

CHROM. 7628

USE OF THERMODYNAMIC SOLUBILITY PARAMETERS FOR THE CHARACTERIZATION OF LIQUID PHASES

T. H. RISBY*, P. C. JURS and B. L. REINBOLD

Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)

SUMMARY

The differential enthalpy of evaporation from solution (ΔH_e^s) is reported for the following functional groups: $-\text{CH}_2-$, $-\text{OH}$, $-\text{O}-$, $>\text{C}=\text{O}$, $-\text{CHO}$, $-\text{OC(O)H}$, and $-\text{OC(O)CH}_3$. These values are reported on seventy-five liquid phases using fifty solutes. The functional group ΔH_e^s values for the liquid phases have been used to rank the selectivity of the liquid phase towards each functional group.

INTRODUCTION

One of the major difficulties which has been experienced in the use of gas chromatography (GC) for qualitative and quantitative analysis has been selecting a stationary liquid phase which will separate a particular solute matrix. As a direct result, a number of theories have been proposed to replace the traditional "Black Magic" art of column selection.

The first approach was propounded by Rohrschneider¹, and it reflected the ability of a liquid phase to retain butadiene as compared to butane. This theory ranked liquid phases by comparison with standard liquid phases, namely squalane and β,β' -oxydipropionitrile.

Subsequent papers have developed this approach further with the use of the following solute systems: (a) benzene and cyclohexane²; (b) ethanol, 2-butanone, benzene, pyridine, and nitromethane³; (c) benzene, butanol, 2-pentanone, nitropropane, pyridine, 2-methyl-2-pentanol, 1-iodobutane, 2-octyne, 1,4-dioxane, and *cis*-hydridene⁴; (d) octane, toluene, ethanol, 2-butanone, dioxane, and nitromethane⁵.

Recently Novák *et al.*⁶ have developed a polarity scale based on the partial molar Gibbs free energy of a methylene group — $\Delta G_e(\text{CH}_2)$ — obtained by using butyl acetate and amyl acetate (or any series of successive acetate homologs). The following relationship was used in this study:

$$\Delta G_e(\text{CH}_2) = \frac{RT}{0.434 \log V_g P^0}$$

* Author to whom all correspondence should be addressed.

TABLE I
LIQUID PHASES

<i>Column reference number</i>	<i>Liquid phase</i>	<i>Column temperatures (°C)</i>	
1	Apiezon J	120.0	160.0
2	Apiezon L	120.0	160.0
3	Apiezon M	120.0	160.0
4	Apiezon N	120.0	160.0
5	Bis-2-ethoxyethyl phthalate	100.0	120.0
6	Carbowax 300	100.0	120.0
7	Carbowax 400	100.0	120.0
8	Carbowax 600	100.0	120.0
9	Carbowax 1000	100.0	120.0
10	Carbowax 1540	100.0	120.0
11	Carbowax 4000	120.0	140.0
12	Carbowax 6000	120.0	140.0
13	Carbowax 20M	120.0	160.0
14	Castorwax	120.0	140.0
15	Citroflex A 4	80.0	100.0
16	Dibutyl tetrachlorophthalate	100.0	120.0
17	Diethylene glycol adipate	120.0	140.0
18	Diethylene glycol sebacate	120.0	140.0
19	Diethylene glycol succinate	120.0	140.0
20	Di-(2-ethylhexyl) adipate	100.0	120.0
21	Di-(2-ethylhexyl) sebacate	100.0	120.0
22	Diisodecyl phthalate	120.0	140.0
23	Dioctyl phthalate	120.0	140.0
24	Dioctyl sebacate	100.0	120.0
25	Docosanol	80.0	100.0
26	Dow Corning 550 fluid	120.0	160.0
27	Dow Corning FS 1265 fluid	120.0	160.0
28	Ethofat 60-25	100.0	120.0
29	Ethylene glycol adipate	120.0	140.0
30	Ethylene glycol sebacate	120.0	140.0
31	Flexol 8N8	120.0	140.0
32	Hallocimid M 18	100.0	120.0
33	Hallocimid M 18 OL	100.0	120.0
34	Hyprose SP 80	100.0	120.0
35	Igepal CO 880	100.0	120.0
36	Iooctyl decyl adipate	100.0	120.0
37	Kroniflex THFP	120.0	140.0
38	Neopentyl glycol adipate	120.0	140.0
39	Neopentyl glycol adipate terminated	120.0	140.0
40	Neopentyl glycol succinate	120.0	140.0
41	Oronite NIW	120.0	160.0
42	Pluronic F 68	100.0	120.0
43	Pluronic F 77	100.0	120.0
44	Pluronic F 88	100.0	120.0
45	Pluronic L 42	120.0	140.0
46	Pluronic L 44	120.0	140.0
47	Pluronic L 61	100.0	120.0
48	Pluronic L 63	100.0	120.0
49	Pluronic L 72	120.0	140.0
50	Pluronic L 81	100.0	120.0

TABLE I (*continued*)

Column reference number	Liquid phase	Column temperatures (°C)	
51	Pluronic P 46	120.0	140.0
52	Pluronic P 65	100.0	120.0
53	Pluronic P 84	100.0	120.0
54	Pluronic P 85	100.0	120.0
55	Polyphenyl ether-5 rings	120.0	160.0
56	Polyphenyl ether-6 rings	120.0	160.0
57	Poly tergent J 300	100.0	120.0
58	Quadrol	100.0	120.0
59	SE 30	120.0	160.0
60	SE 30 polyester NPGA terminated	120.0	140.0
61	SE 31	120.0	160.0
62	SE 52	120.0	160.0
63	Squalane	80.0	100.0
64	Sucrose acetate isobutyrate	120.0	160.0
65	Sucrose octaacetate	120.0	160.0
66	Tergitol NPX	120.0	160.0
67	TMP tripelargonate	120.0	160.0
68	Tricresyl phosphate	100.0	120.0
69	Triethylene glycol succinate	120.0	140.0
70	Triton X 305	120.0	160.0
71	Ucon LB-1715	120.0	160.0
72	Ucon 50 HB-2000	100.0	120.0
73	Versilube F-50	120.0	160.0
74	XF 1150	120.0	160.0
75	Zonyl E 7	100.0	120.0

in which R is the gas constant, T is the column temperature (°K), V_g is the specific retention volume, and P^0 is the saturated vapor pressure. This approach was a major advance over all previous theories since it did not rely upon any empirical scale and was also independent of the column temperature.

Another polarity scale which has also been recently proposed⁷ and was independent of the column temperature was based on the differential molar enthalpy of evaporation of the solute from solution (ΔH_e^s). This concept related the specific retention volume to the reciprocal of the column temperature⁸. This relationship was as follows:

$$\ln V_g = \frac{\Delta H_e^s}{RT} + K_4$$

in which K_4 is a constant. Thus, by the use of this correlation the solute-solvent interaction was quantified for various solute and solvent systems. This study also used the linear relationship between the specific retention volume and the number of carbon atoms in a homologous series of solutes. The gradient of this curve was equal to the change of the specific retention volume per methylene group. If this slope was plotted against the reciprocal of the column temperature (°K), a fundamental unit which was the differential molar enthalpy of evaporation of the methylene group

TABLE II
SPECIFIC RETENTION VOLUMES FOR ETHANE

<i>Column reference number</i>	<i>Ref. 9</i>	<i>Calculated</i>	<i>Ref. 9</i>	<i>Calculated</i>
1	0.6	1.07	0.4	0.72
2	0.6	1.04	0.5	0.80
3	0.7	1.05	0.5	0.78
4	0.6	0.98	0.4	0.75
5	0.4	0.74	0.3	0.65
6	0.3	0.31	0.2	0.32
7	0.3	0.39	0.2	0.34
8	0.2	0.40	0.2	0.34
9	0.2	0.44	0.2	0.36
10	0.3	0.45	0.2	0.39
11	0.2	0.38	0.2	0.33
12	0.2	0.40	0.2	0.35
13	0.3	0.41	0.2	0.29
14	0.4	0.96	0.4	0.87
15	0.8	1.22	0.7	1.12
16	0.4	0.86	0.4	0.73
17	0.1	0.22	0.1	0.23
18	0.2	0.41	0.2	0.40
19	0.1	0.13	0.0	0.10
20	0.9	1.36	0.8	1.20
21	0.9	1.42	0.7	1.23
22	0.6	0.94	0.5	0.80
23	0.6	0.88	0.5	0.80
24	0.9	1.39	0.8	1.16
25	1.0	1.60	0.8	1.46
26	0.5	0.93	0.4	0.69
27	0.4	0.51	0.3	0.36
28	0.4	0.67	0.3	0.66
29	0.2	0.23	0.1	0.26
30	0.2	0.45	0.2	0.44
31	0.4	1.13	0.4	0.86
32	0.9	1.59	0.8	1.26
33	0.7	1.21	0.5	0.94
34	0.2	0.28	0.2	0.25
35	0.3	0.54	0.2	0.48
36	0.8	1.38	0.8	1.33
37	0.3	0.43	0.2	0.38
38	0.3	0.53	0.3	0.48
39	0.3	0.52	0.2	0.49
40	0.3	0.41	0.3	0.40
41	0.5	0.63	0.2	0.39
42	0.4	0.58	0.3	0.48
43	0.3	0.67	0.3	0.58
44	0.4	0.57	0.3	0.50
45	0.4	0.76	0.3	0.65
46	0.4	0.68	0.3	0.56
47	0.4	0.70	0.3	0.64
48	0.4	0.80	0.3	0.67
49	0.4	0.78	0.3	0.63
50	0.6	0.85	0.5	0.77

TABLE II (*continued*)

Column reference number	Ref. 9	Calculated	Ref. 9	Calculated
51	0.4	0.57	0.3	0.45
52	0.5	0.81	0.3	0.64
53	0.5	0.69	0.4	0.64
54	0.5	0.68	0.4	0.61
55	0.4	0.53	0.2	0.35
56	0.3	0.50	0.2	0.33
57	0.5	0.77	0.4	0.63
58	0.3	0.49	0.2	0.41
59	0.7	1.23	0.5	0.91
60	0.8	1.20	0.5	0.93
61	0.7	1.16	0.5	0.81
62	0.7	1.12	0.5	0.78
63	1.1	1.68	1.0	1.51
64	0.5	0.71	0.4	0.49
65	0.3	0.35	0.2	0.26
66	0.4	0.71	0.3	0.45
67	0.8	1.09	0.4	0.77
68	0.4	0.73	0.3	0.60
69	0.1	0.17	0.1	0.16
70	0.2	0.36	0.2	0.27
71	0.5	0.73	0.2	0.46
72	0.6	0.78	0.4	0.65
73	0.7	1.13	0.6	0.80
74	0.4	0.47	0.3	0.30
75	0.2	0.44	0.2	0.36

from the solution $-\Delta H_e^s(\text{CH}_2)$ — was obtained. The idea of additivity of functional groups was also used, and from this assumption the differential molar enthalpy of evaporation from solution was obtained for the $-\text{OH}$, $-\text{NO}_2$, $>\text{C}=\text{O}$, $-\text{C}(\text{H})\text{ Ring}$, and $>\text{N Ring}$ groups on sixteen liquid phases.

The major advantage of this approach⁷ as compared to that suggested by Novák *et al.*⁶ is that it does not require prior knowledge of the saturated vapor pressure of the solutes and can be calculated directly from chromatographic data.

This work is concerned with the extension of these preliminary data⁷ by the use of published GC data.

DATA

The specific retention volumes of the solutes (*n*-alkanes, *n*-alkanols, *n*-alkanals, 2-alkanones, ethers, alkyl formates and alkyl acetates) used in this study were obtained from published results⁹. Table I shows the liquid phases investigated with the column temperatures used and their reference numbers. The reported extrapolated specific retention volumes for ethane and *n*-butane were not used but were recalculated using a weighted least squares computer program. Tables II and III show these values together with the published specific retention volumes and in all cases considerable differences may be observed.

TABLE III
SPECIFIC RETENTION VOLUMES FOR *n*-BUTANE

<i>Column reference number</i>	<i>Ref. 9</i>	<i>Calculated</i>	<i>Ref. 9</i>	<i>Calculated</i>
1	3.2	3.96	1.7	2.13
2	3.4	3.96	1.9	2.34
3	3.4	4.01	1.9	2.31
4	3.2	3.75	1.7	2.21
5	2.1	2.72	1.5	2.10
6	0.9	0.99	0.7	0.90
7	1.0	1.20	0.9	0.95
8	0.9	1.24	0.7	0.96
9	1.0	1.37	0.7	1.04
10	1.1	1.41	0.8	1.13
11	0.8	1.12	0.8	0.89
12	0.9	1.17	0.8	0.93
13	1.0	1.18	0.6	0.72
14	2.3	3.43	1.9	2.65
15	5.2	5.84	3.9	4.48
16	2.9	3.79	2.1	2.79
17	0.5	0.62	0.4	0.57
18	0.9	1.28	0.8	1.09
19	0.3	0.33	0.2	0.24
20	5.2	5.98	3.7	4.58
21	5.2	6.21	3.9	4.69
22	2.7	3.47	2.2	2.63
23	2.8	3.27	2.2	2.60
24	5.2	6.13	3.8	4.49
25	7.1	8.55	5.3	6.39
26	2.7	3.14	1.5	1.88
27	1.2	1.35	0.7	0.78
28	2.0	2.56	1.6	2.17
29	0.6	0.65	0.5	0.64
30	1.0	1.40	0.9	1.25
31	2.5	3.87	2.1	2.71
32	5.2	6.89	3.9	4.86
33	4.4	5.33	3.0	3.69
34	0.8	0.83	0.6	0.66
35	1.3	1.87	1.2	1.49
36	5.0	6.00	3.6	4.88
37	1.1	1.35	0.7	1.08
38	1.3	1.60	1.1	1.32
39	1.2	1.64	1.0	1.38
40	1.1	1.21	0.9	1.04
41	1.7	2.05	0.7	1.07
42	1.6	1.98	1.1	1.49
43	1.8	2.37	1.3	1.79
44	1.7	1.99	1.3	1.55
45	1.9	2.53	1.7	1.94
46	1.7	2.21	1.4	1.64
47	2.0	2.65	1.5	2.13
48	2.3	2.97	1.6	2.19
49	1.8	2.56	1.5	1.87
50	2.9	3.39	2.2	2.66

TABLE III (*continued*)

Column reference number	Ref. 9	Calculated	Ref. 9	Calculated
51	1.5	1.81	1.2	1.32
52	2.3	2.93	1.4	2.05
53	2.2	2.61	1.6	2.10
54	2.0	2.54	1.6	2.01
55	1.7	1.85	0.8	1.02
56	1.4	1.72	0.7	0.94
57	2.5	3.02	1.8	2.22
58	1.3	1.58	0.9	1.18
59	3.2	3.92	1.8	2.33
60	3.0	3.73	1.9	2.61
61	3.0	3.66	1.7	2.05
62	3.0	3.65	1.6	2.03
63	7.2	9.20	6.1	6.88
64	1.8	2.22	1.2	1.29
65	0.9	0.95	0.5	0.60
66	1.8	2.27	1.0	1.22
67	3.4	4.02	1.6	2.26
68	2.0	2.79	1.4	2.04
69	0.3	0.46	0.2	0.39
70	0.9	1.11	0.6	0.68
71	2.0	2.48	1.0	1.29
72	2.4	2.81	1.7	2.07
73	3.1	3.74	1.7	2.11
74	1.2	1.20	0.6	0.65
75	1.0	1.32	0.7	0.99

CALCULATIONS

Alkanes

The first step in the calculations was to determine $\Delta H_e^s(\text{CH}_2)$ and $\Delta H_e^s(\text{CH}_3)$ (the differential molar heat of evaporation of the solute from the solvent) for the normal alkane data. To determine $\Delta H_e^s(\text{CH}_2)$ the following sequence of calculations was performed. A weighted linear least squares fit was made of the set of data for $\ln V_g(T_1)$ vs. n , in which V_g is the specific retention volume, T_1 is the lower of the two temperatures for which data were available, and n is the number of carbons in the compound. Only the data for $n \geq 6$ were used since the reference states that V_g values reported for ethane and *n*-butane were obtained by extrapolation. The slope $a_1(T_1)$ and intercept $a_0(T_1)$ result. The same procedure was used to determine the slope and intercept for the higher temperature: $a_1(T_2)$ and $a_0(T_2)$. (The slopes and intercepts of these two fits were used to obtain calculated values for V_g for ethane and *n*-butane at T_1 and T_2 . These values are reported in Tables II and III.) Then the following equation was used:

$$\Delta H_e^s(\text{CH}_2) = \frac{R[a_1(T_1) - a_1(T_2)]}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (1)$$

These results are reported in Table V. From the results of the linear least squares fits one can also obtain a calculated methyl contribution from the following equation:

$$\Delta H_e^s(\text{CH}_3) = \frac{\{[a_0(T_1) - a_0(T_2)] + [2a_1(T_1) - 2a_2(T_2)]\}R}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (2)$$

The value for $\Delta H_e^s(\text{CH}_3)$ resulting from eqn. 2 is independent of the number of carbon atoms in the compound, and it is called the constant or calculated methyl contribution. This value was used in subsequent computations. The results of eqn. 2 are reported in Table VI.

A second set of $\Delta H_e^s(\text{CH}_3)$ values was calculated for the alkane data by the following sequence of steps. First, the total ΔH_e^s is calculated for an individual alkane as follows:

$$\Delta H_e^s(\text{alkane}, n) = \frac{R[\ln V_g(T_1) - \ln V_g(T_2)]}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (3)$$

Then

$$\Delta H_e^s(\text{CH}_3, n) = \frac{1}{2} [\Delta H_e^s(\text{alkane}) - Z\Delta H_e^s(\text{CH}_2)] \quad (4)$$

in which Z is the number of methylene groups in the alkane. By this procedure a series of $\Delta H_e^s(\text{CH}_3)$ values are computed as a function of carbon number. Then a linear least squares fit is performed on $\Delta H_e^s(\text{CH}_3)$ vs. n to obtain a slope and intercept for these data. Both the individual values of $\Delta H_e^s(\text{CH}_3)$ as a function of n and the slope and intercept were used in the subsequent calculations on the monofunctional compounds.

Monofunctional compounds

A series of computations was performed for each of six classes of compounds: alkanols, alkanals, 2-alkanones, formates, acetates, and dialkyl ethers. In each case the final result was a value for ΔH_e^s (functional group): ΔH_e^s (-OH), ΔH_e^s (-CHO), ΔH_e^s (>C=O), ΔH_e^s (-OC(O)H), ΔH_e^s (-OC(O)CH₃), and ΔH_e^s (-O-). Values for $\Delta H_e^s(\text{CH}_2)$ were calculated for each compound as well.

The first step for each type of compound was to calculate $\Delta H_e^s(\text{CH}_2)$ from the data which form a homologous series. This was done by the procedure described above for alkanes. The values for $\Delta H_e^s(\text{CH}_2)$ calculated for each group of compounds are reported in Table V. Then the ΔH_e^s (functional group) is calculated using these data and values for $\Delta H_e^s(\text{CH}_3)$ from the alkane calculations.

The overall ΔH_e^s (solute) is calculated from the following equation:

$$\Delta H_e^s(\text{solute}) = \frac{R[\ln V_g(T_1) - \ln V_g(T_2)]}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (5)$$

The result is then corrected by subtracting the value of $\Delta H_e^s(\text{CH}_2)$ multiplied by the number of methylene groups in the molecule. The only remaining contributions to the

TABLE IV
NUMBER OF METHYL CORRECTIONS USED FOR COMPOUND TYPES

<i>Compound type</i>	<i>Carbon number for functional compound</i>	<i>Carbon number for alkanes used for CH₃ correction</i>
Alcohols	<i>n</i>	<i>n</i> + 1
Aldehydes	<i>n</i>	<i>n</i>
Methyl ketones	<i>n</i>	<i>n</i> - 1 and 2
Formates	<i>n</i>	<i>n</i>
Acetates	<i>n</i>	<i>n</i> - 1
Dialkyl ethers*	<i>n</i>	$\frac{n}{2}$ + 1

* For the dialkyl ethers the methyl contribution was subtracted twice.

ΔH value are the terminal methyl group(s) and the functional group. The methyl contributions are subtracted in one of two alternative ways as follows.

Procedure I. Subtract the calculated methyl contribution from eqn. 2 regardless of carbon number.

Procedure II. Subtract the methyl contribution obtained earlier using eqns. 3 and 4, wherein the $\Delta H_e^s(\text{CH}_3)$ value used is a function of the carbon number of the

TABLE V
 $\Delta H_e^s(\text{CH}_2)$ IN kcal/mole FOR ALL THE SOLUTES

<i>Column reference number</i>	<i>Alkanes</i>	<i>Alkanols</i>	<i>Alkanals</i>	<i>Alkanones</i>	<i>Formates</i>	<i>Acetates</i>	<i>Ethers</i>
1	0.986	0.926	0.847	0.850	0.795	0.815	0.879
2	1.119	0.926	0.916	0.938	0.901	0.924	0.955
3	1.053	0.950	0.764	0.954	0.859	0.897	0.873
4	1.113	0.876	0.774	0.923	0.861	0.884	0.940
5	0.929	0.787	0.948	0.711	0.784	0.677	0.529
6	0.965	0.694	0.657	0.857	0.715	0.852	0.434
7	0.726	0.695	0.950	0.796	0.596	0.754	0.718
8	0.599	0.578	0.956	0.832	0.462	0.719	0.587
9	0.646	0.688	0.790	0.772	0.618	0.746	0.657
10	0.734	0.718	0.805	0.793	0.737	0.797	0.853
11	0.865	0.681	0.822	0.566	0.637	0.714	0.602
12	0.780	0.710	0.880	0.704	0.664	0.770	0.520
13	0.725	0.729	0.655	0.650	0.645	0.671	0.770
14	1.247	0.959	0.909	0.795	0.778	0.810	0.734
15	1.170	0.776	0.824	0.755	0.768	0.609	0.467
16	1.049	1.125	1.190	0.883	0.812	0.855	0.630
17	0.949	0.906	0.513	0.494	1.321	0.772	0.831
18	0.945	0.972	0.619	0.857	1.243	0.685	0.791
19	0.631	0.408	0.596	0.765	1.184	0.722	0.894
20	1.089	0.904	0.830	0.922	0.882	0.859	0.863
21	1.025	0.966	0.975	0.958	0.977	0.878	0.842
22	0.954	1.116	1.103	0.920	0.871	0.961	0.768
23	1.090	0.982	1.103	0.916	0.902	1.006	0.824
24	0.920	0.949	0.876	0.958	0.794	0.904	0.780

(Continued on p. 182)

TABLE V (continued)

<i>Column reference number</i>	<i>Alkanes</i>	<i>Alkanols</i>	<i>Alkanals</i>	<i>Alkanones</i>	<i>Formates</i>	<i>Acetates</i>	<i>Ethers</i>
25	1.272	0.828	1.510	1.061	1.011	1.050	0.645
26	0.931	0.937	0.904	0.899	0.848	0.855	0.840
27	0.830	0.821	0.720	0.658	0.834	0.762	0.648
28	1.109	0.755	0.995	0.890	0.711	0.046	0.896
29	0.944	0.829	0.684	0.662	1.643	0.881	0.830
30	0.904	0.964	0.664	0.632	1.241	0.799	0.831
31	0.627	0.948	1.008	0.983	0.980	0.978	0.746
32	0.855	0.903	0.946	0.947	1.012	0.840	0.838
33	0.845	0.863	1.087	0.914	0.804	0.935	0.799
34	0.822	0.707	0.983	0.811	0.547	0.805	0.872
35	0.887	0.748	0.912	0.876	0.714	0.856	0.881
36	1.244	0.589	0.880	0.960	0.864	0.863	0.832
37	0.816	0.786	0.900	0.681	0.787	0.830	0.586
38	0.847	0.969	0.614	0.241	1.312	0.756	0.945
39	0.895	1.067	0.645	0.790	1.144	0.771	0.792
40	1.001	1.418	0.639	0.992	1.204	0.676	0.723
41	0.668	0.721	0.653	0.659	0.627	0.777	0.803
42	0.783	0.850	0.755	0.824	0.660	0.791	0.842
43	0.977	0.704	0.725	0.730	0.628	0.644	0.668
44	0.940	0.819	0.705	0.805	0.772	0.774	0.828
45	0.894	0.891	0.937	0.815	0.930	0.920	0.662
46	0.825	0.812	0.942	0.915	0.856	0.856	0.739
47	1.012	0.814	1.191	0.787	0.755	0.697	0.582
48	0.942	0.707	1.089	0.783	0.713	0.637	0.665
49	0.842	0.806	0.870	0.745	0.931	0.879	0.697
50	1.017	0.864	0.847	1.909	0.885	0.843	0.813
51	0.721	0.761	1.044	0.803	0.922	0.841	0.635
52	0.878	0.701	0.956	0.721	0.675	0.653	0.518
53	1.049	0.778	0.743	0.842	0.941	0.796	0.850
54	0.984	0.799	0.713	0.859	0.758	0.844	0.846
55	0.837	0.653	0.968	0.711	0.825	0.810	0.695
56	0.805	0.777	0.860	0.708	0.622	0.824	0.730
57	0.820	0.802	0.836	0.795	0.775	0.838	0.888
58	0.874	0.985	0.875	0.599	0.832	0.670	0.660
59	0.932	0.852	0.729	0.823	0.910	0.832	0.895
60	0.818	1.075	0.868	0.771	0.825	0.786	0.885
61	0.902	0.863	0.811	0.885	0.914	0.843	0.870
62	0.935	0.986	0.703	1.039	0.850	0.823	0.853
63	1.227	1.228	0.764	0.718	0.782	0.742	0.999
64	0.753	0.775	0.853	0.683	0.683	0.780	0.782
65	0.655	0.678	0.563	0.595	0.608	0.688	0.647
66	0.687	0.798	0.811	0.739	0.782	0.823	0.813
67	0.971	1.594	0.799	0.857	0.902	0.912	0.916
68	0.844	0.898	1.092	0.896	0.692	0.814	0.771
69	0.691	1.147	0.188	0.556	1.230	0.725	0.628
70	0.756	0.813	0.813	0.745	0.713	0.793	0.876
71	0.781	0.818	0.660	0.746	0.765	0.785	0.848
72	0.847	0.724	1.150	0.878	0.646	0.845	0.817
73	0.943	0.876	0.808	0.911	0.833	0.799	0.872
74	0.712	0.824	0.714	0.793	0.770	0.755	0.690
75	0.748	0.995	0.756	0.643	0.708	0.708	0.233

TABLE VI
 $\Delta H_e^s(CH_3)$ IN kcal/mole FOR THE *n*-ALKANES

<i>Rank</i>	<i>Column reference number</i>	$\Delta H_e^s(CH_2)$	$\Delta H_e^s(CH_3)$ (<i>constant</i>)
1	25	1.272	0.635
2	14	1.247	0.825
3	36	1.244	0.266
4	63	1.227	0.681
5	15	1.170	0.566
6	2	1.119	1.107
7	4	1.113	1.119
8	28	1.109	0.094
9	23	1.090	0.764
10	20	1.089	0.858
11	3	1.053	1.282
12	53	1.049	0.543
13	16	1.049	1.190
14	21	1.025	1.020
15	50	1.017	0.749
16	47	1.012	0.566
17	40	1.001	0.234
18	1	0.986	1.647
19	54	0.984	0.740
20	43	0.977	1.062
21	67	0.971	1.464
22	6	0.965	-0.270
23	22	0.954	1.292
24	17	0.949	-0.313
25	18	0.945	0.293
26	29	0.944	-0.890
27	73	0.943	1.467
28	48	0.942	1.280
29	44	0.940	0.876
30	62	0.935	1.557
31	59	0.932	1.256
32	26	0.931	1.234
33	5	0.929	0.960
34	24	0.920	1.340
35	30	0.904	0.017
36	61	0.902	1.536
37	39	0.895	0.456
38	45	0.894	1.251
39	35	0.887	0.782
40	52	0.878	1.699
41	58	0.874	1.242
42	11	0.865	0.968
43	32	0.855	1.700
44	38	0.847	0.694
45	72	0.847	1.378
46	33	0.845	1.831
47	68	0.844	1.427
48	49	0.842	1.679
49	55	0.837	1.694

(Continued on p. 184)

TABLE VI (*continued*)

Rank	Column reference number	$\Delta H_e^s(CH_2)$	$\Delta H_e^s(CH_3)$ (constant)
50	27	0.830	1.498
51	46	0.825	1.563
52	34	0.822	0.826
53	57	0.820	1.410
54	60	0.818	2.062
55	37	0.816	0.964
56	56	0.805	1.756
57	42	0.783	1.321
58	71	0.781	1.980
59	12	0.780	1.076
60	70	0.756	1.285
61	64	0.753	1.545
62	75	0.748	1.375
63	10	0.734	0.902
64	7	0.726	0.962
65	13	0.725	1.379
66	51	0.721	1.843
67	74	0.712	1.911
68	69	0.692	0.613
69	66	0.687	1.933
70	41	0.668	2.084
71	65	0.655	1.299
72	9	0.646	1.385
73	19	0.631	1.812
74	31	0.627	2.239
75	8	0.599	1.222

alkane. Since only even-carbon-number alkanes were represented in the data set, the odd carbon number values are obtained by linear interpolation between adjacent values. $\Delta H_e^s(CH_3)$ values for ethane, propane, butane, and pentane were obtained using the calculated slope and intercept from the linear least squares fit of $\Delta H_e^s(CH_3)$ vs. n . Finally, a conversion was done between carbon number of the monofunctional compound and the $\Delta H_e^s(CH_3)$ value used (*cf.* Table IV).

Some examples of the calculation of ΔH_e^s (functional group, n) follow.

Example 1 — CH_3-CH_2-OH , $n = 2$. The overall ΔH_e^s (solute) is calculated from eqn. 5. Then (1), $\Delta H_e^s(CH_2)$, is subtracted. Then the methyl contribution is subtracted: (a) the constant, calculated value for $\Delta H_e^s(CH_3)$ from eqn. 2 can be used, or (b) the value for propane can be used since $n + 1 = 2 + 1 = 3$ in this case. The value for the methyl contribution of propane is derived from the slope and intercept obtained from the linear least squares fit to the data obtained from eqn. 4.

Example 2 — $CH_3-CH_2-CH_2-C(O)-CH_3$, $n = 5$. The overall ΔH_e^s (solute) is calculated from eqn. 5. Then (2), $\Delta H_e^s(CH_2)$, is subtracted. The methyl contribution is subtracted as $\Delta H_e^s(CH_3)$, ethane and $\Delta H_e^s(CH_3)$, butane). Thus, the contributions from both terminal methyl groups are subtracted.

In general the procedure yields a series of ΔH_e^s (functional group, n) values. These are then averaged, and it is these average values which are reported in Tables VIIa and VIIb.

TABLE VIIa

 ΔH_e^s IN kcal/mole FOR FUNCTIONAL GROUPS USING VARYING $\Delta H_e^s(\text{CH}_3)$

Column reference number	$\Delta H_e^s(\text{OH})$	$\Delta H_e^s(\text{CHO})$	$\Delta H_e^s(\text{C=O})$	O 	O 	$\Delta H_e^s(O)$
			$\Delta H_e^s(\text{O}-\text{CH})$	$\Delta H_e^s(\text{O}-\text{C}-\text{CH}_3)$		
1	3.037	3.186	2.326	3.227	4.290	0.781
2	3.217	3.058	2.491	3.241	4.166	0.904
3	3.334	3.709	2.693	3.238	4.202	1.444
4	3.717	3.923	2.745	3.627	4.371	1.211
5	6.033	4.153	4.271	5.116	6.019	2.592
6	8.162	5.893	6.084	5.583	5.877	5.253
7	7.080	3.554	4.067	4.911	5.223	1.924
8	7.752	3.703	4.166	5.805	5.890	2.565
9	6.576	3.563	3.648	4.868	5.122	1.690
10	6.902	4.091	4.572	4.953	5.466	1.516
11	7.464	4.874	5.083	5.811	6.121	2.887
12	7.419	5.049	5.252	6.019	6.306	4.107
13	6.416	4.593	4.172	5.270	5.743	1.145
14	6.851	4.872	5.139	5.578	6.556	3.590
15	6.516	5.196	5.239	5.619	6.898	4.365
16	3.705	2.875	3.242	4.586	5.168	2.157
17	6.451	5.964	7.601	4.478	6.779	3.774
18	6.345	6.437	6.575	5.375	7.633	4.685
19	6.174	6.612	5.081	5.390	8.006	2.317
20	5.588	4.607	4.486	4.720	5.730	2.449
21	5.060	3.770	3.970	4.283	5.287	2.245
22	4.579	3.467	3.458	4.639	4.972	2.413
23	5.342	4.101	4.351	4.824	5.320	2.653
24	4.812	3.855	3.311	4.440	4.967	1.892
25	7.924	1.454	3.281	3.519	4.425	2.685
26	3.628	3.700	3.251	4.018	4.967	1.470
27	3.769	4.637	4.397	4.205	5.411	1.336
28	7.329	4.174	4.950	5.490	7.546	2.550
29	7.450	6.260	8.275	4.265	7.578	5.558
30	5.993	5.513	6.856	4.409	6.504	4.133
31	4.984	3.262	1.186	3.437	4.170	0.420
32	6.420	3.524	2.725	3.506	4.623	0.826
33	6.357	2.863	2.709	4.040	4.310	1.014
34	7.793	2.929	4.356	4.984	5.085	1.547
35	6.988	4.078	4.695	5.332	5.631	2.021
36	7.347	4.389	4.152	4.692	5.705	2.684
37	7.601	5.072	5.461	5.619	5.979	3.743
38	5.568	4.999	5.354	3.461	6.011	1.894
39	5.509	5.312	5.964	4.367	6.040	3.921
40	5.062	5.435	5.598	4.429	6.738	4.030
41	6.124	4.086	3.007	4.662	4.998	0.121
42	6.117	4.585	4.062	5.567	5.607	1.290
43	7.092	5.034	4.139	5.583	6.156	1.738
44	6.555	4.897	4.276	5.155	5.841	1.671
45	6.618	4.351	4.409	4.790	5.436	3.238
46	6.545	4.116	3.560	4.684	5.403	1.970
47	7.464	3.701	5.116	5.783	6.587	3.779
48	7.088	3.489	3.958	5.311	6.215	2.032
49	6.619	4.484	4.053	4.610	5.452	2.369

(Continued on p. 186)

TABLE VIIa (*continued*)

Column reference number	$\Delta H_e^{\circ}(OH)$	$\Delta H_e^{\circ}(CHO)$	$\Delta H_e^{\circ}(C=O)$	O $\Delta H_e^{\circ}(O-CH)$	O $\Delta H_e^{\circ}(O-C-CH_3)$	$\Delta H_e^{\circ}(O)$
50	6.643	4.453	1.286	4.985	5.811	2.722
51	6.708	3.822	3.606	4.736	5.411	2.071
52	6.564	3.570	3.057	5.034	5.609	1.878
53	7.064	4.852	4.481	5.003	5.902	2.136
54	6.802	4.823	4.164	5.210	5.786	2.019
55	4.495	3.120	3.037	4.204	5.205	1.566
56	4.069	3.351	2.927	4.684	4.777	0.941
57	6.434	3.986	3.445	4.516	5.048	0.865
58	6.826	4.061	3.826	3.717	5.143	1.955
59	4.039	3.836	3.003	3.372	4.563	1.080
60	2.841	2.578	2.183	3.543	4.524	0.126
61	3.217	3.233	2.243	3.181	4.338	0.783
62	3.001	3.940	2.250	3.610	4.670	1.001
63	3.176	4.743	4.601	4.852	6.000	1.941
64	5.532	3.066	3.907	5.026	5.452	1.372
65	5.752	4.753	4.232	5.231	5.664	1.639
66	5.564	3.977	2.747	3.987	4.558	0.076
67	3.094	3.888	2.973	3.978	4.895	0.652
68	5.540	3.268	3.165	4.824	5.071	0.962
69	4.954	5.287	5.776	3.567	5.888	1.300
70	6.144	4.262	4.245	4.946	5.484	0.889
71	5.510	3.984	2.807	4.256	4.998	-0.095
72	6.553	2.954	3.562	5.118	5.484	1.394
73	3.527	3.495	2.443	3.519	4.418	1.041
74	4.648	4.034	2.811	3.924	4.887	0.329
75	4.211	4.986	5.163	5.433	6.161	4.011

RESULTS AND DISCUSSION

The results of the calculations for the differential molar enthalpies of evaporation from solution for the methylene groups of the solutes investigated are presented in Table V. These values show reasonable agreement between each homologous series for a particular liquid phase. If Procedures I and II are followed using the results in Table V and the respective values for $\Delta H_e^{\circ}(CH_3)$, then the ΔH_e° (functional group) are obtained which are shown in Tables VI, VIIa and VIIb. An examination of these tables yields an insight into the relative strengths of the various molecular interactions which are occurring between the solutes and the liquid phases. Therefore, the largest differential molar enthalpy for a particular functional group on a liquid phase reflects the maximum interaction, which in turn suggests better separation of solute mixtures containing that functional group. Tables VIIIa and VIIIb show the liquid phases ranked according to the interaction of the solute with the liquid phase where 1 indicates maximum interaction and 75 the minimum. A number of anomalies can be seen immediately in these tables which are due to the action of the addition of a wetting agent to each column packing material; however, the general trend observed in practice is quantified by these tables. The advantages of this system are as follows:

- (1) It is an absolute system, not depending upon any standard.
- (2) It may be easily determined from chromatographic measurements.

TABLE VIIb

 ΔH_e° IN kcal/mole FOR FUNCTIONAL GROUPS USING CONSTANT $\Delta H_e^\circ(\text{CH}_3)$

Column reference number	$\Delta H_e^\circ(\text{OH})$	$\Delta H_e^\circ(\text{CHO})$	$\Delta H_e^\circ(\text{C}=\text{O})$	O $\Delta H_e^\circ(\text{O}-\text{CH})$	O $\Delta H_e^\circ(\text{O}-\text{C}-\text{CH}_3)$	$\Delta H_e^\circ(\text{O})$
1	3.131	3.298	2.614	3.339	4.393	1.032
2	3.418	3.318	3.127	3.507	4.397	1.482
3	3.427	3.826	2.991	3.337	4.305	1.709
4	3.929	4.188	3.398	3.863	4.611	1.799
5	6.425	4.545	5.218	5.508	6.411	3.447
6	8.257	5.931	6.170	5.622	5.962	5.329
7	7.100	3.505	4.077	4.862	5.232	1.826
8	7.725	3.589	4.110	5.690	5.833	2.336
9	6.564	3.539	3.633	4.845	5.107	1.643
10	6.899	4.050	4.556	4.912	5.449	1.433
11	7.659	5.093	5.646	6.029	6.332	3.324
12	7.395	4.928	5.185	5.897	6.238	3.865
13	6.394	4.600	4.146	5.258	5.718	1.159
14	7.151	5.280	6.141	5.986	6.916	4.406
15	6.703	5.383	5.731	5.806	7.084	4.823
16	4.072	3.241	4.157	4.953	5.534	2.981
17	6.507	6.009	7.660	4.523	6.837	3.829
18	6.354	6.399	6.560	5.337	7.617	4.608
19	6.179	6.785	5.143	5.563	7.958	2.605
20	5.601	4.630	4.500	4.744	5.744	2.492
21	5.063	3.776	3.969	4.289	5.286	2.261
22	4.757	3.639	4.004	4.811	5.153	2.757
23	5.594	4.357	5.094	5.079	5.579	3.164
24	4.802	3.841	3.292	4.426	4.948	1.875
25	8.169	1.791	3.932	3.764	4.670	3.293
26	3.728	3.817	3.568	4.135	5.074	1.741
27	3.857	4.760	4.660	4.327	5.516	1.618
28	7.625	4.494	5.822	5.811	7.827	3.192
29	7.491	6.388	8.346	4.393	7.649	5.625
30	5.966	5.448	6.814	4.344	6.462	4.024
31	5.162	3.417	1.840	3.591	4.332	0.729
32	6.395	3.500	2.700	3.481	4.599	0.791
33	6.378	2.884	2.730	4.061	4.331	1.074
34	7.794	2.876	4.336	4.931	5.065	1.442
35	7.009	4.056	4.704	5.310	5.641	1.977
36	7.793	4.918	5.459	5.221	6.169	3.869
37	7.610	4.940	5.415	5.487	5.933	3.477
38	5.573	5.029	5.372	3.491	6.026	1.944
39	5.521	5.294	5.966	4.349	6.042	3.890
40	5.071	5.440	5.607	4.433	6.746	4.038
41	6.104	4.119	3.012	4.665	5.003	0.187
42	6.106	4.573	4.052	5.555	5.597	1.266
43	7.476	5.418	5.104	5.966	6.540	2.588
44	6.774	5.145	4.916	5.404	6.061	2.168
45	6.621	4.278	4.379	4.717	5.407	3.093
46	6.513	4.080	3.520	4.648	5.363	1.883
47	7.869	4.106	6.074	6.188	6.992	4.661
48	7.423	3.824	4.736	5.646	6.549	2.764
49	6.615	4.454	4.037	4.579	5.436	2.308

(Continued on p. 188)

TABLE VIIb (continued)

Column reference number	$\Delta H_e^{\circ}(OH)$	$\Delta H_e^{\circ}(CHO)$	$\Delta H_e^{\circ}(C=O)$	O 	O 	$\Delta H_e^{\circ}(O)$
				$\Delta H_e^{\circ}(O-CH)$	$\Delta H_e^{\circ}(O-C-CH_3)$	
50	6.873	4.722	1.966	5.253	6.059	3.258
51	6.713	3.784	3.581	4.699	5.385	1.997
52	6.991	3.998	4.060	5.461	6.037	2.838
53	7.437	5.279	5.519	5.429	6.288	2.988
54	7.143	5.225	5.111	5.613	6.142	2.824
55	4.643	3.376	3.595	4.450	5.428	2.079
56	4.235	3.559	3.472	4.925	5.007	1.358
57	6.447	4.020	3.457	4.550	5.060	0.933
58	6.832	4.104	3.850	3.759	5.168	2.039
59	4.156	3.983	3.372	3.518	4.692	1.413
60	2.750	2.533	2.097	3.486	4.438	0.050
61	3.286	3.315	2.469	3.263	4.411	0.977
62	3.105	4.064	2.561	3.734	4.784	1.275
63	3.308	4.875	4.978	4.983	6.132	2.293
64	5.529	3.037	3.882	5.014	5.427	1.314
65	5.746	4.781	4.236	5.233	5.668	1.695
66	5.517	3.976	2.707	3.968	4.518	0.076
67	3.214	4.078	3.368	4.152	5.046	1.031
68	5.847	3.575	3.973	5.132	5.379	1.658
69	5.089	5.311	5.910	3.591	6.023	1.340
70	6.131	4.227	4.208	4.928	5.446	0.819
71	5.538	4.085	2.989	4.336	5.064	0.106
72	6.726	3.171	4.137	5.335	5.672	1.826
73	3.593	3.579	2.661	3.604	4.489	1.240
74	4.697	4.195	3.035	4.085	4.981	0.684
75	4.263	5.038	5.215	5.485	6.213	4.083

TABLE VIIIa

RANKING OF LIQUID PHASES ACCORDING TO ΔH_e° (FUNCTIONAL GROUP) USING VARYING $\Delta H_e^{\circ}(CH_3)$

Rank	Column reference number					
	Alkanols	Alkanals	Alkanones	Formates	Acetates	Ethers
1	6	19	29	12	19	29
2	25	18	17	11	18	6
3	34	29	30	8	29	18
4	8	17	18	47	28	15
5	37	6	6	37	15	30
6	47	30	39	15	17	12
7	11	40	69	6	40	40
8	29	39	40	43	47	75
9	12	69	37	14	14	39
10	36	15	38	42	30	47
11	28	37	12	28	12	17
12	43	12	15	75	48	37
13	48	43	75	19	75	14
14	7	38	14	18	43	45
15	53	75	47	35	11	11

TABLE VIIIa (*continued*)

Rank	Column reference number					
	Alkanols	Alkanals	Alkanones	Formates	Acetates	Ethers
16	35	44	11	48	39	50
17	10	11	19	13	5	25
18	14	14	28	65	38	36
19	58	53	35	54	63	23
20	54	54	63	44	37	5
21	51	65	10	72	53	8
22	50	63	20	5	8	28
23	49	27	53	52	69	20
24	45	20	45	64	6	22
25	9	13	27	53	44	49
26	52	42	34	50	50	19
27	44	49	23	34	54	21
28	72	50	44	10	13	16
29	46	36	5	70	20	53
30	15	45	70	7	36	51
31	17	70	65	9	65	48
32	57	28	13	63	35	35
33	32	5	8	68	52	54
34	13	46	54	23	42	46
35	33	23	36	45	72	58
36	18	10	43	51	70	63
37	19	41	7	20	10	7
38	70	35	42	36	49	38
39	41	58	49	46	64	24
40	42	74	21	56	45	52
41	5	57	48	41	51	43
42	30	71	64	22	27	9
43	65	66	58	49	46	44
44	20	62	9	16	23	65
45	38	4	51	57	21	55
46	66	67	72	17	7	34
47	68	24	46	24	55	10
48	64	59	22	40	16	26
49	71	51	57	30	58	3
50	39	21	24	39	9	72
51	23	3	25	21	34	64
52	40	8	26	29	68	27
53	21	47	16	71	57	69
54	31	26	68	27	71	42
55	69	52	52	55	41	4
56	24	9	55	33	22	13
57	74	7	41	26	26	59
58	22	32	59	66	24	73
59	55	73	67	67	67	33
60	75	48	56	74	74	62
61	56	22	74	58	56	68
62	59	56	71	4	62	56
63	27	68	66	62	32	2
64	4	31	4	69	59	70
65	16	61	32	60	66	57
66	26	1	33	73	60	32

(Continued on p. 190)

TABLE VIIIa (continued)

Rank	Column reference number					
	Alkanols	Alkanals	Alkanones	Formates	Acetates	Ethers
67	73	55	3	25	25	61
68	3	64	2	32	73	1
69	61	2	73	38	4	67
70	2	72	1	31	61	31
71	63	34	62	59	33	74
72	67	16	61	2	1	60
73	1	33	60	3	3	41
74	62	60	50	1	31	66
75	60	25	31	61	2	71

TABLE VIIIb

RANKING OF LIQUID PHASES ACCORDING TO ΔH_e° (FUNCTIONAL GROUP) USING CONSTANT $\Delta H_e^{\circ}(\text{CH}_3)$

Rank	Column reference number					
	Alkanols	Alkanals	Alkanones	Formates	Acetates	Ethers
1	6	19	29	47	19	29
2	25	18	17	11	28	6
3	47	29	30	14	29	15
4	34	17	18	43	18	47
5	36	6	6	12	15	18
6	8	30	14	28	47	14
7	11	40	47	15	14	75
8	28	43	39	8	17	40
9	37	15	69	48	40	30
10	29	69	28	6	48	39
11	43	39	15	54	43	36
12	53	14	11	19	30	12
13	48	53	40	42	5	17
14	12	54	53	5	11	37
15	14	44	36	37	53	5
16	54	11	37	75	12	11
17	7	75	38	52	75	25
18	35	38	5	53	36	50
19	52	37	75	44	54	28
20	10	12	12	18	63	23
21	50	36	19	72	44	45
22	58	63	54	35	50	53
23	44	65	43	13	39	16
24	72	27	23	50	52	52
25	51	50	63	65	38	54
26	15	20	44	36	69	48
27	45	13	48	68	6	22
28	49	42	35	23	37	19
29	9	5	27	64	8	43
30	46	28	10	63	20	20
31	17	49	20	16	13	8
32	57	23	45	34	72	49

TABLE VIIIb (continued)

Rank	Column reference number					
	Alkanols	Alkanals	Alkanones	Formates	Acetates	Ethers
33	5	45	34	70	65	63
34	32	70	65	56	35	21
35	13	74	70	10	42	44
36	33	4	16	7	23	55
37	18	41	13	9	16	58
38	19	47	72	22	27	51
39	70	58	8	20	10	35
40	42	71	7	45	70	38
41	41	46	52	51	49	46
42	30	67	42	41	55	24
43	68	62	49	46	64	72
44	65	35	22	49	45	7
45	20	10	68	57	51	4
46	23	57	21	17	68	26
47	38	52	25	55	46	3
48	71	59	64	40	21	65
49	64	66	58	24	7	68
50	39	24	9	29	58	9
51	66	3	55	39	22	27
52	31	48	51	30	9	2
53	69	26	26	71	26	34
54	40	51	46	27	34	10
55	21	21	56	21	71	59
56	24	22	57	67	57	56
57	22	8	4	26	67	69
58	74	73	59	74	56	64
59	55	68	67	33	41	62
60	75	56	24	66	74	42
61	56	9	2	4	24	73
62	59	7	74	25	62	13
63	16	32	41	58	59	33
64	4	31	3	62	25	1
65	27	55	71	73	4	67
66	26	2	33	69	32	61
67	73	61	66	31	66	57
68	3	1	32	59	73	70
69	2	16	73	2	60	32
70	63	72	1	38	61	31
71	61	64	62	60	2	74
72	67	33	61	32	1	41
73	1	34	60	1	31	71
74	62	60	50	3	33	66
75	60	25	31	61	3	60

(3) It is corrected for column temperature, flow-rate, pressure drop and weight of the liquid phase.

(4) It is indicative of the true solubility of the solute in the stationary phase.

(5) It may be used to calculate specific functional-group interaction with the stationary liquid phase.

(6) It may then be used to classify stationary liquid phases not on a vague polarity scale, but on a scale determined by a real indication of the solubility of functional groups.

(7) It may be used to predict specific retention volumes, not only under identical conditions as originally investigated, but also at different temperatures, flow-rates and weights of stationary liquid phases.

It must be emphasized that the values for the ΔH_e^s should not be considered to be absolute since the specific retention volumes were only reported at two temperatures. Also, no polyfunctional group solutes have been investigated although this study is under active investigation.

ACKNOWLEDGEMENTS

We wish to thank W. O. McReynolds of the Celanese Chemical Company and S. T. Preston of the Preston Technical Abstracts Company for permission to use and reproduce the chromatographic data reported in this manuscript.

REFERENCES

- 1 L. Rohrschneider, *Z. Anal. Chem.*, 170 (1959) 256.
- 2 P. Chovin and J. Lebbe, *Communication aux Journées International d'Étude de Méthodes de Séparation Immédiate et de Chromatographie, Paris, juin 1962*.
- 3 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
- 4 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 5 L. Rohrschneider, *Anal. Chem.*, 45 (1973) 1241.
- 6 J. Novák, J. Ruzicková, S. Wičar and J. Janák, *Anal. Chem.*, 45 (1973) 1365.
- 7 B. L. Reinbold, *M.S. Thesis*, Pennsylvania State University, Pennsylvania, Pa., 1974.
- 8 P. E. Porter, C. H. Deal and F. H. Stross, *J. Amer. Chem. Soc.*, 78 (1956) 2999.
- 9 W. O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts Company, Evanston, Ill., 1966.