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A Method for the Calculation of Heats of Solution (ΔH_s) for Organic Compounds from the Number of Constituent Carbon Atoms and the Functional Groups

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The heat of solution (ΔH_s) of several homologous series of linear and monofunctional organic compounds (n-alkanes, n-alcohols, n-aldehyds and esters) in polar stationary phase (Carbowax 1540) can be expressed by $\Delta H_s = a + b \cdot n_R + c \cdot C_G$, where a is a constant, n_R is the number of carbon atoms not belonging to the functional group in the molecule and C_G represents the contribution of each functional group to the ΔH_s value. The accuracy of the ΔH_s values calculated by this equation is sufficient for all the compounds tested (average relative error = 1.92%). C_G can be calculated from the plots ΔH_s versus n_R.

(Keywords: Capillary Gas Chromatography; Heat of solution)

Eine Methode zur Berechnung der Lösungswärmen (ΔH_s) organischer Verbindungen aus der Anzahl der Kohlenstoffatome und Parametern für funktionelle Gruppen

Die Lösungswärmen einiger homologer Reihen von linearen monofunktionellen Verbindungen (n-Alkane, n-Alkohole, n-Aldehyde und Ester) in polarer stationärer Phase (Carbowax 1540) können folgendermaßen ausgedrückt werden: $\Delta H_s = a + b \cdot n_R + c \cdot C_G$, wobei a eine Konstante ist, n_R die Anzahl der C-Atome (exclusive der funktionellen Gruppe) angibt und C_G den Beitrag der funktionellen Gruppe repräsentiert. Die Genauigkeit der von dieser Gleichung wiedergegebenen ΔH_s-Werte ist in allen untersuchten Fällen gut (mittlerer relativer Fehler 1,92%). C_G-Werte können aus ΔH_s — n_R-Diagrammen erhalten werden.

Introduction

Many investigators have published various methods for estimating the thermodynamic properties of organic compounds under ideal conditions, which employ the principle of the group contribution. The

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molecules are separated into atom groups or functional groups and the sum of the contributions of these groups gives the estimated values. A complete study has been carried out by *Yoneda* et al[1].

Gas chromatography is becoming increasingly useful for physiochemical measurements. Several papers[2–4] and two recent books[5,6] have reviewed the applications of gas liquid chromatography for the determination of thermodynamic data.

Different procedures are available for calculating heats of solution (ΔH_s) by gas liquid chromatography from retention data; the methods used by *Oberholtzer* and *Rogers*[7] and *Golovnya* and *Arsenyev*[8,9] may be cited.

In a previous paper[10] heats of solution of different homologous series of esters on Carbowax 1540 stationary phase were determined by using the following equation:

$$\ln(V_R^\circ/T) = -\Delta H_s/RT + C \tag{1}$$

where V_R° is the corrected retention volume, T is the absolute temperature, R is the gas constant and C is a constant of integration.

In this paper the determination of ΔH_s for n-alkanes, n-alcohols and n-aldehydes were carried out by means of the same equation (1) in order to study the possibility to obtain a general equation for accurate calculations of ΔH_s values for organic compounds by using group increments[1]. This additive principle is widely used in GLC for calculating retention parameters with high accuracy[11,12].

Results and Discussion

The ΔH_s values obtained for n-alkanes, n-alcohols and n-aldehydes are listed in Table 1 a and for esters in Table 1 b.

One observes (Tables 1 a, 1 b) that for compounds with the same number of carbon atoms the absolute value of ΔH_s increases in the following order:

$$n\text{-alkanes} < n\text{-aldehydes} \simeq \text{esters} < n\text{-alcohols}$$

A linear correlation between ΔH_s and the number of carbon atoms (n_R) is observed. Slopes, intercepts, and statistics for the straight lines are presented in Table 2. There are good correlation coefficients in all cases.

For the esters, an increase in the length of either the alcohol or the acid chain produces an increases of the slope (Table 2).

Intercept values (C_G) can be considered as the contribution of the functional group to the ΔH_s value.

Table 1a. *Heats of solution* ($-\Delta H_s$) *of n-alkanes, n-alcohols and n-aldehydes* (s = *standard deviation*)

Compound	$-\Delta H_s$ (kcal/mol)	Compound	$-\Delta H_s$ (kcal/mol)	Compound	$-\Delta H_s$ (kcal/mol)
Nonane	7.98	Propanol	10.07	Butanal	7.23
Decane	9.17	Butanol	10.99	Pentanal	8.50
Undecane	10.29	Pentanol	11.92	Hexanal	9.52
Dodecane	11.39	Hexanol	12.80	Heptanal	10.54
		Heptanol	13.89	Octanal	11.63
		Octanol	14.90	Nonanal	12.59
				Decanal	13.72
$\overline{\Delta(\Delta H)}$ =	1.14	$\overline{\Delta(\Delta H)}$ =	0.97	$\overline{\Delta(\Delta H)}$ =	1.08
s =	0.05	s =	0.08	s =	0.10

Table 1b. *Heats of solution* ($-\Delta H_s$) *of esters*[10] (s = *standard deviation*)

	Methyl	Ethyl	Propyl	Butyl	Pentyl	Hexyl	Heptyl	Octyl	$\overline{\Delta(\Delta H)}$	s
ormate	-	-	-	9.52	10.34	11.24	12.24	13.22	0.93	0.08
cetate	-	-	8.52	9.74	10.78	11.70	12.84	13.88	1.04	0.09
ropionate	-	8.65	9.65	10.44	11.42	12.30	13.19	14.07	0.90	0.08
utyrate	9.02	9.61	10.40	11.20	12.06	12.93	13.78	-	0.83	0.04
entanoate	10.04	10.54	11.19	12.04	12.91	13.75	14.55	15.34	0.80	0.08
exanoate	10.85	11.45	12.11	12.90	13.73	14.51	15.25	16.04	0.77	0.06
eptanoate	11.74	12.26	12.97	13.76	-	-	-	-	-	-
ctanoate	12.69	13.15	13.86	14.60	-	-	-	-	-	-
$\overline{(\Delta H)}$ =	0.90	0.90	0.89	0.81	0.74	0.70	-	-		
s =	0.09	0.06	0.13	0.07	0.11	0.10	-	-		

If the esters are considered as a homologous series (R—COOR') a general equation may be obtained for all of them:

$$\Delta H_s = -5.73 - 0.81 \cdot n \tag{2}$$

$N = 44$; $r = 0.991$; $s = 0.254$; $F = 2276$ ($F_{\text{theoret.}} = 7.31$) where: n = total number of carbon atoms of R plus R'; N = number of experimental data; r = correlation coefficient; s = standard deviation; F = experimental value of *Snedecor*'s test.

Table 2. *Plots of ΔH_s vs. n_R and statistics**

Homologous serie	slope	intercept C_G	R	s
$R\text{-}CH_3$	-1.13_5	1.07_5	0.9998	0.033
$R\text{-}CH_2OH$	-0.96	-8.09	0.9994	0.070
R-CHO	-1.06	-4.17	0.9993	0.090
$CH_3COO\text{-}R$	-1.06	-5.43	0.9994	0.076
$C_2H_5COO\text{-}R$	-0.90	-6.89	0.9998	0.043
$C_3H_7COO\text{-}R$	-0.84	-7.90	0.9998	0.035
$C_4H_9COO\text{-}R$	-0.81_5	-8.83	0.9995	0.059
$C_5H_{11}COO\text{-}R$	-0.77	-9.84_5	0.9997	0.042
$C_6H_{13}COO\text{-}R$	-0.75	-10.75	0.9995	0.033
$C_7H_{15}COO\text{-}R$	-0.72_5	-11.69_5	1.0000	0.012
$R\text{-}COOCH_3$	-0.90	-6.35	0.9994	0.055
$R\text{-}COOC_2H_5$	-0.90	-6.91	0.9996	0.051
$R\text{-}COOC_3H_7$	-0.87	-7.76	0.9991	0.087
$R\text{-}COOC_4H_9$	-0.82	-8.82	0.9994	0.067
$R\text{-}COOC_5H_{11}$	-0.74	-9.96	0.9976	0.093
$R\text{-}COOC_6H_{13}$	-0.71	-10.92	0.9978	0.085
$R\text{-}COOC_7H_{15}$	-0.62	-12.07	0.9915	0.148
$R\text{-}COOC_8H_{17}$	-0.56	-13.16	0.9875	0.199

* In all cases the number of experimental points were between 4 and 7. All the equations are with 99% significance (*Snedecor*'s *F* test).

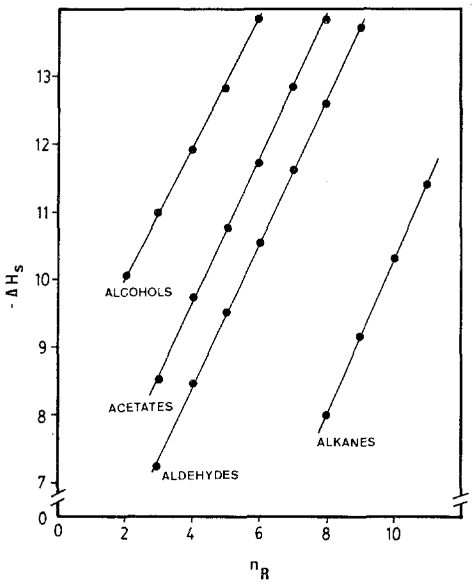

Fig. 1. Plots of heats of solution vs. number of C-atoms for homologous series of alkanes, aldehydes, alcohols and acetates

Table 3. *Values of ΔH_s (experimental) and ΔH_s calculated by eq. (3) for n-alkanes, n-alcohols, n-aldehydes and esters (kcal/mol)*

Compounds	$-\Delta H_s$(exp)	$-\Delta H_s$(calc)	$\lvert E \rvert$(%)
R-CH_3			
Nonane	7.98	8.29	3.94
Decane	9.17	9.19	0.22
Undecane	10.29	10.09	1.99
Dodecane	11.39	10.98	3.59
R-CH_2OH			
Propanol	10.07	9.82	2.46
Butanol	10.99	10.72	2.49
Pentanol	11.92	11.61	2.58
Hexanol	12.80	12.51	2.29
Heptanol	13.89	13.40	3.51
Octanol	14.90	14.30	4.04
R-CHO			
Pentanal	8.50	8.66	1.89
Hexanal	9.52	9.56	0.38
Heptanal	10.54	10.45	0.84
Octanal	11.63	11.35	2.43
Nonanal	12.59	12.24	2.78
Decanal	13.72	13.14	4.24
R-$COOCH_3$			
Methyl Butyrate	9.02	9.41	4.28
" Pentanoate	10.04	10.30	2.61
" Hexanoate	10.85	11.20	3.20
" Heptanoate	11.74	12.09	3.01
" Octanoate	12.69	12.99	2.35
R-$COOC_2H_5$			
Ethyl Propionate	8.65	8.93	3.26
" Butyrate	9.61	9.83	2.27
" Pentanoate	10.54	10.72	1.74
" Hexanoate	11.45	11.62	1.48
" Heptanoate	12.26	12.51	2.08
" Octanoate	13.15	13.41	1.98
R-$COOC_3H_7$			
Propyl Acetate	8.52	8.68	1.84
" Propionate	9.65	9.58	0.81
" Butyrate	10.40	10.47	0.65
" Pentanoate	11.19	11.36	1.55
" Hexanoate	12.11	12.26	1.23
" Heptanoate	12.97	13.15	1.42
" Octanoate	13.86	14.05	1.37
R-$COOC_4H_9$			
Butyl Acetate	9.74	9.47	2.72
" Propionate	10.44	10.37	0.67
" Butyrate	11.20	11.27	0.59
" Pentanoate	12.04	12.16	1.01
" Hexanoate	12.90	13.06	1.22
" Heptanoate	13.76	13.95	1.40
" Octanoate	14.60	14.85	1.70
R-$COOC_5H_{11}$			
Pentyl Acetate	10.78	10.33	4.15
" Propionate	11.42	11.22	1.69
" Butyrate	12.06	12.12	0.53
" Pentanoate	12.91	13.02	0.85
" Hexanoate	13.73	13.92	1.35
R-$COOC_6H_{13}$			
Hexyl Propionate	12.30	11.95	2.83
" Butyrate	12.93	12.85	0.64
" Pentanoate	13.75	13.74	0.05
" Hexanoate	14.51	14.64	0.88

Table 3 (continued)

Compounds	$-\Delta H_s$(exp)	$-\Delta H_s$(calc)	|E| (%)
R-COOC$_7$H$_{15}$			
Heptyl Propionate	13.19	12.82	2.83
" Butyrate	13.78	13.71	0.49
" Pentanoate	14.55	14.61	0.40
" Hexanoate	15.25	15.50	1.66
R-COOC$_8$H$_{17}$			
Octyl Propionate	14.07	13.64	3.07
" Pentanoate	15.34	15.43	0.58
" Hexanoate	16.04	16.32	1.77

Taking into account the contribution of the different functional groups, a general equation for all the homologous series studied was obtained (3):

$$\Delta H_s = -1.94 - 0.90\, n_R + 0.75\, C_G \qquad (3)$$

$N = 57$; $r = 0.991$; $s = 0.267$; $F = 1466$ ($F_{\text{theoret.}} = 4.98$). The C_G values are included in Table 2 since they are the intercepts of the straight lines obtained by plotting ΔH_s vs. n_R for each homologous series. The accuracy of eq. (3) for theoretical calculation of ΔH_s is shown in Table 3. The average relative error ($\bar{E}$) is 1.92%.

Utilization of $C_{G(\text{—COO—})} = -5.73\,\text{kcal mol}^{-1}$ is only useful for esters (eq. 2) because in the general equation better correlations are obtained by using C_G corresponding to each homologous series as can be deduced from the values of the average relative error ($\bar{E}$). Thus, when $C_{G(\text{—COO—})}$ is used for all the esters $\bar{E}$ is 3.39%.

The method proposed here may be applicable to other linear and branching homologous series and stationary phases as well.

Experimental

The heats of solution were calculated from the slopes of the ln (V_R°/T) vs. $1/T$ plots. Dead volume was determined by the Peterson and Hirsch method[13] using measurement on a homologous series of *n*-paraffins (C_9—C_{14}).

Determinations of V_R° were carried out with a Perkin Elmer Chromatograph model 900 equipped with a SIP-1 digital integrator and a counter, model 56. The detection system was flame ionization. One capillary column of Carbowax 1540 + KOH (99:1) made of stainless steel with dimensions of 150 ft × 0.02 in. was used.

The assays were carried out at three different temperatures, 70, 81 and 90 °C. The other experimental conditions and the retention data of the esters, alcohols, alkanes and aldehydes mentioned have been listed in previous paper[14,15]. The calculations were made using a HP-9830 calculator.

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