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DETERMINATION OF SOLVENTS FOR THERMALLY STABLE AROMATIC HETEROCYCLIC POLYMERS

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We have developed and tested a relatively rapid experimental procedure to screen and rank potential solvents for aromatic, heterocyclic polymers. Polymers utilized in the study were meta-phenylene PBI, PDIAB, PBO, and ATQ. Quantitative criteria have been developed for using gas chromatographic data to determine solvents for aromatic, heterocyclic polymers. The criteria require gas chromatographic data and polar and hydrogen-bonding solubility parameters for the solvents of interest.

FOREWORD

Dr. Khalid A. Karim was largely responsible for developing the
experimental techniques used in this project and directed day-to-day
activities in the Polymer-Thermodynamics Laboratory. PBI results were
obtained by Mr. Alan Graham and Mr. Kailash Dangayach. PDIAB results
and PBO results were obtained by Mr. Dangayach and Dr. Karim, respectively.
ATQ and poly(ethylmethacrylate) results were obtained by Mr. Dangayach
and Dr. Karim

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SECTION I

INTRODUCTION

A current critical problem is the lack of suitable solvents for the
processing of thermally stable aromatic, heterocyclic polymers. Such
polymers must often be processed or fabricated in solution because they
will not melt, and suitable solvents must be provided before the poly-
mers can be fully utilized. Attempts to use the relatively few existing
solvents for these polymers give rise to serious deleterious effects.
They tend to be either too corrosive or high boiling and difficult to
remove in the processing. Not only are suitable solvents unavailable
for otherwise useful thermally stable polymers, but current methods of
solvent searches have not provided the kind of data necessary to pro-
mote the discovery of new solvating molecular structures.

The technique of gas-liquid chromatography (GLC) has been utilized
in this work as a rapid and reproducible means of studying solvent inter-
actions with aromatic, heterocyclic polymers in order to develop solvents
or solvent systems for aromatic, heterocyclic polymers.

The polymer studies reported here are for the polymers meta-phenylene
PBI, PBO, PDIAB, and ATQ. Structures for these polymers are shown in
Appendix A. The solvents tested are listed in Appendix B , along with
their relevant physical properties. Gas chromatographic data for all
solvents tested are presented in Appendix C . Results of a study for
ATQ are presented in Appendix D . Finally, in Appendix E we report a
study for poly (ethyl methacrylate). The poly (ethyl methacrylate) study
show how gas chromatography results can be interpreted for molten polymers.

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SECTION II

EXPERIMENTAL PROCEDURE

For each study, we used a gas chromatograph equipped with thermal conductivity detectors. Stainless steel tubes of about 20 cm length, 2.2 mm i.d., and 0.47 mm wall thickness were packed with 40-300 mg of polymer by vibration. Helium was used as the carrier gas and was dried by passage through a gas purifier containing silica gel and molecular sieves. The gas inlet pressure was measured by a sensitive pressure gauge. Flow rates in the range 2-12 ml/min (STP) were used and checked using a bubble flow meter. Injector and detector temperatures were kept at least 20°C higher than the boiling point of the highest-boiling injected samples.

Our sampling technique was based on drawing a sample of a solute using a 1 μℓ Hamilton syringe and flushing out. Usually, traces of the sample are left in the syringe, and we refer to these traces as "residual". Approximately 0.1 μℓ of the residual was injected into the chromatograph.

In most cases, the results obtained depended on sample size, so gas chromatographic results were extrapolated to zero peak height, corresponding to zero sample size.

As we show later, the most reproducible results were usually obtained by using one constant, small helium flow rate of approximately 3-4 ml/min. rather than taking results at several flow rates and extrapolating to zero flow rate.

A schematic diagram of the GLC apparatus is shown in Figure 1. Helium flow was regulated to ± 0.1 ml/min (STP), and oven temperature was controlled to better than ± 0.1°C.

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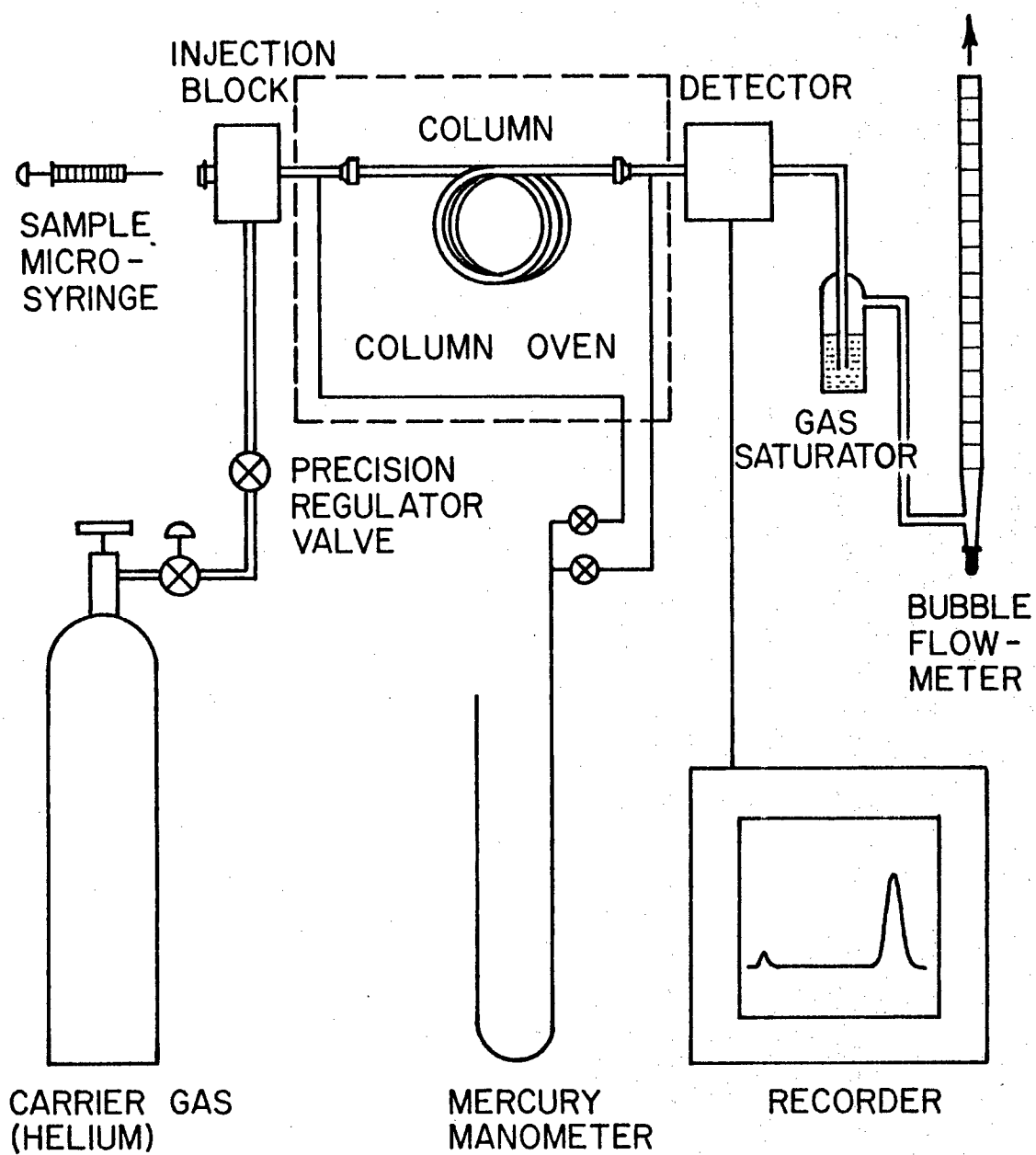
FIGURE 1 - Gas Chromatographic Apparatus

SECTION III

THEORETICAL TREATMENT

Using standard techniques (Cheng and Bonner, 1974), one can calculate the specific retention volume V_g^o corrected to 0°C of each sample injected into the GLC column.

$$V_g^o = F(t_g - t_a) \, J/W \, (273.2/T) \qquad (1)$$

where V_g^o = specific retention volume of injected sample per gram of polymer in the column, cm^3/g.

F = flow rate of helium at ambient temperature, cm^3/min.

t_g = retention time of injected sample, min.

t_a = retention time of air injected with sample, min.

J = correction of flow rate to average column pressure

W = mass of polymer in column, g.

T = ambient temperature in K.

If the carrier gas flow rate F is measured at the column outlet, J is given by the following equation.

$$J = (3/2) \, [(P_i/P_o)^2 - 1] \, / \, [(P_i/P_o)^3 - 1] \qquad (2)$$

where P_i = pressure at column inlet.

P_o = pressure at column outlet

The value of V_g^o is related to the distribution coefficient k for the injected solvent [Meyer (1973)]. The distribution coefficient is defined by

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$$k = \frac{x}{p} \tag{3}$$

where x = mole fraction of the solvent in the stationary phase

p = partial pressure of the solvent in the gas phase

The relation between k and V_g^o is simple.

$$k = \frac{M_2}{273.2\ R} V_g^o \tag{4}$$

Where R is the gas constant and M_2 is the polymer molecular weight

From the value of V_g^o, one can calculate standard partial molar Gibbs energy ($\Delta\bar{g}_1^\infty$) and partial molar enthalpy ($\Delta\bar{h}_1^\infty$) for the following process. The gas chromatographic process at equilibrium, at temperature T and 1 atm, is the transfer of one molecule of injected solvent from the gas phase to the pure polymer stationary phase (in our case, the polymer surface). Thus, we may calculate $\Delta\bar{g}_1^\infty$ and $\Delta\bar{h}_1^\infty$ as follows:

$$\Delta\bar{g}_1^\infty = -RT\ \ln\left(\frac{M_2}{273.2\ R} V_g^o\right) \tag{5}$$

and
$$\Delta\bar{h}_1^\infty = RT^2\ d(\ln V_g^o)/dT \tag{6}$$

where T is column temperature.

Based on justifications offered by Dwyer and Karim (1975), $\Delta\bar{g}_1^\infty$ and $\Delta\bar{h}_1^\infty$ can be represented to a first approximation as linear sums of terms due to polarizability, dipole moment, and association (e.g., hydrogen bonding).

$$\Delta\bar{g}_1^\infty = a'\alpha_1 + b'\mu_1 + X' \tag{7}$$

and
$$\Delta\bar{h}_1^\infty = a\alpha_1 + b\mu_1 + X \tag{8}$$

where α_1 = solvent polarizability

μ_1 = solvent dipole moment

a, a', b, b' = constants

X, X' = interaction parameters.

Dwyer and Karim (1975) have shown that X represents the enthalpy of chemical association (e.g., hydrogen bonding or change-transfer complexing).

We shall see in later sections of this report that the individual contributions to $\Delta \bar{g}_1^{\infty}$ and $\Delta \bar{h}_1^{\infty}$ provide insight into the nature of solvent interactions with aromatic, heterocyclic polymers.

All of the aromatic, heterocyclic polymers discussed in this report have glass transition temperatures in excess of approximately 300°C. Therefore the interactions under study are those involving adsorption of a solvent on the surface of a glassy polymer. We shall therefore refer to our results as those derived from gas-solid chromatography (GSC).

For glassy polymers, it is unfortunately not possible to derive solution activity coefficients or Flory-Huggins interaction parameters because diffusion of the injected solvent into the polymer cannot occur during the time scale of the experiment. Our analysis of results is therefore limited to evaluation of thermodynamic data representing only surface adsorption, such as $\Delta \bar{g}_1^{\infty}$ and $\Delta \bar{h}_1^{\infty}$.

SECTION IV

RESULTS FOR PBI, PDIAB, AND PBO WITH SINGLE SOLVENTS

Three polymers, meta-phenylene PBI, PDIAB, and PBO, were tested with a battery of up to 69 candidate solvents using gas-solid chroma-

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tography (GSC). Temperatures ranged from 140°C to 250°C. A fourth polymer, ATQ, was tested in a different manner. The ATQ results are presented in Appendix D.

The repeat-unit structures of PBI, PDIAB, and PBO are shown in Appendix A. Solvents and their physical properties are tabulated in Appendix B . GSC data are tabulated in Appendix C, and calculated values of $\Delta \bar{g}_1^{\infty}$ are given in Appendix C.

Interpretation of $\Delta \bar{g}_1^{\infty}$ Results

In order to understand the $\Delta \bar{g}_1^{\infty}$ results, we have plotted $\Delta \bar{g}_1^{\infty}$ for each polymer at a temperature of approximately 150°C. For each polymer, $\Delta \bar{g}_1^{\infty}$ is plotted versus solvent polarizability (gas phase polarizability at 25°C). The $\Delta \bar{g}_1^{\infty}$ plots are given in Figs. 2, 3, and 4. The normal alkanes form a reference line for each polymer (Dwyer and Karim, 1975; Appendix E).

The qualitative appearance of Figures 2, 3, and 4 is nearly identical. Substances which can form hydrogen bonds with the polymers or can associate by electron charge-transfer complexing give strong interactions (large distances above the alkane reference line). Particularly strong interactions are exhibited by acids, acetamides, amines, alcohols, and ketones. Halogenated compounds do not tend to exhibit extremely large interactions.

In order to eliminate the effect of purely dispersion forces from the measured data, we plot the values of $(\Delta \bar{g}_1^{\infty})_{ad}$, the distance between the data in Figures 2, 3, and 4, and their respective alkane lines, versus solvent dipole moment. The $(\Delta \bar{g}_1^{\infty})_{ad}$ results are shown in

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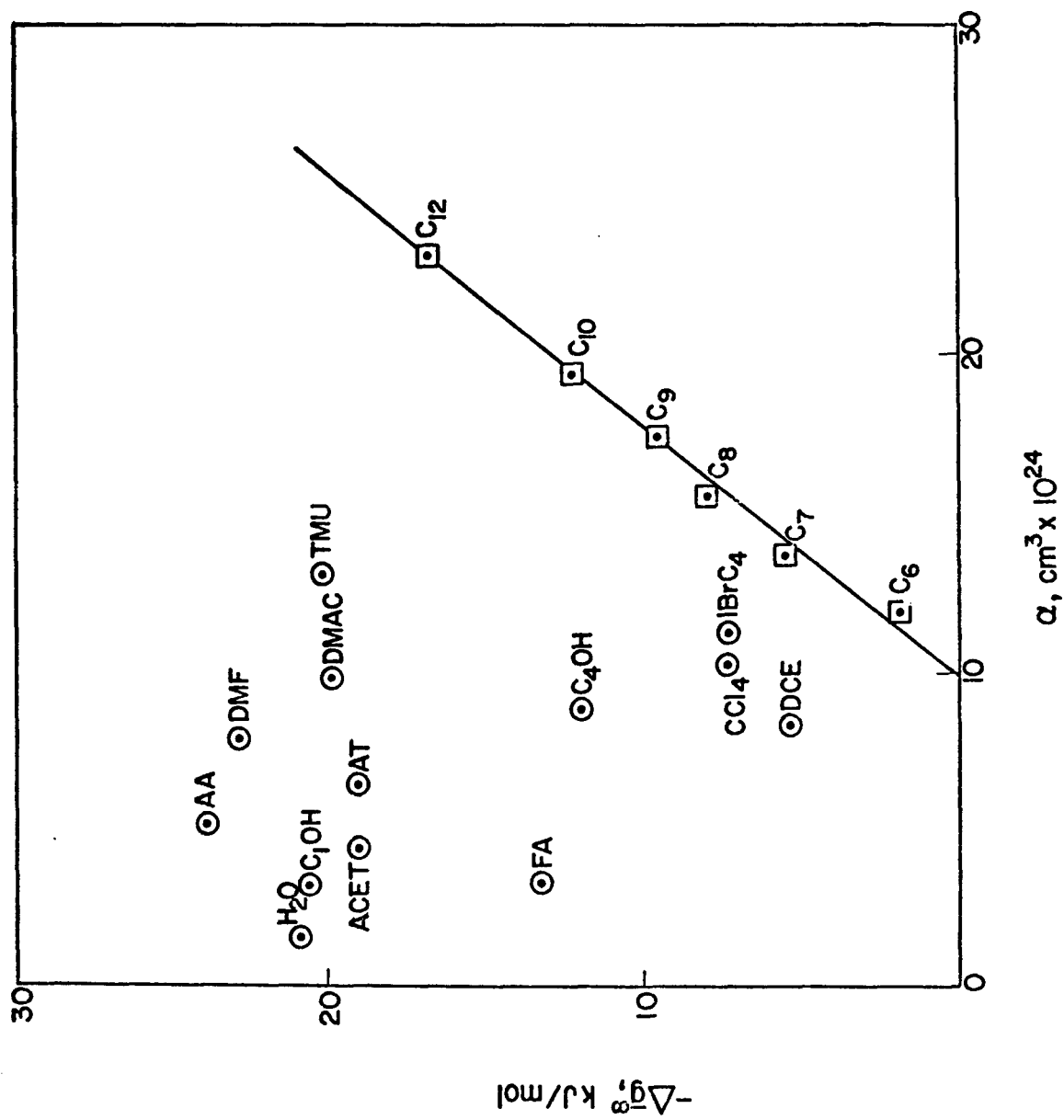
FIGURE 2 – Partial Molar Gibbs Energy of Interaction for Solvents in PBI at 141.8°C.
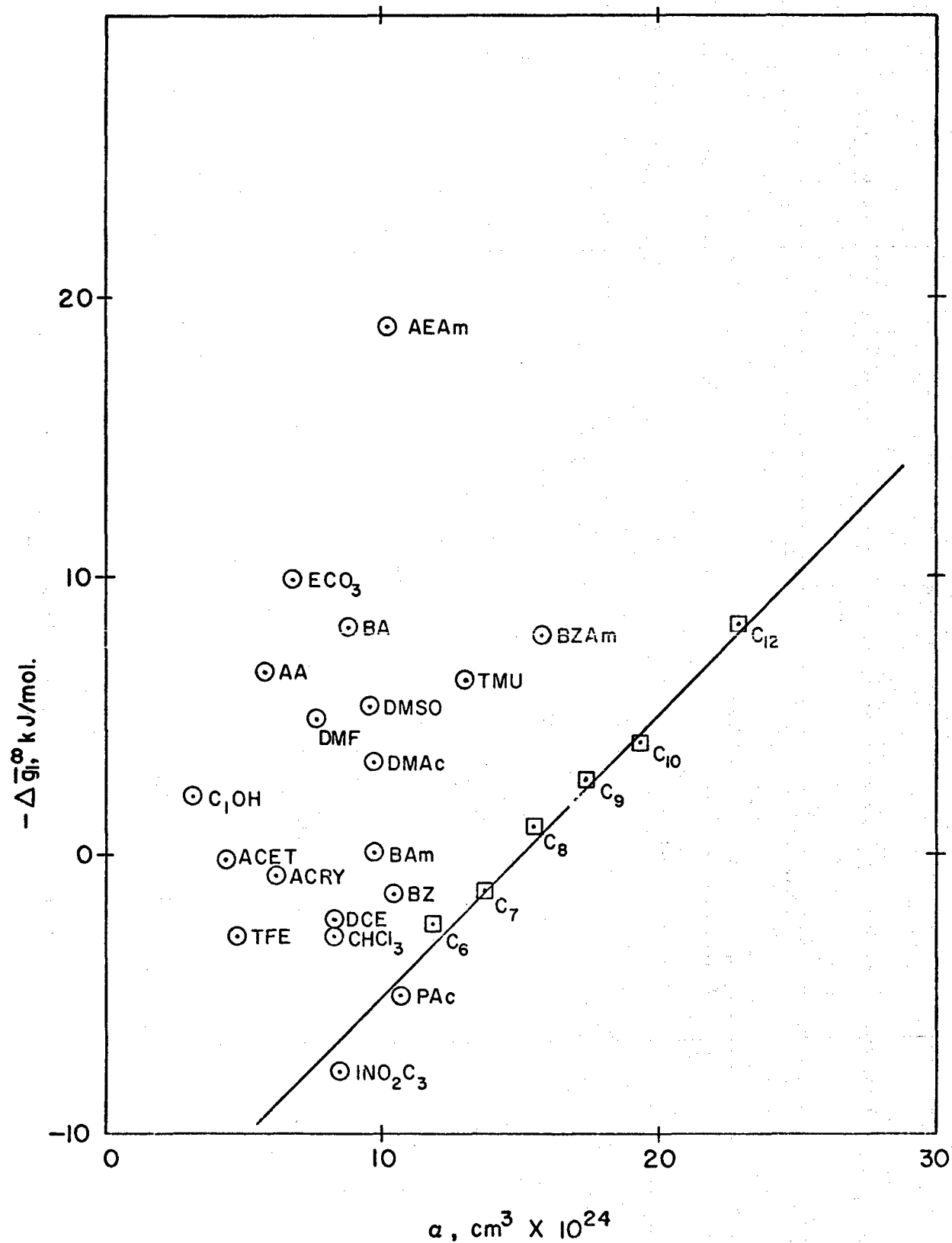
FIGURE 3 - Partial Molar Gibbs Energy of Interaction for Solvents in PDIAB at 150°C.

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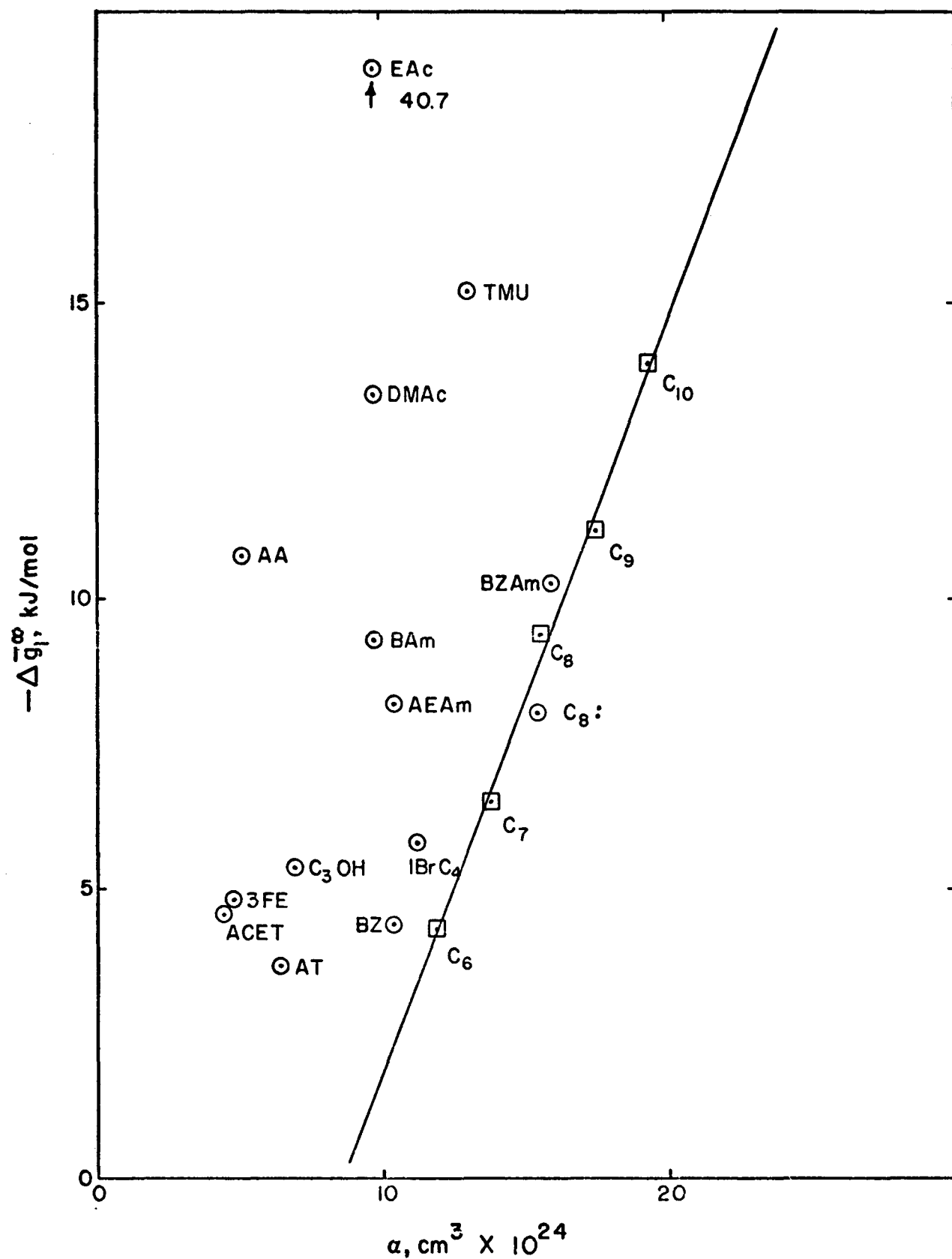
FIGURE 4 - Partial Molar Gibbs Energy of Interaction for
Solvents in PBI at 149°C.

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Figures 5, 6, and 7, respectively, for PBI, PDIAB, and PBO. Only data for representative compounds are plotted in Figs. 5-7.

The solid lines in Figs. 5-7 are determined by a statistical fit of data for polar substances which would not be expected to form hydrogen bonds with or to associate with the polymer studied.

The distance of the data above the polar reference line is denoted by X'. The value of X' represents the contribution of "specific interactions" such as hydrogen bonding, electron charge-transfer association, or chemical reaction.

A few compounds fall below the reference line. In most instances this occurs because the alkanes are not a suitable reference for all substances (Dwyer and Karim, 1975). Also, experimental error in the dipole moment assignments can cause compounds to fall below the polar reference line.

The classes of compounds which exhibit the greatest specific interactions are the organic acids, amides, acetamides, alcohols, and amines.

While the data illustrated in Figures 2-7 indicate which functional groups form the strongest bonds with PBI, PDIAB, and PBO, the data do not indicate which of the solvents tested do in fact dissolve the polymer. The data indicate only which substances have one of the characteristics required of solvents for these polymers: strong specific associations. We will return to this point later.

There is, however, another type of useful information that can be obtained from values of $\Delta \bar{g}_1^\infty$. To illustrate this, we plot $\Delta \bar{g}_1^\infty$ at two temperatures for several substances interacting with PBI, PDIAB, and PBO. The plots are given in Figs. 8, 9, and 10 for PBI, PDIAB, and PBO, respectively.

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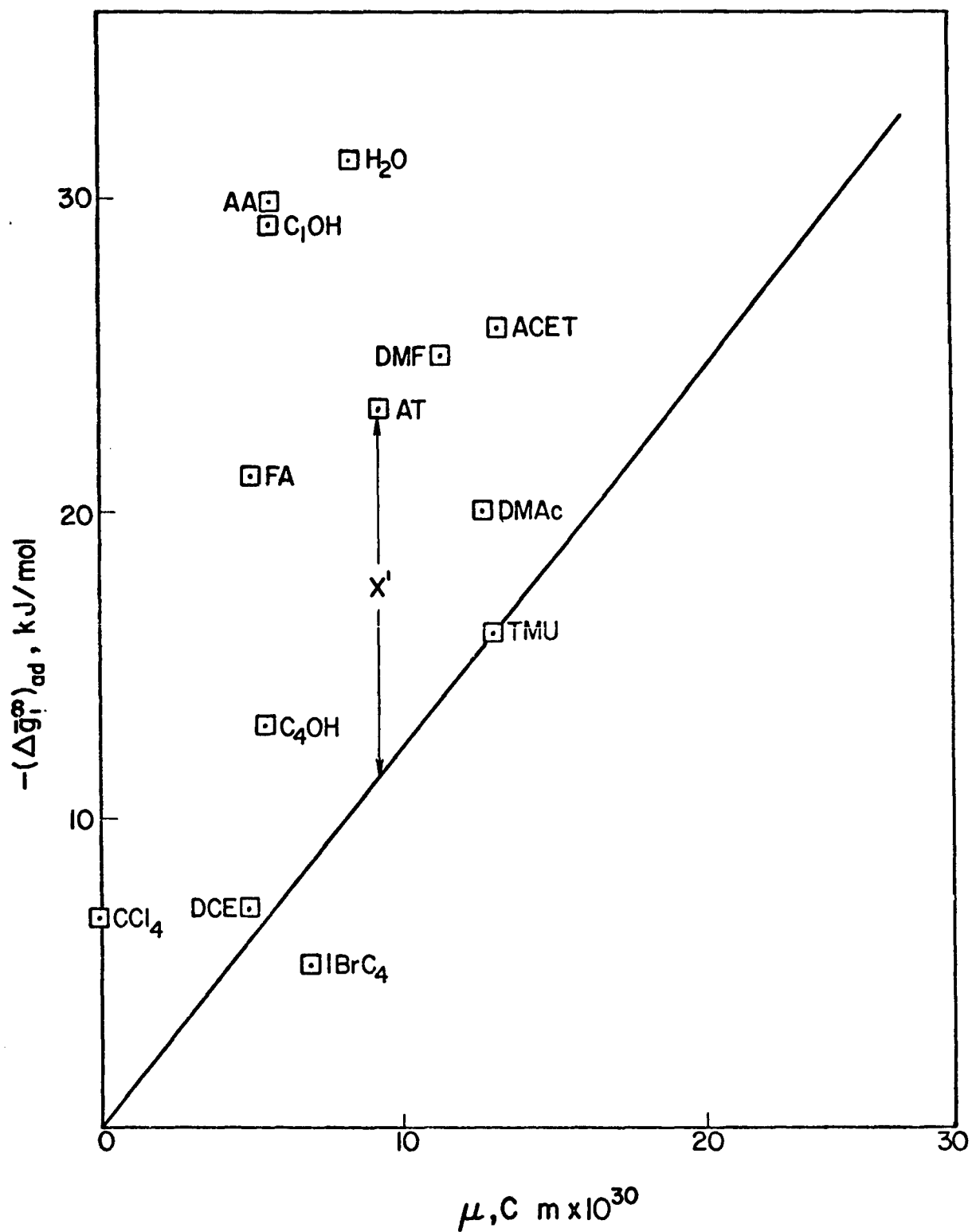
FIGURE 5 - Specific Interactions for Solvents in
PBI at 141.8°C.
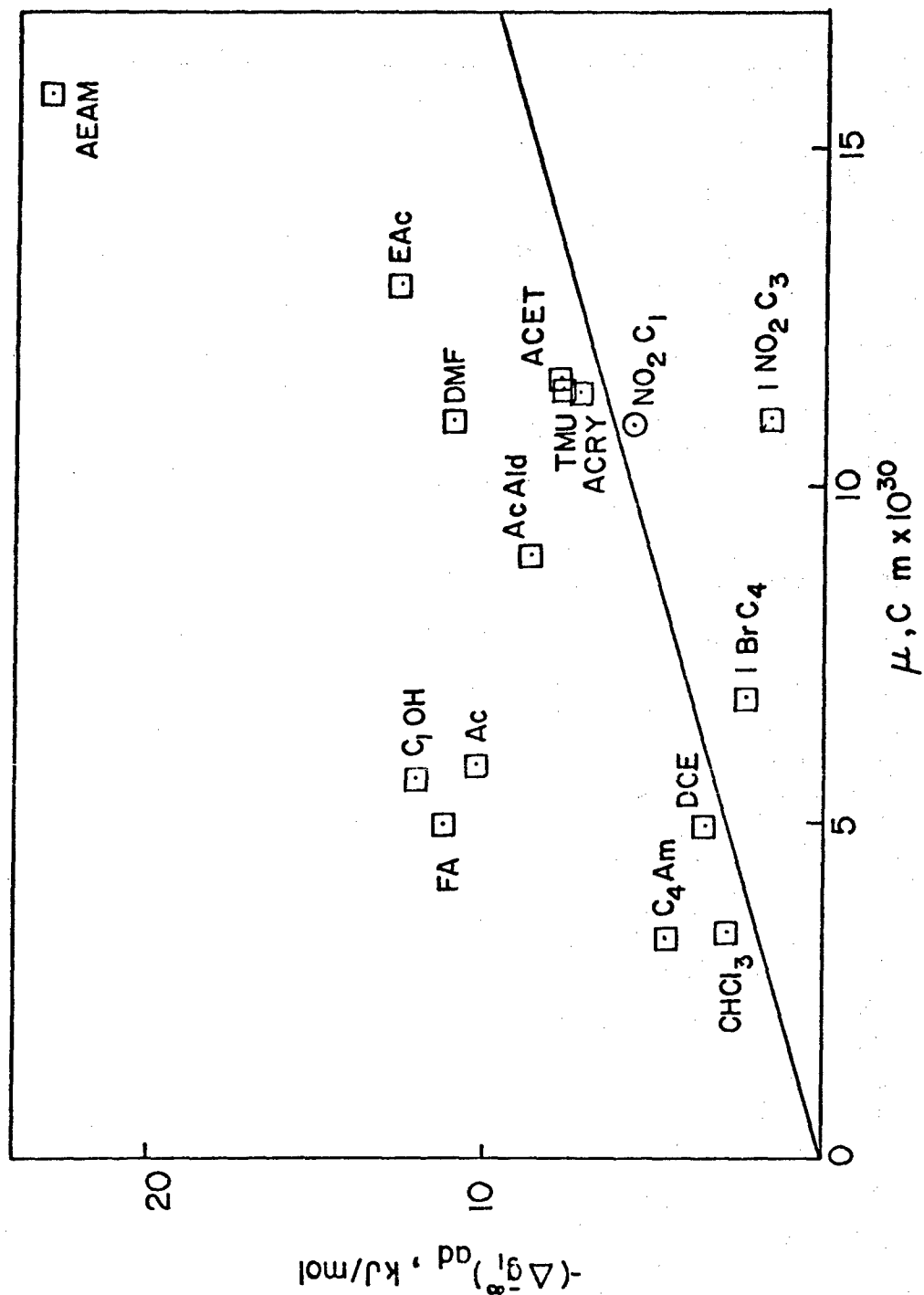
FIGURE 6 – Specific Interactions for Solvents in PDIAB at 150°C.

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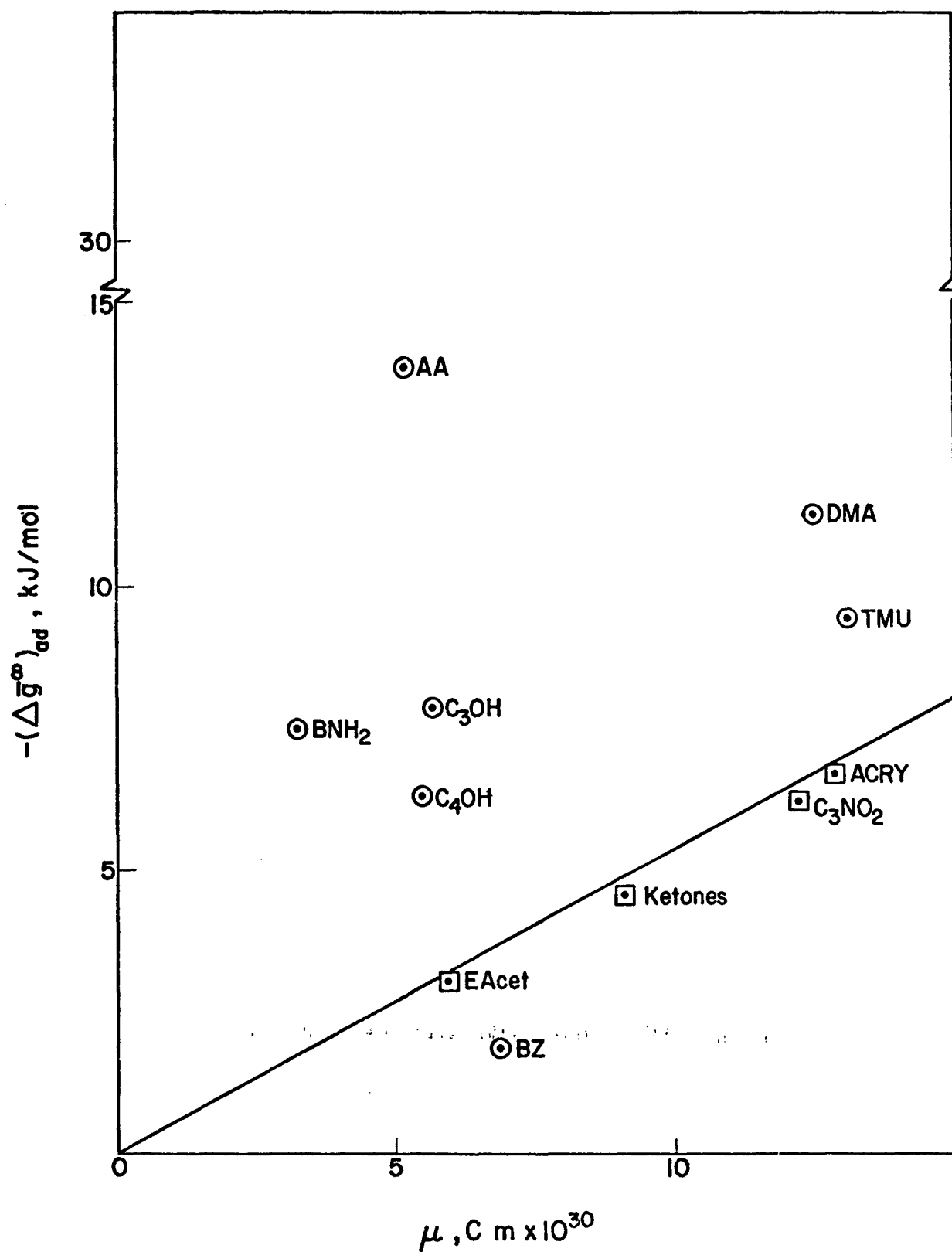
FIGURE 7 - Specific Interactions for Solvents in PBO
at 149°C.

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If the specific interaction contributing to $\Delta\bar{g}_1^\infty$ is hydrogen bonding or charge-transfer complexing, one would expect that $\Delta\bar{g}_1^\infty$ would <u>decrease</u> with <u>increasing</u> temperature for a given solvent. The decrease would be brought about by the increasing kinetic energy of each molecule, tending to break the weak bonding associated with specific interactions. This would result in a smaller fraction of the solvent molecules interacting with polymer at high temperatures, thus lowering $\Delta\bar{g}_1^\infty$ (Prausnitz, 1969; Prigogine and Defay, 1954). As seen in Figures 8-10, precisely such behavior is exhibited by alcohols and Lewis acids such as chloroform. "Non-specifically" interacting substances such as alkanes also behave similarly due to weakening of van der Waals forces at high temperatures.

There are, however, some notable exceptions to this pattern: DMF, DMAc, acetylethanolamine, and acetic acid (in the case of PBI only). We classify solvents whose interactions with polymers strengthen with increasing temperature as "reactive solvents".

In order for $\Delta\bar{g}_1^\infty$ to decrease with increasing temperature, as it does for the solvents noted above, a net endothermic process ($\Delta\bar{h}_1^\infty > 0$) must occur since from classical thermodynamics

$$\left(\frac{\partial (\Delta\bar{g}_1^\infty / T)}{\partial T} \right)_p = -\frac{\Delta\bar{h}_1^\infty}{T^2} \tag{9}$$

Formation of hydrogen bonds and the like between a polymer and a solvent diffusing onto the polymer surface from a low-pressure gas phase in the chromatograph is an exothermic process ($\Delta\bar{h}_1^\infty < 0$). This indicates that for a "reactive solvent" other mechanisms, which are endothermic, must be at work in addition to specific interaction.

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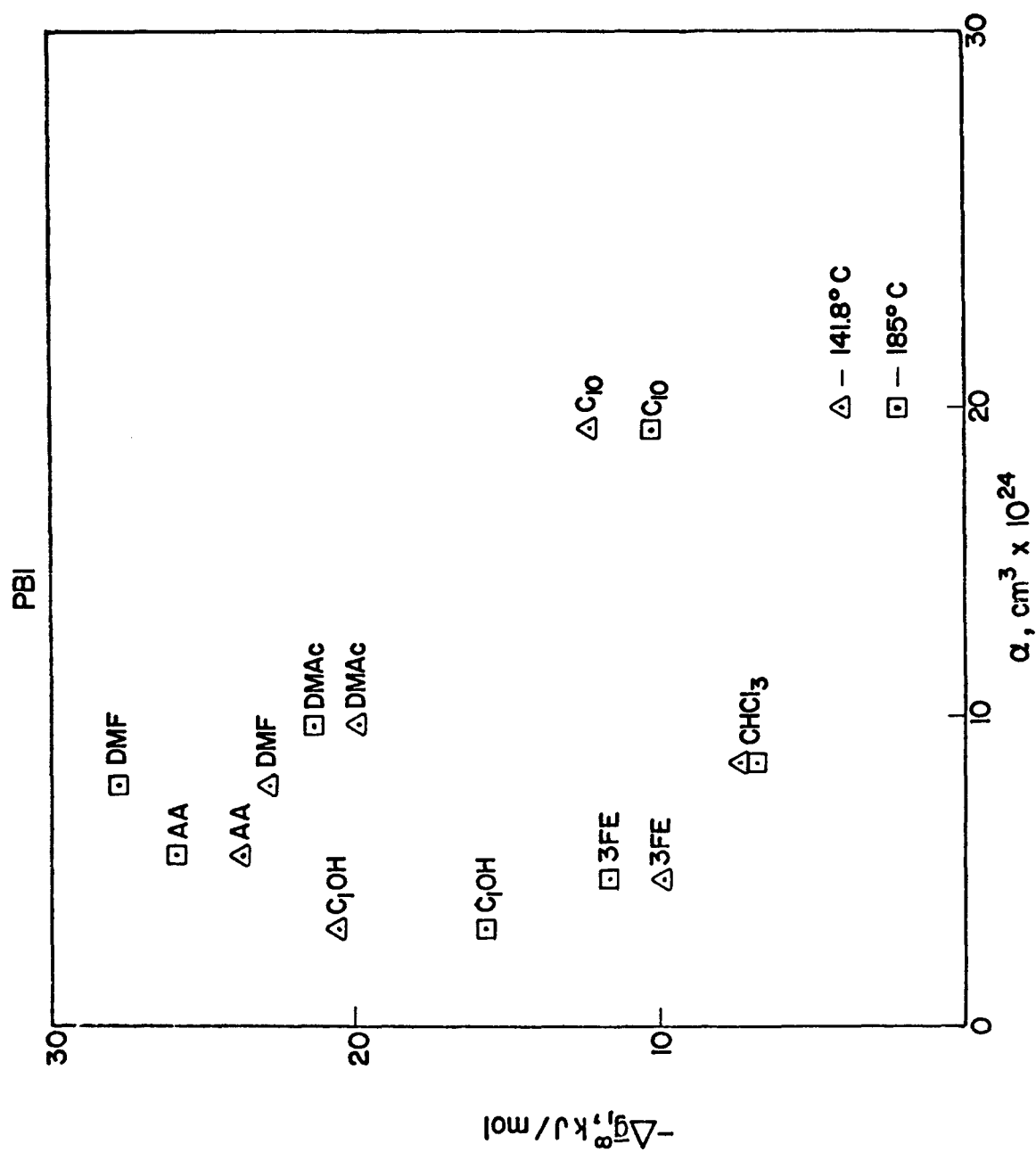
FIGURE 8 - Effect of Temperature on Partial Molar Gibbs Energy
Results for PBI

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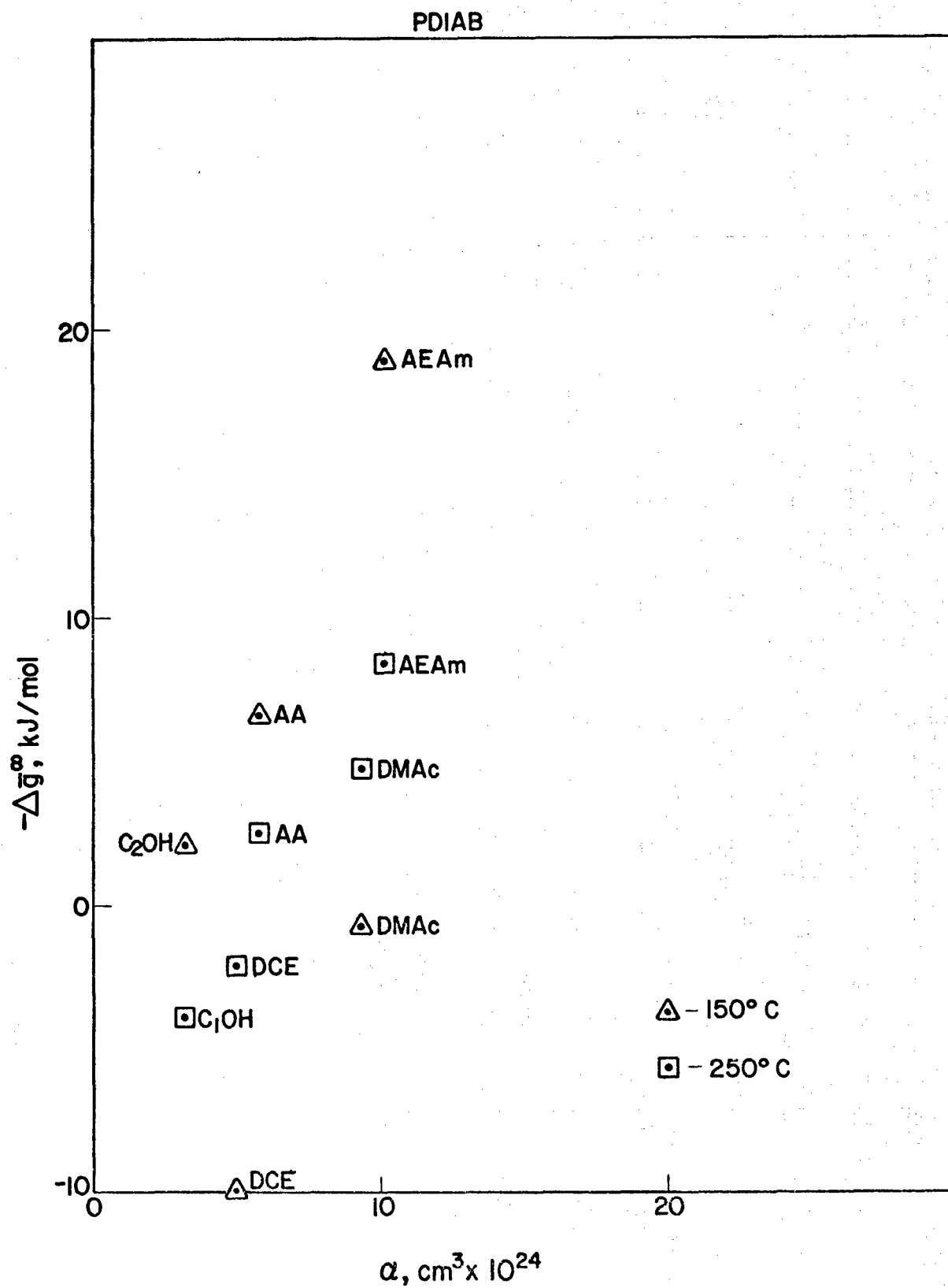
FIGURE 9 - Effect of Temperature on Partial Molar Gibbs
Energy Results for PDIAB.

$-\Delta \bar{g}^{\infty}$, kJ/mol

△ EAc
↑ 40.7
⊡ EAc

⊡ DMAc

△ C_{10}

△ DMAc

⊡ C_{10}

△ AA

⊡ AA

△ IC_4OH

⊡ IC_4OH

△ $IBrC_4$

⊡ $IBrC_4$

△ - 149°C

⊡ - 185°C

0   10   20

α, cm^3 x 10^{24}
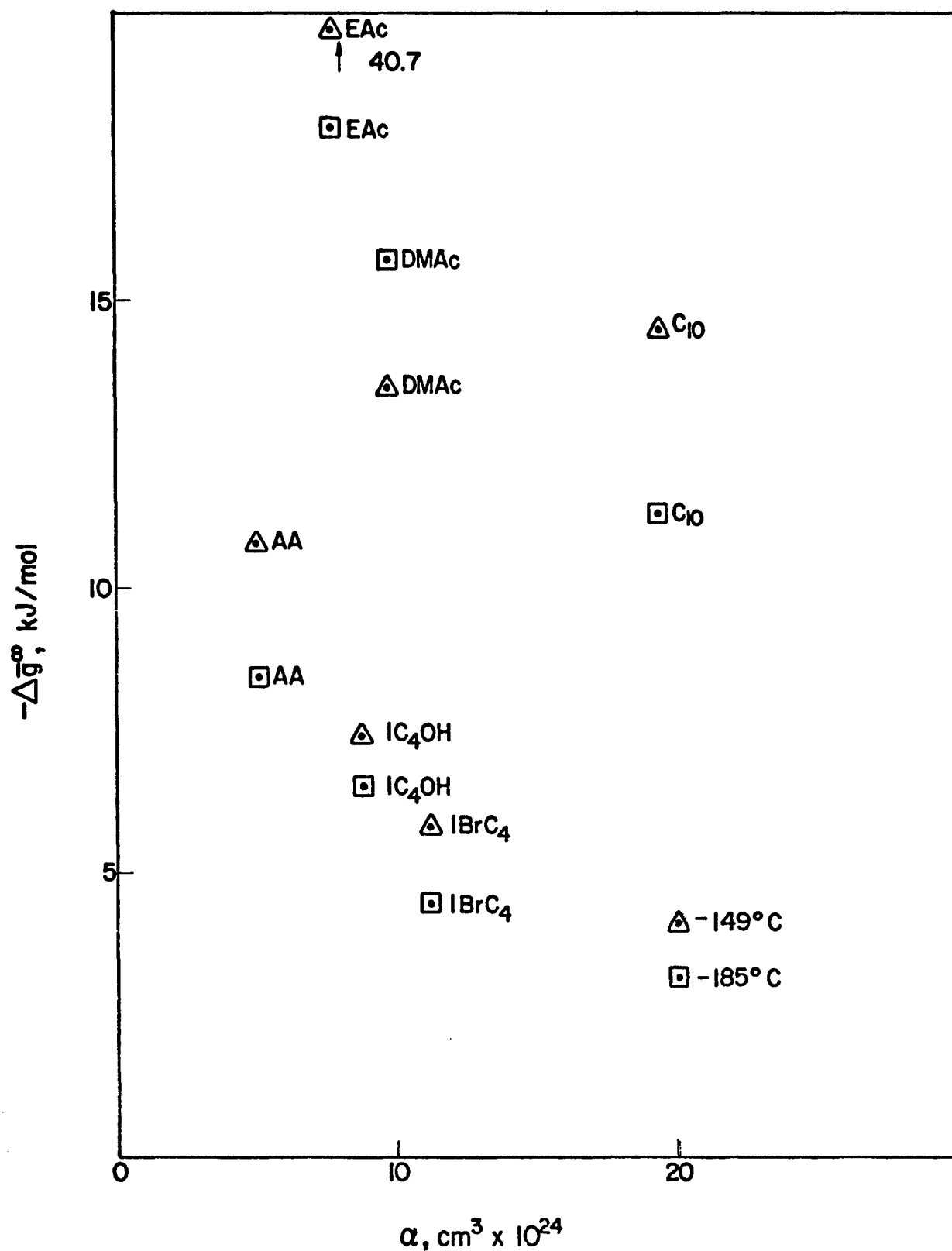
FIGURE 10 - Effect of Temperature on Partial Molar Gibbs
Energy Results for PBO.

There is one direct, experimental indication that reaction may be occuring between some of the test solvents and the polymers. When acetic acid (AA) is injected into GSC columns packed with PBI, at 150°C or 185°C, three peaks (in addition to air) are observed in rapid succession. Two are small and one is quite large in area. Blank runs with acetic acid give only one peak (followed much later by a water peak). The two small peaks may be reaction by-products. Unfortunately, we have not yet been able to identify the small peaks.

We now turn to a discussion of PBI, PDIAB, and PBO separately.

meta-phenylene PBI

There are several known non-acid solvents for PBI. Among them are DMAc and DMF. At low temperatures (~25°C) some fluorinated compounds are also solvents for PBI.

Representative data for PBI at 142°C are given in Figures 2, 5, and 8. As can be seen in Figure 2, many solvents show strong interactions with PBI. A large difference between the $\Delta \bar{g}_1^\infty$ value of a solvent and the alkane reference line does not mean that the solvent will dissolve PBI. It merely means that there is strong bonding with the polymer. An extreme example is water. Figure 2 indicates that water has nearly the strongest interaction with the polymer of any substance tested. In order to understand the reason for the interaction, we plot $(\Delta \bar{g}_1^\infty)_{ad}$ versus solvent dipole moment in Figure 5. If X' $[(= (\Delta \bar{g}_1^\infty)_{ad} - (\Delta \bar{g}_1^\infty)_{ad\ polar,\ non\text{-}assoc})]$ is significantly greater than zero, then there is very strong specific association at work. In the case of water, the interaction is almost certainly extensive hydrogen bonding. Figure 5 shows that molecules such as acetic

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acid and methanol, which should be able to form hydrogen bonds of nearly
the same strength as those of water, have X' values nearly equal to that
of water.

Why, then, are acetic acid and methanol not good solvents for PBI,
where as DMF and DMAc are solvents for PBI, even though their X' values
are smaller than that of water? The answer to this question lies not
so much in the strength of bonding but in the effect of the bonding.

In order to dissolve thermally stable polymers, a solvent must not
only bond with one molecule but must be able to reduce inter-and intrachain
bonding which cause polymer chain stiffness. The molecules DMF and DMAc
contain postively charged nitrogen atoms and negatively charged carboxyl
groups.

$$
CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - N \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}
\qquad\qquad
CH_3 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - N \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}
$$
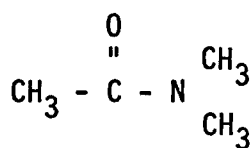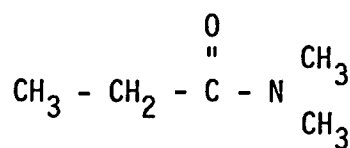
DMF   DMAc

The charged nitrogen and C=O groups can interact strongly with the polymer
chain. The DMF and DMAc molecules are also sufficiently bulky that they
probably prevent interaction of PBI segments from different polymer chains.

Based on the preceding argument, good solvents for PBI are probably
charged species which are sufficiently bulky to block inter-chain bonding
and exhibit moderately large X' values.

Another reason that some solvents dissolve PBI substantially better
than others is shown in Figure 11. Formamide is not as good a solvent

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(a)

PBI   Chain   Chain   Interaction

(b)

PBI   With   Formamide   Replacing   Chain
                Chain   Interaction

(c)

PBI   During   Dimethylformamide   Solvation
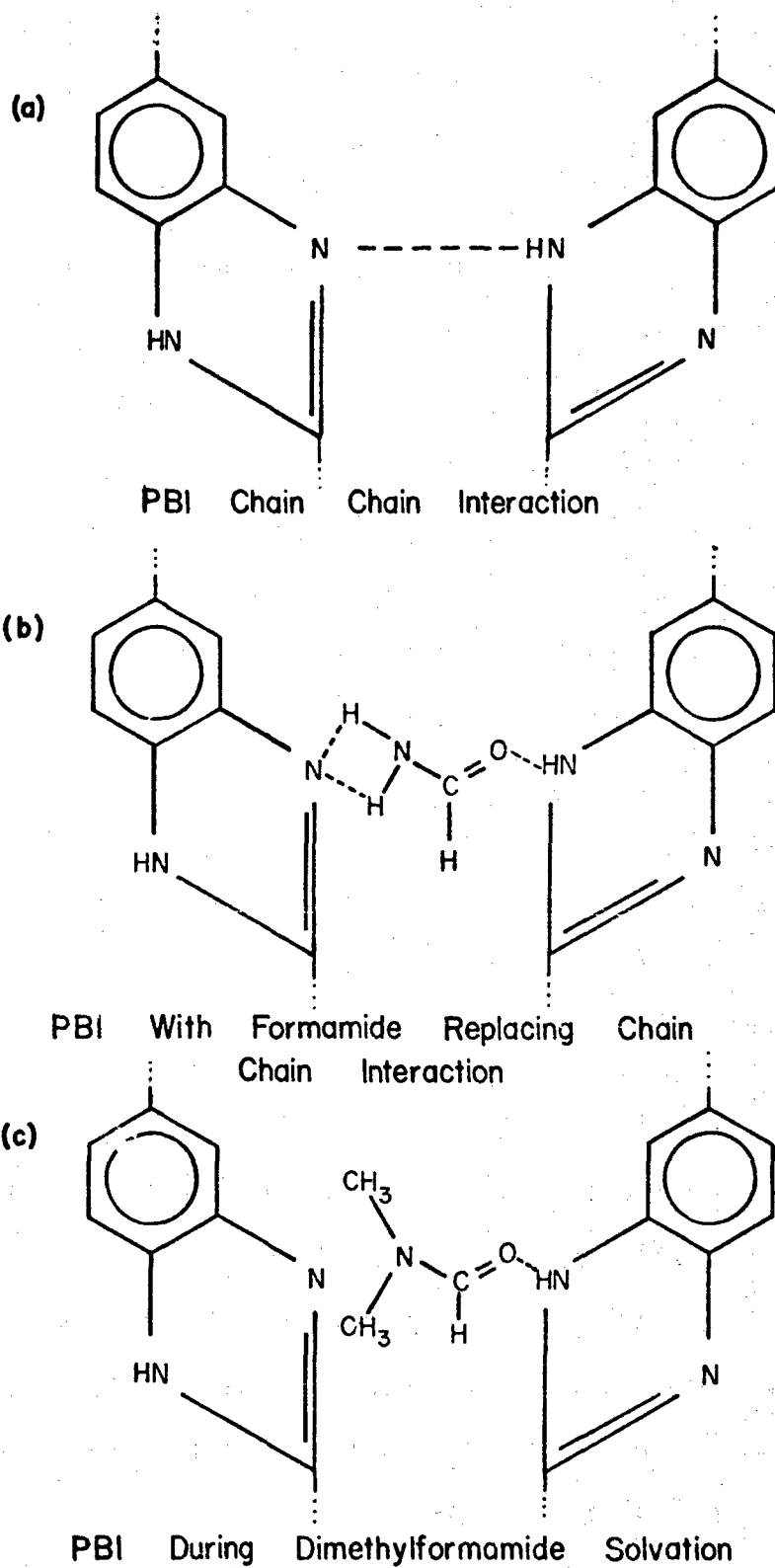
FIGURE 11 - Effect of Solvent Structure
on Interchain Bonding

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for PBI as DMF. A possible reason for this can be seen in Figure 11. As shown in part (b) of Figure 11, formamide can, in effect, replace a chain-chain interaction in PBI, not forcing chain separation. As shown in part (c) of Figure 11, the pendant methyl groups of DMF prevent bonding with two PBI chains. Thus if a DMF molecule hydrogen bonds with a PBI segment, an interchain bond between two PBI segments must be broken. This allows the PBI chain with DMF bonded to it to become more flexible than in its pure state and easier to dissolve.

As seen from Figure 8, the best solvents for PBI also appear to interact endothermaically: $\Delta \bar{g}_1^{\infty}$ increases with increasing temperature. This behavior may indicate that some mechanism similar to a reversible chemical reaction is occurring.

Since PBI is the only polymer we have worked with that is soluble in several compounds, we have attempted to devise a ranking scheme that has a one-to-one correspondence with actual solubility results. By analogy with the definition of weight-fraction, activity coefficient of a solvent in a molten polymer (Bonner and Prausnitz, 1973), we have defined an empirical, "pseudo" activity coefficient for surface interactions.

$$\Omega_1^{\infty}{}_{ps} \simeq \lim_{w_1 \to 0} (a_1/w_1) \simeq \frac{273.2 \, R}{P_1^{S} V_g^{\circ} M_1} \tag{9}$$

where P_1^{S} = solvent vapor pressure at column temperature

R = gas constant

M_1 = solvent molecular weight

w_1 = weight fraction solvent in solution

We performed beaker-scale solubility tests of PBI in four solvents at 91°C (the highest temperature at which we could practically conduct

the studies). Weighed samples of PBI were placed in beakers filled with a solvent at 91°C. The solvent level was replenished to keep the volume of solvent constant. After 24 hours the liquid above the polymer was removed and discarded. The undissolved polymer was dried and weighed to determine its percent weight loss by dissolution in the solvent.

The results of the beaker-scale study are shown in Table 1. The values of $\Omega_1^\infty {}_{ps}$ shown in Table 1 were obtained by plotting $\Omega_1^\infty {}_{ps}$ values at 148°C and 185°C on a semi-logarithmic plot versus reciprocal temperature and extrapolating linearly to 91°C.

A small value of $\Omega_1^\infty {}_{ps}$ should indicate better solubility, and it is clear that the trend shown in Table 1 indicates that polymer solubility in a solvent does increase as activity coefficient decreases.

PDIAB

Only one partial solvent that is purely organic in nature has been found for PDIAB: n-acetylethanolamine. We have been able to form films of PDIAB with n-acetylethanolamine, but PDIAB solubility is quite limited in this solvent.

Figure 3 shows that n-acetylethanolamine has a large $\Delta \bar{g}_1^{-\infty}$ value of 19 kJ/mol at 150°C.

Acetylethanolamine shows temperature behavior typical of weak association, as shown in Figure 9. The $\Delta \bar{g}_1^{-\infty}$ value for acetylethanolamine decreases as temperature increases. Better solvents tend to exhibit the opposite behavior.

The solvents which appear to interact most strongly with PDIAB are amides, amines, acetamides, carbonates, and organic acids.

TABLE 1

COMPARISON OF SOLUBILITY

RANKING BY STATIC AND GSC METHODS AT 91°C

Substance	Weight Per Cent Polymer Loss by Beaker Test	Activity Coefficient
Acetic Acid	38.5	0.66
2-(ethoxyethoxyethanol)	28.7	1.90
1-Butanol	18.3	5.60
n-Decane	12.5	15.50

PBO

The compounds which interact most effectively with PBO are of the same type as for PDIAB. One exception, shown in Figure 3, is N-ethylacetamide, which interacts extremely effectively with PBO.

Although N-ethylacetamide does not dissolve bulk samples of PBO readily, the interaction with PBO is so strong that it is surprising that dissolution does not occur. Figure 10 provides a possible clue as to why PBO does not dissolve in N-ethylacetamide. Unlike DMAc, a so-called "reactive" solvent, the interaction ($\Delta \bar{g}_1^\infty$) between PBO and N-ethylacetamide decreases as temperature increases, behaving strictly as a strongly associating solvent and not a "reactive" solvent.

We saw earlier that the organic substances that dissolve PBI easily tend to be "reactive" solvents. The only reactive solvent for PBO that we tested was DMAc. Apparently the strength of interaction between DMAc and PBO is not great enough to overcome the bonding keeping PBO in solid form.

Comparison of Results for PBI, PDIAB, and PBO

The only polymer, of the three discussed here, for which we have discovered single organic solvents is PBI. We have shown that there are single solvents that form very strong interactions with PDIAB and PBO.

The solvents that interact strongly enough with PBI to dissolve it tend to exhibit interactions whose strength increases with increasing temperature. This trend is similar to a chemisorption process. We have classified these as "reactive" solvents.

The solvents which are "reactive" solvents tend to have structures, parts of which can become ionically charged. In addition, solvents for

polymers of the type being studied here must have strong interactions with the polymer chain in order to compete with and to overcome interchain bonding. Because the polymer chains of interest here can bond between themselves forming a rigid matrix, any potential solvent must be able to break some interchain bonding in order to make the chains flexible enough to dissolve.

We have not presented results for $\Delta \bar{h}_1^{-\infty}$ in this report because these results appear to be quite uncertain. The $\Delta \bar{h}_1^{\infty}$ results obtained from our GSC data are probably precise to no better than ± 10 percent. We have therefore chosen to base our discussions and conclusions on $\Delta \bar{g}_1^{-\infty}$ results, which we believe are precise to better than ± 3 percent.

In the case of PBI, we have shown that there is a direct relationship between polymer solubility and pseudo activity coefficient $(\Omega_1^{\infty}{}_{ps})$. Unfortunately, we cannot use pseudo activity coefficients to correlate results in general because in many cases the solvent vapor pressure (p_1^{s}) cannot be determined or is not available.

In the following section we develop an alternate method of correlating and predicting solubility results.

SECTION V

CORRELATION AND PREDICTION OF SOLUBILITY

One of the principal conclusions that we can draw from the preceding discussions is that the dissolution of aromatic, heterocyclic polymers is achieved because of polar forces and forces of specific interaction, not because of dispersion forces.

As we show in the polyethylmethacrylate study in Appendix V, polar forces are adequately represented in correlations by Hansen's polar solubility parameter, δ_p. The reason for this is that δ_p is directly proportional to dipole moment (μ).

$$\delta_p = 9.5 \ \mu/Vm^{1/2}$$

where Vm is molar volume. In addition, polar forces are central-field forces and have uniform characteristics, regardless of the source of the force.

Unfortunately, one cannot use Hansen's hydrogen-bonding solubility parameter, δ_h, reliably for mixtures. The reason for this is that δ_h represents the strength of specific association <u>in the pure solvent</u> (or polymer) and not in a mixture. The strength of hydrogen bonding in a mixture can be substantially different than that of either pure component. As a replacement for δ_h, we use X', which is the experimentally measured energy of specific interaction.

In order to demonstrate the use of X' in predicting solubility, we have prepared in Figure 12 a plot of X' versus δ_p for solvents in PBI at 141.8°C. The two known solvents for PBI for which we have X' values
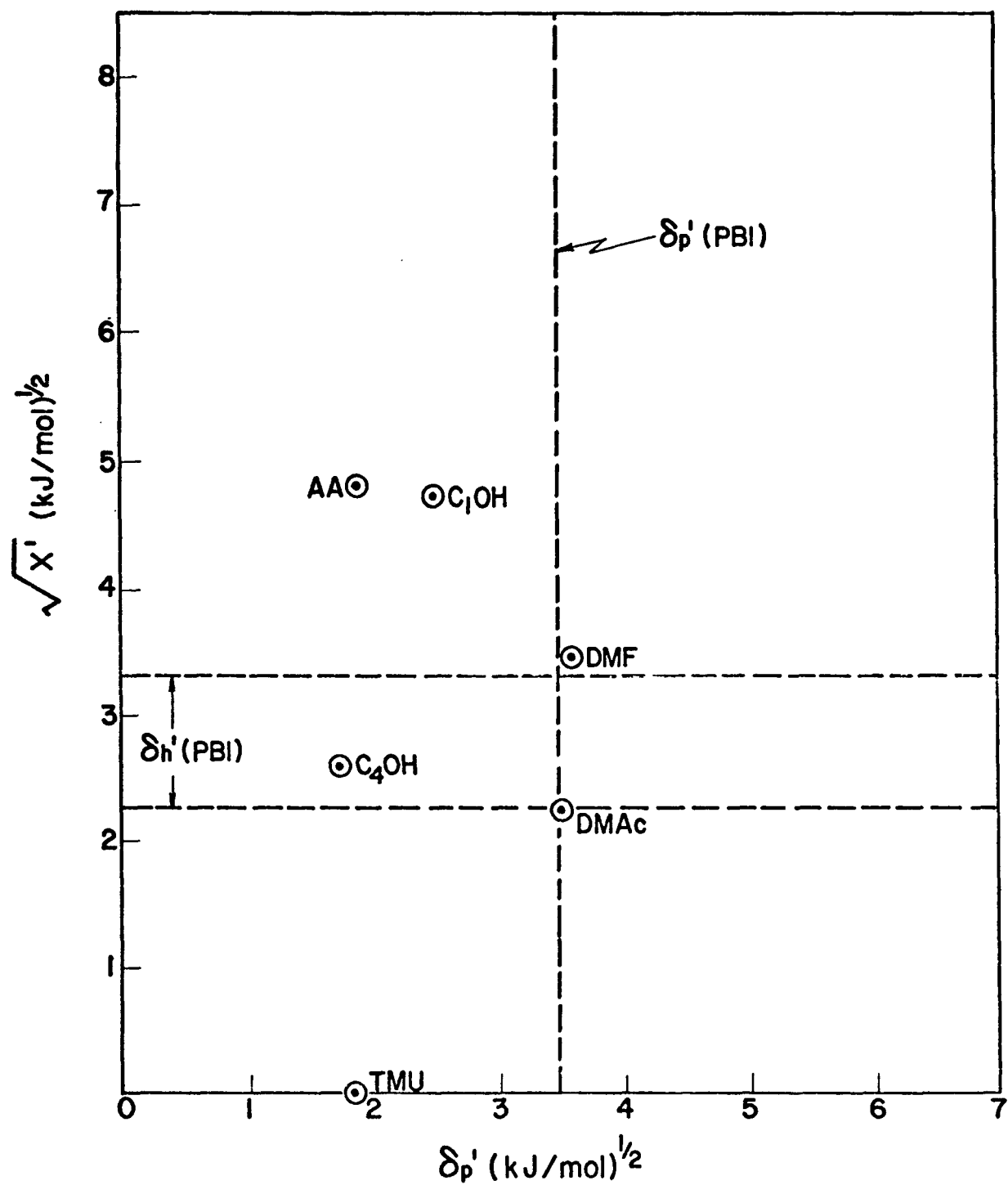
FIGURE 12 - Solubility Plot for PBI at 141.8°C.
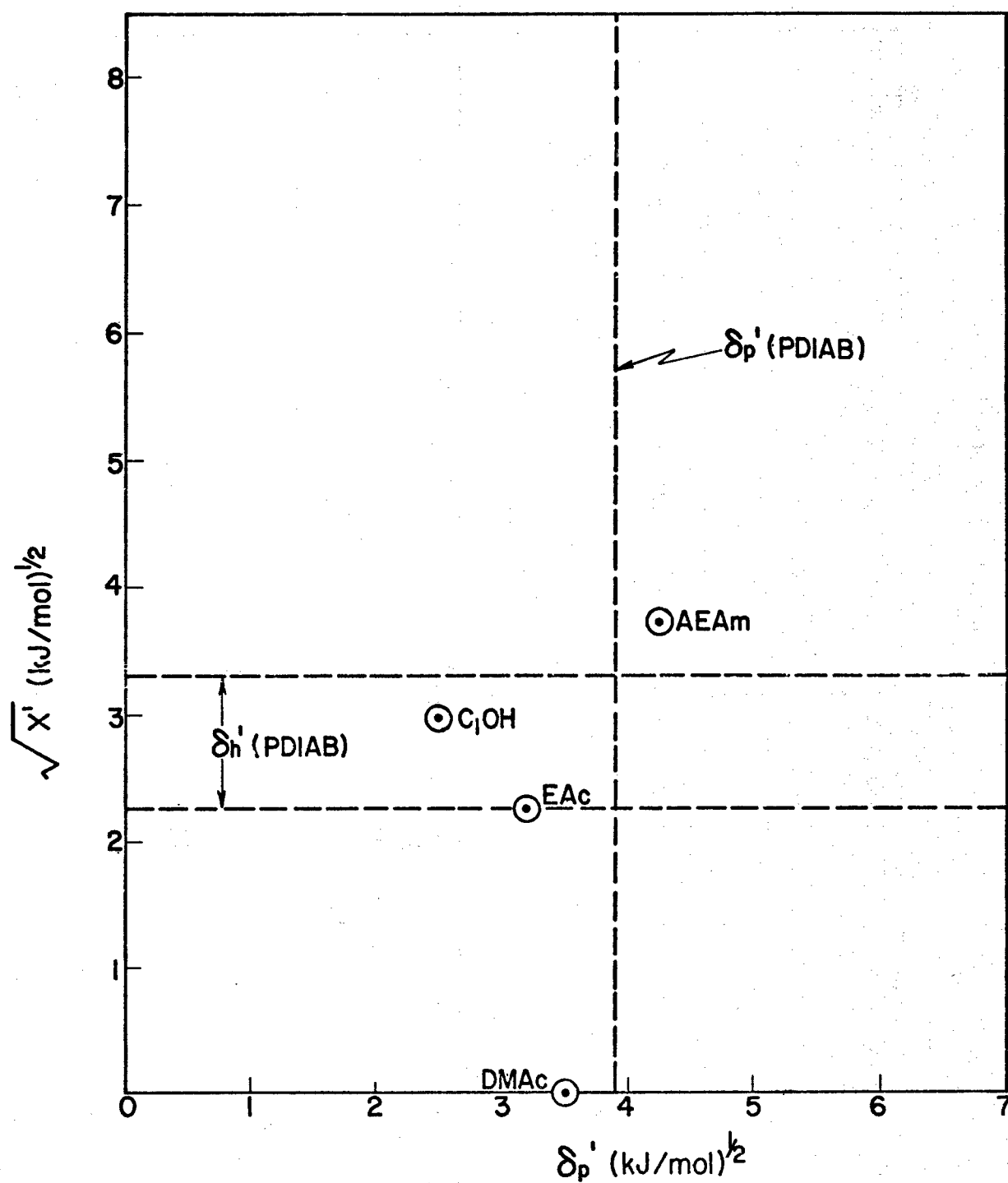
FIGURE 13 - Solubility Plot for PDIAB at 150°C.
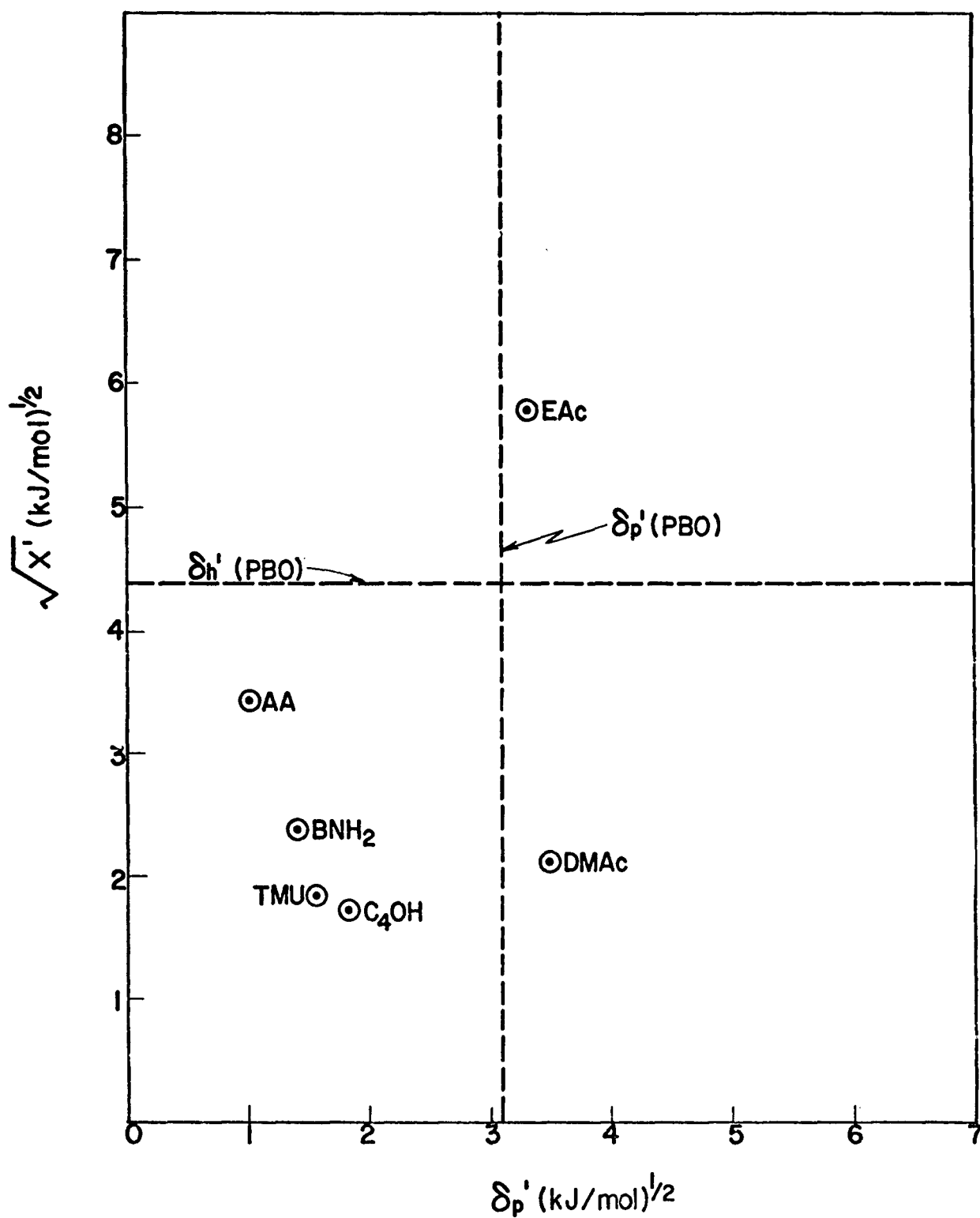
FIGURE 14 - Solubility Plot for PBO at 149°C.

are DMF and DMAc. From the placement of the DMF and DMAc points in Figure 12, one can hypothesize that solvents having δ_p values between 3 and 4 $(kJ/mol)^{1/2}$ and X' values from 2 to 4 $(kJ/mol)^{1/2}$ are probably good solvents for PBI. Acetic acid and methanol can dissolve limited amounts of PBI. Their X' values are higher than those of DMAc or DMF, but their δ_p values are less than 3 $(kJ/mol)^{1/2}$.

It is also possible to compute δ_h for PBI from group contributions (Hansen, 1971). There is some uncertainty in the group contribution of (-C=N-) to δ_h for PBI. The limits of δ_h are shown in Figure 12. The value of δ_h gives an indication of the strength of interchain bonding which must be overcome by a solvent.

The polar solubility parameter δ_p for PBI can be calculated from group contributions (Hansen, 1971). The δ_p value for PBI is shown in Figure 12. We denote quantities converted to dimensions of $(kJ/mol)^{1/2}$ by a superscript ' in Figures 12, 13, and 14.

We give sample calculations in Appendix F to show how δ_p and δ_h can be calculated from group contribution methods.

Figure 12 shows clearly that DMF and DMAc should be solvents for PBI if we accept the reasonable hypothesis that a solvent should have δ_p' and X' values close to those of the polymer.

We test our hypothesis further in Figures 13 and 14 for PDIAB and PBO, respectively. The compound n-acetylethanolamine (AEAm) is a marginal solvent for PDIAB in that it dissolves enough PDIAB to form films. It can be seen in Figure 13 that n-acetylethanolamine falls closest to the intersection of estimated δ_h' and δ_p' values for PDIAB.

In the case of PBO, illustrated in Figure 14, several compounds have δ_p values similar to that of PBO. However, none has an X' value near the δ_h' value of PBO. Solvents for PBO should have δ_p' and X' values of approximately 3.1 $(kJ/mol)^{1/2}$ and 4.4 $(kJ/mol)^{1/2}$, respectively.

SECTION VI

CONCLUSION

We have developed an experimental procedure to screen solvents for thermally stable polymers. We have used meta-phenylene PBI to refine our analysis. We have studied the para- systems PDIAB and PBO. Although we have discovered no good, single organic solvents for PDIAB and PBO, we have determined criteria required of good solvents for PDIAB and PBO. The criteria are equally applicable to any aromatic, heterocyclic polymer.

Our work in progress now involves a search for solvents whose physical structures indicate that they may satisfy the solubility criteria for para - systems. In addition, we are now investigating solvent systems which contain two organic solvents and solvent systems consisting of an aprotic solvent and an ionic salt.

APPENDIX A

POLYMER STRUCTURES
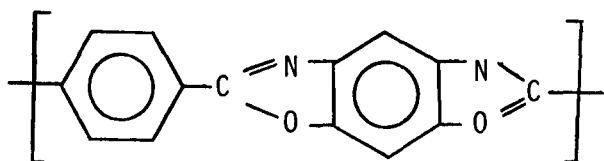
PBO
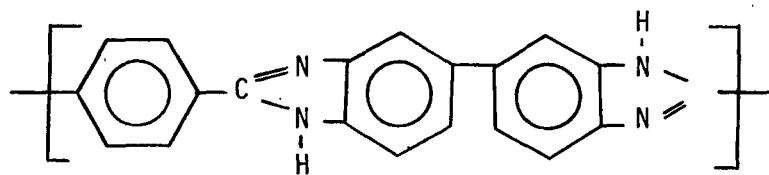
PDIAB
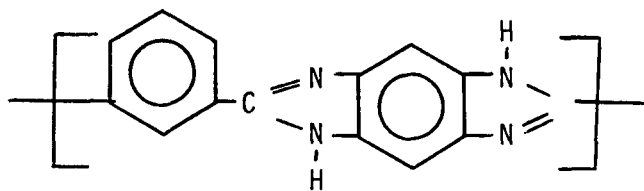
m - PHENYLENE PBI

APPENDIX B

SOLVENTS AND PHYSICAL PROPERTIES

Solvent	Acronym	$\alpha \times 10^{24}/cm^3$	$\mu \times 10^3$ C m	$\delta_d,(cal/cm^3)^{1/2}$	$\delta_p,(cal/cm^3)^{1/2}$	$\delta_h,(cal/cm^3)^{1/2}$
Acetaldehyde	Ac Ald	4.49	9.07	7.1	3.9	6.6
Acetic Acid	AA	5.12	5.80	7.6	5.1	3.4
Acetone	AT	6.43	9.3	7.8	5.7	5.0
Acetic Anhydride	A Anh	8.81	9.34	7.6	5.1	3.4
Acetone	AT	6.43	9.3			
N-Acetylethanolamine	AE Am	10.22				
Acetonitrile	ACET	4.40	13.21	7.5	8.8	3.0
Acrylonitrile	ACRY	6.19	12.77	8.0	8.5	3.3
Allyl alcohol	AOH	6.75	5.33	7.9	5.3	8.2
Aniline	AN					
Benzene	BZ	10.40	0	9.0	0	1.0
Benzylamine	BZ Am	15.91				
Bromobenzene						
1-Bromobutane	1 BrC$_4$	11.25	6.94			
2-Bromobutane	2 BrC$_4$	11.25	7.44			
n-Butanol	C$_4$OH	8.76	5.57	7.8	2.8	7.7
Butylacetate	BAcet	12.5	6.13			
n-Butylamine	BAm	9.72	3.33	7.9	2.2	3.9
iso-Butylamine	iBAm	9.55				

Solvent	Acronym	$\alpha \times 10^{24}/cm^3$	$\mu \times 10^3 C\,m$	$\delta_d, (cal/cm^3)^{1/2}$	$\delta_p, (cal/cm^3)^{1/2}$	$\delta_h, (cal/cm^3)^{1/2}$
Butyraldehyde	BAld	8.17	9.07	7.3	2.0	5.2
Butyric Acid	BA	8.81				
Carbon Tetrachloride	CCl$_4$	10.24	0	8.7	0	0.3
Chlorobenzene						
Chloroform	CHCl$_3$	8.32	3.40	8.7	1.5	2.8
Cyclohexane						
n-Decane	C$_{10}$	19.3	0	7.7	0	0
1,2-Dichloroethane	DCE	8.34	5.00			
Diethylamine	DEAm	9.62	3.07	7.3	1.1	3.0
Dihydroperfluoro butanol	DH PF B					
1,1-Dihydroperfluoro propanol	DH PF P					
Dimethylacetamide	DMAc	9.7	12.70	8.2	5.6	5.0
Dimethylformade	DMF	7.84	11.34	8.5	6.7	5.5
2,6-Dimethyl-3-heptene	DMC$_7$:	15.4				
2,4-Dimethyl-3-pentanone	DMC$_5$0					
Dimethyl sulfoxide	DMSO	9.61		9.0	8.0	5.0
1,3-Di(trifluoromethyl) benzene	2(TFM)BZ					

Solvent	Acronym	$\alpha \times 10^{24}/cm^3$	$\mu \times 10^3 C\ m$	$\delta_d,(cal/cm^3)^{1/2}$	$\delta_p,(cal/cm^3)^{1/2}$	$\delta_h,(cal/cm^3)^{1/2}$
n-Dodecane	C_{12}	23.0	0	7.8	0	0
Ethanol	C_2OH					
2-Ethoxy ethanol	EOE	8.47	7.			
2(2-Ethoxy Ethoxy) ethanol	$(EO)_2E$	12.33				
N-Ethylacetamide	EAc	9.68	13		(5.28)	(4.08)
Ethyl acetate	EAcet	8.83	5.93			
Ethyl benzene	EB	14.17	1.97	8.7	0.3	0.7
Ethyl cyclohexane						
Ethyl carbonate	ECO_3	6.81				
Ethyl diamine	EDAm	7.21	6.64	8.1	4.3	8.3
Formic Acid	FA	3.28	5.07	7.0	5.8	8.1
n-Heptane	C_7	13.71	0	7.5	0	0
2-Heptene	$C_7:$	13.54				
Hexamethyl phosphoramide				9.0	4.2	5.5
n-Hexane	C_6	11.85	0	7.3	0	0
2-Hexene	$C_6:$	11.69				
Methanol	C_1OH	3.23	5.7	7.4	6.0	10.9

Solvent	Acronym	$\alpha \times 10^{24}/cm^3$	$\mu \times 10^3 C \cdot m$	$\delta_d, (cal/cm^3)^{1/2}$	$\delta_p, (cal/cm^3)^{1/2}$	$\delta_h, (cal/cm^3)^{1/2}$
3-Methyl-2-butanone	MBONE	10.09				
Methylcyclohexane	McC$_6$					
Nitrobenzene	NO$_2$BZ					
Nitroethane	NO$_2$C$_2$	6.74	11.81	7.8	7.6	2.2
Nitromethane	NO$_2$C$_1$	4.95	11.91	7.7	9.2	2.5
1-Nitropropane	1NO$_2$C$_3$	8.48	12.01			
2-Nitropropane	2NO$_2$C$_3$	8.48	12.44	7.9	5.9	2.0
n-Nonane	C$_9$	17.42	0	7.6	0	0
iso-Octane	iC$_8$	15.95		7.0	0	0
1-Octene	C$_8$:	15.36	1.13			
n-Octane	C$_8$	15.54	0	7.6	0	0
Perfluorotributyl amine	PFTBA					
1,2-Propanediamine	PDA	9.46				
n-Propanol	C$_3$OH	6.90	5.64	7.8	3.3	8.5
Propionic Acid	PA	6.97	5.83			
Propionic Anhydride	PAnh	12.50				
Propionitrile	PRO					

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Solvent	Acronym	$\alpha \times 10^{24}/cm^3$	$\mu \times 10^3 C \cdot m$	$\delta_d, (cal/cm^3)^{1/2}$	$\delta_p, (cal/cm^3)^{1/2}$	$\delta_h, (cal/cm^3)^{1/2}$
Propyl Acetate	C_3Acet	10.67	6.00			
Propyl Ether	C_3OC_3					
Tetramethyl Urea	TMU	13.04	13.06	8.2	4.0	5.4
Toluene	TOL	12.34	1.23	8.8	0.7	1.0
Triethyl Phosphate	TEP		10.0			
2,2,2-Trifluoro methanol						
2,2,2-Trifluoro ethanol						
Water	H_2O	1.59	8.34	7.6	7.8	20.7

APPENDIX C

GSC DATA FOR

PBI, PDIAB, AND PBO

PDIAB   PBI   PBO

Solvent	V_g/g ml^{-1} (PDIAB)			$-\Delta g_1^\infty$/kJ g-mol^{-1} (PDIAB)			V_g/g ml^{-1} (PBI)		$-\Delta g_1^\infty$/kJ g-mol^{-1} (PBI)		V_g/g ml^{-1} (PBO)			$-\Delta g_1^\infty$/kJ g-mol^{-1} (PBO)	
	150°C	200°C	250°C	150°C	200°C	250°C	141.8°C	185°C	141.8°C	185°C	149°C	185°C	221°C	149	185
Acetaldehyde	0.763	0.142	0.097	1.35	1.02	10.64					15.50	8.57		8.05	6.12
Acetic acid	7.390	0.209	1.977	-6.64	-0.51	-2.47	1113.6	1014.4	23.32	25.94	34.10	15.67	5.97	10.78	8.41
Acetic anhydride	2.320	0.167	0.613	-2.56	0.38	2.62		∞			29.23	21.38	4.92	10.23	9.59
Acetone		1.87	0.218		2.01	7.13	125.3	53.4	19.04	14.72	4.63	3.81		3.67	3.02
N-Acetylethanolamine	242.8	7.817	7.739	-18.92	-14.74	-8.40					16.26	17.77		8.17	8.89
Acetonitrile	1.083	1.018	0.704	0.118	0.38	2.02	278.4	69.5	19.04	11.74	5.79	4.13		4.54	3.33
Acrylonitrile	0.886	0.001	0.400	0.83	26.89	4.48	348.0	72.2	19.80	15.87	6.27	4.62		4.83	3.76
Allyl alcohol	0.611	~0	~0	2.13							8.58	5.48		5.93	4.41
Aniline												20.74	11.13		
Benzene	0.763	0.073	0.279	1.35	10.74	6.04					5.53	4.52		4.38	3.68
Benzylamine	0.383	0.457	1.523	-7.86	-3.58	-1.42					31.40			10.49	
Bromobenzene													10.37		
1-Bromobutane	0.916	~0	0.188	0.71		7.76	12.2	8.9	8.25	7.90	8.32	5.59		5.82	4.48
2-Bromobutane	0.672	~0	~0	1.80							6.48	3.89		4.94	3.10
n-Butanol	1.313	0.256	0.461	0.56	5.81	3.86	34.8	13.8	11.86	9.58	13.16	4.19	3.75	7.42	6.51
Butylacetate	0.507	0.043	0.188	2.79	12.80	7.76					18.39	13.09		8.52	7.73
n-Butylamine	1.160	0.057	0.691	-0.72	4.6	2.10					25.31		10.88	9.73	11.03
iso-Butylamine	1.220	~0	0.188	-0.30	7.76	7.76								8.84	

PDIAB PBI PBO

Solvent	PDIAB $V_g/\text{g ml}^{-1}$			PDIAB $-\Delta\bar{g}_1^\infty/\text{kJ g-mol}^{-1}$			PBI $V_g/\text{g ml}^{-1}$		PBI $-\Delta\bar{g}_1^\infty/\text{kJ g-mol}^{-1}$		PBO $V_g/\text{g ml}^{-1}$			PBO $-\Delta\bar{g}_1^\infty/\text{kJ g-mol}^{-1}$	
	150°C	200°C	250°C	150°C	200°C	250°C	141.8°C	185°C	141.8°C	185°C	149°C	185°C	221°C	149	185
Butyraldehyde	~0	~0	~0	-8.17	-1.95	-1.42					6.95			5.19	
Butyric acid	11.42	0.302	1.553	4.57		2.41					51.80	25.76	7.96	12.25	10.30
Carbon tetrachloride	0.305	~0	0.643				3.6	2.9	7.35	3.70	3.36	2.74		2.63	1.77
Chlorobenzene													7.89		
Chloroform	0.507	~0	0.346	2.79		5.1	9.4	6.8	7.35	6.88	3.85	2.74		3.11	1.76
Cyclohexane											4.09	2.79		3.33	1.84
n-Decane	3.482	1.809	0.473	3.99	-1.88	3.75	39.1	16.61	12.26	10.27	86.14	33.29	8.43	14.03	11.28
1, 2 - Dichloroethane	0.611	0.177	0.691	2.13	0.15	9.93	5.3	15.9	5.36	10.13					
Diethylamine	0.855	0.097	0.340	0.95	2.74	5.19					34.59	23.86		10.82	10.01
Dihydroperfluoro butanol	3.970	0.969	0.443	4.45	0.57	4.03					13.44	7.26		7.50	5.52
1, 1 - Dihydroperfluoro propanol	1.435	0.372	0.643	-0.87	4.34	2.41					7.49	4.52		5.45	3.68
Dimethylacetamide	4.337	2.419	0.946	-4.76	-3.03	0.734	357.73	307.38	19.90	21.39	74.01	105.6	13.29	13.49	15.68
Dimethylformamide	4.550	1.078		-4.93	0.151		835.17	1649.49	22.83	27.80	18.83	9.75	8.19	8.69	
2, 6 - Dimethyl-3-heptene	1.527	0.724	0.764	-1.09	1.72	1.66									
2, 4 - Dimethyl-3-pentanone	2.767	0.730	0.315	-3.18	1.78	5.51					13.80	9.52		6.51	6.51
Dimethyl sulfoxide	5.190	1.018	1.735	-5.39	0.38	-1.90	∞	∞							

PDIAB   PBI   PBO

Solvent	PDIAB V_g/g ml^{-1}			PDIAB $-\Delta\bar{g}_1^\infty$/kJ g-mol^{-1}			PBI V_g/g ml^{-1}		PBI $-\Delta\bar{g}_1^\infty$/kJ g-mol^{-1}		PBO V_g/g ml^{-1}			PBO $-\Delta\bar{g}_1^\infty$/kJ g-mol^{-1}	
	150°C	200°C	250°C	150°C	200°C	250°C	141.8°C	185°C	141.8°C	185°C	149°C	185°C	221°C	149	185
1, 3-Di(trifluoromethyl) benzene	1.590	~0		2.26							13.16	7.79		7.42	5.75
n-Dodecane	11.850	4.064	2.857	8.30	-5.05	-4.07	146.2	55.8	16.81	14.89		135.59	23.76	14.04	16.6
Ethanol							556.8	94.0	21.43	16.88					
2-Ethoxy ethanol	2.749	0.896	0.315	2.80	5.32	5.51	313.2	258.2	19.44	20.73				9.01	9.01
2(2-Ethoxy-Ethoxy) ethanol	32.070	2.734	1.613	11.80	3.51	1.58	911.7	284.3	19.44	20.73	33.49			10.71	
N-Ethylacetamide	10.990	0.382	1.613	8.04	-2.88	-1.59					105.8	25.18	15.74	4.07	16.21
Ethylacetate	~0	0.226	0.340		6.30	5.18					6.58	5.11	4.56	4.91	4.15
Ethylbenzene		1.018	0.443		0.38	4.03					18.42	7.77	2.80	8.61	
Ethylcyclohexane											12.47			7.24	
Ethylene carbonate	18.63	2.663		-9.88	3.41	-1.75	∞	169.0		19.12	33.43	28.24	24.23	10.70	11.28
Ethylenediamine	4.150	0.362	1.674	-4.60	-2.66	2.10					18.20	14.22	6.44	8.57	8.04
Formic acid	1.527	0.417	0.691	-1.09	-3.22		51.5	10.45	13.21	8.51	10.09	5.58	2.22	6.50	4.48
n-Heptane	0.765	0.250	0.097	1.34	6.74	10.64	5.45	3.93	5.46	4.78	9.98			6.46	
2-Heptene	0.489	0.384		2.91	4.21										
Hexamethyl phosphoramide	42.45	18.990	7.618	12.80	11.14	-8.34	∞	∞			5.41			4.30	
n-Hexane	0.55	0.128	~0	2.50	8.53		1.95	2.3	1.91	2.74					

PDIAB PBI PBO

Solvent	PDIAB V_g/g ml^{-1}			PDIAB $-\overline{\Delta g_1}^\infty$/kJ g-mol^{-1}			PBI V_g/g ml^{-1}		PBI $-\overline{\Delta g_1}^\infty$/kJ g-mol^{-1}		PBO V_g/g ml^{-1}			PBO $-\overline{\Delta g_1}^\infty$/kJ g-mol^{-1}	
	150°C	200°C	250°C	150°C	200°C	250°C	141.8°C	185°C	141.8°C	185°C	149°C	185°C	221°C	149	185
2-Hexene	2.932	0.761	0.552	3.38	1.52	3.07	438.5	68.3						4.10	2.72
Methanol	2.030	0.445	0.461	2.09	3.63	3.86			20.60	15.66					4.24
3-Methyl-2-butanone	1.527	~0	~0	-1.09							6.69	5.24		4.97	3.55
Methylcyclohexane											6.77	4.37	1.58	5.09	
Nitrobenzene												46.78	15.04		5.02
Nitroethane	0.763	~0		1.35	2.13						7.86	5.95	2.24	5.42	
Nitromethane		0.611	0.226	0.946		6.30	7.35					7.61	3.93		6.06
1-Nitropropane	0.366	~0	0.188	3.93		7.76					11.32	8.45	2.81	6.82	4.49
2-Nitropropane	0.582	~0	0.946	2.31		0.74					6.69	5.59		4.97	
n-Nonane	2.382	0.256	0.188	2.65	3.60	7.76	20.83	9.79	7.58	8.26	38.55	17.131	5.28	11.21	8.75
iso-Octane	1.283	0.256	0.704	0.48	5.81	2.02					8.67	5.04	2.11	5.96	4.09
1-Octene	0.489	0.256	0.582	2.91	5.81	2.85	11.0	8.1	7.89	7.52	15.57	9.59	4.79	8.02	6.54
n-Octane	1.470	0.299		0.96	5.20		11.62	5.33	8.07	5.94	19.25	9.23	3.51	8.76	6.40
Perfluorotributylamine	1.313	~0	0.643	-0.63	2.41						67.73			13.18	10.88
1, 2 - Propanediamine	2.260	0.042	0.188	-2.47	5.81	7.76									10.43
n-Propanol	0.382	0.317	0.346	3.79	4.96	5.10					7.31	6.55	2.22	5.36	5.09
Propionic acid	9.467	0.107	1.856	-7.51	2.12	-2.20					44.74	21.38	6.49	11.70	9.59

PDIAB   PBI   PBO

| Solvent	V_g/g ml^{-1} (PDIAB)			$-\Delta\bar{g}_1^\infty$/kJ g-mol^{-1} (PDIAB)			V_g/g ml^{-1} (PBI)		$-\Delta\bar{g}_1^\infty$/kJ-mol^{-1} (PBI)		V_g/g ml^{-1} (PBO)			$-\Delta\bar{g}_1^\infty$/kJ g-mol^{-1} (PBO)	
	150°C	200°C	250°C	150°C	200°C	250°C	141.8°C	185°C	141.8°C	185°C	149°C	185°C	221°C	149	185
Propionic anhydride	2.932	0.117	0.795	-3.38	1.78	1.49					44.62	20.29	5.85	11.72	9.39
Propionitrite	0.257	~0	0.946	5.18		0.74					6.27			4.83	
Propyl acetate		~0									10.23	7.74		6.46	2.72
Propyl ether											10.04	5.71		6.48	4.57
Tetramethyl urea	6.719	1.523	0.279	-6.30	-1.21	6.04	389.8	158.3	20.20	18.86	120.28			15.20	
Toluene	0.794	0.496	~0	1.21	3.42	-3.42	863.0	169.1	22.94	19.12	11.29	8.09	4.39	6.89	5.89
Triethyl phosphate		7.415	2.462		-7.43	4.82									
2,2,2-Trifluoromethanol	0.763	1.627	0.370	1.35	1.47										
2,2,2-Trifluoroethanol	0.489	0.165	~0	2.91	7.53		33.4	15.1	23.13	21.10	4.94	2.74	1.29	3.99	1.78
Water	∞	50.06	6.253	∞	-14.95	-7.47	487.2	132.2	20.96	18.18					

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APPENDIX D

SOLVENT INTERACTIONS

WITH "ATQ"

Introduction

At the request of Dr. T. E. Helminiak, we have done a study of solvent interactions with a polymer known as "ATQ". The polymer structure is shown below:
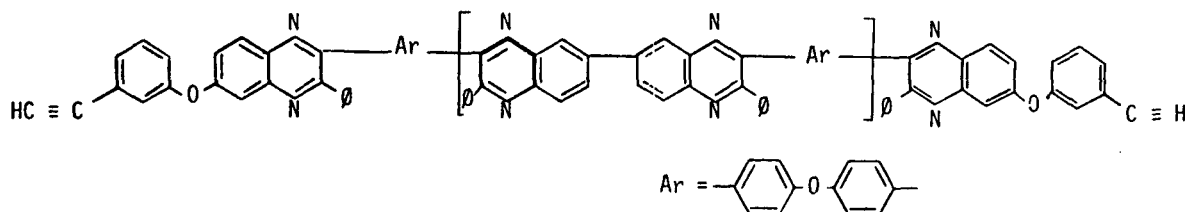
The objective of the study was to compare the solvent power of a group of solvents with that of dioxane at 100°C and to determine whether or not there exist solvents for ATQ which are slightly easier to remove from the polymer than dioxane.

Materials

The solvents used in the study are listed in Table 2. The solvents tested were arbitrarily limited to those with boiling points less than approximately 100°C. This limitation was imposed because solvents with boiling points greater than the maximum processing temperature for ATQ would be difficult to remove from ATQ solution by means other than steam stripping or solvent leaching.

The ATQ sample was obtained from the Air Force Materials Laboratory in oligomeric form. The oligomer was cured to polymer under helium at 300°C for five hours.

TABLE 2

SOLVENT RETENTION VOLUMES
AT 100°C WITH ATQ

Solvent	Code	V_g°	Polarizability $(\alpha) \times 10^{24}$ cm^{-3}	Dipole Moment(μ) C. m.$\times 10^{30}$
n-hexane	1	4.24	11.85	0
n-heptane	2	6.98	13.71	0
n-octane	3	13.20	15.54	0
2-hexene	4	11.56	11.56	–
2-heptene	5	13.38	13.38	–
1-octene	6	12.45	15.36	1.13
iso-octane	7	8.455	15.95	0
methanol	8	19.57	3.195	5.63
1-butanol	9	20.27	8.760	5.57
ethanol	10	19.13	5.07	5.67
2,2,2-trifluroethanol	11	10.84	4.74	–
2-chloroethanol	12	22.77	6.34	–
allyl alcohol	13	31.14	6.75	–
propyl acetate	14	13.57	10.67	6.00
n-butyl acetate	15	14.58	12.51	6.13
nitromethane	16	58.58	4.95	11.91
nitroethane	17		6.74	11.81
2-nitropropane	18	13.14		12.54
1-nitropropane	19	38.70	8.48	12.01
3-methyl-2-butanone	20	5.44		–
2,4-dimethyl-3-pentanone	21	10.16		–
1,4-dioxane	22	14.86	9.66	4.50
formic acid	23	21.07	3.37	5.20
iso-butyl amine	24	9.520		4.23
1,2-propane diamine	25	7.152	7.94	–
α-chlorotoluene	26	351.9	6.37	–
chloroform	27	18.31	1.00	3.40
1-chloropropane	28	12.49	8.17	6.83
carbon tetrachloride	29	9.980	10.24	0
methylene chloride	30	25.13	6.42	6.47
chlorobenzene	31	80.11	13.91	5.70
acetonitrile	32	38.10	4.40	13.21
acrylonitrile	33	37.15	6.19	12.77
acetaldehyde	34	5.38	4.49	9.00
butyraldehyde	35	17.89	8.17	9.07
benzene	36	18.00	10.40	0
water	37	19.92	1.59	6.08

Experimental Procedure

Approximately 0.0865g of ATQ oligomer was coated on 1.7 g of Fluoropak 80 (80/100 mesh) substrate. The ATQ-coated substrate was packed into 2 ft of 1/8-inch i.d., 316 stainless steel tubing. The packed tubing was used as the column in a Varian 920 Gas Chromatograph with a thermal conductivity detector.

The oven temperature of the chromatograph was kept at 100.0 ± 0.1 °C, and the injector block temperature was kept at 150.0 ± 0.1 °C.

Sample injection sizes were of the order of 0.01 $\mu\ell$ of solvent vapor. Solvent retention times were extrapolated to zero peak height using several different solvent sample sizes for each particular solvent.

Helium carrier gas flowrate was kept constant at 5 mℓ/min (STP).

Data Reduction

Solvent retention volumes (V_g^o) were calculated, using air as a reference from the following formula (Cheng and Bonner, 1974).

$$V_g^o = Q(273.15/T)(t_g - t_a)(f_p/m_2) \qquad (1)$$

where   Q = helium flow rate at room temperature

   T = room temperature, °K

   t_g = solvent retention time

t_a = air retention time

$$f_p = \frac{3}{2} \, [(p_i/p_o)^2 - 1]/[(p_i/p_o)^3 - 1]$$

p_i = column inlet pressure

p_o = column outlet pressure

m_2 = mass of polymer coated in column.

Using an adaptation of the method of Dwyer and Karim (1975), the natural logarithm of V_g° of each solvent tested was plotted versus its respective polarizability. The distance between the alkane reference curve and the data is denoted by $\Delta(\ln V_g^\circ)$. The value of $\Delta(\ln V_g^\circ)$ is then plotted versus solvent dipole moment.

A reference line is established for non-associating solvents. The difference between the associating solvent data and values on the reference line is denoted X'. The value of X' is a direct measure of the Gibbs energy of interaction between the solvent and ATQ (Meyer, 1973; Dwyer and Karim, 1975). Thus, the larger the value of X', the stronger the interaction between solvent and ATQ.

Values of X' are listed in Table 3.

TABLE 3

VALUES OF X' AT 100°C IN ATQ

Solvent	Code	X'
α-chlorotoluene	26	3.12
formic acid	23	1.54
water	37	1.34
1-nitropropane	19	0.84
1-butanol	9	0.78
nitromethane	16	0.74
1,4-dioxane	22	0.63
methylene chloride	30	0.45
chloroform	27	0.16
n-propyl acetate	14	~ 0
1-chloropropane	28	~ 0
butyraldehyde	35	~ 0
acrylonitrile	33	~ 0
acetonitrile	32	~ 0
chlorobenzene	31	- 0.22
butyl acetate	15	- 0.46

Discussion of Results

Dioxane is a non-polar molecule, but only one oxygen atom in its structure can interact with the polymer surface at a time. We have therefore assigned a dipole moment to dioxane using the structure shown below to compute the dipole moment.
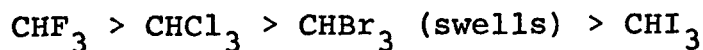
$$CH_3 - O - CH_3$$

The resulting dipole moment for dioxane is approximately 4.5×10^{-30} C.-m. As can be seen from the X' values, the best solvent we tested was α-chlorotoluene. Beaker-scale solubility tests show that although formic acid, water, nitromethane, and nitropropane exhibit strong interactions with ATQ, they are not good solvents.

Methylene chloride and chloroform, while solvents for ATQ, do not interact as strongly with the polymer as dioxane. Methylene chloride and chloroform should therefore be slightly easier to remove from ATQ than dioxane.
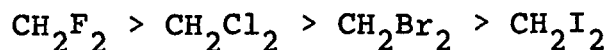
The negative X' values for chlorobenzene and butylacetate are probably due to experimental error and should be taken as essentially zero.

Beaker-scale solubility studies were carried out using 1,2-dibromoethane; 1,2-dichloroethane; bromoform; and pentachloro-ethane. 1,2-dibromoethane only swells ATQ, while 1,2-dichloro-thane dissolves ATQ. Pentachloroethane dissolves ATQ about as
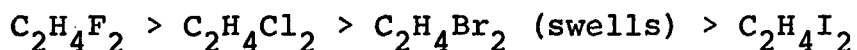
rapidly as chloroform. We therefore propose the following qualitative ranking of halogenated solvents in terms of their affinity for ATQ.

$$CHF_3 > CHCl_3 > CHBr_3 \text{ (swells)} > CHI_3$$

$$\lor$$

$$CH_2F_2 > CH_2Cl_2 > CH_2Br_2 > CH_2I_2$$

$$\lor$$

$$C_2H_4F_2 > C_2H_4Cl_2 > C_2H_4Br_2 \text{ (swells)} > C_2H_4I_2$$

Conclusion

Methylene chloride and chloroform are probably more easily removed from solution with ATQ than dioxane. However, based on beaker-scale studies in combination with gas-chromatographic results, a solvent that is relatively easy to remove from ATQ but is also relatively inexpensive is 1,2-dichloroethane.

A solubility ranking of halogenated solvents has been proposed for ATQ.

Other solvents worthy of process testing, based on their molecular structure, are diiodomethane and methyliodide.

APPENDIX E

THERMODYNAMIC INTERPRETATION OF

SOLUTE-POLYMER INTERACTIONS AT

INFINITE DILUTION

Gas liquid chromatography (GLC) has proved to be an accurate technique for measuring thermodynamic properties of binary solutions, providing that the volatilities of the two components differ considerably (Cruickshank, et al., 1966, 1968; Conder, et al., 1969; Cadogan, et al., 1969; Meyer, 1973). In recent years various attempts have been made to standardize a common approach for the determination of thermodynamic data for binary polymer solutions from GLC measurements (Smidsrød and Guillet, 1969; Summers, et al., 1972; Newman and Prausnitz, 1973; Cheng and Bonner, 1974).

Our main objective here is to explain, in terms of measured thermo-dynamic data, the intermolecular interaction forces that operate in polymer solutions under GLC conditions. We also intend to develop mathematical models to identify types of interactions in terms of the molecular properties of the solution components. Similar studies were made by Dwyer and Karim (1975) for binary solutions of low molecular weight substances, and the following semi-empirical model was developed:**

**We have used the symbol ΔH_S with the same meaning as the symbol $\Delta \bar{H}_S$ in the paper of Dwyer and Karim (1975). We have eliminated the superscript bar (-) to avoid possible confusion with partial molar quantities.

$$-\Delta H_S = a \, \alpha_2 + b\mu_2 + X \tag{1}$$

or, including the molecular properties of the stationary phase, equation (1) becomes:

$$-\Delta H_S = a_1 \alpha_1 \alpha_2 + b_1 \mu_1 \mu_2 + X_1 \tag{2}$$

where ΔH_S is the heat of solution of a solute in a solvent, and it is calculated from the specific retention volume at 0°C (V_g°) by the following equation:*

$$\frac{d \ln V_g^{\circ}}{dT} = \frac{\Delta H_S}{RT^2} \tag{3}$$

The specific retention volume used here is defined by

$$V_g^{\circ} = F \, (t_g - t_r) \, \frac{273.15}{T} \, \frac{1}{m_2} \, f_p \tag{4}$$

wehre F = carrier gas flow rate measured at room temperature,

   T = room   temperature in K,

   t_g = retention time (to peak maximum) of solute,

   t_r = retention time (to peak maximum) of air,

   m_2 = mass of polymer coated on Fluoropak in the column,

---

*
    As Dwyer and Karim (1975) point out, equation (3) only gives an approximate value of ΔH_S. However, due to uncertainties in the values of polarizability and dipole moment, further refinement of equation (3) for use in conjunction with equation (1) is unwarranted.

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

P_i = column inlet pressure,

P_o = column outlet pressure.

The a's and b's in equations (1) and (2) are empirical constants character-istic of solute and solvent. The terms α_1 and α_2 are the polarizabilities of the solvent and the solute, respectively, and μ_1 and μ_2 are their dipole moments. Finally, X and X_1 are terms expressing the magnitude of the specific interactions which are defined in a previous paper by Dwyer and Karim (1975).

In order to demonstrate the applicability of the technique embodied in equations (1) and (2) to polymer solutions, we used poly (ethyl methacrylate) as the stationary liquid phase (solvent) and a variety of monofunctional aliphatic and aromatic compounds as solutes.

Experimental

A Varian Aerograph Model 920 Gas Chromatograph containing thermal conductivity detectors was used in this study. Columns of stainless steel tubes of about 2 m length, 2.2 mm i.d., and 0.47 mm wall thickness were packed with 3.30 g poly (ethyl methacrylate) supported on acid-washed, 80 - 100 mesh Fluoropak 80. The number average molecular weight (M_n) of the polymer determined by gel permeation chromatography is equal to 144,000. The polymer was carefully deposited on the solid support from solution in chloroform. The Fluoropak packing was coated with 1 g

TABLE 4

DIPOLE MOMENTS, POLARIZABILITY, AND HEATS OF SOLUTION OF
SOLUTES IN POLY (ETHYL METHACRYLATE)

Solute	Code No	Polarizability $\alpha \times 10^{24}/cm^3$	Dipole Moment $\mu \times 10^{30}/C\ m$	Heats of Solution $-\Delta H_S$(experimental)/ $kj\ mol^{-1}$	$\Delta H_S/kj\ mol^{-1}$ calculated from Eq. 11	X^* $\Delta H_S(exp)-\Delta H_S(calc)$
n-Heptane	1	13.71	0	23.50	23.84	
n-Octane	2	15.54	0	28.06	28.40	
n-Nonane	3	17.42	0	33.00	33.67	
n-Decane	4	19.30	0	38.91	39.60	
1-Octene	5	15.36	1.13	28.34	30.78	?
n-Butyl bromide	6	11.22	6.94	39.00	35.91	0
Nitromethane	7	4.95	11.91	39.90	37.48	
Nitroethane	8	6.74	11.81	43.34	40.07	
1-Nitropropane	9	8.48	12.01	46.93	43.53	
Methyl cyanide	10	4.40	13.21	41.29	39.92	
Ethyl cyanide	11	6.26	13.51	42.18	43.59	
Acrylonitrile	12	6.19	12.77	39.27	41.61	
Di-n-propyl ether	13	12.57	3.43	28.23	29.90	
n-Butyl amine	14	9.72	3.33	33.52	23.89	9.63
Methyl ethyl ketone	15	8.24	9.24	36.87	36.12	
Dimethyl ketone	16	9.60	6.43	37.00	31.48	
Methyl cyclohexane	17	12.90	0	18.56	21.98	
Ethyl cyclohexane	18	14.72	0	21.27	26.29	?
n-Butyl acetate	19	12.51	6.13	39.96	36.59	0
n-Propyl acetate	20	10.67	6.00	36.80	35.57	
n-Butyraldehyde	21	8.17	9.07	36.98	35.57	
Benzene	22	10.40	0	35.99	16.77	
Toluene	23	12.34	1.23	40.59	23.85	
Ethyl benzene	24	14.17	1.97	43.90	29.91	
Chlorobenzene	25	12.32	5.70	49.37	35.09	
Bromobenzene	26	13.49	5.67	49.72	37.63	
n-Propyl alcohol	27	6.90	5.64	40.38	24.77	15.61
n-Butyl alcohol	28	8.76	5.57	41.18	27.77	13.41
n-Pentyl alcohol	29	10.64	5.54	41.84	31.22	10.62
Chloroform	30	8.32	3.40	37.42	21.52	15.90
Carbon tetrachloride	31	10.24	0	9.16	16.46	
Propionic acid	32	8.81	5.83	33.91	28.52	5.39
Cyclohexane	33	10.71	0	15.49	17.37	

* Small values of (X) are within experimental error and they are approximated to zero.
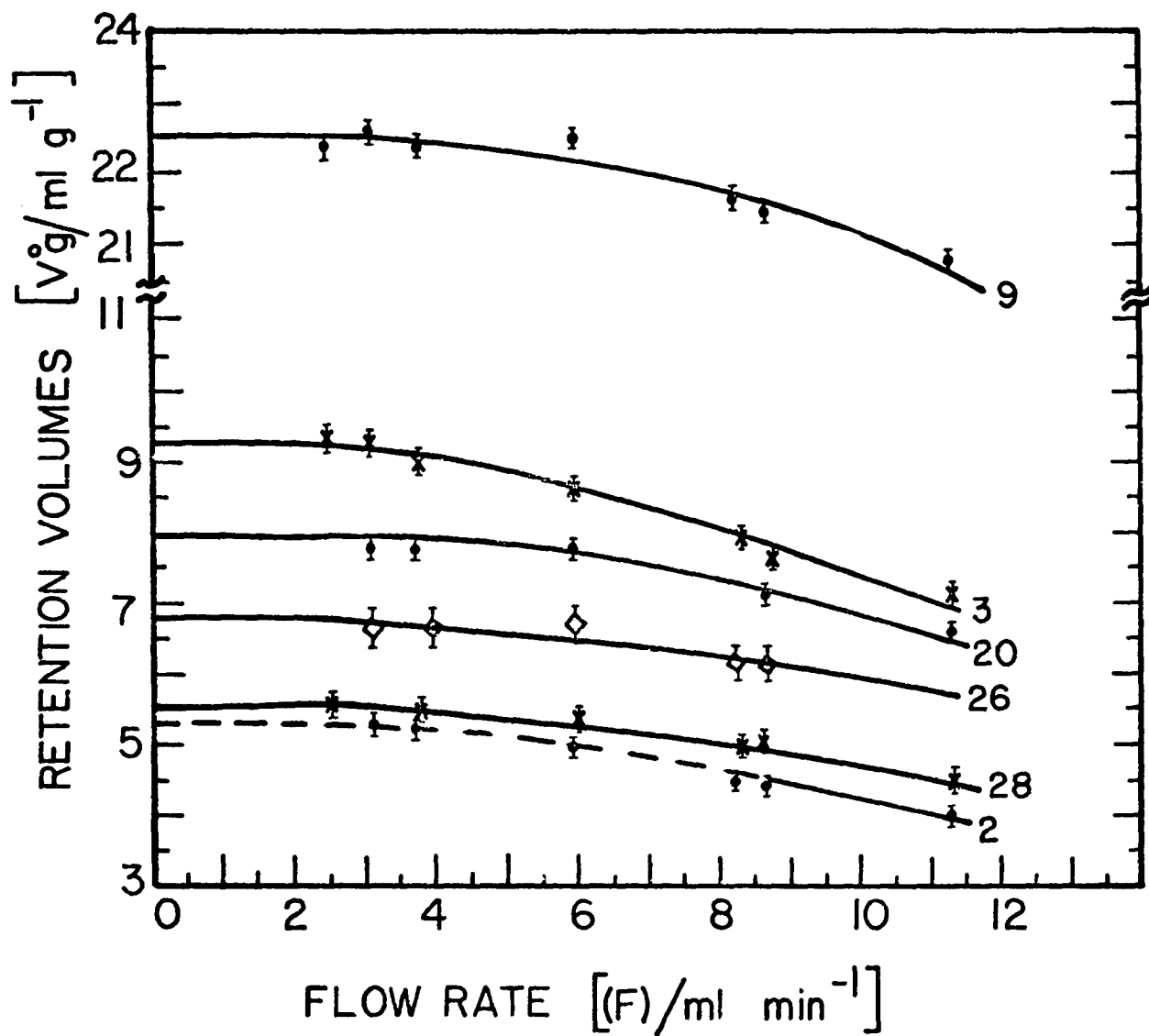
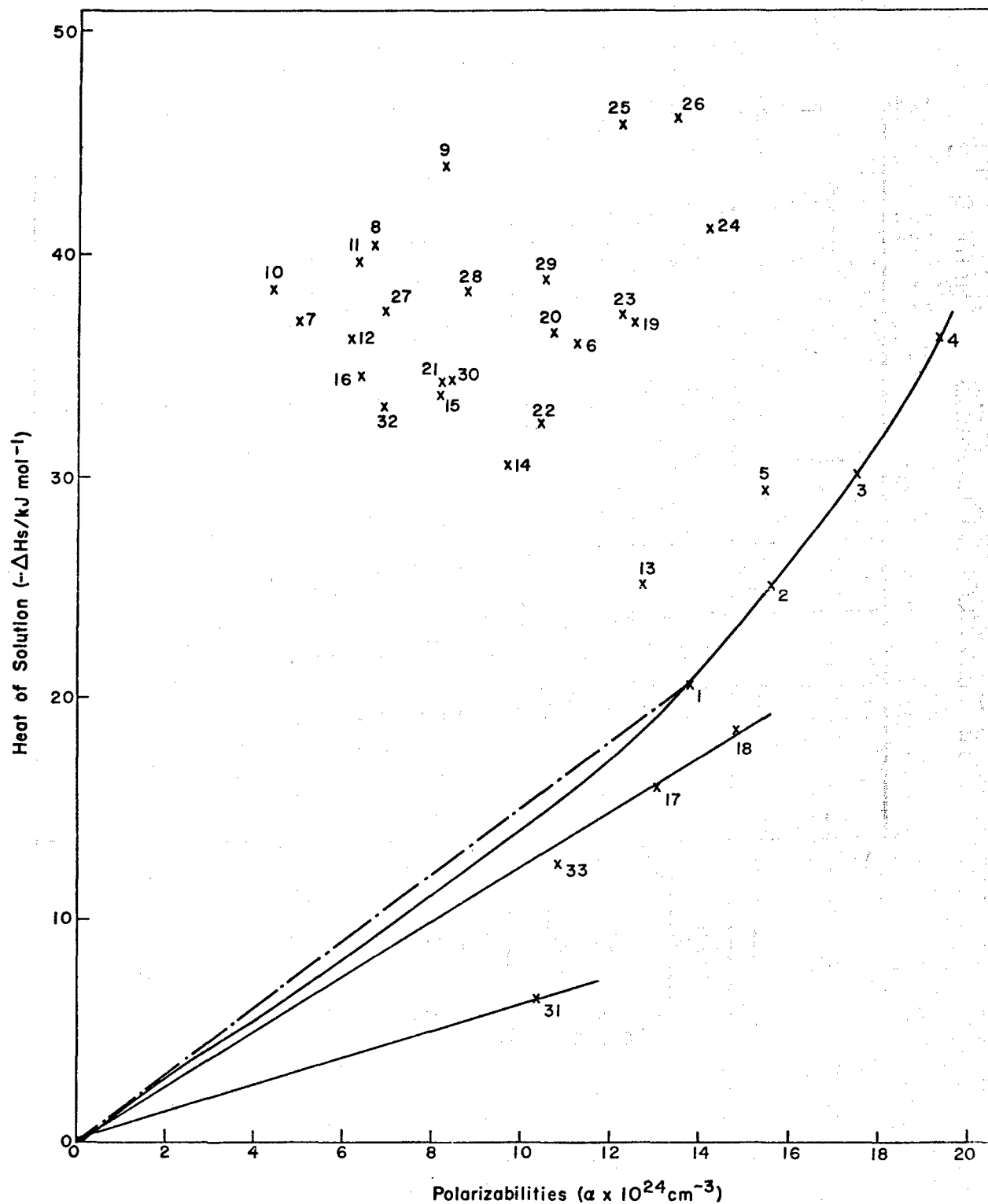FIGURE 15 - Effect of Flow Rate on Specific Retention
Volume at 418K

FIGURE 16 - Heat of Solution as a Function of Polarizability for Solutes in Poly(ethyl methacrylate)

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n-Alkanes were used to determine the reference curve when determining the dipolar and specific interaction contributions of the polar solutes to the heat of solution. A plot of ΔH_S vs. polarizability α of solutes is shown in Figure 16. The polarizabilities listed in Table 4 and used in Figure 16 are taken as the arithmetic average of the three principal components of polarizability, i.e. $\alpha_2 = \dfrac{\alpha_x + \alpha_y + \alpha_z}{3}$. The curve for n-alkanes was found to be fit by the following polynomial:

$$-\Delta H_S = 1.500\alpha_2 - 0.010\alpha_2^2 + 0.002\alpha_2^3 \tag{6}$$

The solid curve through points 1, 2, 3, and 4 in Figure 16 is that determined using equation (6).

The reference curve for chloroform was taken to be a line passing through the point of carbon tetrachloride and the origin (the solid line through point 31 in Figure 16), while that for the aromatic compounds was initially taken to be a line having zero intercept and passing through the points of the cyclic alkanes (the solid line through points 33, 17, and 18 in Figure 16).

The heats of solution of the polar compounds which are estimated from the vertical differences above the relevent reference curve will be referred to as ΔH_{ad}. These values are measures of the strength of the interaction due to the permanent electrical forces in the polar molecules and also due to specific interactions. Values below the relevent reference curve will be referred to as ΔH_n. It follows that ΔH_S is the sum of two contributions identified by the type of molecular interaction:

$$-\Delta H_S = \Delta H_{ad} + \Delta H_n \tag{7}$$

For non-polar solutes, equation (7) will be reduced to the following form:

$$-\Delta H_S = \Delta H_n \tag{8}$$

The curve of the alkanes expressed by equation (6) can be approximated for simplicity by a straight line passing through the origin, introducing a maximum error of 5 percent in the values of ΔH_{ad}. Equation (6) will then be reduced to:

$$-\Delta H_S = 1.71\alpha_2 \tag{9}$$

Equation (9) gives the dashed line in Figure 16.

A linear correlation was found to exist between ΔH_{ad} and the dipole moments of the solutes, as shown in Figure 17. A similar correlation also exists when ΔH_{ad} is estimated from the straight line approximation represented by equation (9), as shown in Figure 18. The slight scatter around the line is probably due to the exculsion of the contribution of the permanent quadrupoles and higher multipole moments and also the choice of the proper values of dipole moments. Vapor-state values for dipole moments were used whenever possible. The solid lines in Figures 17 and 18 are least-squares fits (forced through the origin) of data for compounds which because of their chemical structures should not have specific interactions with poly (ethyl methacrylate). Compounds not exhibiting specific inter-
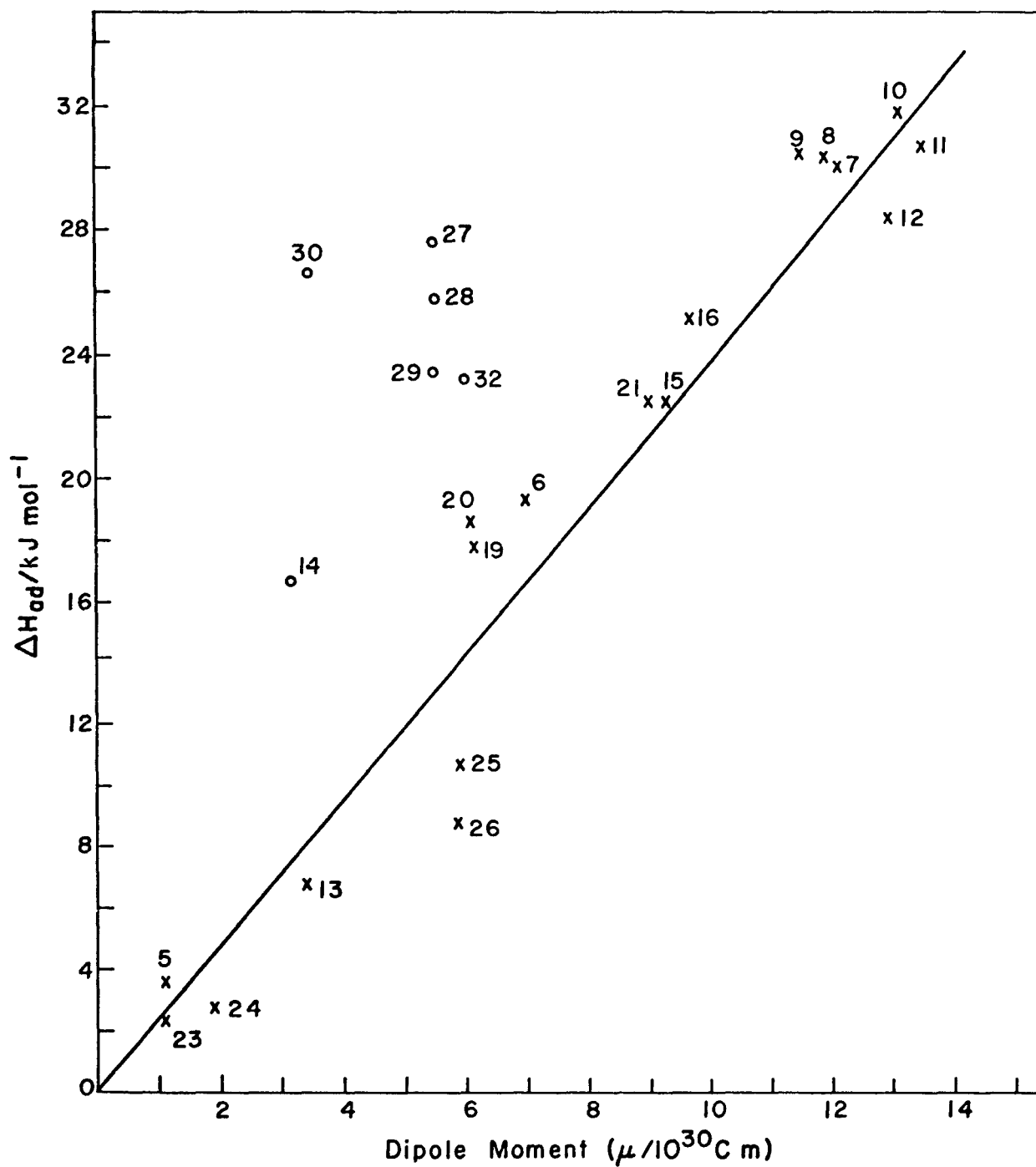
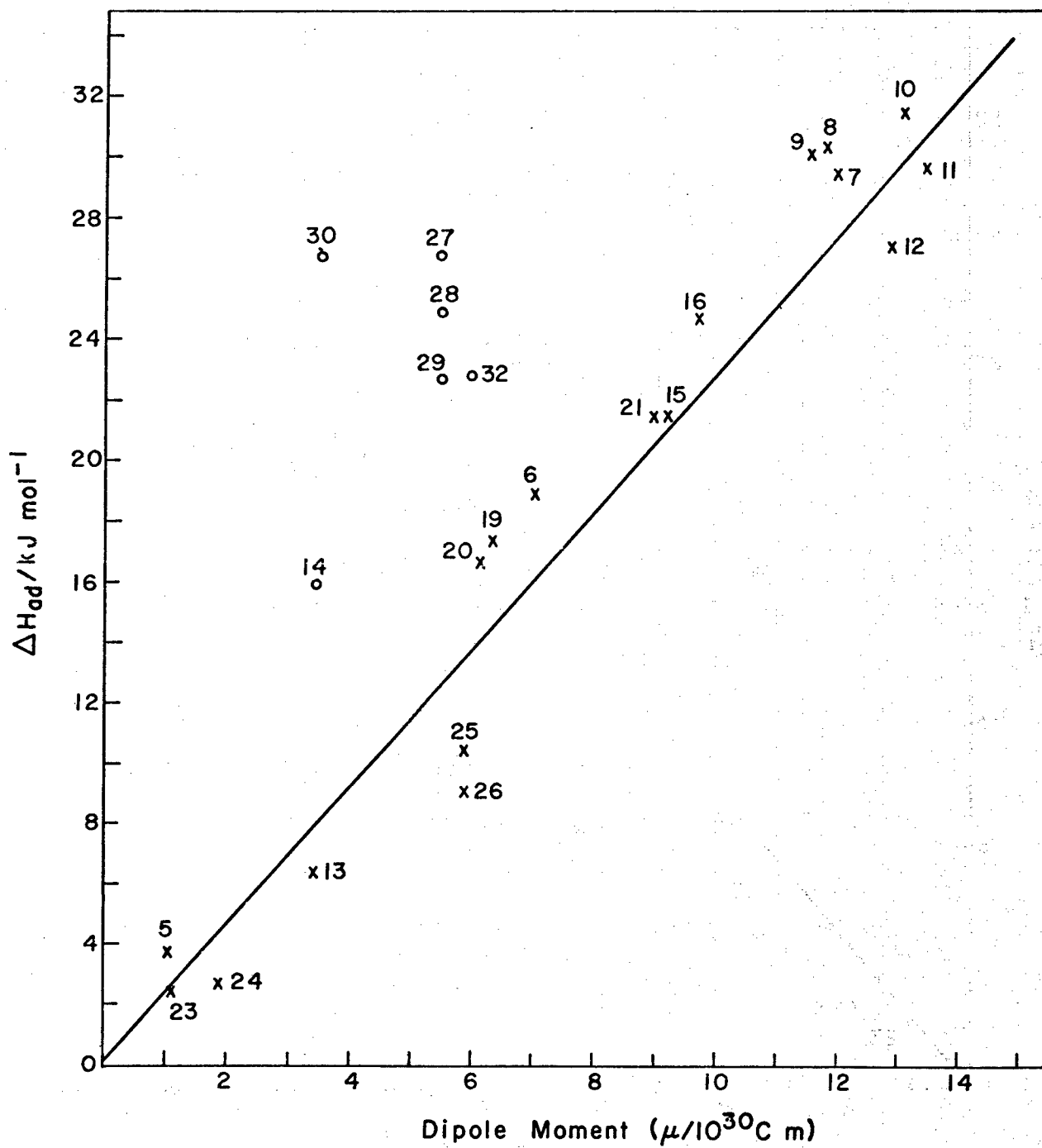FIGURE 17 - Plot of ΔH_{ad} for Solutes in Poly(ethyl methacrylate) vs. Solute Dipole Moment

FIGURE 18 - Plot of ΔH_{ad} (from straight line approximation) for Solutes in Poly(ethyl methacrylate) vs. Solute Dipole Moment

$$\frac{\Delta H_S \ (\underline{n}\text{-alkane})}{\omega \ (\underline{n}\text{-alkane})} = \frac{\Delta H_S \ (\text{Branched alkane})}{\omega \ (\text{Branched alkane})} \qquad (12)$$

where ω is the acentric factor defined by Pitzer (1955).

Knowing the heat of solution of an $\underline{n}$-alkane, it is possible to estimate with good accuracy the heat of solution of its isomers from equation (12).

Taking the cyclic paraffins as a reference for the polar, aromatic compounds, the polar, aromatic solutes were found to have excessively large values of ΔH_{ad}, when compared with the ΔH_{ad} that would be predicted by the solid line in Figure 17 for molecules having dipole moments equivalent to those of polar, aromatic compounds. Benzene, which is non-polar, would have had a ΔH_{ad} corresponding to a dipole moment of approximately 7×10^{30} C. m. using cyclic paraffins as a reference. We conclude that the cyclic paraffins are not a proper reference for the aromatics in the combined treatment of aliphatics and aromatics.

If benzene, toluene and ethyl benzene were to be used as a reference-curve solutes for other polar aromatic compounds, then the values of ΔH_{ad} would be lower than the true values and would fall well below the lines of Figures 17 and 18. This is due to the fact that an additional heat of solution (ΔH_{ad}) which results from dipolar interaction of toluene and ethyl benzene with the polymer is included in the values of ΔH_S for toluene and ethyl benzene. This value will then introduce an error in the measured ΔH_{ad} values for bromobenzene and chlorobenzene equivalent to about 2. kJ mol^{-1}. Knowing the dipole moments of toluene and ethyl

actions with the polymer are indicated by the symbol "χ" in Figures 17 and 18.

Points which are well above the line belong to compounds exhibiting specific interactions. The vertical distances above the dipole-dipole line are measures of the magnitude of such interactions.

From Figures 16 and 17 we suggest the following mathematical model which relates ΔH_S to the molecular properties of the solutes:

$$-\Delta H_S = a_3 \alpha_2 + b_3 \mu_2 + X \tag{10}$$

where a_3 (=1.71) and b_3 (=2.52) are empirical constants representing the slopes of plots of ΔH_S vs. α and ΔH_{ad} vs. μ, respectively.

According to equation (6) a more accurate form of equation (10) is

$$-\Delta H_S = 1.500 \alpha_2 - 0.010 \alpha_2^2 + 0.002 \alpha_2^3 + b_3 \mu_2 + X \tag{11}$$

Values of ΔH_S calculated from equation (11) are listed in Table 2.

Molecular Shape of Solutes

The shape of the non-polar molecules forming the reference line was found to be an important criterion in justifying the above relationships. It was found by Dwyer and Karim (1975) that branched polar compounds should have a reference curve composed of similarly branched alkanes. A method is developed here to account for such structural changes, and it is summarized by the following equation:

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benzene, this error was estimated from an extrapolation procedure in Figure 17. We may safely conclude that the reference curve for bromobenzene and chlorobenzene is a line passing through the point of benzene and below the points of toluene and ethyl benzene. Such a procedure is necessary in order to generalize the correlations developed here for combined study of aliphatic and aromatic compounds.

When considering aromatic systems only it is possible to assume that the cyclic paraffins are reference solutes representing the reference curve. This assumption will not change the overall interaction selectivity scale, except for benzene.

From Figures 17 and 18 it appears that alcohols, amines, and chloroform exhibit significant specific interactions in the polymer solution. This behavior may be attributed to the formation of hydrogen bonds between these solutes and the polymer.

Conclusion

The correlations between heats of solution at infinite dilution of binary systems and the molecular parameters of the two components developed by Dwyer and Karim (1975) have been extended to describe interactions in polymer solutions. The correlations were found to apply to the polymer studied here. We have also extended the correlations of Dwyer and Karim (1975) to allow for structural changes in the solute molecules by employing Pitzer's acentric factor (1955). In order to obtain true solution thermodynamic data, the study was conducted at temperatures greater than the melting range of the polymer. It was possible to isolate the contributions of solute polarizability, dipole moment, and other solute-polymer

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polymer per 10 g Fluoropak. Helium was used as the carrier gas and was dried by passage through a gas purifier containing silica gel and molecular sieve. The gas inlet pressure was measured by a Heise Pressure Gage (0 - 100 psig, 0.1 div). Flow rates in the range of 2 - 12 ml/min (STP) were used at room temperature and repeatedly checked during the experiment using a bubble flow meter. Injector and detector temperatures were kept 20°C higher than the boiling point of the highest-boiling solute. Our sampling technique was based on drawing a sample of a solute by 1 μl Hamilton syringe and flushing out. Usually, traces of the sample are left in the syringe, and we will refer to these traces as "residual". Approximately 0.1 μl of the residual was injected into the chromatograph. By using such small samples we found that there is no dependence of retention time on sample size over a large range of sample sizes studied, i.e., 0.1 μl - 0.5 μl of the residual. Fluoropak 80 was used as solid support due to its low surface energy and resulting minimal adsorptive capacity.

Results and Discussion

Specific retention volumes (V_g^o) of a variety of monofunctional organic solutes were determined. In order to obtain equilibrium retention volumes, it was necessary to extrapolate the values of V_g^o to zero flow rate as illustrated in Figure 15. Measurements of V_g^o were performed at seven different flow rates, and over the range of 2 - 12 ml/min (STP) for all the solutes studied, the retention volumes were independent of the flow rate if the latter was less than 4 ml/min. Errors in V_g^o values at flow rates of 2 ml/min become as great as 2 percent. Therefore, we

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chose flow rates of approximately 4 ml/min in order to obtain equilibrium data with optimum reproducibility. A detailed discussion of the zero-flow rate extrapolation procedure was presented by Lichtenthaler et al. (1974). The following empirical relation was suggested:

$$V_g^o = c \exp (-d \cdot F^2) \tag{5}$$

where c and d are temperature dependent constants, and F is the flow rate in ml/min (STP).

Interactions between polar molecules are mainly due to (i) the permanent electrical forces (dipoles), (ii) quadrupoles and higher multi-pole moments, and (iii) hydrogen bonding together with charge-transfer and coordination forces. Interactions due to the latter type of electrical forces will be referred to in this work as "specific interactions".

For a non-polar solute in solution with a polar polymer, the type of interaction is mainly due to the induced electric moments which arise from the short-lived perturbation of the electron positions during collision or near collision. Interactions due to dispersion forces are always present in any solute-solvent systems.

A similar procedure to that used by Dwyer and Karim (1975) in determining the contribution of the above interaction parameters individually to the chromatographically measured heats of solution will be adopted in this work.

Values of ΔH_S of the solutes in the polymer together with their molecular parameters are listed in Table 4.

interaction to the heat of solution. This approach can be used to help in predicting optimum solubility characteristics based on well-defined molecular parameters.

In a subsequent paper, we will show how to analyze data of the type presented in this paper to improve Hansen's three-dimensional solubility parameter method for predicting solubility of polymers in polar and hydrogen-bonding solvents.

APPENDIX F

CALCULATION OF SOLUBILITY

PARAMETERS USING GROUP CONTRIBUTIONS

Hansen (1971) presents a group contribution method for calculating δ_p and δ_h. We illustrate the calculation of δ_p for n-ethylacetamide. The structure is

$$CH_3 - C - N \overset{\displaystyle O}{\underset{\displaystyle}{\big\|}} \begin{array}{c} C_2H_5 \\ \diagup \\ \diagdown \\ H \end{array}$$
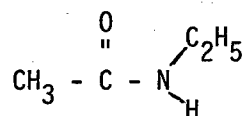
Groups contributing to polarity and δ_p are C=O and NH. Using Hansen group contributions

$$V\,\delta_p = \Sigma \text{ (all polar groups)} \qquad\qquad \text{(VI-1)}$$

where V is molar volume. In our case,

$$V\,\delta_p = V\,\delta_p(C=O) + V\,\delta_p(NH)$$

$$= (390 + 100)\ (\text{cal-cm}^3)^{1/2}/g\ \text{mol}$$

$$\delta_p = \frac{490(\text{cal-cm}^3)^{1/2}}{g\ \text{mol}} \left| \frac{0.937\ g}{\text{cm}^3} \right| \frac{g\ \text{mol}}{87g} = 5.28\ (\text{cal/cm}^3)^{1/2}$$

To calculate δ_h for n-ethylacetamide, one uses the relation (Hansen, 1971)

$$V\,\delta_h^{\ 2} = \Sigma \text{ (all H-bonding groups)} \qquad\qquad \text{(VI-2)}$$

or $\qquad V\,\delta_h^{\ 2} = V\,\delta_p^{\ 2}(C=O) + V\,\delta_h^{\ 2}(NH)$

$$= (800 + 750)\ \text{cal/g mol}$$

$$= 1550\ \text{cal/g mol}$$

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$$\delta_h = \left[\frac{1550 \text{ cal}}{\text{g mole}} \middle| \frac{0.937 \text{ g}}{\text{cm}^3} \middle| \frac{\text{g mol}}{87\text{g}} \right]^{1/2}$$

$$\delta_h = 4.08 \ (\text{cal/cm}^3)^{1/2}$$

Calculation of δ_p and δ_h is the same for polymers except that all computations should be based on a signle repeat unit and using the true polymer density.

SECTION VIII

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