 \cdot 10^{-5} T^2$ $r = 0.999$
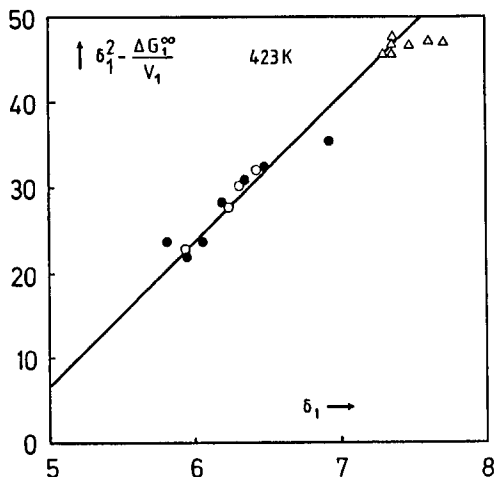
The δ_2 for high temperature 7.1 from the slope and $\delta_2 = 7.6$ from the intercept at 466 K agree well with those obtained by DiPaola-Barany and Guillet[2] with other solute probes. The extrapolated solubility parameter for 298 K is 9.46 from intercept and 8.82 from slope respectively. The average, 9.14 is in good agreement with δ_2, from swelling or viscosity measurements[11], 9.10. Thus, the capability of gas chromatography as an alternative to the conventional methods is confirmed.

Fig. 9: Plot $\delta_1^2 - \Delta G_1^\infty / V_1$ versus δ_1 for all solutes studied

The thermodynamic informations received by gas chromatography on poly(styrene) with a broad series of solutes will be useful in connection with an improved interpretation of solution properties as well as of polymer miscibility. In a further contribution corresponding investigation on polymer blends will be reported.

ACKNOWLEDGEMENT

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