The $T/2V^{1/2}$ Ratio: Solubility Parameter Substitute

Sir:

$T/2V^{1/2}$ ratios (T, normal b.p. in K; V, molar volume at 25°C) were observed in limited work (1) to be measures of polarity and possible substitutes for solubility parameters (SP; $MPa^{1/2}$). $T/2V^{1/2}$ ratios have a great advantage because data on b.p. and molar volumes are plentiful and easily determined. Because of these advantages and the importance of SP (2–4), the earlier work was extended; several hundred $T/2V^{1/2}$ ratios were found to be similar to their corresponding SP.

References 2, 5–7, which provide more than 800 SP values, were the principal data sources. Some SP values (6) were calculated from molar vaporization energy [EvM (J/mol)] and molar volume, V (Eq. 1), or from gram vaporization energy [Hv (J)] and density, d, at 25°C (Eq. 2):

$$SP = (EvM/V)^{1/2} \quad [1]$$

$$SP = (d\ Hv)^{1/2} \quad [2]$$

Some of the numerous SP values and corresponding $T/2V^{1/2}$ ratios examined in the present work are shown in Tables 1–3 (organic compounds) and Table 4 (inorganic compounds).

The data used to compare SP values and $T/2V^{1/2}$ ratios in Tables 1–3 were from References 2 and 5. Data from Reference 6 were used to compare SP values and $T/2V^{1/2}$ ratios for approximately 300 compounds. Agreement of the two values was excellent with only a few exceptions.

Although the several hundred compounds of the study ranged widely in M.W. and structure and in SP values (from 11.8 for propane to 48 for water), the $T/2V^{1/2}$ ratios were closely similar in most instances to the corresponding SP values. The principal exceptions were the SP of some carboxylic acids, alcohols, and glycols, where the differences were sometimes about 2 $MPa^{1/2}$. Differences were small for some alcohols and glycols, e.g., benzyl alcohol, 0.12; tetrahydrofurfuryl alcohol, 0.40; triethylene glycol, 0.17; and glycerol, 0.84 (6). Because of the good agreement of $T/2V^{1/2}$ ratios with

TABLE 1
Comparison of Solpars[a] ($MPa^{1/2}$) with $T/2V^{1/2}$, Where T Is Normal b.p. (K) and V Is Molar Volume at 25°C: Oxygen Compounds[b,c]

Compound	SP	SP less $T/2V^{1/2}$	Compound	SP	SP less $T/2V^{1/2}$
Methyl ethyl ether	15.47	–0.42	Acrolein	20.11	–0.19
Di-isopropyl ether	14.44	–0.12	2-Ethylhexanol	17.21	0.22
Dihexyl ether	16.37	–0.12	3-Methoxybutanal	19.18	–0.40
Diphenyl ether	20.66	0.33	1,2,3,6-Tetrahydrobenzaldehyde	20.55	–0.39
Tetrahydrofuran	18.52	0.29	Ethanol	26.15	–3.21
Ethyl acetate	18.23	–0.60	Decanol	20.52	–2.35
Isobutyl isobutanoate	15.84	0.30	2-Hexanol	20.54	–2.15
Hexyl hexanoate	16.96	–0.02	2-Decanol	18.03	–0.38
2-Ethylhexyl 2-ethylhexanoate	16.18	–0.19	Glycol ethyl ether	21.91	–1.20
Ethyl acetoacetate	20.11	0.10	Glycol nonyl ether	17.70	–0.80
Methyl benzoate	20.85	0.20	Ethylene chlorohydrin	26.50	–2.00
Ethyl salicylate	20.08	0.00	Ethylene cyanohydrin	31.04	–0.61
Acetone	19.68	–0.54	Acetic acid	26.48	–0.70
Ethyl butyl ketone	17.43	0.31	Propanoic acid	25.51	–1.61
Isobutyl heptyl ketone	16.27	0.05	Hexanoic acid	23.90	–2.55
Acetylacetone	19.50	0.84	2-Ethyl butanoic acid	23.53	–2.74
Cyclohexanone	21.32	–0.31	Methacrylic acid	26.82	–3.45
2,5-Hexanedione	21.14	0.29	1,2,3,6-Tetrahydro-benzoic acid	25.72	–2.11
Acetaldehyde	20.19	–0.77			
Hexanal	18.23	–0.18			

[a]Solubility parameters, or solpars (SP), are in units of $MPa^{1/2}$ ($J^{1/2}$ $cm^{-3/2}$).
[b]Data from Hoy (2,5).
[c]SP (Hildebrands, in Refs. 2, 5) were multiplied by 2.046 to get SP in units of $MPa^{1/2}$.

Paper no. J10709 in *JAOCS 81*, 519–521 (May 2004).

TABLE 2
Comparison of Solpars[a] ($MPa^{1/2}$) with $T/2V^{1/2}$, Where T Is Normal b.p. (K) and V Is Molar Volume at 25°C: Hydrocarbons; Nitrogen, Halogen, and Sulfur Compounds[b,c]

Compound	SP	SP less $T/2V^{1/2}$	Compound	SP	SP less $T/2V^{1/2}$
Pentane	14.36	–0.03	2-Ethylhexyl chloride	16.63	0.53
Cyclopentane	16.53	0.20	2-Chloro-1,3-butadiene	17.17	0.05
1-Pentene	14.47	–0.04	Bromoethane	18.21	–0.27
3-Ethyl hexane	15.41	0.20	Bromochloromethane	21.22	–0.43
Benzene	18.74	–0.06	Bromotrichloromethane	18.56	0.41
Decane	15.8	0.04	Bromobenzene	20.15	0.54
Butylamine	17.72	0.54	Iodomethane	20.17	0.23
Hexylamine	17.29	0.27	1-Iodobutane	18.25	0.61
Diethylamine	16.45	0.35	1-Iodo-2 methylpropane	17.75	0.59
Dihexylamine	17.02	–0.33	Iodobenzene	20.52	1.30
Triethylamine	15.18	0.15	2-Thiapropane	18.44	–0.37
Tributylamine	15.88	–0.14	2-Thiabutane	17.94	–0.15
2-Ethylhexylamine	17.27	–0.04	Thiacyclopentane	20.52	0.29
Di(2-ethylhexyl)amine	15.96	0.00	Thiophene	20.09	–0.07
4-Ethyl-2,6-dimethylmorpholine	17.25	0.03	2 Methylthiophene	19.48	0.06
Fluorobenzene	18.45	–0.02	3-Methylthiophene	19.54	0.13
p-Fluorotoluene	18.24	0.27	Methylthioethyl acrylate	20.11	0.03
Chlorobutane	17.13	–0.02	Vinyl *S*-ethylmercapto-ethyl ether	18.93	–0.20

[a]Solubility parameters, or solpars (SP), are in units of $MPa^{1/2}$ ($J^{1/2}$, $cm^{-3/2}$).
[b]Data from Hoy (2,5).
[c]SP (Hildebrands, in Refs. 2, 5) were multiplied by 2.046 to get SP, in units of $MPa^{1/2}$.

TABLE 3
Comparison of Solpars[a] ($MPa^{1/2}$) with $T/2V^{1/2}$, Where T Is Normal b.p. (K) and V Is Molar Volume at 25°C: Miscellaneous Compounds[b,c]

Compound	SP	SP less $T/2V^{1/2}$	Compound	SP	SP less $T/2V^{1/2}$
1-Acetoxy-1,3-butadiene	19.38	–0.47	2-Ethyl-3-methyl-1,5 pentanediol	24.55	–2.71
Allyl acetoacetate	20.46	–0.21	5-Ethyl-2 nonanone	17.49	–0.08
N-(2-Aminoethyl) ethanolamine	28.13	–2.49	3-Heptene-2 one	19.05	–0.16
N-(2-Aminoethyl)piperazine	21.44	0.10	2,4 Hexadienal	21.54	–0.20
Benzyl glycol ether	22.21	–0.13	*N*-(2-Hydroxyethyl) morpholine	22.42	0.10
Butadiene dioxide	24.10	–0.68	*N*-(2-Hydroxyethyl) piperidine	24.06	–0.67
Butyl lactate	20.13	–1.26	Methoxytriglycol	22.02	–1.21
γ-Butyrolactone	26.33	0.93	1-Methyl naphthalene	20.26	1.52
ε-Caprolactone	25.90	–1.28	1-Nonylnapthalene	18.56	0.89
2,5-Diethoxytetrahydrofuran	17.31	–0.08	*N*-Phenylethanol amine	25.74	–0.81
Diethoxytriglycol	18.33	–0.69	2,2-Dimethylpropanal	16.78	–0.16
Diethyl 2-ethyl-2-methyl glutarate	17.13	0.09	1,1,3,3 Tetraethoxypropane	16.76	–0.88
3,9-Diethyl-6-tridecanol	17.02	–0.33	1,1,3,3 Tetramethoxyhexane	17.29	–0.44
Diglycol chlorohydrin	24.80	–1.90	N,N,N,N-Tetramethyl-1,2-ethylene diamine	16.04	0.08
Di-isopropylethanolamine	18.91	–0.96	Triallylamine	15.82	0.33
Diketene	23.57	–0.80	Triglycol dichloride	20.89	–0.39
Dimethoxytetraglycol	19.66	–1.19	2,6,8-Trimethyl-4 nonanol	16.94	–0.46
Ethoxytriglycol	20.79	0.83	Vinyl 2-ethylhexanoate	16.55	–0.16
2-Ethyl-1,3-butadiene	15.37	0.82	Vinyl 2,6,8-trimethyl-4-nonyl ether	15.26	0.00
4-Ethyl-2,6-dimethylmorpholine	17.25	0.03			

[a]Solubility parameters, or solpars (SP), are given in units of $MPa^{1/2}$ ($J^{1/2}/cm^{-3/2}$).
[b]Data from Hoy (2,5).
[c]SP (Hildebrands, in Refs. 2, 5) were multiplied by 2.046 to get SP, in units of $MPa^{1/2}$.

SP values, it seems reasonable to consider the ratios as SP substitutes.

Another advantage of the expression $T/2V^{1/2}$ = SP is that any one component of the expression can be calculated when the other two are known. For example, the equation $T = 2V^{1/2}$ SP can be used to estimate approximate normal b.p. The SP, 26.15, and molar volume, 142.64, of glycerol trinitrate (6) were used to estimate the approximate b.p. of 625 K.

TABLE 4
Comparison of Solpars[a] (MPa$^{1/2}$) with $T/2V^{1/2}$, Where T Is Normal b.p. (K) and V Is Molar Volume at 25°C: Inorganic Compounds[b]

Compound	SP	SP less $T/2V^{1/2}$	Compound	SP	SP less $T/2V^{1/2}$
Arsenic trichloride	22.06	–0.12	Nitric acid	30.01	–2.09
Arsenic trifluoride	26.00	–2.33	Pentaborane	16.32	–0.09
Boron tribromide	18.12	0.42	Phosphorus tribromide	21.02	1.67
Boron trichloride	29.03	–0.14	Phosphorus trichloride	18.43	0.26
Bromine	23.50	–0.38	Phosphoryl chloride	19.69	–0.08
Bromine pentafluoride	19.57	–0.95	Silicon tetrabromide	17.79	1.37
Bromine trifluoride	29.58	–1.04	Silicon tetrachloride	15.50	0.04
Chromyl chloride	21.91	–0.26	Sulfur trioxide	31.23	–6.61
Cyanogen chloride	30.94	–2.03	Sulfuryl chloride	18.54	0.57
Dimethyl mercury	21.01	0.44	Thionyl chloride	19.77	0.64
Germanium tetrachloride	17.14	–0.30	Tin chloride	18.15	0.04
Hexaborane	17.90	0.11	Titanium chloride	18.74	0.82
Hydrazine	36.36	1.02	Tribromosilane	18.89	0.25
Hydrogen cyanide	24.50	–0.72	Trichlorosilane	15.11	0.06
Hydrogen peroxide	44.96	–2.02	Trisilane	14.02	0.17
Iodine pentafluoride	23.93	–1.53	Vanadium fluoride	27.43	–6.4
Molybdenum fluoride	17.52	–0.63	Water	47.92	–4.03
Nickel carbonyl	14.56	–0.72			

[a]Solubility parameters, or solpars (SP) are in units of MPa$^{1/2}$, (J$^{1/2}$cm$^{-3/2}$).
[b]Data from Reference 6.

ACKNOWLEDGMENTS

We thank Matt and Kevin Franklin for important calculations.

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[Received August 4, 2003; accepted February 17, 2004]

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