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**Characterization of the
 π^* Scale of
Solvent Polarity-Polarizability**

By

Scott William Goffinet

Thesis

**for the
Degree of Bachelor of Science
in
Chemical Engineering**

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For Dad

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List of Symbols

- π^* : Kamlet-Taft solvatochromic scale number
- μ : Dipole moment, Debeyes
- α : Polarizability, cm^3
- I : Ionization potential, electron volts
- n_D : Index of refraction
- λ : nonpolar solubility parameter, $(\text{cal}/\text{cm}^3)^{1/2}$
- τ : MOSCED polarity parameter
- $\Delta\pi^*$: difference between calculated and experimental π^*
- ID : compound identification number
- n : number of compounds
- α_{KT} : Kamlet-Taft acidity scale
- β_{KT} : Kamlet-Taft basicity scale
- s : Kamlet-Taft π^* susceptibility
- V_m : Molar volume, cm^3/mol .
- N_0 : Avogadro's number
- κ : Boltzman's constant
- T : Absolute temperature, K

Summary

The objective of this research was to determine the relative contributions of dispersion, polarity, and polarizability forces to the Kamlet-Taft π^* scale [1]. In order to achieve this objective, quantitative descriptions of these intermolecular forces were required. Therefore, the key to the reduction of π^* into its separate components rested upon the representation of these forces. The ultimate utility of this research lies in its application to the MOSCED equation [2,3,4,].

In order to accurately characterize π^* and its fundamental contributors, a large database of physical properties was required. The database was constructed with the intent of the ready application of the results to the MOSCED model. Consequently, the 144 solvents in the MOSCED database [5] were used as the core. An additional 19 compounds were added for diversity. Since the requisite physical property data were not available for all 163 compounds the greatest number that could be used was 90.

The criteria used for determining the functional form used to approximate π^* were: the physical appeal of the form, and its ease of integration into the MOSCED system. The principal form used is given below.

$$\pi^* = a(L) + b(K) + c(D) + d \quad (1)$$

where: a, b, c, and d are adjustable parameters and

L: London force term (dispersion)

K: Keesom force term (dipole - dipole, polarity)

D: Debye force term (dipole induced - dipole, polarizability).

The forces were represented in the form of pairwise interaction potentials as shown below [6].

$$L = 1.2015 \times 10^{-5} \alpha^2 I$$

$$K = 6.6667 \times 10^{-16} \mu^4 / \kappa T$$

$$D = 2.000 \times 10^{-4} \mu^2 \alpha$$

$$\text{units: erg} \cdot \text{cm}^6 \times 10^{-57}$$

The overall results of this project were positive, even though the numerical accuracy of the correlation for π^* was not equivalent to previous work [7]. The average $\Delta\pi^*$ value for the 90 solvent set was ± 0.20 . This value was substantially reduced by categorizing the solvents into sets and using a separate intercept for each set. With five sets the average $\Delta\pi^*$ was ± 0.10 . It is important to realize when Equation 1 was used to describe π^* , a very small portion of the contributions to π^* came from dipole-dipole interactions. This is contrary to established belief [8].

Introduction

The π^* scale of solvent polarity-polarizability was introduced in 1977 by M. J. Kamlet, J. L. Abboud, and R. W. Taft as a method of measuring solvent polarity and polarizability effects on free energy related properties. The term was introduced as [9]:

$$XYZ = XYZ_0 + a\alpha_{\text{KT}} + b\beta_{\text{KT}} + s\pi^* \quad (2)$$

The XYZ could be a reaction rate, equilibrium constant, or a spectral position. It was the spectral shift property on which π^* was defined. Hydrogen bonding interactions were eliminated from π^* by the way in which the scale was developed, leaving polarity and polarizability interactions to make up π^* .

The motivation for this research stemmed from a desire to incorporate π^* into the estimation of the MOSCED τ parameter. Successful utilization of π^* to predict τ values would reduce the number of MOSCED parameters per compound from 1+ to 0+ [10]. Ideally this would be done by developing an adequate predictive model for π^* from which the polar contribution could be extracted easily. It was this intention that dictated the choice of the function used to model π^* . The major simplifying assumption implied by the use of this form was that the intermolecular forces are independent and additive. While other researchers [11,12,13,14,15,16,17] have sought to describe π^* on the basis of a reaction field model, [18,19,20] the approach taken here was fundamentally different. The major difference between the two approaches is that the reaction field models are based upon a point dipole immersed in a continuum dielectric medium; whereas the model used in this study based π^* on pairwise interactions.

Procedure

The database used was compiled with the intention of providing a wide range of π^* values. Benzyl acetate possessed the largest π^* , 1.19, and n-butane had the smallest at -0.11. Each of the 11 MOSCED groups was represented in the database. The database was composed of 90 compounds, 75 of which are polar. Tables 1a, 1b, 2a, and 2b display the database in order of identification number and also in order of their MOSCED grouping.

In several of the fitting attempts the compounds were separated into sets. This was done so that the intercepts, d , could be separately adjusted for each set. Table 2b shows in general the π^* 's for any given MOSCED group cluster together. Another method of segregating the compounds used was on the basis of polarity. Compounds with nonzero dipole moments were treated separately than those with no dipole moment. This reduced the number of compounds which could be fit at any one time and reduced the range of π^* that a set of parameters had to represent.

Several different functional forms were tried in an attempt to provide a numerically accurate and physically appealing characterization of π^* . Those not discussed in the Results section may be found in the Appendix. In order to test these various functional forms and methods of grouping compounds, a FORTRAN program was written which utilized an IMSL minimization routine. This program provided values for the adjustable parameters giving the best fit of calculated π^* 's to experimental values. A complete listing of the FORTRAN code is given in the Appendix. While the use of a minimization routine provides the best mathematical agreement between calculated and experimental π^* 's, it does not insure the most realistic physical description.

Results

Even though the expression used to approximate π^* did not provide adequately accurate predictions, the results did provide insight into the relative contributions to π^* . Since polarizability data was available for only 56 of the 90 compounds in the database, the Lorentz-Lorenz approximation for polarizability was used. It is.

$$\alpha = (3/4\pi N_0)(n_D^2 - 1)/(n_D^2 + 2)$$

Introducing this approximation definitely decreased the accuracy to which π^* could be fit, but it is felt the benefits gained by additional compounds being made available by using this estimation outweighed that negative aspect. Also, in order to utilize all 90 compounds, the ionization potential of each was assumed equal. Therefore, the ionization potential was lumped into a, the adjustable parameter associated with the London force term.

The results using the best fit parameters are shown below.

$$\pi^* = a(L) + b(K) + c(D) + d$$

a = 0.000
b = 0.000
c = 2.070
d = 0.372
n = 90
ave. $\Delta\pi^* = \pm 0.205$

a = 0.000
b = 0.000
c = 1.890
d = 0.399
n = 75 (polar only)
ave. $\Delta\pi^* = \pm 0.175$

a = 0.377
b = 0.005
c = 1.429
d₁ = -0.115
d₂ = 0.033
d₃ = 0.273
d₄ = 0.486
d₅ = 0.135
n = 71, (polar)
(MOSCED gp. 10 excl.)
ave. $\Delta\pi^* = \pm 0.097$

The adjustable parameters were constrained to be non-negative in keeping with the original goals of the model. Figures 1, 2, and 3 show the variance of $\Delta\pi^*$ with π^* . It is seen from these Figures that only when multiple intercepts are used is an acceptable distribution of $\Delta\pi^*$ observed. The important information to be gathered

from these results is the overall contribution of each force to π^* , that is, the adjustable parameter associated with each force multiplied by the compound's individual London, Keesom, or Debye term. In the last set of data, the average London, Keesom, and Debye contributions were 12.3%, 0.3%, and 16.9% respectively. Clearly the largest contribution to π^* is the intercept. This fact makes the use of this form to estimate τ prohibitive since such a large portion of π^* is not assigned to any particular interaction. The much smaller than expected contribution by the dipole-dipole forces is probably due to the nature of the form used to represent it. Because these interactions were proportional to μ^4 small changes in the dipole moment caused large fluctuations in the estimated Keesom force. The scale of Keesom forces predicted by μ^4 range from 0 to 261, while the π^* values range from -0.11 to 1.19. Simply using a linear function of the Keesom forces did not facilitate adequate fitting.

Conclusions

1. The functional form used to approximate π^* did not provide results as accurate as those used by previous researchers.
2. The partition of π^* by using pairwise interactions is not correct.
3. Application of the results of this study to MOSCED parameter estimation is not, at present, feasible. However, the results of earlier studies are equally inapplicable.
4. In the cases where the average error was acceptable (different intercepts for each set of compounds), the model predicted an unexpectedly small Keesom force contribution.
5. The representation of the dipole-dipole interactions by μ^4 is too sensitive to small changes in the dipole moment.

Recommendations

1. Future attempts to discern the separate contributions to π^* should not be based on pairwise interactions.
2. In order to correctly portray the dispersion contribution to π^* , a homomorph technique [21] should be used (see Appendix).
3. Before pursuing another method of modelling π^* , a modification of the previous work should be attempted, so as to make it integrable into the MOSCED model.

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Appendix

Table 1a

Physical Property Data

V	RI	LDA	I	ID	COMPOUND
72.0	1.628		10.08	1	CARBON DISULFIDE
96.5	1.460		11.47	2	CARBON TETRACHLORIDE
80.7	1.446		11.10	4	CHLOROFORM
64.1	1.424		9.30	6	DICHLOROMETHANE
40.5	1.328		10.84	8	METHANOL
53.7	1.381	8.22	11.10	9	NITROMETHANE
52.2	1.344	8.02	12.20	11	ACETONITRILE
99.6	1.338			12	1,1,1-TRICHLOROETHANE
79.1	1.445		11.12	14	1,2-DICHLOROETHANE
72.0	1.392	8.04	10.98	16	NITROETHANE
58.4	1.361	7.80	10.49	19	ETHANOL
70.4	1.366	7.98	11.84	20	PROPIONITRILE
74.4	1.359	7.68	9.69	21	ACETONE
80.4	1.360		10.61	22	ETHYL FORMATE
79.3	1.361		10.27	23	METHYL ACETATE
89.0	1.402	8.06	10.81	24	1-NITROPROPANE
77.0	1.430	8.35	9.12	25	DIMETHYL FORMAMIDE
90.1	1.394	7.95	10.71	26	2-NITROPROPANE
88.1	1.388		10.82	28	N-PROPYL CHLORIDE
74.8	1.386	7.79	10.10	31	N-PROPANOL
89.6	1.379	7.64	9.50	32	2-BUTANONE
96.3	1.378		10.15	33	METHYL PROPIONATE
81.1	1.407	8.36	9.42	34	TETRAHYDROFURAN
97.3	1.377		10.54	35	N-PROPYL FORMATE
97.8	1.372	7.60	10.11	36	ETHYL ACETATE
84.2	1.422		9.13	37	DIOXANE
104.5	1.402		10.67	39	N-BUTYL CHLORIDE
100.4	1.333	6.94	10.63	42	N-BUTANE
91.5	1.399	7.79	10.04	43	N-BUTANOL
80.5	1.510	9.90	9.30	44	PYRIDINE
94.1	1.407	8.20	10.53	47	CYCLOPENTANE
109.6	1.371	7.23	9.50	50	1-PENTENE
105.8	1.392	7.72	9.32	55	3-PENTANONE
106.5	1.390		9.37	56	2-PENTANONE
115.0	1.384		10.04	57	N-PROPYL ACETATE
113.7	1.388		10.07	58	METHYL BUTYLATE
114.5	1.384		10.00	59	ETHYL PROPIONATE
115.3	1.358	7.17	10.35	61	N-PENTANE
116.4	1.354		10.32	62	ISOPENTANE
108.1	1.410	7.87		63	1-PENTANOL
102.3	1.552	9.84	9.92	64	NITROBENZENE
101.8	1.525		9.07	65	CHLOROBENZENE

Table 1a
Physical Property Data

V	RI	LDA	I	ID	COMPOUND
89.1	1.501	9.20	9.24	66	BENZENE
89.0	1.551	9.88	8.51	67	PHENOL
91.1	1.586	9.83	7.70	68	ANILINE
101.4	1.447		8.72	69	CYCLOHEXENE
103.6	1.451	8.84	9.14	70	CYCLOHEXANONE
108.1	1.426		9.80	72	CYCLOHEXANE
125.0	1.388		7.70	73	1-HEXENE
105.4	1.467			78	CYCLOHEXYANOL
132.0	1.392	7.65	9.56	79	N-BUTYL ACETATE
130.8	1.375	7.33	10.18	80	N-HEXANE
124.7	1.418			86	N-HEXANOL
139.0	1.401		7.50	87	TRIETHYLAMINE
102.6	1.528		9.71	88	BENZONITRILE
106.3	1.497	8.95	3.82	91	TOLUENE
109.1	1.517		8.21	92	ANISOLE
146.6	1.388	7.47	9.90	98	N-HEPTANE
116.9	1.534	9.57	9.27	101	ACETOPHENONE
122.5	1.496	9.01	8.76	102	ETHYL BENZENE
123.3	1.496	8.83	8.44	103	P-XYLENE
120.6	1.506		8.56	104	O-XYLENE
162.6	1.397			109	N-OCTANE
157.8	1.430			110	N-OCTANOL
118.1	1.627			111	QUINOLINE
142.4	1.523			113	BENZYL ACETATE
178.7	1.405			117	N-NONANE
189.6	1.418		7.23	118	TRIPROPYLAMINE
156.0	1.490		8.69	120	N-BUTYL BENZENE
194.9	1.412	7.85		126	N-DECANE
227.5	1.422			128	N-DODECANE
94.3	1.396	7.08	9.60	145	1-BUTENE
88.3	1.423		9.30	146	CYCLOPENTENE
72.2	1.368	7.38	10.97	147	ETHYL CHLORIDE
55.4	1.339		11.30	148	METHYL CHLORIDE
123.4	1.497		8.58	149	M-XYLENE
94.3	1.023		9.20	150	FLOUROBENZENE
105.5	1.495		8.98	151	BROMOBENZENE
142.2	1.381		9.27	152	DI-N-PROPYL ETHER
57.1	1.332		10.20	153	ACETALDEHYDE
73.4	1.364		9.98	154	PROPIONALDEHYDE
66.0	1.366		8.86	155	ETHYL AMINE

Table 1a

Physical Property Data

V	RI	LDA	I	ID	COMPOUND
83.0	1.387		8.78	156	N-PROPYL AMINE
99.3	1.403		8.71	157	N-BUTYL AMINE
104.2	1.386		8.01	158	DI-ETHYL AMINE
94.3	1.363		7.82	159	TRI-METHYL AMINE
18.1	1.333		12.60	160	WATER
125.7	1.400		8.12	161	NAPHTHALENE
138.9	1.283		7.55	162	ANTHRACENE
181.9	1.594		8.10	163	PHENANTHRACENE

V: Molar volume, ml

RI: Refractive index

LDA: Nonpolar Solubility parameter, $(\text{cal./ml})^{0.5}$

I: Ionization Potential, eV

Table 1b

Physical Property Data

MU	ALPHA	PST	IGRP	ID	COMPOUND
0.00	88.0	0.00	10	1	CARBON DISULFIDE
0.00	105.0	0.28	02	2	CARBON TETRACHLORIDE
1.01	82.3	0.58	02	4	CHLOROFORM
1.60	64.8	0.82	02	6	DICHLOROMETHANE
1.70	32.3	0.40	03	8	METHANOL
3.46	73.7	0.85	07	9	NITROMETHANE
3.92	44.8	0.75	05	11	ACETONITRILE
1.78	107.0	0.49	02	12	1,1,1-TRICHLOROETHANE
1.41	80.0	0.81	02	14	1,2-DICHLOROETHANE
2.40	96.3	0.80	07	16	NITROETHANE
1.69	51.1	0.40	03	19	ETHANOL
4.02	62.4	0.70	05	20	PROPIONITRILE
2.88	63.9	0.71	04	21	ACETONE
1.93	80.1	0.61	06	22	ETHYL FORMATE
1.72	69.4	0.60	06	23	METHYL ACETATE
3.66		0.78	07	24	1-NITROPROPANE
3.82	78.1	0.88	10	25	DIMETHYL FORMAMIDE
3.73		0.75	07	26	2-NITROPROPANE
2.05	100.0	0.39	02	28	N-PROPYL CHLORIDE
1.68	67.4	0.40	03	31	N-PROPANOL
3.30	81.3	0.67	04	32	2-BUTANONE
1.70		0.55	06	33	METHYL PROPIONATE
1.63		0.58	06	34	TETRAHYDROFURAN
1.90		0.60	06	35	N-PROPYL FORMATE
1.90	97.0	0.55	06	36	ETHYL ACETATE
0.40	100.0	0.55	10	37	DIOXANE
2.05	113.0	0.39	02	39	N-BUTYL CHLORIDE
0.05	82.0	-0.11	00	42	N-BUTANE
1.66	88.8	0.40	03	43	N-BUTANOL
2.19	95.0	0.87	09	44	PYRIDINE
0.00	91.5	-0.01	00	47	CYCLOPENTANE
0.40		0.08	01	50	1-PENTENE
2.70	99.3	0.72	04	55	3-PENTANONE
2.50	99.3	0.65	04	56	2-PENTANONE
1.80		0.53	06	57	N-PROPYL ACETATE
1.70		0.53	06	58	METHYL BUTYLATE
1.80		0.50	06	59	ETHYL PROPIONATE
0.00	99.9	-0.08	00	61	N-PENTANE
0.13		-0.06	00	62	ISOPENTANE
1.70		0.40	03	63	1-PENTANOL
4.22	129.0	1.01	08	64	NITROBENZENE
1.69	123.0	0.71	08	65	CHLOROBENZENE

Table 1b

Physical Property Data

MU	ALPHA	PST	IGRP	ID	COMPOUND
0.00	107.4	0.59	08	66	BENZENE
1.45	111.0	0.72	03	67	PHENOL
1.60	121.0	0.73	08	68	ANILINE
0.60	107.0	0.10	01	69	CYCLOHEXENE
3.10		0.76	04	70	CYCLOHEXANONE
0.30	109.0	0.00	00	72	CYCLOHEXANE
0.40		0.08	01	73	1-HEXENE
1.70	115.6	0.45	03	78	CYCLOHEXANOL
1.80		0.51	06	79	N-BUTYL ACETATE
0.00	119.0	-0.04	00	80	N-HEXANE
1.80		0.40	03	86	N-HEXANOL
0.90	131.0	0.14	09	87	TRIETHYLAMINE
4.18	125.0	0.90	08	88	BENZONITRILE
0.36	123.0	0.55	08	91	TOLUENE
1.38		0.73	08	92	ANISOLE
0.00	136.0	-0.02	00	98	N-HEPTANE
3.00	150.0	0.90	08	101	ACETOPHENONE
0.40	142.0	0.53	08	102	ETHYL BENZENE
0.10	141.0	0.51	08	103	P-XYLENE
0.50	149.0	0.51	08	104	O-XYLENE
0.00	159.0	0.01	00	109	N-OCTANE
2.00		0.40	03	110	N-OCTANOL
2.29		0.92	08	111	QUINOLINE
1.80		1.19	08	113	BENZYL ACETATE
0.73		0.02	00	117	N-NONANE
1.29		0.14	09	118	TRIPROPYLAMINE
0.00		0.49	08	120	N-BUTYL BENZENE
0.00	191.0	0.03	00	126	N-DECANE
0.00	227.0	0.05	00	128	N-DODECANE
0.30	79.7	0.08	01	145	1-BUTENE
0.90	91.0	0.10	01	146	CYCLOPENTENE
2.00	64.0	0.47	02	147	ETHYL CHLORIDE
1.90	47.2	0.82	02	148	METHYL CHLORIDE
0.30	142.0	0.51	08	149	M-XYLENE
1.40	103.0	0.62	08	150	FLOUROBENZENE
1.50	147.0	0.79	08	151	BROMOBENZENE
1.20	125.0	0.24	10	152	DI-N-PROPYL ETHER
2.50	45.9	0.67	04	153	ACETALDEHYDE
2.70	65.0	0.65	04	154	PROPIONALDEHYDE
1.30	40.1	0.32	09	155	ETHYL AMINE

Table 1b

Physical Property Data

MU	ALPHA	PST	IGRP	ID	COMPOUND
1.30	92.0	0.31	09	156	N-PROPYL AMINE
1.30	135.0	0.31	09	157	N-BUTYL AMINE
1.10	102.0	0.25	09	158	DI-ETHYL AMINE
0.60	81.0	0.16	09	159	TRI-METHYL AMINE
0.80	14.5	1.09	10	160	WATER
0.00	165.0	0.70	08	161	NAPHTHALENE
0.00	254.0	0.80	08	162	ANTHRACENE
0.00	388.0	0.80	08	163	PHENANTHRACENE

MU: Dipole Moment, Debye

ALPHA: Polarizability, ml x 10⁻²⁵

PST: Pi-Star

IGRP: MOSCED Group classification

Table 2a

Physical Property Data

V	RI	LDA	I	IGRP	ID	COMPOUND
130.8	1.375	7.33	10.18	00	80	N-HEXANE
178.7	1.405			00	117	N-NONANE
116.4	1.354		10.32	00	62	ISOPENTANE
100.4	1.333	6.94	10.63	00	42	N-BUTANE
115.3	1.358	7.17	10.35	00	61	N-PENTANE
194.9	1.412	7.85		00	126	N-DECANE
108.1	1.426		9.80	00	72	CYCLOHEXANE
162.6	1.397			00	109	N-OCTANE
94.1	1.407	8.20	10.53	00	47	CYCLOPENTANE
227.5	1.422			00	128	N-DODECANE
146.6	1.388	7.47	9.90	00	98	N-HEPTANE
125.0	1.388		7.70	01	73	1-HEXENE
88.3	1.423		9.30	01	146	CYCLOPENTENE
109.6	1.371	7.23	9.50	01	50	1-PENTENE
94.3	1.396	7.08	9.60	01	145	1-BUTENE
101.4	1.447		8.72	01	69	CYCLOHEXENE
99.6	1.438			02	12	1,1,1-TRICHLOROETHANE
72.2	1.368	7.38	10.97	02	147	ETHYL CHLORIDE
79.1	1.445		11.12	02	14	1,2-DICHLOROETHANE
96.5	1.460		11.47	02	2	CARBON TETRACHLORIDE
88.1	1.388		10.82	02	28	N-PROPYL CHLORIDE
55.4	1.339		11.30	02	148	METHYL CHLORIDE
64.1	1.424		9.30	02	6	DICHLOROMETHANE
80.7	1.446		11.10	02	4	CHLOROFORM
104.5	1.402		10.67	02	39	N-BUTYL CHLORIDE
89.0	1.551	9.88	8.51	03	67	PHENOL
40.5	1.328		10.84	03	8	METHANOL
105.4	1.467			03	78	CYCLOHEXANOL
91.5	1.399	7.79	10.04	03	43	N-BUTANOL
157.8	1.430			03	110	N-OCTANOL
108.1	1.410	7.87		03	63	1-PENTANOL
58.4	1.361	7.80	10.49	03	19	ETHANOL
74.8	1.386	7.79	10.10	03	31	N-PROPANOL
124.7	1.418			03	86	N-HEXANOL
57.1	1.332		10.20	04	153	ACETALDEHYDE
74.4	1.359	7.68	9.69	04	21	ACETONE
89.6	1.379	7.64	9.50	04	32	2-BUTANONE
73.4	1.364		9.98	04	154	PROPIONALDEHYDE
106.5	1.390		9.37	04	56	2-PENTANONE
103.6	1.451	8.84	9.14	04	70	CYCLOHEXANONE
105.8	1.392	7.72	9.32	04	55	3-PENTANONE
70.4	1.366	7.98	11.84	05	20	PROPIONITRILE

Table 2a

Physical Property Data

V	RI	LDA	I	IGRP	ID	COMPOUND
52.2	1.344	8.02	12.20	05	11	ACETONITRILE
113.7	1.388		10.07	06	58	METHYL BUTYLATE
97.8	1.372	7.60	10.11	06	36	ETHYL ACETATE
114.5	1.384		10.00	06	59	ETHYL PROPIONATE
96.3	1.378		10.15	06	33	METHYL PROPIONATE
115.0	1.384		10.04	06	57	N-PROPYL ACETATE
80.4	1.360		10.61	06	22	ETHYL FORMATE
81.1	1.407	8.36	9.42	06	34	TETRAHYDROFURAN
132.0	1.392	7.65	9.56	06	79	N-BUTYL ACETATE
97.3	1.377		10.54	06	35	N-PROPYL FORMATE
79.3	1.361		10.27	06	23	METHYL ACETATE
90.1	1.394	7.95	10.71	07	26	2-NITROPROPANE
89.0	1.402	8.06	10.81	07	24	1-NITROPROPANE
53.7	1.381	8.22	11.10	07	9	NITROMETHANE
72.0	1.392	8.04	10.88	07	16	NITROETHANE
101.8	1.525		9.07	08	65	CHLOROBENZENE
118.1	1.627			08	111	QUINOLINE
122.5	1.496	9.01	8.76	08	102	ETHYL BENZENE
120.6	1.506		8.56	08	104	O-XYLENE
156.0	1.490		8.69	08	120	N-BUTYL BENZENE
94.3	1.023		9.20	08	150	FLOUROBENZENE
123.3	1.496	8.83	8.44	08	103	P-XYLENE
106.3	1.497	8.95	8.82	08	91	TOLUENE
102.6	1.528		9.71	08	88	BENZONITRILE
116.9	1.534	9.57	9.27	08	101	ACETOPHENONE
109.1	1.517		8.21	08	92	ANISOLE
181.9	1.594		8.10	08	163	PHENANTHRACENE
125.7	1.400		8.12	08	161	NAPHTHALENE
142.4	1.523			08	113	BENZYL ACETATE
123.4	1.497		8.58	08	149	M-XYLENE
91.1	1.586	9.83	7.70	08	68	ANILINE
102.3	1.552	9.84	9.92	08	64	NITROBENZENE
105.5	1.495		8.98	08	151	BROMOBENZENE
138.9	1.283		7.55	08	162	ANTHRACENE
89.1	1.501	9.20	9.24	08	66	BENZENE
189.6	1.418		7.23	09	118	TRIPROPYLAMINE
139.0	1.401		7.50	09	87	TRIETHYLAMINE
104.2	1.386		8.01	09	158	DI-ETHYL AMINE
83.0	1.387		8.78	09	156	N-PROPYL AMINE
66.0	1.366		8.86	09	155	ETHYL AMINE

Table 2a

Physical Property Data

V	RI	LDA	I	IGRP	ID	COMPOUND
94.3	1.363		7.82	09	159	TRI-METHYL AMINE
99.3	1.403		8.71	09	157	N-BUTYL AMINE
80.5	1.510	9.90	9.30	09	44	PYRIDINE
142.2	1.381		9.27	10	152	DI-N-PROPYL ETHER
72.0	1.628		10.08	10	1	CARBON DISULFIDE
77.0	1.430	8.35	9.12	10	25	DIMETHYL FORMAMIDE
18.1	1.333		12.60	10	160	WATER
84.2	1.422		9.13	10	37	DIOXANE

IGRP: MOSCED group number

- 0: alkanes
- 1: alkenes
- 2: halogens
- 3: alcohols
- 4: aldehydes/ketones
- 5: nitriles
- 6: esters
- 7: nitros
- 8: aromatics
- 9: amines
- 10: misc.

Table 2b

Physical Property Database

MU	ALPHA	PST	IGRP	ID	COMPOUND
0.00	119.0	-0.04	00	80	N-HEXANE
0.73		0.02	00	117	N-NONANE
0.13		-0.06	00	62	ISOPENTANE
0.05	82.0	-0.11	00	42	N-BUTANE
0.00	99.9	-0.08	00	61	N-PENTANE
0.00	191.0	0.03	00	126	N-DECANE
0.30	109.0	0.00	00	72	CYCLOHEXANE
0.00	159.0	0.01	00	109	N-OCTANE
0.00	91.5	-0.01	00	47	CYCLOPENTANE
0.00	227.0	0.05	00	128	N-DODECANE
0.00	136.0	-0.02	00	98	N-HEPTANE
0.40		0.08	01	73	1-HEXENE
0.90	91.0	0.10	01	146	CYCLOPENTENE
0.40		0.08	01	50	1-PENTENE
0.30	79.7	0.08	01	145	1-BUTENE
0.60	107.0	0.10	01	69	CYCLOHEXENE
1.78	107.0	0.49	02	12	1,1,1-TRICHLOROETHANE
2.00	64.0	0.47	02	147	ETHYL CHLORIDE
1.41	80.0	0.81	02	14	1,2-DICHLOROETHANE
0.00	105.0	0.28	02	2	CARBON TETRACHLORIDE
2.05	100.0	0.39	02	28	N-PROPYL CHLORIDE
1.90	47.2	0.82	02	148	METHYL CHLORIDE
1.60	64.8	0.82	02	6	DICHLOROMETHANE
1.01	82.3	0.58	02	4	CHLOROFORM
2.05	113.0	0.39	02	39	N-BUTYL CHLORIDE
1.45	111.0	0.72	03	67	PHENOL
1.70	32.3	0.40	03	8	METHANOL
1.70	115.6	0.45	03	78	CYCLOHEXANOL
1.66	88.8	0.40	03	43	N-BUTANOL
2.00		0.40	03	110	N-OCTANOL
1.70		0.40	03	63	1-PENTANOL
1.69	51.1	0.40	03	19	ETHANOL
1.68	67.4	0.40	03	31	N-PROPANOL
1.80		0.40	03	86	N-HEXANOL
2.50	45.9	0.67	04	153	ACETALDEHYDE
2.88	63.9	0.71	04	21	ACETONE
3.30	81.3	0.67	04	32	2-BUTANONE
2.70	65.0	0.65	04	154	PROPIONALDEHYDE
2.50	99.3	0.65	04	56	2-PENTANONE
3.10		0.76	04	70	CYCLOHEXANONE
2.70	99.3	0.72	04	55	3-PENTANONE
4.02	62.4	0.70	05	20	PROPIONITRILE

Table 2b

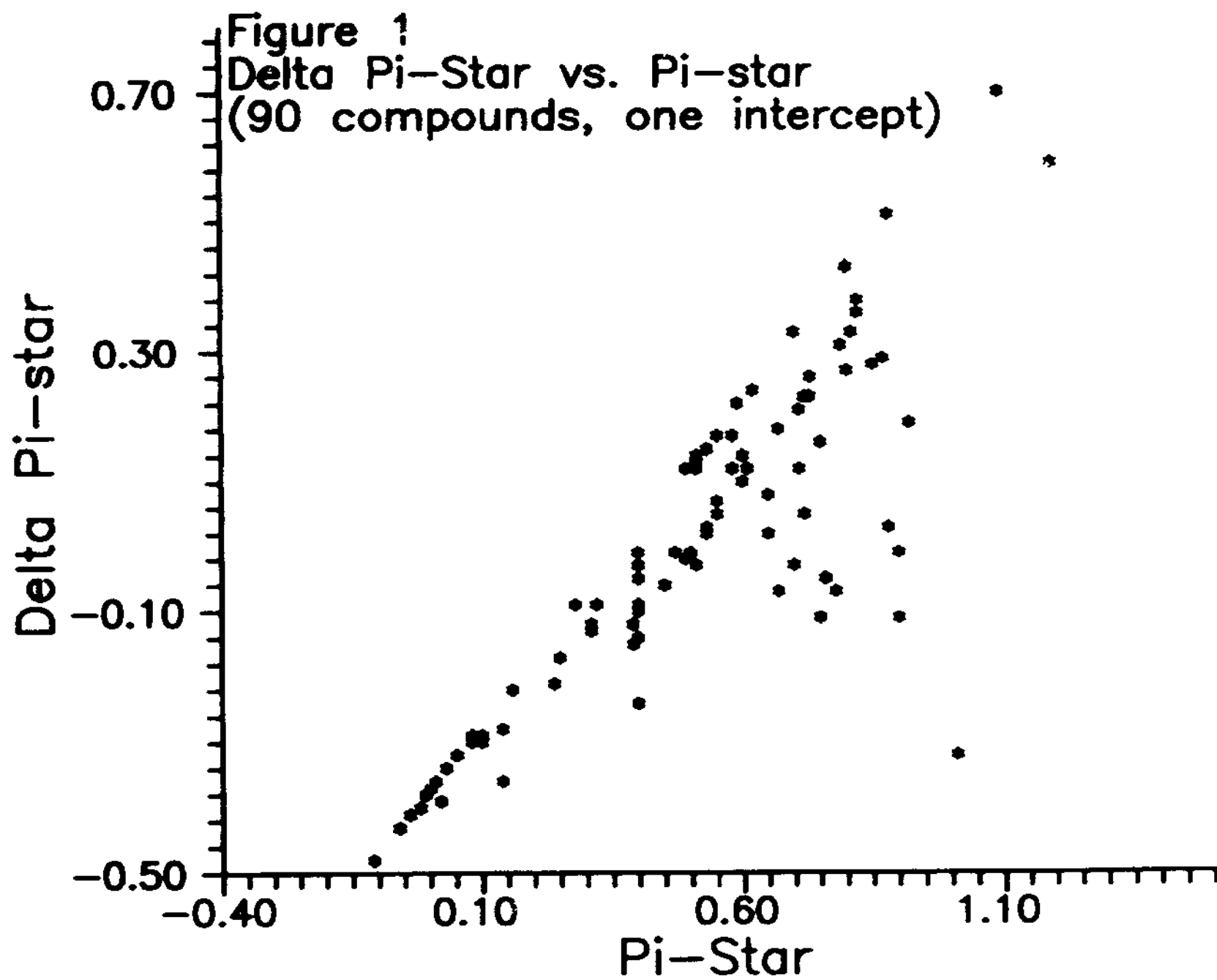
Physical Property Database

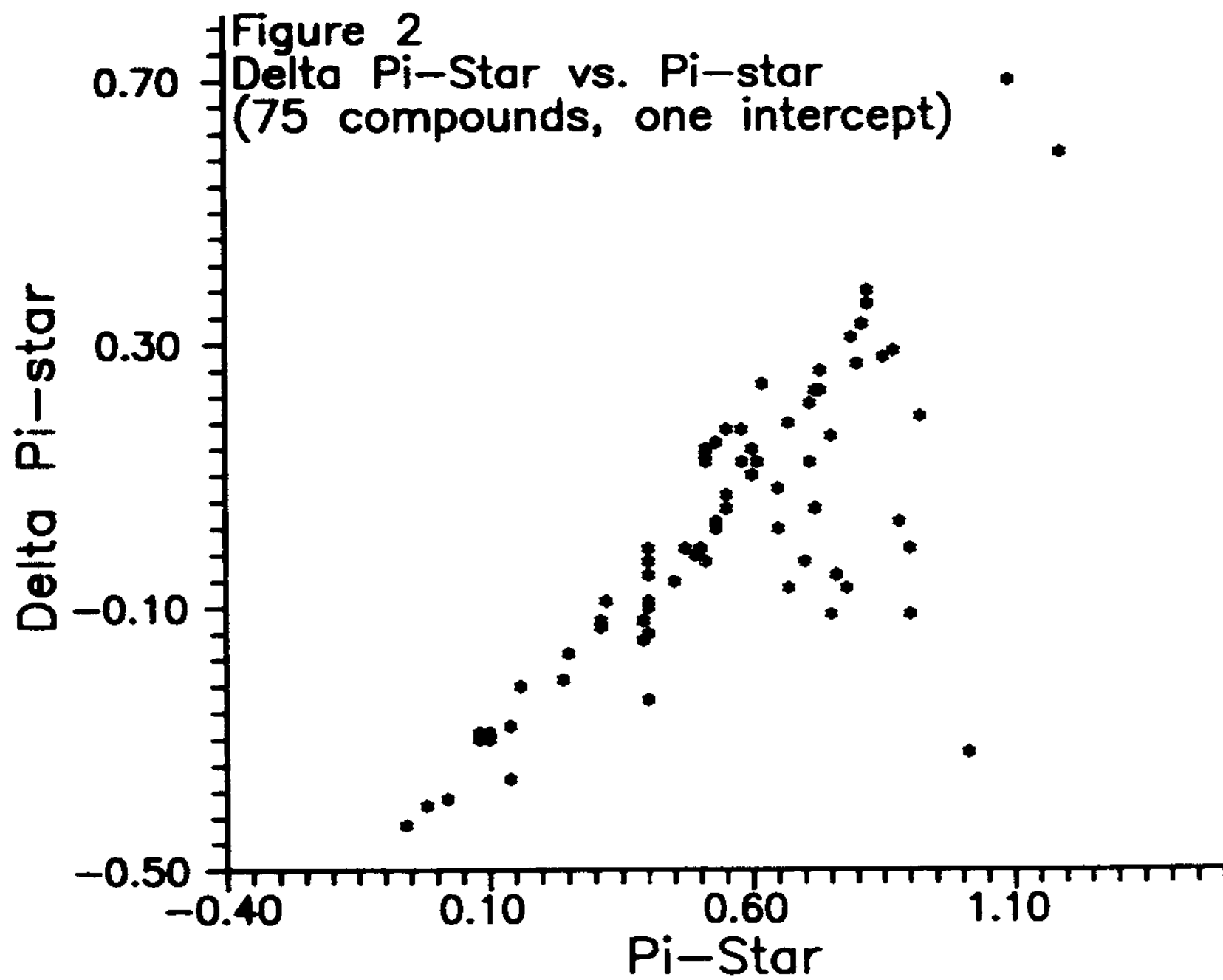
MU	ALPHA	PST	IGRP	ID	COMPOUND
3.92	44.8	0.75	05	11	ACETONITRILE
1.70		0.53	06	58	METHYL BUTYLATE
1.90	97.0	0.55	06	36	ETHYL ACETATE
1.80		0.50	06	59	ETHYL PROPIONATE
1.70		0.55	06	33	METHYL PROPIONATE
1.80		0.53	06	57	N-PROPYL ACETATE
1.93	80.1	0.61	06	22	ETHYL FORMATE
1.63		0.58	06	34	TETRAHYDROFURAN
1.80		0.51	06	79	N-BUTYL ACETATE
1.90		0.60	06	35	N-PROPYL FORMATE
1.72	69.4	0.60	06	23	METHYL ACETATE
3.73		0.75	07	26	2-NITROPROPANE
3.66		0.78	07	24	1-NITROPROPANE
3.46	73.7	0.85	07	9	NITROMETHANE
2.40	96.3	0.80	07	16	NITROETHANE
1.69	123.0	0.71	08	65	CHLOROBENZENE
2.29		0.92	08	111	QUINOLINE
0.40	142.0	0.53	08	102	ETHYL BENZENE
0.50	149.0	0.51	08	104	O-XYLENE
0.00		0.49	08	120	N-BUTYL BENZENE
1.40	103.0	0.62	08	150	FLOUROBENZENE
0.10	141.0	0.51	08	103	P-XYLENE
0.36	123.0	0.55	08	91	TOLUENE
4.18	125.0	0.90	08	88	BENZONITRILE
3.00	150.0	0.90	08	101	ACETOPHENONE
1.38		0.73	08	92	ANISOLE
0.00	388.0	0.80	08	163	PHENANTHRACENE
0.00	165.0	0.70	08	161	NAPHTHALENE
1.80		1.19	08	113	BENZYL ACETATE
0.30	142.0	0.51	08	149	M-XYLENE
1.60	121.0	0.73	08	68	ANILINE
4.22	129.0	1.01	08	64	NITROBENZENE
1.50	147.0	0.79	08	151	BROMOBENZENE
0.00	254.0	0.80	08	162	ANTHRACENE
0.00	107.4	0.59	08	66	BENZENE
1.29		0.14	09	118	TRIPROPYLAMINE
0.90	131.0	0.14	09	87	TRIETHYLAMINE
1.10	102.0	0.25	09	158	DI-ETHYL AMINE
1.30	92.0	0.31	09	156	N-PROPYL AMINE
1.30	40.1	0.32	09	155	ETHYL AMINE

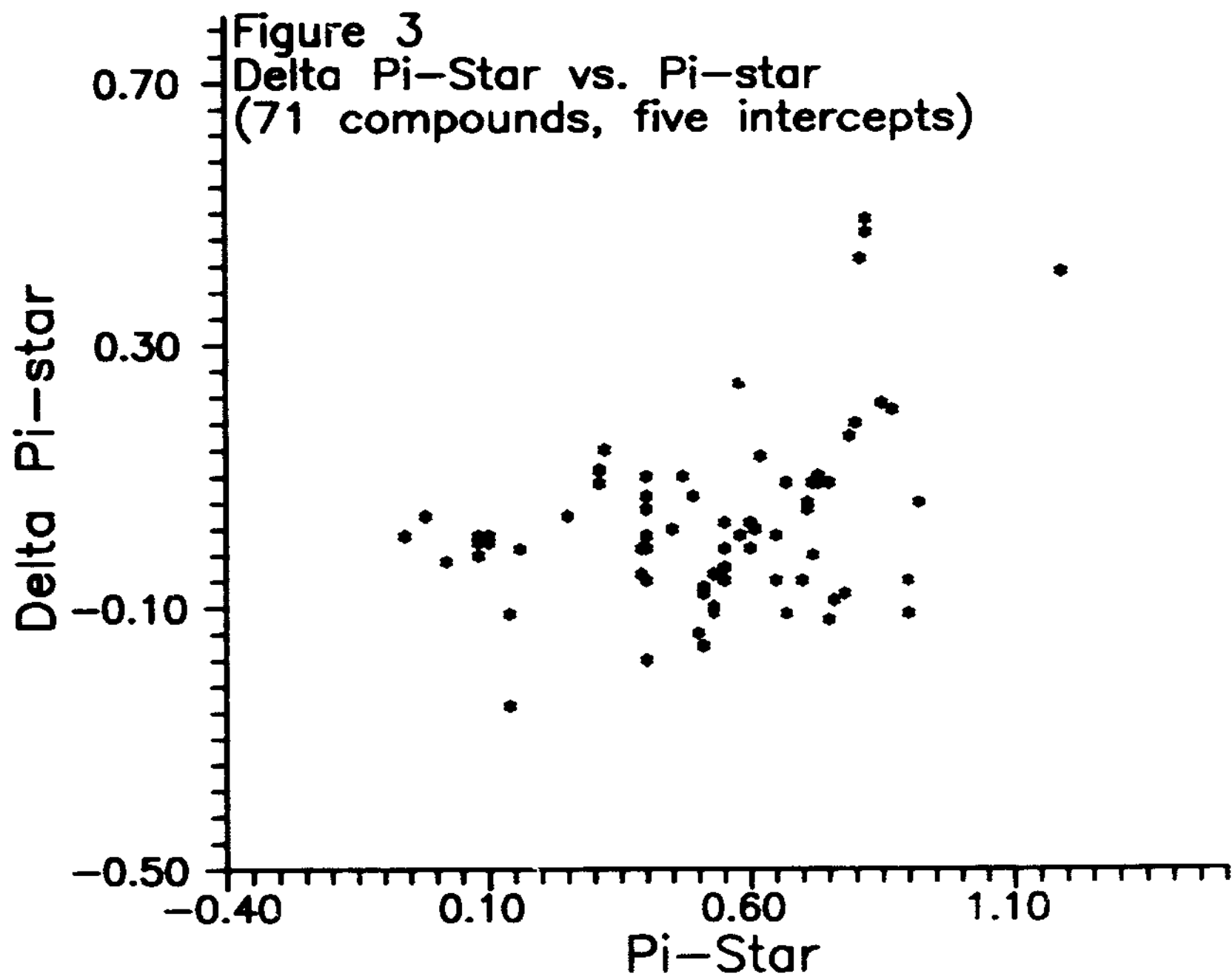
Table 2b

Physical Property Database

MU	ALPHA	PST	IGRP	ID	COMPOUND
0.60	81.0	0.16	09	159	TRI-METHYL AMINE
1.30	135.0	0.31	09	157	N-BUTYL AMINE
2.19	95.0	0.87	09	44	PYRIDINE
1.20	125.0	0.24	10	152	DI-N-PROPYL ETHER
0.00	88.0	0.00	10	1	CARBON DISULFIDE
3.82	78.1	0.88	10	25	DIMETHYL FORMAMIDE
0.80	14.5	1.09	10	160	WATER
0.40	100.0	0.55	10	37	DIOXANE







```

C*****
C***** *****
C
C THIS PROGRAM FITS AN AN EMPIRICAL EQUATION TO THE KAMLET- **
C TAFT PI-STAR SCALE OF SOLVENT POLARITY/POLARIZABILITY. **
C      DEVELOPED BY: S. W. GOFFINET **
C      10 FEB. 1989 **
C*****
C***** *****
C
C      PROGRAM PSFIT
C
C ***** DECLARE EXTERNAL SUBROUTINE USED IN IMSL ***
C
C      EXTERNAL SRPSFIT
C
C ***** DECLARE VARIABLES *****
C
C      DOUBLE PRECISION V,IP,ALPHA,PST,PERR,LC,KC,DC,APPO,APNP,RAT1
1      RAT2,RAT3,PSTCALC,LT,KT,DT,TEMP,BK,DUMV,
2      DUMIP,DUMMU,DUMALPHA,DUMPST,BOUNDS,BOTTOM,
3      TOP,G,AVERR,MINERR,MAXERR,SUMERR,INTERMED,
4      WORK(500),X(4),MU,DIFF,DIV1,DIV2,DIV3,
5      PL,PK,PD,A,EX,RI,DUMRI,PF
      INTEGER NPAR,NDATA,NSRSCH,II,DUMID,DUMIGRP,DUMUSE,ID,
1      IGRP,USE,JJ,ROW,COL,NSIG,ITER,IER,IWORK(4),RND,B
C
C ***** DEFINE VARIABLE BLOCKS ***** *
C
C      COMMON NDATA,ITER,IER,DIFF(163),RND,DIV1,DIV2,DIV3,PF
      COMMON PSTCALC(163),RAT1(163),RAT2(163),RAT3(163),EX(15)
      COMMON/PROP/ V(163),IP(163),MU(163),ALPHA(163),PST(163),
1      USE(163),ID(163),IGRP(163),RI(163)
      COMMON/DUMPROP/ DUMV(163),DUMIP(163),DUMMU(163),
1      DUMALPHA(163),DUMPST(163),DUMUSE(163),
2      DUMID(163),DUMIGRP(163),DUMRI(163)
      COMMON/IMSL/ BK,NSRSCH,TEMP,LT(163),DT(163),KT(163),
1      APPO,APNP,AVERR,SUMERR,LC(163),DC(163),
2      MINERR,MAXERR,PERR(163),KC(163)
      COMMON/BNDS/ BOUNDS(4,2),BOTTOM(4),TOP(4)
      COMMON/JF/ PL(163),PK(163),PD(163),A(3),B(50)
C
C      CHARACTER * 27 NAME(163),DUMNAME(163)

```

```
C
C ***** OPEN INPUT AND ECHO FILES*****
C
  OPEN(1,FILE='PSPROP.DAT',STATUS='OLD')
  OPEN(92,FILE='RESABS.DAT',STATUS='NEW')
  OPEN(3,FILE='PSPROP.ECH',STATUS='NEW')
  OPEN(6,FILE='BNDABS.DAT',STATUS='OLD')
  OPEN(7,FILE='BOUNDS.ECH',STATUS='NEW')
C
C ***** CALL INPUT SUBROUTINE *****
C
  CALL RDAT(NAME)
C
  NPAR = 4
  NSIG = 2
  ITER = 0
  NSRSCH = 100
  TEMP = 298.15
  BK = 1.38048*10.0**(-16)
  MINERR = 100.0
  MAXERR = 0.0
  AVERR = 0.0
  SUMERR = 0.0
C
C
  WRITE(92,*) 'NUMBER OF PARAMETERS ADJUSTED: ', NPAR
  WRITE(92,*) 'NUMBER OF SOLVENTS USED: ', NDATA
  WRITE(92,*) 'NUMBER OF INITIAL SEARCH POINTS: ', NSRSCH
C
C ***** CALL IMSL MINIMIZATION ROUTINE *****
C
  CALL ZXMWD(SRPSFIT,NPAR,NSIG,BOTTOM,TOP,NSRSCH,X,G,WORK,
1          IWORK,IER)
C
C ***** CALL OUTPUT SUBROUTINE *****
C
  CALL OUTPUT(NAME,X)
C
  STOP
  END
C
C
```

```

C*****
C
C          SUBROUTINE SECTION
C
C*****
C
C          *****
C***** INPUT SUBROUTINE RDAT ***** *
C          *****
C
C          SUBROUTINE RDAT(NAME)
C
C
C***** DECLARE VARIABLES *****
C
C          DOUBLE PRECISION V,IP,ALPHA,PST,PERR,LC,KC,DC,APPO,APNP,RAT1,
1             RAT2,RAT3,PSTCALC,LT,KT,DT,TEMP,BK,DUMV,
2             DUMIP,DUMMU,DUMALPHA,DUMPST,BOUNDS,BOTTOM,
3             TOP,G,AVERR,MINERR,MAXERR,SUMERR,INTERMED,
4             WORK(500),X(4),MU,DIFF,DIV1,DIV2,DIV3,
5             PL,PK,PD,A,EX,RI,DUMRI,PF
C          INTEGER NPAR,NDATA,NSRSCH,II,DUMID,DUMIGRP,DUMUSE,ID,
1             IGRP,USE,JJ,ROW,COL,NSIG,ITER,IER,IWORK(4),RND,B
C
C
C***** DEFINE VARIABLE BLOCKS ***** *
C
C          COMMON NDATA,ITER,IER,DIFF(163),RND,DIV1,DIV2,DIV3,PF
C          COMMON PSTCALC(163),RAT1(163),RAT2(163),RAT3(163),EX(15)
C          COMMON/PROP/ V(163),IP(163),MU(163),ALPHA(163),PST(163),
1             USE(163),ID(163),IGRP(163),RI(163)
C          COMMON/DUMPROP/ DUMV(163),DUMIP(163),DUMMU(163),
1             DUMALPHA(163),DUMPST(163),DUMUSE(163),
2             DUMID(163),DUMIGRP(163),DUMRI(163)
C          COMMON/IMSL/ BK,NSRSCH,TEMP,LT(163),DT(163),KT(163),
1             APPO,APNP,AVERR,SUMERR,LC(163),DC(163),
2             MINERR,MAXERR,PERR(163),KC(163)
C          COMMON/BNDS/ BOUNDS(4,2),BOTTOM(4),TOP(4)
C          COMMON/JF/ PL(163),PK(163),PD(163),A(3),B(50)
C
C          CHARACTER * 27 NAME(163),DUMNAME(163)
C
C***** READ IN DATA ***** *
C
C          NDATA = 0
C
C          READ(6,*)((BOUNDS(II,JJ),JJ=1,2),II=1,4)
C          DO 66 II = 1,4
C             BOTTOM(II) = BOUNDS(II,1)
C             TOP(II) = BOUNDS(II,2)

```

```

66  CONTINUE
    DO 119 II = 1,15
        READ(6,*)EX(II)
119  CONTINUE
C
    JJ = 1
    DO 77 II = 1,163
        READ(1,11)DUMV(II),DUMRI(II),DUMIP(II),DUMMU(II),DUMALPHA(II),
1          DUMPST(II),DUMUSE(II),DUMIGRP(II),DUMID(II),
2          DUMNAME(II)
C
C
C
C          IF (DUMUSE(II).GT.EX(14)) GO TO 77
C
C          IF (DUMMU(II).GT.EX(13)) GO TO 77
          IF (DUMMU(II).LT.EX(12)) GO TO 77
C
C          IF (DUMIGRP(II).EQ.EX(1)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(2)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(3)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(4)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(5)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(6)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(7)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(8)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(9)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(10)) GO TO 77
          IF (DUMIGRP(II).EQ.EX(11)) GO TO 77
C
          V(JJ) = DUMV(II)
          RI(JJ) = DUMRI(II)
          IP(JJ) = DUMIP(II)
          MU(JJ) = DUMMU(II)
          ALPHA(JJ) = DUMALPHA(II)
          PST(JJ) = DUMPST(II)
          USE(JJ) = DUMUSE(II)
          IGRP(JJ) = DUMIGRP(II)
          ID(JJ) = DUMID(II)
          NAME(JJ) = DUMNAME(II)
          NDATA = NDATA + 1
C
C          WRITE(3,12)V(JJ),RI(JJ),IP(JJ),MU(JJ),ALPHA(JJ),PST(JJ),USE(JJ),
1          IGRP(JJ),ID(JJ),NAME(JJ)
C
C          JJ = JJ + 1
C
C 77  CONTINUE
C
C

```

```

11 FORMAT (4X,F5.1,1X,F5.3,1X,F5.2,1X,F4.2,1X,F5.1,1X,F5.2,1X,I1,1X,
1      I2,1X,I3,1X,A27)
12 FORMAT (F5.1,1X,F5.3,1X,F5.2,1X,F4.2,1X,F5.1,1X,F5.2,1X,I1,1X,I2,
1      1X,I3,1X,A27)
C
C
C ***** ECHO PARAMETER BOUNDS *****
C
C
C
C
C      DO 55 II = 1,4
C          WRITE(7,*) 'BOTTOM FOR X',II, '= ', BOTTOM(II)
C          WRITE(7,*) 'TOP FOR X',II, '= ', TOP(II)
55      CONTINUE
C
C      WRITE(92,*) ' BOUNDS FOR ADJUSTABLE PARAMETERS'
C      WRITE(92,31)BOTTOM(1),TOP(1)
C      WRITE(92,32)BOTTOM(2),TOP(2)
C      WRITE(92,33)BOTTOM(3),TOP(3)
C      WRITE(92,34)BOTTOM(4),TOP(4)
31      FORMAT(1X,'LONDON PARM.:',1X,F8.5,1X,'-',1X,F9.5)
32      FORMAT(1X,'KEESOM PARM.:',1X,F8.5,1X,'-',1X,F9.5)
33      FORMAT(1X,'DEBYE PARM.:',1X,F8.5,1X,'-',1X,F10.5)
34      FORMAT(1X,'INTERCEPT.:',1X,F8.5,1X,'-',1X,F8.5)
C
C      WRITE(92,*)
C      WRITE(92,*)'POLARITY RANGE (deb.): '
C      WRITE(92,29)EX(12),EX(13)
29      FORMAT(22X,F6.3,3X,F6.3)
C      WRITE(92,*)'GROUPS EXCLUDED: '
C      WRITE(92,18)(EX(II), II = 1,11)
18      FORMAT(1X,F4.1)
C
C      RETURN
C      END
C
C
C *****
C ***** FUNCTION SURROUTINE PSFIT *****
C *****
C
C
C      SUBROUTINE SRPSFIT(NPAR,X,G)
C
C
C ***** DECLARE VARIABLES *****
C
C
C      DOUBLE PRECISION V,IP,ALPHA,PST,PERR,LC,KC,DC,APFO,APNP,RAT1,
1      RAT2,RAT3,PSTCALC,LT,KT,DT,TEMP,BK,DUMV,

```

```

2          DUMIP,DUMMU,DUMALPHA,DUMPST,BOUNDS,BOTTOM,
3          TOP,G,A VERR,MINERR,MAXERR,SUMERR,INTERMED,
4          WORK(500),X(4),MU,DIFF,DIV1,DIV2,DIV3,
5          PL,PK,PD,A,EX,RI,DUMRI,PF
C
C      INTEGER NPAR,NDATA,NSRSCH,II,DUMID,DUMIGRP,DUMUSE,ID,
1          IGRP,USE,JJ,ROW,COL,NSIG,ITER,IER,IWORK(4),RND
C
C
C ***** DEFINE VARIABLE BLOCKS *****
C
C      COMMON NDATA,ITER,IER,DIFF(163),RND,DIV1,DIV2,DIV3,PF
C      COMMON PSTCALC(163),RAT1(163),RAT2(163),RAT3(163),EX(15)
C      COMMON/PROP/ V(163),IP(163),MU(163),ALPHA(163),PST(163),
1          USE(163),ID(163),IGRP(163),RI(163)
C      COMMON/DUMPROP/ DUMV(163),DUMIP(163),DUMMU(163),
1          DUMALPHA(163),DUMPST(163),DUMUSE(163),
2          DUMID(163),DUMIGRP(163),DUMRI(163)
C      COMMON/IMSL/ BK,NSRSCH,TEMP,LT(163),DT(163),KT(163),
1          APPO,APNP,A VERR,SUMERR,LC(163),DC(163),
2          MINERR,MAXERR,PERR(163),KC(163)
C      COMMON/BNDS/ BOUNDS(4,2),BOTTOM(4),TOP(4)
C      COMMON/JF/ PL(163),PK(163),PD(163),A(3)
C
C      CHARACTER * 27 NAME(163),DUMNAME(163)
C
C      G = 0.0
C      ITER = ITER + 1
C
C ***** BEGIN IMSL LOOP *****
C
C ***** CALCULATION OF PI-STAR *****
C
C ***** UNITS OF LT, KT, AND DT ARE ERG CM^6 x 10^-57 *****
C
C      IF (EX(15).EQ.2.0) GO TO 653
C
C      DO 190 II = 1,NDATA
C      LT(II) = 0.000012015*(ALPHA(II)**2.0)*IP(II)
C      KT(II) = (6.6667*10.0**(-16)*(MU(II)**4.0))/(BK*TEMP)
C      DT(II) = 0.0002*ALPHA(II)*MU(II)**2.0
C
C      PSTCALC(II)=LT(II)*X(1)+KT(II)*X(2)+DT(II)*X(3)+X(4)
C      ERRSQ = (PSTCALC(II)-PST(II))**2
C      G = G + ERRSQ
190 CONTINUE
C      IF (EX(15).EQ.1.0) GO TO 654
653 WRITE(7,*)
C

```



```

DO 191 II = 1,NDATA
PF = 3.96401*V(II)*(((RI(II)**2)-1.0)/((RI(II)**2)+2.0))
LT(II)=0.000012015*(PF**2)
KT(II)=(6.6667*(10.0**(-16.0))*(MU(II)**4.0))/(BK*TEMP)
DT(II)=0.0002*PF*(MU(II)**2.0)

```

```

C PSTCALC(II)=LT(II)*X(1)+KT(II)*X(2)+DT(II)*X(3)+X(4)
ERRSQ = (PSTCALC(II)-PST(II))**2.0
G = G + ERRSQ

```

```

191 CONTINUE

```

```

C 654 WRITE(7,*)

```

```

C RETURN
C END

```

```

C *****
C ***** OUTPUT SUBROUTINE *****
C *****

```

```

C SUBROUTINE OUTPUT(NAME,X)

```

```

C DOUBLE PRECISION V,IP,ALPHA,PST,PERR,LC,KC,DC,APPO,APNP,RAT1,
1 RAT2,RAT3,PSTCALC,LT,KT,DT,TEMP,BK,DUMV,
2 DUMIP,DUMMU,DUMALPHA,DUMPST,BOUNDS,BOTTOM,
3 TOP,G,AVERR,MINERR,MAXERR,SUMERR,INTERMED,
4 WORK(500),X(4),MU,DIFF,DIV1,DIV2,DIV3,
5 PL,PK,PD,A,EX,RI,DUMRI,PF
INTEGER NPAR,NDATA,NSRSCH,II,DUMID,DUMIGRP,DUMUSE,ID,IGRP,
1 USE,JJ,ROW,COL,NSIG,ITER,IER,IWORK(4),RND

```

```

C ***** DEFINE VARIABLE BLOCKS *****

```

```

C COMMON NDATA,ITER,IER,DIFF(163),RND,DIV1,DIV2,DIV3,PF
COMMON PSTCALC(163),RAT1(163),RAT2(163),RAT3(163),EX(15)
COMMON/PROP/ V(163),IP(163),MU(163),ALPHA(163),PST(163),
1 USE(163),ID(163),IGRP(163),RI(163)
COMMON/DUMPROP/ DUMV(163),DUMIP(163),DUMMU(163),
1 DUMALPHA(163),DUMPST(163),DUMUSE(163),
2 DUMID(163),DUMIGRP(163),DUMRI(163)
COMMON/IMSL/ BK,NSRSCH,TEMP,LT(163),DT(163),KT(163),
1 APPO,APNP,AVERR,SUMERR,LC(163),DC(163),
2 MINERR,MAXERR,PERR(163),KC(163)
COMMON/BNDS/ BOUNDS(4,2),BOTTOM(4),TOP(4)
COMMON/JF/ PL(163),PK(163),PD(163),A(3)

```

```

C

```

```

C
C CHARACTER * 27 NAME(163),DUMNAME(163)
C
C SUMERR = 0.0
C JJ = 0
C
C ***** DELTA PI-STAR CALCULATED *****
C
C APPO = 0.0
C DO 99 II = 1,NDATA
C   DIFF(II) = PSTCALC(II)-PST(II)
C   APPO = APPO + DIFF(II)**2
99 CONTINUE
C
C DO 101 II = 1,NDATA
C   IF (PST(II).NE.0.0) THEN
C     PERR(II) = 100.0*(SQRT(((PSTCALC(II)-PST(II))/PST(II))**2))
C   ENDIF
C   IF (PST(II).EQ.0.0) THEN
C     PERR(II) = 99.9
C   ENDIF
C   IF (ABS(DIFF(II)).GT.MAXERR) THEN
C     MAXERR = ABS(DIFF(II))
C   ENDIF
C   IF (ABS(DIFF(II)).LT.MINERR) THEN
C     MINERR = ABS(DIFF(II))
C   ENDIF
C   SUMERR = ABS(DIFF(II)) + SUMERR
C   JJ = JJ + 1
C
101 CONTINUE
C
C AVERR = SUMERR/JJ
C
C ***** RESULTS DISPLAYED *****
C
C
C WRITE(92,*)
C WRITE(92,*)' SUM OF RESIDUALS SQUARED '
C WRITE(92,93)APPO
93 FORMAT(10X,F6.3)
C WRITE(92,*)
C WRITE(92,*)' AVE ABS ERR MIN ABS ERR MAX ABS ERR'
C WRITE(92,47)AVERR,MINERR,MAXERR
47 FORMAT(7X,F5.3,10X,F5.3,10X,F5.3)
C WRITE(92,*)
C WRITE(92,*)' ADJUSTABLE PARAMETERS'
C WRITE(92,21)X(1)
C WRITE(92,22)X(2)

```

```

WRITE(92,23)X(3)
WRITE(92,24)X(4)
21 FORMAT(1X,'LONDON PARAM.:',1X,F10.5)
22 FORMAT(1X,'KEESOM PARAM.:',1X,F10.5)
23 FORMAT(1X,'DEBYE PARAM.:',1X,F10.5)
24 FORMAT(1X,'INTERCEPT :',1X,F8.5)
WRITE(92,*)
WRITE(92,*)'ITERATIONS = ',ITER
WRITE(92,*)'NUMBER OF SOLVENTS = ',NDATA
WRITE(92,*)
WRITE(92,*)'NAME                ID PI-STAR  CALC.',
1      ' %ERR  DIFF'
DO 64 II = 1,NDATA
WRITE(92,42)NAME(II),ID(II),PST(II),PSTCALC(II),PERR(II),DIFF(II)
64 CONTINUE
C
42 FORMAT(1X,A27,1X,I3,3X,F5.2,3X,F5.2,2X,F6.1,3X,F4.2)
C
WRITE(92,*)
WRITE(92,*)'NAME                ID LONDON  KEESOM',
1      ' DEBYE'
WRITE(92,*)
DO 68 II = 1,NDATA
WRITE(92,46)NAME(II),ID(II),LT(II),KT(II),DT(II)
68 CONTINUE
C
46 FORMAT(1X,A27,1X,I3,2X,F6.3,2X,F6.3,2X,F6.3)
C
WRITE(92,*)
C
DO 707 II = 1, NDATA
LC(II) = LT(II)*X(1)
KC(II) = KT(II)*X(2)
DC(II) = DT(II)*X(3)
RAT1(II) = LC(II)/KC(II)
RAT2(II) = KC(II)/DC(II)
RAT3(II) = LC(II)/DC(II)
707 CONTINUE
C
DO 383 II = 1, NDATA
PL(II) = (LC(II)/PST(II))*100.0
PK(II) = (KC(II)/PST(II))*100.0
PD(II) = (DC(II)/PST(II))*100.0
383 CONTINUE
C
A(1) = 0.0
A(2) = 0.0
A(3) = 0.0
DO 350 II = 1,NDATA
A(1) = A(1) + PL(II)

```

```

      A(2) = A(2) + PK(II)
      A(3) = A(3) + PD(II)
350 CONTINUE
      A(1) = (A(1)/NDATA)
      A(2) = (A(2)/NDATA)
      A(3) = (A(3)/NDATA)
C
      WRITE(92,*)
      WRITE(92,*)'AVERAGE:  % LON.  % KEES.  % DEB.'
      WRITE(92,84)A(1),A(2),A(3)
84  FORMAT(13X,F4.1,6X,F4.1,3X,F4.1)
      WRITE(92,*)'NAME           ID  % LON.  % KEES.',
1      '           % DEB.'
      DO 336 II = 1,NDATA
      WRITE(92,88)NAME(II),ID(II),PL(II),PK(II),PD(II)
336 CONTINUE
C
88  FORMAT(1X,A27,2X,I3,3X,F4.1,5X,F4.1,6X,F4.1)
C
      DIV1 = X(1)/X(2)
      DIV2 = X(2)/X(3)
      DIV3 = X(1)/X(3)
C
      WRITE(92,*)'  LP/KP  KP/DP  LP/DP'
      WRITE(92,67)DIV1,DIV2,DIV3
67  FORMAT(4X,F7.1,4X,F7.1,4X,F7.1)
C
      WRITE(92,*)
      WRITE(92,*)' NAME           ID  LC  KC',
1      '           DC'
C
      DO 909 II = 1,NDATA
      WRITE(92,37)NAME(II),ID(II),LC(II),KC(II),DC(II)
909 CONTINUE
C
37  FORMAT(1X,A27,1X,I3,4X,F5.3,4X,F5.3,4X,F5.3)
C
      WRITE(92,*)
      WRITE(92,*)' NAME           ID  LC/KC  KC/DC',
1      '           LC/DC'
C
      WRITE(92,*)
      DO 404 II = 1,NDATA
      WRITE(92,69)NAME(II),ID(II),RAT1(II),RAT2(II),RAT3(II)
404 CONTINUE
C
69  FORMAT(1X,A27,1X,I3,2X,F5.1,2X,F5.1,2X,F5.1)
C
      WRITE(92,*)'*****'
      WRITE(92,*)

```

C

```
WRITE(92,*)  
RETURN  
END
```

Summary of Alternative Functional Forms

Presented below are the functional forms which were tested but proved less effective than that presented in the text.

$$\pi^* = \text{Ln}(a(L) + b(K) + c(D) + d)$$

$$\pi^* = L^a + K^b + D^c + d$$

$$\pi^* = a(K) + b(D) + c(K)(D) + d$$

$$\pi^* = 1/V_m(a(L) + b(K) + c(D)) + d$$

An additional method for calculating π^* utilized a homomorph technique in order to represent the dispersion contribution. In this method the traditional dispersion term was replaced by λ^2 , the nonpolar solubility parameter [22,23]. For the 35 compounds for which λ was available, an average $\Delta\pi^*$ of ± 0.13 was achieved. In contrast, $\Delta\pi^*$ was ± 0.17 for these 35 compounds when α^2 was used to calculate the London term. By using λ^2 to calculate the London term, the adjustable parameter must have dimensions since λ has dimensions of cohesive energy density, $(\text{cal./cm}^3)^{1/2}$ and the other terms have units of $\text{erg}\cdot\text{cm}^6$. Despite the small number of compounds available for which λ was available, the improved results over calculation with α^2 show promise for representing π^* as a cohesive energy density. An alternative application of this technique would be to use the polarizability of a compound's homologue in the calculation of the compound's dispersion term.