

Enthalpies of Solution and Excess Enthalpies of Oxo Compounds by Capillary Gas Chromatography

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Abstract

The temperature dependence of retention data is measured for 5 *n*-alkanes and 35 aliphatic ketones and aldehydes on capillary columns using 4 bonded stationary phases: dimethyl polysiloxane (HP-1), phenyl methyl polysiloxane (HP-50), trifluoropropyl methyl polysiloxane (DB-210), and polyethylene glycol (HP-Innowax). A novel equation is deduced from the expressions describing the thermodynamic relations of the specific retention volume. The enthalpy of solution, $Q_{\text{sol}}H^\circ$, is determined from the fits of $\ln(k/T)$ versus $1/T$, where k is the retention factor and T is the column temperature. The excess enthalpy H^E is determined from the enthalpy of vaporization in the middle of the temperature range (the enthalpy of vaporization is available from the literature) and from $Q_{\text{sol}}H^\circ$. The $Q_{\text{sol}}H^\circ$ values of the *n*-alkanes decrease with increasing column polarity on the McReynolds scale, whereas those of the alkanals and ketones tend to increase. The values of H^E show that, with increasing polarity of the stationary phase, the stronger interaction with the C=O group is cancelled out by a similar decrease in interaction with the apolar part of the solute. With increasing molecular size of the *n*-alkanes, the solute-stationary phase interaction is increasingly less able to compensate the energy necessary for hole formation in the stationary phase.

Introduction

Gas chromatography (GC) is a useful technique for the investigation of solute-stationary phase (solvent) interactions. The gas-liquid equilibrium in a GC column is generally characterized by the distribution constant or by the free energy, the molar enthalpy and entropy of solution ($Q_{\text{sol}}H^\circ$ and $Q_{\text{sol}}S^\circ$, respectively). In this respect, $Q_{\text{sol}}H^\circ$ is the most important and frequently investigated function for representing the solute-stationary phase interaction. From its value, one can determine the lowest temperature at which the stationary phase can be applied and select the best solvent for the polymer stationary phase (1) and the solvent for rinsing the bonded phase in the capillary column. In certain cases, the enthalpy of vaporization can

be determined from $Q_{\text{sol}}H^\circ$ (2). Its value reveals a change in the structure of the stationary liquid phase with temperature (e.g., in liquid crystals)(3) and therefore the lower limit of its applicability in analysis. It serves as a basis for the interpretation of polarity and selection mechanisms (4). $Q_{\text{sol}}H^\circ$ with $Q_{\text{sol}}S^\circ$ may be used to predict the retention factor and therefore the retention time on a given stationary phase.

The growing interest in capillary columns with a relatively inert wall has necessitated the study of the thermodynamic characteristics of the new bonded phases.

The basic relationships describing the solution process involve the specific retention volume at 0°C, V_g (5).

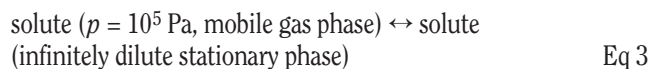
Two basic thermodynamic functions of the distribution process (i.e., the molar enthalpy and entropy of solution) can be determined by means of the van't Hoff equation from the temperature dependence of the distribution constant K :

$$\ln K = -\frac{Q_{\text{sol}}H^\circ}{RT} + \frac{Q_{\text{sol}}S^\circ}{R} \quad \text{Eq 1}$$

where T is the column temperature, R is the molar gas constant, and K is the distribution constant of the distribution process. Similarly, for the Henry constant, a simple relation exists between K , V_g , and the relative molar mass of the stationary phase M (6):

$$V_g = \frac{273 RK}{M} \quad \text{Eq 2}$$

When the following distribution process is applied,



V_g can be determined from the analytical conditions

$$V_g = \frac{F_c j (t_R - t_M) 273}{W_S T} \quad \text{Eq 4}$$

where F_c is the carrier gas flow rate, j is the compressibility correction factor, t_R is the retention time of the solute, t_M is the

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column dead time, and W_S is the mass of the stationary phase.

$\mathcal{Q}_{sol}H^\circ$ is usually determined from the slope of $\ln V_g$ versus $1/T$ plots (7,8). The measurement of V_g is relatively easy if a packed column is used. However, the difficulty in the determination of V_g for analyses with a capillary column is twofold: the mass of the stationary phase is ambiguous because the film thickness is not uniform and not accurately known, and the measurement of the carrier flow rate at low speed may be uncertain (9).

It should be mentioned that the heat of solution can also be calculated independently from the temperature dependence of retention data; empirical retention time versus boiling point relations are suitable for the estimation of $\mathcal{Q}_{sol}H^\circ$ values on apolar and slightly polar columns (10).

The retention factor (capacity ratio) k (11,12) has also been employed as an alternative for the determination of $\mathcal{Q}_{sol}H^\circ$. The parameter k is preferably used because of the simplicity of its determination from the chromatogram.

$$k = \frac{t_R}{t_M} - 1 \quad \text{Eq 5}$$

There are differences in $\mathcal{Q}_{sol}H^\circ$ determined from the fit $\ln k$ or $\ln V_g$ versus $1/T$. The reason for this is the different standard state, concentration, or pressure of the solute in the gas phase (Eq 3) (6).

The solution process consists of the condensation and mixing of the pure compound with the solvent. $\mathcal{Q}_{sol}H^\circ$ is divided into two parts:

$$\mathcal{Q}_{sol}H^\circ = -\mathcal{Q}_{vap}H^\circ + H^E \quad \text{Eq 6}$$

where $\mathcal{Q}_{vap}H^\circ$ is the enthalpy of vaporization and H^E is excess enthalpy (the energy needed or liberated during the transfer of 1 mol of pure liquid solute into 1 mol of infinitely dilute solution).

H^E can be calculated from Eq 6 using the experimental $\mathcal{Q}_{sol}H^\circ$ and $\mathcal{Q}_{vap}H^\circ$ values. $\mathcal{Q}_{vap}H^\circ$ is known with appropriate accuracy (0.1–0.3%) for several compounds, generally at the boiling point or in a standard state (i.e., conditions rarely applicable in GC) (13,14).

The calculation of $\mathcal{Q}_{vap}H^\circ$ for several organic compounds at any temperature by a semiempirical method from accurate data sets was recently suggested, with a reported maximum error of approximately 2%:

$$\mathcal{Q}_{vap}H^\circ = A \exp(-\alpha T_R)(1 - T_R)^a \quad \text{Eq 7}$$

where T_R is the reduced temperature and A and a can be determined from group values (15).

In the present paper, a convenient method for the determination of $\mathcal{Q}_{sol}H^\circ$ from the retention

Table I. Characteristics of Capillary Columns

Notation	Column	Stationary phase*	Inner diameter (mm)	Film thickness (μm)	Length (m)	Polarity [†]
A	HP-1	dimethyl polysiloxane	0.32	1.05	50	222
B	HP-50	50% phenyl methyl polysiloxane	0.32	0.5	30	884
C	J&W DB-210	50% trifluoropropyl methylpolysiloxane	0.32	0.5	30	1520
D	HP-Innowax	polyethylene glycol	0.32	0.5	30	2308

* All phases are bonded.
[†] Sum of the first five McReynolds constants (5,16).

Table II. Estimation of H^E of n -Alkanes from $-\mathcal{Q}_{sol}H^\circ$ and $\mathcal{Q}_{vap}H^\circ$ Values on Different Stationary Phases*

		Column A	Column B	Column C	Column D	$\mathcal{Q}_{vap}H^\circ_{353}^\dagger$
n -Hexane	$-\mathcal{Q}_{sol}H^\circ$	28.93 ± 0.21 (27.59) [‡]	26.36 ± 0.15 (26.9) [§]	24.18 ± 0.14	21.02 ± 0.25	28.87
	H^E	-0.06	2.51	4.69	7.85	
n -Heptane	$-\mathcal{Q}_{sol}H^\circ$	33.26 ± 0.27 (32.6)	30.49 ± 0.16 (31) [§]	28.06 ± 0.17	24.53 ± 0.18 (26.8) [#]	33.44
	H^E	0.18	2.95	5.38	8.91	
n -Oktane	$-\mathcal{Q}_{sol}H^\circ$	37.46 ± 0.11 (36.7)	34.45 ± 0.13 (35.2) [§]	31.70 ± 0.17	28.23 ± 0.25 (30.8) [#]	37.94
	H^E	0.48 (-0.08)**	3.49	6.24	9.71	
n -Nonane	$-\mathcal{Q}_{sol}H^\circ$	42.04 ± 0.20 (40.8)	38.49 ± 0.15	35.54 ± 0.14	31.88 ± 0.21 (34.5) [#]	42.43
	H^E	0.39 (0.18)**	3.94	6.89	10.55	
n -Decane	$-\mathcal{Q}_{sol}H^\circ$	46.41 ± 0.25 (44.5)	42.38 ± 0.14 (43.9) [§]	39.05 ± 0.17	35.48 ± 0.20 (38.5) [#]	46.98
	H^E	0.57 (0.55)**	4.60	7.93	11.5	

* In kJ/mol within the temperature range 323–383 K. H^E values are calculated using Eq 6.

[†] Calculated from references 13 and 14 and Eq 11.

[‡] n -C₃₆H₇₄, 373.15 (7).

[§] OV17, T = 333–423 K (19).

^{||} SE30, T = 333–423 K (19).

[#] PEG20M, T = 333–393 K (19).

**SE30, T = 393 K (20).

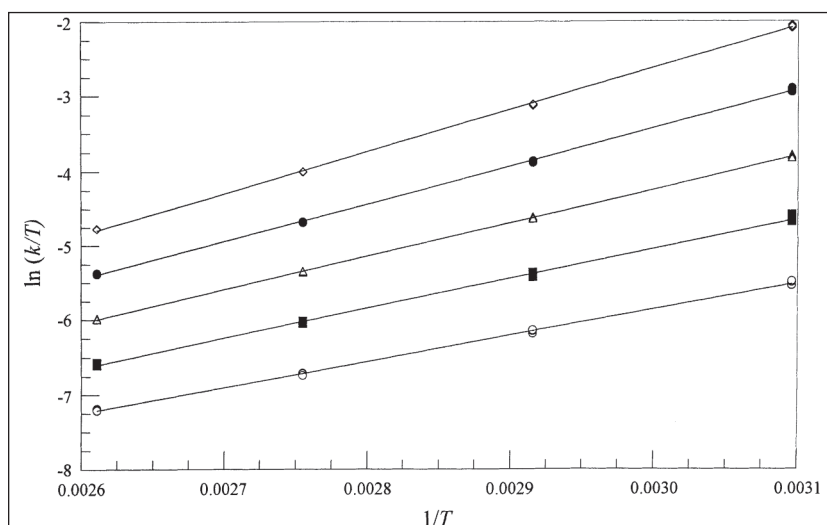


Figure 1. Dependence of $\ln(k/T)$ on $1/T$ on column A. \circ , *n*-hexane; \blacksquare , *n*-heptane; \triangle , *n*-octane; \bullet , *n*-nonane; \diamond , *n*-decane.

Table III. $-\Delta_{\text{sol}}H^\circ$ for Selected Ketones and Aldehydes*

Solute	Column A	Column B	Column C	Column D
Acetone	23.88 ± 0.23	26.74 ± 0.08	29.53 ± 0.11	29.03 ± 0.13
2-Butanone	27.50 ± 0.32	30.74 ± 0.19	32.64 ± 0.14	31.73 ± 0.15
2-Pentanone	31.05 ± 0.20	34.38 ± 0.16	36.25 ± 0.18	34.35 ± 0.16
3-Pentanone	31.72 ± 0.21	34.81 ± 0.16	35.84 ± 0.19	34.03 ± 0.10
3-Methyl-2-butanone	30.37 ± 0.14	33.08 ± 0.11	34.97 ± 0.17	32.53 ± 0.16
2-Hexanone	35.85 ± 0.16	38.36 ± 0.20	40.01 ± 0.22	37.85 ± 0.17
3-Hexanone	36.42 ± 0.22	38.20 ± 0.16	39.14 ± 0.26	37.05 ± 0.29
4-Methyl-2-pentanone	33.89 ± 0.25	36.15 ± 0.18	37.65 ± 0.34	35.02 ± 0.25
3,3-Dimethyl-2-butanone	32.33 ± 0.14	34.38 ± 0.16	36.68 ± 0.28	32.58 ± 0.19
3-Methyl-2-pentanone	34.23 ± 0.12	36.35 ± 0.17	37.95 ± 0.18	34.81 ± 0.13
2-Heptanone	40.79 ± 0.23	42.37 ± 0.14	43.57 ± 0.27	41.12 ± 0.17
3-Heptanone	40.24 ± 0.26	42.13 ± 0.18	42.92 ± 0.25	40.06 ± 0.13
4-Heptanone	40.20 ± 0.23	41.46 ± 0.19	42.27 ± 0.24	38.93 ± 0.22
5-Methyl-2-hexanone	39.28 ± 0.29	40.94 ± 0.17	43.98 ± 0.27	39.74 ± 0.19
2,4-Dimethyl-3-pentanone	35.77 ± 0.17	37.44 ± 0.18	40.27 ± 0.38	34.23 ± 0.18
5-Methyl-3-heptanone	42.68 ± 0.25	44.01 ± 0.22	45.54 ± 0.35	41.20 ± 0.22
2-Methyl-3-heptanone	42.74 ± 0.24	43.53 ± 0.17	44.72 ± 0.30	40.53 ± 0.15
3-Octanone	45.56 ± 0.34	46.73 ± 0.30	47.12 ± 0.30	44.12 ± 0.21
5-Nonanone	49.07 ± 0.33	49.98 ± 0.36	50.25 ± 0.31	46.53 ± 0.21
Acetaldehyde	17.86 ± 0.23	21.95 ± 0.28	23.90 ± 0.12	25.56 ± 0.24
Propanal	22.93 ± 0.21	26.82 ± 0.13	27.57 ± 0.14	28.62 ± 0.30
Acrolein	22.50 ± 0.15	26.17 ± 0.14	27.40 ± 0.12	29.96 ± 0.20
<i>i</i> -Butanal	26.11 ± 0.20	28.49 ± 0.18	29.93 ± 0.15	28.91 ± 0.19
Butanal	27.24 ± 0.20	30.29 ± 0.21	31.61 ± 0.16	31.14 ± 0.28
<i>i</i> -Valeraldehyde	29.30 ± 0.20	32.34 ± 0.18	33.39 ± 0.10	31.98 ± 0.12
2-Methylbutanal	30.45 ± 0.25	32.71 ± 0.14	34.00 ± 0.17	31.89 ± 0.22
<i>trans</i> -2-Butenal	29.45 ± 0.22	33.23 ± 0.15	34.60 ± 0.13	35.69 ± 0.17
Valeraldehyde	31.71 ± 0.37	34.59 ± 0.19	35.17 ± 0.18	34.05 ± 0.12
Trimethylacetaldehyde	27.63 ± 0.24	29.41 ± 0.14	31.33 ± 0.13	27.54 ± 0.15
Hexanal	36.30 ± 0.12	38.65 ± 0.17	38.88 ± 0.20	37.74 ± 0.26
2-Ethylbutanal	34.38 ± 0.12	36.48 ± 0.15	36.96 ± 0.23	34.66 ± 0.20
3,3-Dimethylbutanal	32.01 ± 0.18	34.17 ± 0.18	35.72 ± 0.19	33.15 ± 0.21
Heptanal	40.67 ± 0.18	42.47 ± 0.13	42.51 ± 0.22	41.42 ± 0.15
Octanal	45.19 ± 0.31	46.82 ± 0.22	47.44 ± 0.35	45.15 ± 0.22
2-Ethylhexanal	43.03 ± 0.29	44.02 ± 0.18	45.04 ± 0.16	41.09 ± 0.17

* $\ln k/\text{mol}$ in the temperature range 323–383 K.

factor of the solute is suggested. Another aim of the paper is to show that this new method is equivalent to that of V_g in the determination of $\Delta_{\text{sol}}H^\circ$ using a new equation that gives results comparable to other determinations on a packed column. The observed characteristics in the solution enthalpies of *n*-alkanes and aliphatic oxo compounds (branching, position of the carbonyl group, and polarity of the stationary phase) are interpreted.

Experimental

In this study, selected *n*-alkanes, aliphatic ketones, and aldehydes were chosen as model compounds. They were purchased from Fluka AG (Buchs, Switzerland) and Aldrich (Milwaukee, WI) and were used without further purification. The retention measurements were performed with a 5890 Hewlett-Packard series II GC with an HP 3365 ChemStation. A flame ionization detector (FID) and a split/splitless injector in split mode were used. The carrier gas was nitrogen. A constant inlet pressure was applied, and the carrier flow rate was set to the minimum range of the height equivalent to one theoretical plate (HETP).

The characteristics of the capillary columns are summarized in Table I. Column A was an HP-1 (Hewlett-Packard, Palo Alto, CA), column B was an HP-50 (Hewlett-Packard), column C was a DB-210 (J&W Scientific, Folsom, CA), and column D was an HP-Innowax (Hewlett-Packard). The stationary phases were selected to cover a wide range of polarity (16) and to display different types of interactions with the oxo compounds. The retention times were measured at 50, 70, 90, and 110°C, with three injections at each temperature.

Theory

The relationship between V_g and k can be expressed by substituting $F_c = V_M^\circ/jt_M$ into Eq 4, where V_M° is the corrected gas hold-up volume and $(t_R - t_M) = k t_m$:

$$V_g = \frac{273 k V_M^\circ}{W_s T} \quad \text{Eq 8}$$

Upon substitution of Eq 8 into Eq 2 and after algebraic transformations, the following equation is obtained:

$$\ln \frac{k}{T} = \frac{-\Delta_{\text{sol}}H^\circ}{RT} + \frac{\Delta_{\text{sol}}S^\circ}{R} + \ln \frac{W_s R}{M V_M^\circ} \quad \text{Eq 9}$$

The second and third terms on the right-hand side of Eq 9 are temperature-independent;

therefore, $\mathcal{Q}_{\text{sol}}H^\circ$ can be determined from the slope of the linear function $\ln(k/T)$ versus $1/T$. The usefulness of the theoretically derived Eq 9 remains to be proved.

Evaluation of the experimental results

The experimental t_R data were evaluated by a method similar to that used previously (17). t_M was estimated by the Marquardt method with the software ProStat (Poly Software International, Sandy, UT) via the equation

$$\ln(t_R - t_M) = aI + b \quad \text{Eq 10}$$

where I is the retention index of at least 4 n -alkanes whose retention indices bracket the retention index of the given carbonyl compound.

Because the applied temperature range is near or below the boiling point in most cases, the temperature dependence of $\mathcal{Q}_{\text{vap}}H^\circ$ is expected to be small with behavior close to linear. The use of $\mathcal{Q}_{\text{vap}}H^\circ$ calculated for 353 K (the midpoint of the temperature range of the GC analyses), therefore, should not result in a significant error in the determination of H^E_{353} . $\mathcal{Q}_{\text{vap}}H^\circ_{353}$ could also be calculated using Kirchhoff's law

$$\mathcal{Q}_{\text{vap}}H^\circ_T = \mathcal{Q}_{\text{vap}}H^\circ_{298} + [C_p(\text{g}) - C_p(\text{l})]\mathcal{Q}T \quad \text{Eq 11}$$

with the standard $\mathcal{Q}_{\text{vap}}H^\circ_{298}$ and molar heat capacities of the compounds in the liquid and gaseous states. The heat capacities were taken from Shaw (18). The $\mathcal{Q}_{\text{vap}}H^\circ_{353}$ data calculated with Equations 7 and 11 agree within 1% for the n -alkanes. $\mathcal{Q}_{\text{vap}}H^\circ_{298}$

for oxo compounds was either calculated from Eq 7 or taken directly from the experimental data in the literature. As a result of the experimental errors in $\mathcal{Q}_{\text{sol}}H^\circ$ and the literature $\mathcal{Q}_{\text{vap}}H^\circ$ values, the accuracy in H^E is lower than the two decimals indicated.

Results and Discussion

To test Eq 9, $\mathcal{Q}_{\text{sol}}H^\circ$ was determined for various n -alkanes. The $\ln(k/T)$ versus $1/T$ fit gave an excellent straight line (Figure 1). The correlation coefficient was generally 0.9995–0.9999. The $\mathcal{Q}_{\text{sol}}H^\circ$ -s (all negative in sign) determined from this graph for the n -alkanes, together with some reference data, are given in Table II, and those for the oxo compounds are given in Table III. A comparison of the $\mathcal{Q}_{\text{sol}}H^\circ$ data for the n -alkanes with some literature data shows the equivalency of the two methods: the determination of $\mathcal{Q}_{\text{sol}}H^\circ$ for the fits of $\ln V_g$ or $\ln(k/T)$ versus $1/T$.

Although $\mathcal{Q}_{\text{sol}}H^\circ$ is temperature dependent, it can be considered constant within a narrow temperature range. We could not find any experimental results on the nonlinearity of the slope $-\mathcal{Q}_{\text{sol}}H^\circ/R$. For many organic compounds, $\mathcal{C}_p^\circ[\text{g}] - \mathcal{C}_p^\circ[\text{l}] \approx -54 \text{ J K}^{-1} \text{ mol}^{-1}$, according to the Sidgwick rule (14). The excess heat capacities of hydrocarbons on phthalate esters (24) were approximately 20–50 $\text{J K}^{-1} \text{ mol}^{-1}$. Therefore, increasing the temperature results in a less negative value of $-\mathcal{Q}_{\text{vap}}H^\circ$ and a more positive value of H^E ; that is, these two effects may largely cancel each other out, so that their influences that are highly dependent on the solute and stationary phases are greatly decreased.

$\mathcal{Q}_{\text{sol}}H^\circ$ values of n -alkanes increase as the polarity of the stationary phase increases, whereas for the most volatile n -alkanes (Figure 2), the opposite is true. H^E data calculated for selected oxo compounds are listed in Table IV.

The polarities of the ketones, characterized by the dipole moments, are approximately the same. The excess enthalpy (and therefore the solubility) decreases with the size of the apolar carbon chain on apolar column A. Column B is a column of medium polarity; the H^E values are about the same because the polar and apolar effects cancel each other out. The excess enthalpy increases on the polar columns C and D similar to the size of the apolar part of the molecule. The stronger interaction between the C=O group and the stationary phase of increasing polarity is cancelled out by a similar decrease in the interaction with the apolar part of the solute.

Column C is a selective column for oxo compounds, because there are weak complex bonds between the fluorine atoms in the CF_3 group of the stationary phase and the C=O group of the solute. The energy released in the interaction with the stationary phase compensates the strong dipole–dipole, dipole-induced dipole, and dispersive forces between the oxo compounds. The tendencies observed in Table IV are therefore less pronounced for column C than for column D.

Table IV. Estimation of H^E * Data of Some Ketones and Aldehydes from $\mathcal{Q}_{\text{vap}}H^\circ$ and $\mathcal{Q}_{\text{sol}}H^\circ$

	Column A	Column B	Column C	Column D	$\mathcal{Q}_{\text{vap}}H^\circ_{353}$
Acetone	3.93	1.07	-1.72	-1.22	27.81 [†]
2-Butanone	3.80	0.56	-1.34	-0.43	31.30 [‡]
2-Pentanone	3.82	0.49	-1.38	0.52	34.87 [‡]
3-Pentanone	3.27	0.18	-0.85	0.96	34.99 [‡]
3-Methyl-2-butanone	2.89	0.18	-1.71	0.73	33.26 [‡]
2-Hexanone	3.77	1.26	-0.39	1.77	39.62 [‡]
3-Hexanone	2.38	0.6	-0.34	1.75	38.80 [‡]
4-Methyl-2-pentanone	3.14	0.88	-0.62	2.01	37.03 [‡]
3,3-Dimethyl-2-butanone	2.31	0.26	-2.04	2.06	34.64 [§]
3-Methyl-2-pentanone	2.62	0.50	-1.10	2.04	36.85
2-Heptanone	2.35	0.77	-0.43	2.02	43.14 ^{*,}
3-Heptanone	2.69	0.80	0.01	2.87	42.93 ^{*,}
4-Heptanone	2.53	1.27	0.46	3.80	42.73 ^{*,}
2,4-Dimethyl-3-pentanone	2.78	1.11	-1.72	4.32	38.55
2-Methyl-3-heptanone	1.86	1.07	-0.12	4.07	44.60
3-Octanone	2.39	1.22	0.83	3.83	47.95 ^{*,}
5-Nonanone	1.79	0.88	0.61	4.33	50.86 ^{*,}
Propanal	3.44	-0.45	-1.2	-2.25	26.37
<i>i</i> -Butanal	2.48	0.1	-1.34	-0.32	28.59
Butanal	3.35	0.30	-1.02	-0.55	30.59

* Eq 6 at 353 K in kJ/mol.

† Eq 11, references 11 and 18.

‡ Reference 21.

§ Reference 22.

|| Reference 15.

Reference 23.

The slopes of the lines $\mathcal{Q}_{\text{sol}}H^\circ(n\text{-alkanal})$ and $\mathcal{Q}_{\text{sol}}H^\circ(n\text{-alkane})$ versus N_C are approximately the same, except in the case of column D (Table V).

Extrapolation of the line $\mathcal{Q}_{\text{sol}}H^\circ$ versus N_C for the n -alkanes to zero carbon number leads to intercepts around $\mathcal{Q}_{\text{sol}}H^\circ = 0$; a hypothetical hydrocarbon with $N_C = 0$ undergoes no interaction with the stationary phase. Above $N_C = 2$, the decrease in enthalpy of solution is attributed to the presence of the CH_2 unit, which accounts for 4.4–4.5 kJ/mol on an apolar column for n -alkanes and n -alkanals. For 2-ketones, a value of 4.3 kJ/mol has been reported (25).

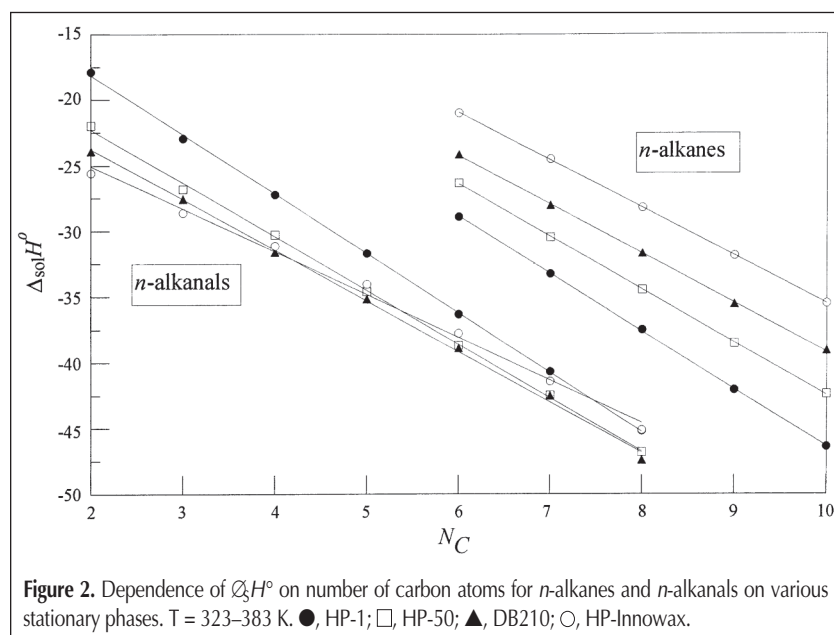


Figure 2. Dependence of $\mathcal{Q}_{\text{sol}}H^\circ$ on number of carbon atoms for n -alkanes and n -alkanals on various stationary phases. $T = 323\text{--}383\text{ K}$. ●, HP-1; □, HP-50; ▲, DB210; ○, HP-Innowax.

Table V. Results of Linear Regressions $\mathcal{Q}_{\text{sol}}H^\circ = a \times N_C + b$ for n -Alkanes and n -Alkanals*

Column	Parameter	n -Alkanes	n -Alkanals
A	a Value	4.374 ± 0.033	4.518 ± 0.0349
	b Value	2.628 ± 0.270	9.106 ± 0.188
	Correlation coefficient r	0.99991	0.99985
	Fischer statistics	17372	16702
	Residual error s (kJ mol ⁻¹)	0.105	0.185
B	a Value	4.004 ± 0.022	4.081 ± 0.053
	b Value	2.402 ± 0.180	14.107 ± 0.287
	Correlation coefficient r	0.99995	0.99957
	Fischer statistics	11847	5863
	Residual error s (kJ mol ⁻¹)	0.070	0.282
C	a Value	3.722 ± 0.034	3.849 ± 0.072
	b Value	1.930 ± 0.277	16.053 ± 0.388
	Correlation coefficient r	0.99987	0.99912
	Fischer statistics	11847	2853
	Residual error s (kJ mol ⁻¹)	0.108	0.381
D	a Value	3.627 ± 0.016	3.249 ± 0.106
	b Value	-0.788 ± 0.131	18.566 ± 0.569
	Correlation coefficient r	0.99997	0.99736
	Fischer statistics	50662	946
	Residual error s (kJ mol ⁻¹)	0.051	0.559

* N_C , number of carbon atoms.

The lines for the n -alkanals intersect at different points. The smaller the difference in polarity of the phases, the higher the N_C values of the n -alkanals at the intersection points. The longer the carbon chain in the aldehyde, the less the column polarity affects $\mathcal{Q}_{\text{sol}}H^\circ$ (see the similarity of the $\mathcal{Q}_{\text{sol}}H^\circ$ data for n -octanal in columns A–D and B–C in Table III). A comparison of $\mathcal{Q}_{\text{sol}}H^\circ$ and H^E for the straight-chain heptanone isomers (Tables III and IV) shows that the greater the column polarity and the more symmetrical the ketone, the more positive H^E and $\mathcal{Q}_{\text{sol}}H^\circ$ are. These two observations can be explained by the behavior of the solute in the cavities of the stationary phase. The chain is not straight; it may

fold back and shield the polar group from the stationary phase. The solute–stationary phase interaction is even less able to compensate the increase in energy necessary for hole formation. Here, only the columns with polar groups (e.g., columns C and D) have real effects when the alkane chain is less soluble in polar phases, and there is more freedom for the apolar part of the molecule to move independently from the stationary phase. Similar conclusions were drawn from a comparison of $\mathcal{Q}_{\text{sol}}H^\circ$ for 2-ketones and n -alkanes on the $n\text{-C}_{36}\text{H}_{74}$ phase (25), but differences in the slopes for n -alkanes and n -alkanals on columns A and B were not observed.

Some opinions concerning the usefulness and accuracy of H^E determined using Eq 6 are skeptical, because it is the difference between two large quantities ($\mathcal{Q}_{\text{sol}}H^\circ$ and $\mathcal{Q}_{\text{vap}}H^\circ$) (26). However, $\mathcal{Q}_{\text{sol}}H^\circ$ and $\mathcal{Q}_{\text{vap}}H^\circ$ can presently be determined fairly exactly (calorimetrically and by GC methods), so the difference can be considered realistic. At any rate, capillary GC offers a simple method relative to calorimetric methods for the determination of H^E in dilute solutions.

Conclusion

In the case of capillary columns, the enthalpy of solution determined from the slope of the graph $\ln(k/T)$ versus $1/T$ can be equivalent to that determined from the slope of $\ln V_g$ versus $1/T$. H^E values of n -alkane and oxo compounds derived from $\mathcal{Q}_{\text{sol}}H^\circ$ and $\mathcal{Q}_{\text{vap}}H^\circ$ functions can characterize the selective, polar, apolar, and molecular interactions between the stationary phase and the solute if the $\mathcal{Q}_{\text{vap}}H^\circ$ determinations are similarly accurate enough. The observed tendencies in $\mathcal{Q}_{\text{sol}}H^\circ$ can explain the behavior of the solute in the cavities of the stationary phase.

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