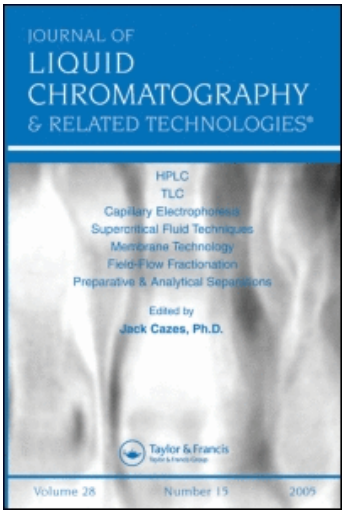

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DETERMINATION OF ACTIVITY COEFFICIENTS OF OXYGENATED HYDROCARBONS BY LIQUID-LIQUID CHROMATOGRAPHY

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ABSTRACT

A study of the thermodynamics of solutions of oxygenated aliphatic and aromatic hydrocarbon solutes in water by a method that combines gas-liquid and liquid-liquid chromatography is presented. Solute infinite dilution activity coefficients in water were determined by liquid-liquid chromatography using water as mobile phase and squalane as stationary phase. Because of the highly polar nature of water, the possible contribution of interfacial adsorption to the retention mechanisms in liquid-liquid chromatography was assessed. The activity coefficients are all large reflecting the poor solubility of organic compounds in water. The greater the organic nature of the solute, the larger is the value of its activity coefficient. While the absolute accuracy of the data cannot be predicted, the reproducibility of the results is at worse ±10%. Comparison of the results with literature data obtained by independent techniques shows reasonably good agreement.

INTRODUCTION

Reliable liquid phase activity coefficient data is of practical and theoretical importance in physical chemistry and chemical engineering. It is useful in estimating quantities such as solubility limits, Henry's law

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constants, octanol-water partition coefficients and multi-component phase equilibria. Solute-mobile phase solution thermodynamic data may also help to explain the critical role of the mobile phase in retention and selectivity in high-pressure liquid chromatography.

Various static techniques can be used to obtain activity coefficient data (1-4) but they are often laborious.

Gas-liquid chromatography (GLC) is now well established as an extremely useful technique for the study of solution thermodynamics, partly because of its simplicity and partly due to the fact that comparison of static with GLC-derived solute activity coefficient data was made early in the history of the development of the technique (5,6). Unfortunately GLC is only suited for systems of volatile solutes in non-volatile solvents.

Liquid-liquid chromatography (LLC) has been known long before the inception of GLC but it has never become as powerful a tool for physical measurements, even though a thermodynamic theory of solute retention in LLC has been available for many years (7,8). LLC have certain advanatages over other methods, but like GLC it is also restricted in terms of the systems that are amenable for study. A basic requirement is that the mobile and stationary phases must be completely immiscible and both must have sufficient solvency for the solutes. Consequently solutes must be of medium polarity and one of the two phases must invariably be polar, thus complicating the retention mechanism with interfacial adsorption and resistance to mass transfer problems.

Unlike the GLC method, only ratios of the activity coefficients of a solute at infinite dilution in the mobile and stationary phases can be obtained by LLC (7,8). In order to obtain solute activity coefficients in one of the phases it is necessary to use independent means to determine the corresponding quantity in the other phase.

Although the literature has not been extensive, a number of reports have appeared in which LLC was used for the measurement of thermodynamic

properties (9.13). Locke (9) combined GLC with LLC using squalane as a common stationary phase to measure the activity coefficients of aliphatic and aromatic hydrocarbons in acetonitrile. In another experiment Locke (10) used the same technique with glycerol as stationary phase to study the thermodynamics of aliphatic alcohols in n-heptane. Comparison with data obtained by static methods showed good agreement for certain solutes and not so good for others. For solutes with low solubility in one or both phases the LLC/GLC derived activity coefficient data were too large compared with static values. The discrepancy was attributed to solute adsorption at the liquid-liquid interface.

Alessi and Kikic studied the systems aniline/squalane and aniline or acetonitrile/Apiezon L (11-13) and compared their results with static and GLC-derived values. They also observed discrepancy, but attributed it to the mutual solubiliity of the two phases used in LLC. They argued that the LLC-derived values pertain to the mutually saturated phases and concluded that the LLC method will yield accurate results only if the mobile and stationary phases are completely immiscible (9). Support for this view was obtained when results obtained with Apiezon L as stationary phase were compared with static measurements (13).

It appears that combined LLC/GLC is a promising technique, but additional studies with different systems are needed to better appreciate its capabilities and limitations.

In the present study we sought to investigate the feasibility of using the combined LLC/GLC method for the measurements of activity coefficients of oxygenated organic compounds in water. Squalane was used as the common stationary phase and water was used as the mobile phase in LLC. This represents the first use of water as mobile phase in LLC for the purpose of deriving of solution thermodynamic quantities.

Water has been previously used as stationary phase in GLC by Pollard and Hardy (14). Pecsar and Martin were however, the first to report a

detailed study of solution thermodynamics with water as a GLC stationary phase (15). More recently Shaffer and Daubert (16) obtained activity coefficients of oxygenated organic compounds in water and compared their results with static values.

EXPERIMENTAL

Gas-Liquid Chromatography

A Perkin-Elmer Sigma 1B gas chromatograph equipped with dual column, forced air oven, two flame ionization detectors, electronic carrier gas flow controllers and a Sigma 10 Data Station was employed. Column inlet pressure was measured with an auxiliary instrument pressure gauge accurate to ±0.2 psi, and column outlet pressure was read off a barometer. Oven temperatures were independently calibrated with a thermocouple. Temperature control was found accurate to within ±0.2°C. Retention data was directly recorded by the on line data station. An average of three measurements was taken for each point. The retention time of methane was used to correct for column dead volume. Flow rates were mesured with a soap bubble flow-meter. All solute peaks except for acetone apppeared to be symmetric. 10.10% squalane on highly inert chromosorb W-HP were used in order to minimize any contribution to retention from adsorption of solute at the gas-liquid or liquid-solid interfaces.

Liquid-Liquid Chromatography

A simple liquid chromatographic system was assembled consisting of a 1000 ml solvent bottle, a de-bubbler, a liquid metering pump (Glenco HPLC pumping system), a pressure gauge (Pye Unicam LC3), a UV detector with a 206 nm filter (Glenco), and a 10 mV potentiometeric recorder. Samples were admitted with a 10 µl Hamilton syringe, through an on-column injector.

The columns were 4 ft x 4 mm i.d. stainless steel. The characteristics of the liquid chromatography columns are presented in Table I. Percent loading of each packing material was determined gravimetrically. A pre-column (4 ft x 4 mm i.d.) packed with the same material as the separation column was used and both columns were coiled and immersed in a temperature regulated water bath. No temperature fluctuations greater than ±0.1°C were detectable over extended periods of operation. Flow rates were measured with a calibrated 25 ml volumetric flask and the measurements were periodically repeated thoughout the operation. All retention measurements were read off the recorded chromatograms. The chart speed was routinely checked with a stop watch. A small amount of squalane was initially stripped off the column by the passage of several liters of water through the column during the initial conditioning. After that no further loss of squalane was detected over extended periods of operation. Percent squalane was checked gravimetrically at the end of each set of measurements. Column interstitial (dead) volume was determined by a weight difference procedure similar to that of Slaats et al (17). Approximately, 200 ml of water and methanol were sequentially pumped through the column to achieve equilibration with each solvent. After each equilibration, the column and its content of stationary phase and solvent were weighed to the nearest 1 mg. The column dead volume was then calculated using the equation:

$$V_m = \frac{M_{H_2O} - M_{CH_3OH}}{\rho_{H_2O} - \rho_{CH_3OH}} \qquad \ldots\ldots (1)$$

where M_{H_2O} and M_{CH_3OH} are the weights of the columns equilibrated with water and methanol respectively. The density (ρ) of water and methanol were literature values at the temperature of the experiment. The small extra column dead volume contribution from the connecting tubing and detector, were taken into account. The magnitude of the dead volume obtained by this measurement represents the maximum volume within the column accessible

TABLE I. Characteristics of the liquid chromatography columns.

Column Number[a]	% Squalane[b]	Mass packing (gm)	Mass squalane W_L(gm)	Dead volume[c] (cm^3)	V_L (cm^3)
I	10.24	7.2755	0.7450	19.91	0.9289
II	14.26	7.8072	1.1133	18.70	1.388
III	19.99	7.8448	1.5682	19.59	1.955
IV	25.94	8.1250	2.1076	18.45	2.628

a - All columns were 4 ft x 4 mm i.d.

b - The only support used was chromosorb W-HP 100/120 mesh.

c - The small extra column contribution is included in this number.

to a molecule of a size comparable to the above solvent molecules. Because of the non porous nature of the coated support used, solute molecules which are larger in size than solvent molecules are expected to experience the same dead volume.

RESULTS AND DISCUSSION

First, we present a brief review of the relevant equations of the thermodynamic theory of solute retention in LLC as developed by Martire and Locke (7,8).

Solute net retention volume (V_N) is given by:

$$V_N = V_R - V_M = KV_L \qquad \ldots\ldots (2)$$

where V_R is solute retention volume; V_M is the column interstitial (dead) volume, K is the solute distribution coefficient, and V_L is the volume of stationary phase in the column. In order to present an expression free from chromatographic operating parameters, the specific retention volume (V_g) is defined as:

$$Vg \quad \frac{V_N}{W_L} = \frac{K}{\rho_L} \qquad \ldots\ (3)$$

where W_L is the mass of stationary phase in the column and ρ_L is the density of the stationary phase at the column temperature.

Choosing the pure liquid solute as the standard state of the solute in the solution and selecting standard atmospheric pressure as the reference pressure for the solution, it could be shown that:

$$\ln Vg = \ln \frac{\gamma_2^{m,\infty} M_m}{\gamma_2^{s,\infty} M_s \rho_m(T)} + \frac{\bar{p}-1}{RT} (\bar{V}_2^m - \bar{V}_2^s) \qquad \ldots\ (4)$$

where $\gamma_2^{m,\infty}$ and $\gamma_2^{s,\infty}$ are the solute infinite-dilution activity coefficients at the column temperature and standard atmospheric pressure in the mobile phase (m) and the stationary phase (s); M_m and M_s are the molar masses of the mobile and stationary phases respectively; $\rho_m(T)$ is the eluent density at T; $\bar{p}$ is the mean column presure and V_2^m and V_2^s are the solute partial molar volumes in the mobile and stationary phases respectively. As indicated by the above authors, the last term in the r.h.s. is negligibly small at moderate pressures, and since no attempt was made in this work to study the pressure dependence of Vg, the following simplificatin could be safely used.

$$Vg = \frac{\gamma_2^{m,\infty} M_m}{\gamma_2^{s,\infty} M_s \rho_m(T)} \qquad \ldots\ (5)$$

In chromatography, we ordinarily want K values in the range from 1 to 100. For $K < 1$, solutes elute very fast and their separation becomes difficult. For $K > 100$, solute retention times are excessively high. These conditions imply that both the mobile and stationary phases be good solvents for the solute, but that the stationary phase be a better solvent than the mobile phase. The fact that immiscible solvents are required in

LLC implies that the activity coefficients of the solute will be distinctly different in the two phases. Consequently, their ratio encountered in eqn.(4) will differ from unity, and this is why LLC works as a separation technique.

The temperature dependence of the retention volume is given as:

$$\frac{R d\ln Vg}{d(1/T)} = \Delta H_2^e + RT^2 \alpha_m \quad \ldots\ldots (6)$$

where ΔH_2^e is the partial molar enthalpy of transfer of solute from mobile to stationary phase (the difference in the partial molar excess enthalpies of mixing of solute with the mobile and stationary phases respectively); and α_m is the coefficient of thermal expansion of the mobile phase.

Solute specific retention volumes (Vg) were obtained for all solutes at three temperatures through eqns. (2) and (3), utilizing the apparatus and procedures outlined under Experimental. The Vg's reported in Table II represent the average of three retention volume measurements for each solute at each temperature. To ensure that the values obtained are unique to the solute-solvent system and independent of the particular column used and the experimental conditions, the effect of sample size, flow rate and liquid phase loadings were examined. Several experiments were conducted using different flow rates (1-3 ml/min) and different sample sizes (0.2 - 2 µl) to confirm that the retention volumes were independent of flow rate and sample size. To determine whether liquid phase loading affects retention measurements, Vg values for a set of solutes were obtained at 30°C on four different columns. The characteristics of the columns are presented in Table I and the Vg data, together with the average Vg and the percent relative standard deviation for each solute are given in Table III. Except for propionaldehyde which has a small retention volume, the agreement among the data is considered acceptable. Furthermore, the agreement among the data improves with increasing retention volume. It is to be noted, however,

TABLE II. Solute specific retention volume in the system squalane/water.

Solute	Vg(ml g^{-1}) 25°C	30°C	35°C
acetone	1.234	1.241	1.253
ethyl methyl ketone	1.547	1.702	1.827
2-pentanone	3.108	2.967	3.179
3-pentanone	3.277	3.506	4.669
2-heptanone	19.04	14.02	16.52
acetaldehyde	1.433	1.243	1.518
propionaldehyde	1.348	1.134	1.205
n-butyraldehyde	1.756	1.884	1.756
ethyl acetate	3.008	2.757	3.108
n-propyl acetate	7.881	8.559	9.247
iso-propyl acetate	6.885	6.552	7.672
n-butyl acetate	29.58	33.00	37.11
phenol	1.338	1.400	1.253
o-cresol	2.102	2.415	2.434
m-cresol	1.675	1.789	1.960
p-cresol	1.841	1.817	1.808

TABLE III. Solute Vg values on four columns with different liquid phase percent loadings at 30°C.

solute	percent loading 10.24	14.26	19.99	25.94	Average Vg	Relative % standard deviation
propionaldehyde	1.295	1.347	1.244	1.134	1.255	7.36
ethyl acetate	2.953	2.864	2.866	2.757	2.860	2.83
3-pentanone	3.838	3.907	3.720	3.506	3.743	4.69
n-propyl acetate	8.831	8.939	8.585	8.559	8.730	2.13
n-butyl acetate	34.11	33.41	33.22	33.00	33.44	0.68

that the deviations are higher than expected on the basis of reproducibility of Vg values on a single column.

The experiment leading to the data presented in Table III was primarily conducted in order to assess the significance of the contribution of interfacial adsorption mechanisms to solute retention. Because of the nature of LLC, either the mobile phase or the stationary phase must be polar. For this reason, the problem of solute adsorption on the surface of the polar phase cannot be overlooked. It is clear, however, that the magnitude of the interfacial effects is not always predictable and must be investigated on a system by system basis. Thermodynamic information nevertheless could still be retrieved from retention data of systems exhibiting interfacial adsorption. This is usually accomplished by expanding the retention equation to (18):

$$V_N = KV_L + K'A_L \qquad \ldots\ldots\ldots (7)$$

where K' is the liquid surface adsorption partition coefficient; A_L is the liquid phase surface area; and the other terms are as defined earlier. Realising that Vg is equal to the net retention volume (V_N) per gram of stationary phase, equation 7 may be rearranged to:

$$Vg = K/\rho_L + K'(A_L)/(W_L) \qquad \ldots\ldots\ldots (8)$$

where ρ_L and W_L are the density and mass of liquid phase in the column. In the absence of interfacial effects, plots of Vg versus $1/W_L$ will be horizontal to the x-axis, while sloping or even curved lines are indicative of interfacial adsorption.

Figure 1 shows Vg versus $1/W_L$ plots for our systems with data obtained from Tables I and III. In all cases horizonatal lines could be drawn through the points if the experimental error indicated in Table III could be tolerated. It appears, however, that the retention volumes are slightly but systematically increasing with decrease of W_L. This indicates that

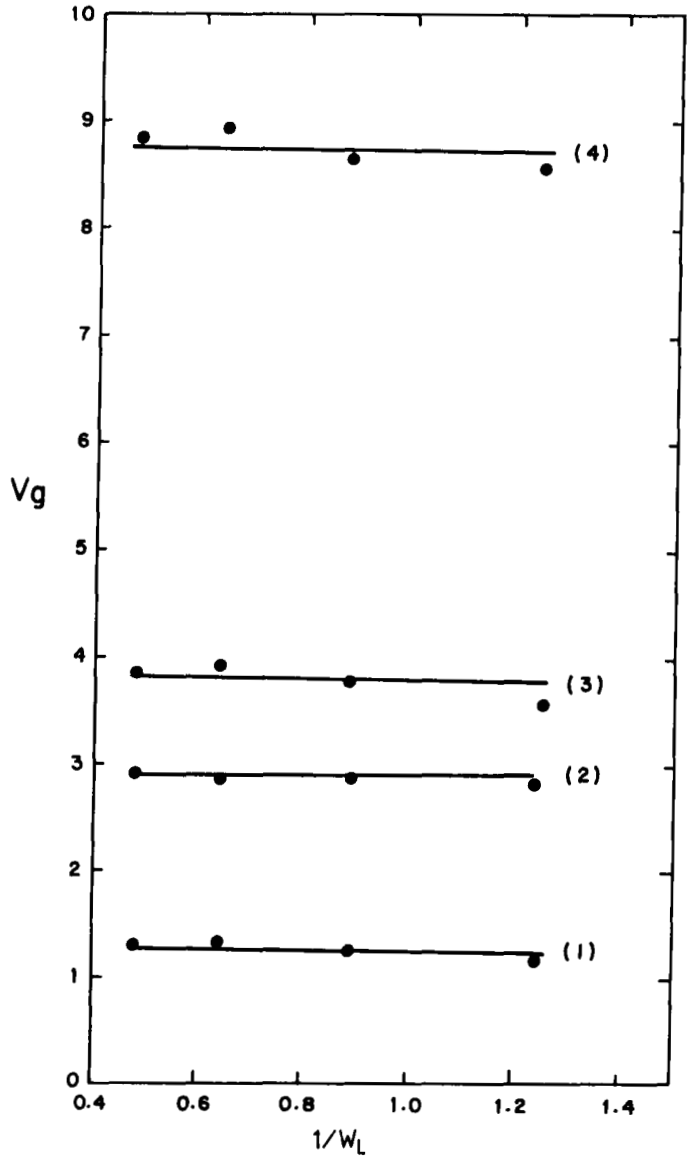

Figure 1. Vg versus $1/W_L$ plots. Solutes :
(1)= propionaldehyde ; (2)= ethyl acetate ;
(3)= 3-pentanone;and (4)= n-propyl acetate .

interfacial effects become increasingly more significant with lightly loaded columns as the surface to bulk ratio increase. With this initial check on the reliability of the data and the magnitude of the errors involved we proceed to analysis of the LLC thermodynamic data generated on the 25.94% column and reported in Table II.

In order to calculate $\gamma_2^{m,\infty}$ according to eq. (5), it is necessary to have $\gamma_2^{s,\infty}$ for the same set of solutes. This data was obtained by a GLC experiment, the details of which are presented elsewhere (19). The results for non-polar and slightly polar solutes agree with literature values to within ±1% (20). The polar oxygenated hydrocarbons did not reproduce as well because of the dependence of retention data on sample size. The accuracy in the $\gamma_2^{s,\infty}$ values for acetone and methyl ethyl ketone, which represent the worse scatter of our results, was within ±5%.

$\gamma_2^{s,\infty}$ and $\gamma_2^{m,\infty}$ at 25°C, 30°C and 35°C are presented in Table IV. Solute activity coefficients in water are all large verifying the expected poor solubility of organic compounds in water. The greater the organic character of a solute, the larger is the value of its activity coefficient. Large LLC derived activity coefficients are usually treated with suspicion (9) because of the possibility of complications to the solution process from interfacial adsorption. While the absolute accuracy of our data cannot be predicted, the reprodicibility of the Vg data presented in Table III suggests that the error is not greater than the standard deviation given in the Table. Such percentage errors in infinite dilution activity coefficient data can generally be tolerated. It has been suggested (21), for example, that a ±10% variation in activity coefficient data does not affect predictions of vapor-liquid equilibria. The data is also useful for the estimation of solubility limits, octanol - water partition coefficients, and Henry's law constants.

An estimate of the degree of accuracy of the data is provided by comparing in Table V, volume fraction based activity coefficients for certain

TABLE IV. Infinite dilution activity coefficients of solutes in water and in squalane.

Solute	25°C		30°C		35°C	
	$\gamma_2^{s,\infty}$	$\gamma_2^{m,\infty}$	$\gamma_2^{s,\infty}$	$\gamma_2^{m,\infty}$	$\gamma_2^{s,\infty}$	$\gamma_2^{m,\infty}$
acetone	2.142	61.86	2.039	59.11	1.945	56.85
ethyl methyl ketone	1.816	65.74	1.772	72.32	1.733	73.86
2-pentanone	1.857	135.1	1.802	125.0	1.749	129.7
3-pentanone	1.761	134.8	1.704	139.6	1.653	180.0
2-heptanone	1.980	882.2	1.911	626.0	1.850	713.0
acetaldehyde[a]	0.877	29.40	0.896	26.04	0.9165	32.45
propionaldehyde[a]	1.534	48.67	1.513	40.10	1.486	41.79
n-butyraldehyde[a]	1.684	69.2	1.638	72.11	1.596	65.38
ethyl acetate	1.513	107.1	1.500	96.63	1.478	107.1
n-propyl acetate	1.632	301.6	1.572	314.4	1.515	326.8
iso-propyl acetate	1.550	251.2	1.527	233.8	1.497	268.0
n-butyl acetate	1.525	1058	1.489	1155	1.547	1261
phenol	17.96	551.2	15.14	495.3	12.84	375.3
o-cresol	8.211	403.1	6.722	379.4	5.536	314.4
m-cresol	14.68	574.3	13.26	554.3	11.98	547.7
p-cresol	17.17	738.2	14.40	611.6	12.09	510.0

solutes with independent measurements reported by Wasik et al (22). This set of data was selected from scarce literature sources because of its reliability. The method used for the generation of the literature data was developed at the National Bureau of Standards over a period of five years (23) and has been validated for this type of measurements. In order to facilitate the comparison our $\gamma_2^{m,\infty}$ data (Table IV) was converted from mole fraction based activity coefficients to volume-fraction based activity coefficients.

The agreement among the data presented in Table V is quite statisfactory considering that we are comparing two independent techniques. The coincidence of the values for acetaldehyde is probably fortuitous and one of the two values for m-cresol must be in error.

Turning our attention to the effect of temperature on the retention volume, we find that in most systems studied by others with organic

TABLE V. Comparison of volume-fraction based activity coefficients in water at 25°C by LLC and generator-column methods.

Solute	$\gamma_\phi^{m,\infty}$(ours)[a]	$\gamma_\phi^{m,\infty}$(Lit.)
acetaldehyde	9.30	9.33
ethyl acetate	19.7	14.1
3-pentanone	22.9	17.8
n-propyl acetate	47.2	43.7
n-butyl acetate	144	132
m-cresol	99.0	331

a - $\gamma_\phi = \gamma_x \frac{\rho_s M_w}{\rho_w M_s}$ where ϕ = volume fraction ;

x = mole fraction ; ρ = density ; M = molar mass ;

s= solute and w = water.

solvents (9,10) plots of the logarithm of Vg versus reciprocal temperature were linear, thus enabling the determination of ΔH_2^e according to eqn.(6). The effect of temperature in our systems is strikingly different because of the complex nature of solubility of organic compounds in water. No apparent trends are observed and depending on the solute, Vg may increase or decrease with increasing temperature, but not necessarily in a linear fashion. It is also observed that some solutes have maxima and others have minima in Vg and in $\gamma_2^{m,\infty}$ values in the temperature range studied. This trend was also observed by Pecsar and Martin (15) with infinite dilution activity coefficients of organic solutes in water. The absolute values of the activity coefficients for some of their solutes that overlap our set of solutes are, however, considerably different from our data.

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