

## THE USE OF PRECISE RETENTION DATA FOR THE DETERMINATION OF MOLAR HEATS OF SOLUTION

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The molar heats of solution of n-alkanes in n-squalane were measured by capillary gas chromatography. The three methods for the calculations of the molar heats of solution from the adjusted retention times, retention indices and the relative retentions were compared. The accuracy and precision of these methods of calculation were evaluated and measures were proposed to improve the attained measuring precision related primarily to the instrumentation employed.

At present, gas chromatography is among the most frequently used research methods. While the principal emphasis is placed on its analytical application, it is being used more and more in physicochemical measurements. For the GLC system, the study of the thermodynamic properties of infinitely dilute solutions is particularly important<sup>1-20</sup>. Gas chromatography is particularly attractive because of a number of advantages over conventional methods, such as rapidity, simplicity, low demands on the purity of the substances, easy and rapid control of the temperature and the large amount of data available from a single experiment. In addition, the precision of the measured data does not change at low concentrations, whereas conventional methods yield results for these concentrations only as a result of extrapolation.

The experimental basis for the calculation of physicochemical data from gas chromatographic measurements are the determined values of the retention times. Consequently, sufficient attention must be paid to the precision and accuracy of the retention times measured. Recently, this subject has been studied in an ever increasing number of works<sup>21-29</sup>.

Errors in the measurement of retention data can result from: 1) improper instrumentation, *i.e.* from incorrect measurement of retention times and incorrect control of the experimental temperature and the carrier gas flow-rate; 2) undefined composition of the liquid stationary phase or from its loss or chemical changes during the measurement; 3) non-linear distribution isotherm resulting in unsymmetrical elution curves (it is thus necessary to inject small sample amounts<sup>30</sup>); 4) incomplete separation of components of the mixture, resulting in a shift of the peak maxima; 5) adsorption of components on the surface of the support or in the gas-liquid interface<sup>31+34</sup>, which can be suppressed by correct choice of the stationary phase, its percent coating and deactivation of the support surface; 6) imprecise determination of the dead time<sup>3,5</sup>, and 7) slow response of the detection and recording system. All the above possible sources of error in measuring the retention data were taken into account in the construction of the gas chromatograph and in the choice of the solutes and of the liquid stationary phase.

The purpose of this work was precise measurement of the retention data and its application to the calculation of molar heats of solution. (The molar heats of solu-

tion,  $\Delta H_s$ , are negative and are equal to the differential heats of vapourization from solution at infinite dilution, but have the opposite sign<sup>14</sup>.) The measurements were carried out on a open tubular column to ensure effective separation<sup>36</sup>. Squalane was chosen as the liquid stationary phase because of its defined structure and the amount of data published for this phase permitting evaluation of the precision and accuracy of measurement<sup>27,37-39</sup>. The studied substances were hydrocarbons C-5 to C-8 whose separation on squalane has been repeatedly successfully confirmed, and which were available in the required purity and amount. The molar heats of solution were calculated from the retention times, retention indices and relative retentions. A method<sup>40</sup> which takes into consideration the non-ideal behaviour in the gaseous state was employed. If a narrow temperature range is employed (about 1°C) then only the adjusted retention times can be used for the calculation and specific retention volumes need not be employed, which simplifies the measurement and improves the precision. In addition to the adjusted retention times, the retention indices<sup>41</sup> and the relative retentions were also used for calculation of  $\Delta H_s$ . The necessary values of the molar heats of solution of standard n-alkanes were determined by measuring the temperature dependence  $\log V_g$  vs  $1/T$  on a packed column.

## EXPERIMENTAL

### Materials

Stationary phase: Squalane (Becker Delft, the Netherlands). Support: Chromosorb W, 40/60 mesh (Carlo Erba, Milan, Italy). Solutes: n-pentane, n-hexane, n-heptane, n-octane, 2-methylpentane, 3-methylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylhexane, 2,4-dimethylhexane, 2,5-dimethylhexane, 2,2,3-trimethylbutane, 2,3,4-trimethylpentane, cyclopentane, cyclohexane, 1-hexene, 1-heptene, 1-octene — all API hydrocarbon standards (USA). Benzene *p.a.*, hexane *p.a.*, toluene *p.a.*, chloroform *p.a.*, acetone *p.a.* Lachema Brno. Czechoslovakia.

### Apparatus

The measurements were carried out on a gas chromatograph constructed according to the requirements on precise measurement of the retention times<sup>29</sup>.

It consisted of the following components: 1) A system for controlling and measuring the carrier gas flow-rate. A constant pressure gradient was maintained in the column by two Negretti-Zambra pressure regulators placed in series. At the inlet of each an overpressure of 1 atm was maintained. This arrangement permitted regulation of the pressure gradient with a precision of 0.001 atm. The pressure gradient was measured with a DeWitt manometer calibrated to 0.05 atm. 2) A system for regulating and measuring the temperature. An air thermostat developed in our laboratory was employed<sup>42</sup>. It has a working range of 30–300°C and a temperature stability of  $\pm 0.01^\circ\text{C}$ . The temperature was measured with a mercury thermometer with 0.1°C divisions. 3) The injection system consisted of the injection block itself and a splitter. The injection block was heated by a heating coil to 130°C. 5  $\mu\text{l}$  of the vapour of the hydrocarbon mixture and 2  $\mu\text{l}$  of methane were injected with a splitting ratio of 1 : 500, corresponding to about  $10^{-9}$  g of the

individual components of the mixture injected into the column. 4) The chromatographic column was a stainless steel capillary, 18 m long and 0.25 mm in diameter. Before coating the column was cleaned by washing with 10 ml portions of organic solvents in the following order: hexane, benzene, chloroform, acetone, water, acetone, chloroform, benzene. After cleaning, the column was coated with a 5% squalane solution in benzene by the dynamic method. The volume of the solution forced through the column was approximately equal to three times the column volume. A constant flow-rate was maintained by connecting a 6 m capillary in series. The column was then stabilized by passage of nitrogen for 5 hours at laboratory temperature and 12 hours at 75°C. 5) The detection system consisted of a flame-ionization detector (Becker-Delft) and an amplifier (Perkin-Elmer, type F 11). The detector was heated by a metal block. A voltage of 150 V was applied to the detector electrodes. 6) A recorder (Electronic 19 — Honeywell) with a pen slewing rate of 0.5 s.

The measurements with the packed column were carried out on a commercial gas chromatograph Carlo Erba, Fractovap Model C with a flame ionization detector. A glass column was used, 140 cm long and with an internal diameter of 0.35 cm, packed with 10% squalane on Chromosorb W (80/100 mesh). An electrical digital stop-watch was used to measure the retention times. All calculations were carried out on a Hewlett Packard 9830A computer.

The amounts of stationary phase in the open tubular column and in the packed column were found by rinsing the phase with solvent, evaporating the solvent and weighing the residue. The calculated average film thickness in the open tubular column was 0.39  $\mu\text{m}$ ; the permeability  $K$  was  $19.4 \cdot 10^{-6} \text{ cm}^2$ .

## RESULTS

Under optimal separation conditions, *i.e.*  $H_{\text{ef},\text{min}} = 0.18 \text{ cm}$ ,  $u_{\text{min}} = 11 \text{ cm/s}$ , the retention times of two artificially prepared mixtures of hydrocarbons were measured on the open tubular column coated with squalane in the temperature range 50–60°C in one-degree intervals. Methane was added to each sample to determine the dead time. An average of 4–6 measurements were carried out for each temperature and mixture. The adjusted retention times, the relative retentions with respect to n-heptane and the retention indices were calculated from the measured retention times.

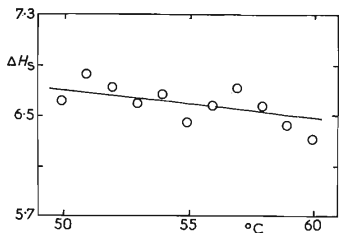


FIG. 1  
The Temperature Dependence of the Molar Heat of Solution,  $\Delta H_s$  (kcal/mol)

The molar heats of solution,  $\Delta H_s$ , were calculated from the adjusted retention times according to the relationship given in ref.<sup>40</sup>. The constants necessary for the calculation were taken from tables<sup>43,44</sup>. The hydrocarbon densities required for calculation of the molar volumes in the required temperature range 60–61°C were obtained by extrapolation of the values for 20, 25 and 30°C. The set of values of  $\Delta H_s$  obtained was evaluated by the linear regression method assuming a linear dependence of  $\Delta H_s$  on temperature. Fig. 1 depicts this dependence for 2-methylpentane. In view

TABLE I

Molar Heats of Solution of Hydrocarbons in Squalane Calculated from Adjusted Retention Times (A), Relative Retentions (B) and Retention Indices (C)

Hydrocarbon	A		B	C
	50–51°C	60–61°C	50–60°C	50–60°C
n-Pentane	5.90	5.86	5.89	5.87
Cyclopentane	6.35	6.27	6.37	6.37
2-MePe	6.53	6.42	6.67	6.65
1-Hexene	7.05	6.81	6.92	6.80
3-MePe	6.75	6.74	6.74	6.75
n-Hexane	6.96	7.06	7.01	6.85
2,2-diMePe	7.02	6.99	7.15	6.99
2,4-diMePe	7.18	7.17	7.31	7.14
Benzene	6.88	7.01	6.90	6.98
2,2,3-triMeBu	7.12	6.87	7.13	6.97
3,3-diMePe	7.24	7.17	7.39	7.24
Cyclohexane	7.13	6.99	7.26	7.06
2-MeHex	7.64	7.34	7.72	7.59
2,3-diMePe	7.76	7.41	7.64	7.51
3-MeHex	7.62	7.48	7.79	7.66
1-Heptene	8.02	7.93	7.87	7.75
n-Heptane	8.05	7.90	8.12	8.12
2,5-diMeHex	8.33	8.13	8.29	8.34
2,4-diMeHex	8.23	8.21	8.36	8.33
Toluene	8.26	8.03	8.14	8.10
2,3,4-triMePe	8.40	8.30	8.42	8.39
2,3-diHex	8.86	8.41	8.69	8.62
4-MeHept	8.78	8.82	8.82	8.66
3-MeHept	8.85	8.77	8.90	8.83
1-Octane	8.87	8.82	8.97	8.98
n-Octane	9.12	9.16	9.29	9.29

of the low temperature dependence of  $\Delta H_s$ , the narrow temperature interval employed and the precision of the method, which equals at most 50–80 cal/mol for the hydrocarbons studied, the dependence can be considered linear. The  $\Delta H_s$  values for 50 and 60°C, calculated from the obtained regression straight line equations, are given in Table I.

The quantities necessary for calculation of  $\Delta H_s$  from the relative retentions were found from measurements on the packed column with squalane. The retention times of n-pentane, n-hexane, n-heptane and benzene were measured at 50, 60 and 80°C. The specific retention volumes  $V_g$  and the slope of the  $\log V_g$  vs  $n$  dependence were calculated from the retention times ( $n$  is the number of carbon atoms in the n-alkane molecule); the molar heats of solution were calculated from the slope of the  $\log V_g$  vs  $1/T$  dependence. In Table II are given the average values of  $V_g$  from 6 measurements, along with the standard deviations, and are compared with the literature data<sup>25,45</sup>. The agreement confirms the correctness of the experiments performed. The slopes for 50°C,  $b = 0.440$  and 60°C,  $b = 0.417$  were determined from the plot of  $\log V_g$  against the number of carbons in the n-alkanes. From the slope of the dependence of  $\log V_g$  on  $1/T$  for the given hydrocarbons were calculated the molar heats of solution of n-pentane (5.87 kcal/mol), n-hexane (6.85 kcal/mol), n-heptane (18.12 kcal/mol) and benzene (7.08 kcal/mol). The molar heats of solution of a number of hydrocarbons were calculated from the relative retentions with respect to n-heptane and from the retention index values<sup>41</sup> and are given in Table I.

## DISCUSSION

The precision and accuracy of the measured retention data are important for the comparison of the calculated heats of solution. The precision of the determined relative retentions is illustrated in Table III, which lists the retention indices at 50

TABLE II  
Specific Retention Volumes of Hydrocarbons in Squalane

Hydrocarbon	50°C			60°C			80°C		
	$V_g$	$s$	$V_g^{25}$	$V_g$	$s$	$V_g^{25}$	$V_g$	$s$	$V_g^{25}$
n-Pentane	55.3	0.3	55.2	41.4	0.2	41.4	25.1	0.1	25.7
n-Hexane	152.2	0.9	151.6	109.6	0.5	108.4	60.2	0.3	61.3
n-Heptane	417.5	2.1	—	282.5	1.1	—	142.2	0.6	142.9
Benzene	221.2	1.3	220.7	158.2	0.8	159.2	87.0	0.4	—

and 60°C, together with the standard deviations. The average magnitude of the standard deviation  $s$  is 0.1  $I$ , in agreement with the value given for the measurement of retention times with a stopwatch. The accuracy of the measurement was evaluated by comparing the obtained retention indices and their temperature dependences with the published data<sup>46</sup>. It is clear from Table III that very good agreement was obtained for all the hydrocarbons except benzene, for which a difference of 0.8  $I$  was found.

The attained precision of determination of the adjusted retention times ( $s_r \approx 0.1\%$ ) is not sufficient for determining  $\Delta H_s$  with a precision of 1% as stated by the authors<sup>40</sup>. The average  $\Delta H_s$  values for 50 and 60°C are in good agreement with the  $\Delta H_s$  values calculated from the relative retentions and from the retention indices measured

TABLE III  
Comparison of the Retention Indices and Their Temperature Coefficients for Hydrocarbons on Squalene

Hydrocarbon	$I_{50}$	$s$	$I_{50}^{46}$	$I_{60}$	$s$	10 $dI/dT$	10 $dI/dT^{46}$
Cyclopentane	565.78	0.23	565.7	566.97	0.20	1.19	1.38
2-MePe	569.82	0.13	569.7	569.96	0.13	0.14	0.17
1-Hexene	582.43	0.16	582.3	582.59	0.10	0.16	0.24
3-MePe	584.17	0.12	584.2	584.63	0.14	0.46	0.45
2,2-diMePe	625.55	0.03	525.6	626.25	0.19	0.70	0.65
2,4-diMePe	629.78	0.18	629.8	630.03	0.02	0.25	0.35
Benzene	638.07	0.16	637.2	640.65	0.14	2.58	2.32
2,2,3-triMeBu	639.55	0.17	639.7	641.07	0.08	1.52	1.44
3,3-diMePe	658.70	0.10	658.9	660.06	0.05	1.36	1.32
Cyclohexane	662.58	0.14	662.7	664.90	0.06	2.32	2.22
2-MeHex	666.63	0.11	666.6	666.77	0.04	0.14	0.17
2,3-diMePe	671.68	0.18	671.7	672.49	0.06	0.81	0.85
3-MeHex	676.16	0.08	676.2	676.53	0.01	0.39	0.36
1-Heptene	681.96	0.10	681.8	682.23	0.04	0.27	0.25
2,5-diMeHex	728.37	0.16	728.4	728.69	0.09	0.32	0.30
2,4-diMeHex	731.83	0.15	731.9	732.36	0.07	0.53	0.51
Toluene	745.38	0.10	745.4	747.86	0.08	2.48	2.40
2,3,4,-triMePe	752.00	0.09	752.4	753.64	0.08	1.34	1.38
2,3-diMeHex	759.99	0.09	760.1	760.70	0.09	0.70	0.72
4-MeHept	767.18	0.08	767.2	767.37	0.01	0.19	0.26
3-MeHept	772.07	0.06	772.3	772.49	0.15	0.42	0.31
1-Octene	781.26	0.05	781.2	781.49	0.08	0.23	0.28

in the same temperature interval (Table I). The largest difference was 3%. The increase in the heat of solution temperature dependence is about 15 cal/mol. K and corresponds to the theory. To determine the temperature-dependence of the heat of solution more precisely, the absolute retention times would have to be measured more precisely. In our case, it would be possible to increase the length of the open tubular column, measure the retention times automatically, thermostat the carrier gas flow-rate regulators and make the reading of the experimental temperature more precise.

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