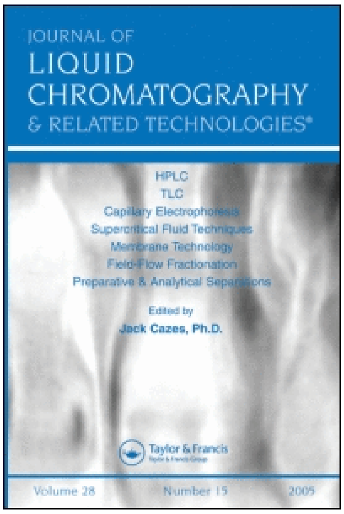

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SOLUTE RETENTION IN COLUMN LIQUID CHROMATOGRAPHY. X. DETERMINATION OF SOLUTE INFINITE-DILUTION ACTIVITY COEFFICIENTS IN METHANOL, WATER, AND THEIR MIXTURES, BY COMBINED GAS-LIQUID AND LIQUID-LIQUID CHROMATOGRAPHY

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ABSTRACT

The Raoult's-law activity coefficients of 3- to 7-carbon aliphatic aldehyde, ketone, ester, and alcohol solutes at infinite dilution in methanol, water, and mixtures of the two and in polydimethylsiloxane, all at 293-308 K, have been determined for the first time by appropriate combination of GLC and LLC retention data. The latter data are reported in terms of mole fractions, while the former are given in concentration units of molality. However, interpretation of the data is difficult because of the multiplicity of the retention mechanisms. Nevertheless, the combined GLC/LLC technique, which had been applied previously only to pure solvents, is said to offer a number of advantages over static techniques for the determination of solute infinite-dilution activity coefficients with volatile solvents, especially with mixtures of solvents.

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INTRODUCTION

Solute activity coefficients in common organic solvents are of considerable theoretical and practical interest and importance in physical chemistry and chemical engineering insofar as such data can be employed to characterize solution behavior, e.g. estimation of solubility limits, Henry's-law constants, partition coefficients, multicomponent phase equilibria, and so forth. Activity coefficients at infinite dilution are of particular interest, because they provide a measure of the behavior of a single solute molecule completely surrounded by solvent. Such data therefore generally reflect the maximum extent of solute-solvent nonideality, free from solute-solute interactions.

However, infinite dilution activity coefficients γ^{∞} are for the most part difficult to determine experimentally, the requisite static techniques for example being somewhat tedious and time-consuming (1-5). In contrast, for systems that are amenable to the techniques involved, chromatographic methods [gas-liquid chromatography (GLC) in particular] are well-known to offer a number of advantages generally in physicochemical measurements (6,7); and are capable of accuracy of better than ± 1% in the determination especially of infinite-dilution activity coefficients and related thermodynamic quantities (8,9).

Although the GLC technique is limited primarily to the study of volatile solutes with solvents of vapor pressure less than ca. 0.1 torr at the column temperature, the use of volatile solvents is not entirely precluded (10-12). The major difficulty that arises in doing so is of course stripping of the stationary phase from the column, which can be overcome at least to some extent by nonsteady-state (13) and reversed-flow (14) techniques.

In contrast, liquid-liquid chromatography (LLC), which is broadly compatible with solvents of virtually any volatility, has several advantages over GLC for the measurement of partition data. First, all mobile-phase interactions are taken account of in deriving solute-solvent activity coefficients. Also, since the mobile phase is incompressible at moderate pressures, any ambiguities surrounding pressure correction factors are obviated. However, LLC is limited by other factors. For example, the mobile and stationary phases must obviously be immiscible, yet each must exhibit sufficient solvency for the solutes such that the retention volumes are neither too close to the column void volume nor too large to compromise the accuracy of their measurement. Since one of the two (immiscible) phases must generally be polar in order to satisfy these criteria, interfacial adsorption and mass transfer nonequilibrium effects may well be significant and must be corrected for if the resultant solution data are to be of any value. (Taking an experimental measure of uncertainties of these kinds is a difficult task under any circumstance, which most likely accounts for the scarcity of LLC-derived thermodynamic data.)

Unlike GLC, only the ratio of the activity coefficients of a solute at infinite dilution in the mobile and stationary phases can be measured by LLC (15,16). Thus, in order to obtain the solute activity coefficient in one phase, a separate technique must be used to assess the corresponding quantity in the other phase. For example, Locke (17) made use of squalane stationary phase in both GLC and LLC, and obtained the activity coefficients of aliphatic and aromatic hydrocarbons by GLC and the solute activity-coefficient ratios (acetonitrile mobile phase) by LLC. He also reported the use of glycerol as the common stationary phase in studies of the thermodynamics of solution of aliphatic alcohols in n-heptane (18). In addition, comparison of his results with data obtained by static methods gave good agreement for most of the solutes tested. However, those with poor solubility in one or both of the phases gave GLC/LLC-derived activity coefficients that were significantly larger than the static-derived values. (The discrepancies were attributed to solute adsorption at the liquid-liquid interface.)

Alessi and Kikic employed substantially the same methodology for systems comprised of aniline/squalane, and aniline/Apiezon L (19-22). In their work, solute activity-coefficient ratios in the two phases were first determined by LLC, followed by calculation of the activity coefficients in aniline alone by multiplying the ratio data by the GLC-determined activity coefficients with squalane or Apiezon L stationary phases. A comparison of their results with those obtained independently by GLC for aniline stationary phase also showed that discrepancies between the LLC- and GLC-derived data could be accounted for by the mutual solubility of the mobile and stationary phases employed in the former technique. Thus, while their static- and GLC-determined activity coefficients could be said to correspond to the behavior of solutes with neat solvents, the LLC values actually pertained to mobile and stationary phases that were mutually saturated. They therefore argued that the LLC technique can yield accurate activity coefficients only if the common solubility of the stationary and mobile phases is negligible.

Further support for this view was derived from comparison of GLC and LLC data at 275 K, at which temperature the mutual solubilities of aniline and squalane are very low (19), and for which the activity-coefficient data were in substantial agreement. Activity coefficients at infinite dilution in the carrier were obtained with Apiezon L as the GLC/LLC stationary phase and aniline or acetonitrile as the (LLC) mobile phase that also agreed well with static values (21). Thus, it appears that appropriate combination of GLC and LLC retention data can in fact yield solute activity coefficients as well as the related excess thermodynamic properties of solution that are of reasonable precision and accuracy, and which, moreover, would otherwise be difficult to obtain by conventional means.

Nevertheless, and in view of the limited number of pertinent studies that have been carried out to date, further scrutiny of a variety of sytems is called for in assessing the utility of LLC for measurements of these kinds. We have therefore sought in this work to extend the combined GLC/LLC technique to systems comprised of methanol, water, and their mixtures as LLC mobile phases with polydimethylsiloxane (PDMS) as the stationary phase; with aliphatic aldehyde, ketone, ester, and alcohol solutes of 3 to 7 carbons selected so as to represent a variety of functionalities. The choice of PDMS was predicated on its near-complete insolubility in methanol as well as water. In addition, it has been used extensively as a GLC stationary phase, and specific retention volumes of high accuracy for a large number of hydrocarbon solutes are available with it (23). Moreover, while water has been used previously as a stationary phase in GLC (10) and as a mobile phase for the purpose of combination of GLC and LLC retention data (24), the current work represents to the best of our knowledge the first occasion that infinite-dilution activity coefficients have been obtained in this way for methanol and methanol/water mixtures.

THEORY

Gas-Liquid Chromatography

Solute activity coefficients at infinite dilution in the stationary phase are related to GLC-measured specific retention volumes $V_g^o/\text{cm}^3\ \text{g}^{-1}$ by the well-known expression (6):

$$V_g^o = 273\ R\ /\ {}^{x}\gamma_p^{S,\infty}\ p_A^o\ M_B \tag{1}$$

where M_B/Da is the molecular weight of the stationary phase B, p_A^o/torr is the saturation vapor pressure of the bulk solute A, and the units on V_g^o pertain to the STP volume/cm^3 of carrier gas per gram stationary phase required to elute the solute peak maximum into the last theoretical plate of the column. ${}^{x}\gamma_p^{S,\infty}$ is the Raoult's-law mole-fraction based infinite dilution activity coefficient of the solute in the stationary phase, where the subscript p indicates that the fugacity correction has not been applied (for simplicity we leave this until later). However, the mole-fraction convention leads to some awkwardness in the retention data, particularly with stationary phases of high M_B, for which, given a finite retention volume, the solute activity coefficient must approach zero. This prompted Huber, Fritz, and Kovats (25,26) to advocate the use of molal-based activity coefficients ${}^{m}\gamma_p^{S,\infty}$ where, in terms of Raoult's law,

$$p_A = {}^{m}\gamma_p^{S,\infty}\ m_A^S\ p_A^o \tag{2}$$

where m_A^S is the solute molality in the solution S (= A + B). Further, since the molality and mole-fraction based concentration conventions are related by:

$$m_A^S = 10^3\ x_A^S\ /\ M_B\ x_B^S \tag{3}$$

and since, recalling the conventional form of Raoult's law,

$$p_A = {}^{x}\gamma_p^S\ x_A^S\ p_A^o \tag{4}$$

it follows that:

$${}^{x}\gamma_p^S = 10^3\ {}^{m}\gamma_p^S/\ M_B\ x_B^S \tag{5}$$

In the event that the solute is at infinite dilution in B, eqn. 5 reduces to:

$$ {}^{x}\gamma_{p}^{S,\infty} = 10^{3}\ {}^{m}\gamma_{p}^{S,\infty} \,/\, M_{B} \qquad (6)$$

The solute specific retention volume and molal-based activity coefficient are therefore related by:

$$ V_{g}^{o} = 273\ R \,/\, 10^{3}\ {}^{m}\gamma_{p}^{S,\infty}\ p_{A}^{o} \qquad (7)$$

An expression for V_g^o in terms of the solute infinite-dilution weight-fraction based activity coefficient ${}^{w}\gamma_{p}^{S,\infty}$ can be derived in the same manner:

$$ V_{g}^{o} = 273\ R \,/\, {}^{w}\gamma_{p}^{S,\infty}\ p_{A}^{o}\ M_{A} \qquad (8)$$

where M_A is the molecular weight of the solute.

In the present instance, since $M_B > 10^5$ Da, eqns. 7 and 8 are more suited than eqn. 1 for making comparisons of solute retentions since the latter forms of the infinite-dilution activity coefficient are independent of the stationary-phase molecular weight.

The fugacity and virial corrections to solute molal-based activity coefficients are given in combined form by the expression:

$$ \ln {}^{m}\gamma_{A}^{S,\infty} = \ln {}^{m}\gamma_{p}^{S,\infty} - p_{A}^{o}(B_{AA} - \bar{V}_{A})/RT + P\ (2B_{AB} - \bar{V}_{A})/RT \qquad (9)$$

where T is the column temperature in K, R is the gas constant, P is the average column pressure, $\bar{V}_A$ is the molar volume of the solute, B_{AA} is the bulk-solute second-interaction virial coefficient, and B_{AB} is the mixed ("cross") solute-carrier second virial coefficient. Typically, B_{AB} with helium carrier is on the order of $\bar{V}_A$. Also, $\bar{V}_A$ is generally small compared to B_{AA}. Eqn. 9 can therefore be approximated as:

$$ \ln {}^{m}\gamma_{A}^{S,\infty} = \ln {}^{m}\gamma_{p}^{S,\infty} - (p_{A}^{o}\ B_{AA})/RT \qquad (10)$$

There are a number of other assumptions implicit in the above derivations, as well as some precautions that must be observed in the application of eqns. 1 through 10. These are all widely recognized, however, and few difficulties arise on their account.

Liquid-Liquid Chromatography

The thermodynamics of solute retentions in LLC have been considered in detail by Locke and Martire (15,16). Briefly, it is convenient to define a net retention volume of the form:

$$V_N = V_R^o - V_M = K_R V_S \tag{11}$$

where, since the carrier is assumed to be incompressible (i.e., j = 1),

$$V_R^o = V_R \tag{12a}$$

$$V_M = V_A \tag{12b}$$

The mobile-phase linear velocity is directly proportional to the pressure drop across the column, where the mean column pressure P is simply the arithmetic mean of the inlet and outlet pressures. Accordingly, it can be shown that (15,16):

$$\ln V_g^T = \ln({}^x\gamma_A^{M,\infty} M_C) / ({}^x\gamma_A^{S,\infty} M_B \rho_C) + (P - 1)(v^M - v^S)/RT \tag{13}$$

where V_g^T is the solute specific retention volume at the column temperature T; ${}^x\gamma_A^{M,\infty}$ and ${}^x\gamma_A^{S,\infty}$ are the infinite-dilution activity coefficients in the mobile (M) and stationary (S) phases; M_B and M_C are the molecular weights of the pure stationary (B) and mobile (C) phases, respectively; ρ_C is the mobile-phase density at T; P is the mean column pressure as before; and v^M and v^S are the solute partial molar volumes in M and S. The last term on the right-hand side of eqn. 13 is negligibly small at moderate pressures, and the relation can therefore be simplified to the form:

$$V_g^T = ({}^x\gamma_A^{M,\infty} M_C) / ({}^x\gamma_A^{S,\infty} M_B \rho_C) \tag{14}$$

In instances where ${}^{m}\gamma_A^{S,\infty}$ is preferred, eqn. 14 becomes:

$$V_g^T = ({}^{x}\gamma_A^{M,\infty} \; M_C) \; / \; (10^3 \; {}^{m}\gamma_A^{S,\infty} \; \rho_C) \qquad (15)$$

The importance of activity coefficients to liquid-chromatographic separations is brought out clearly by eqns. 14 and 15. Also, if activity coefficients could somehow be forecast, then specific retention volumes (hence, separations) could be predicted in advance. Unfortunately, however, and despite notable advances, calculational methods such as UNIFAC are not yet sufficiently accurate for these purposes, as pointed out most recently by Park and Carr (27).

EXPERIMENTAL

Apparatus

The analytical liquid chromatograph used throughout this work was a Varian Model 5000. A Knauer differential refractometer was employed as the detector. The injector was a Valco valve with a 10-mm^3 external sample loop.

Column Preparation

Two columns were used during the course of the LLC work. The first was 58.6 cm x 7.65 mm i.d., and the second was 15 cm x 4.6 mm i.d., the latter being employed for the measurement of retention volumes of long-retained solutes in water-rich mobile phases. A precolumn 15 cm by 4.6 mm i.d., packed with the same material as was contained in the main column, was employed to dampen residual pressure fluctuations, as well as to bring the mobile phase to thermal equilibrium. Prior to packing the empty columns were flushed with dilute hydrochloric acid, distilled water, and acetone; and then dried under a flow of nitrogen.

The solid support in all instances was Johns-Manville Chromosorb G, 120-140 mesh, acid-washed and DMCS-treated. Liquid loadings consisted of approximately 10% w/w OV-1 polydimethylsiloxane (PDMS) from Ohio Valley Specialty Chemical Co.

Column packings were prepared by dissolving tared amounts of OV-1 in chloroform. Preweighed solid support was then added to the solution in a round-bottom flask to form a slurry (additional solvent was added if required to cover the solid support). Mixtures were gently dried on a rotary evaporator; the wet packings were then transferred to an evaporating dish and dried completely (with frequent stirring) in an air oven at 333 K.

Following each set of retention measurements, the percentage loading of stationary phase of the (used) packing was determined by rinsing (boiling toluene) tared portions held in gooch crucibles, followed by drying the extracted support under vacuum at 385 K for at least 12 h. Several repetitions were usually required to reach a constant weight of the support. The results of replicate trials agreed to within ± 1%.

Mobile Phases

Fisher HPLC-grade methanol (MeOH) was employed as received; water was doubly distilled. Mobile-phase solutions were prepared by volume in the amounts: 100, 90, 70, 50, 30, 10, and 0% MeOH. Each batch was prepared fresh, and was degassed in an L&R Model T-9 ultrasonic bath.

Solutes

The bank of test solutes consisted of the aliphatic aldehydes propionaldehyde, butyraldehyde, and valeraldehyde; the aliphatic ketones 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, and 2-heptanone; the aliphatic esters methyl acetate, methyl propionate, methyl butyrate, methyl valerate, and methyl caproate; and the aliphatic alcohols n-propanol, n-butanol, n-pentanol, n-hexanol, and n-heptanol. All were from Chem Service.

Procedures

Constant temperature was maintained by enclosing both the precolumn and the column together in a glass jacket through which was circulated water from a Neslabs Exacal thermostat. The column temperature was monitored with a Hewlett-Packard Model 2802A Platinum Resistance system. The eluent was brought to temperature by immersing a length of ca. 1 m of the solvent line in the bath prior to attachment to the precolumn.

The columns were allowed to equilibrate with each new mobile phase at a given temperature under conditions of constant flow, equilibration being judged satisfactory when the baseline was stable. During the course of each set of measurements, the flow rate was monitored continuously at the detector outlet by means of a graduated and thermostated pipet.

All retentions were measured from stripchart recordings of the chromatograms, which were also checked routinely with a stopwatch. The average of at least three measurements was taken for each data point.

Void Volume Determination

As discussed by us elsewhere (28), determination of the column void volume is not trivial. V_M for the alcohol solutes was taken in this work as the retention volume of methanol with pure methanol mobile phase that gave a solute activity coefficient of unity. The void volume for the ester and ketone solutes was obtained by extrapolating their retentions to zero carbon number. However, this procedure was found to yield inconsistent results for the aliphatic aldehydes, for which the V_M determined for the alcohol solutes was employed. The results were: 17.0, 16.9, 16.9, and 16.9 cm^3 for the alcohol and aldehyde solutes at 293, 298, 303, and 308 K, respectively; 17.6, 17.4, 16.8, and 16.7 cm^3 for the ketone solutes; and 17.5, 17.2, 16.9, and 16.7 cm^3 for the ester solutes.

RESULTS AND DISCUSSION

Gas-Liquid Chromatography

The pertinent physical properties of the solutes required for calculation of the virial and other thermodynamic quantities are provided in Table 1. All but four data were taken from ref. 29; the values for 2-hexanone, 2-heptanone, methyl valerate, and methyl caproate were estimated by the technique of Forman and Thodos (30). The Antoine constants required for calculation of the solute vapor pressures are given in Table 2, and were taken from the sources indicated. The solute vapor pressures at the four experimental temperatures of this work are then presented in Table 3. The vapor pressures of methyl butyrate, methyl valerate, and methyl caproate were taken directly from the graphs given in ref. 31. The requisite data for n-heptanol were available only at temperatures higher than 315 K and so, were extrapolated from those provided in ref. 31. Plots of ln p_A^o were

TABLE 1

Physical Properties of the Solutes (29)

Solute	M/Da	T^c/K	$V^c/cm^3\ mol^{-1}$
Propionaldehyde	58.080	496.	223.
Butyraldehyde	72.107	524.	278.
Valeraldehyde	86.134	554.	333.
2-Propanone	58.080	508.1	209.
2-Butanone	72.107	535.6	267.
2-Pentanone	86.134	564.0	301.
2-Hexanone	100.161	587.5	375. [a]
2-Heptanone	114.19	609.2	430. [a]
Methyl acetate	74.080	506.8	228.
Methyl propionate	88.107	530.6	282.
Methyl butyrate	102.134	554.4	340.
Methyl valerate	116.161	591.3	395. [a]
Methyl caproate	130.188	607.2	450. [a]
n-Propanol	60.069	536.7	218.5
n-Butanol	74.123	562.9	274.
n-Pentanol	88.150	586.	326.
n-Hexanol	102.177	610.	381.
n-Heptanol	116.204	633.	435.

[a] Values estimated by the method of Forman and Thodos (30).

found to be linear in T^{-1} as well as carbon number n for all but the ester homologs. For example, the values for methyl valerate and methyl caproate deviated quite substantially from the linear regression of ln p_A^o with carbon number for the remaining ester solutes; the former data should therefore be regarded as approximate.

The second-interaction virial coefficients, Table 4, were calculated from the equation of corresponding states of McGlashan and Potter (33; see also refs. 34,35):

$$B_{AA} = V_A^c\Big[0.430 - 0.886(T_A^c/T) - 0.694(T_A^c/T)^2 - 0.0375(n_A - 1)(T_A^c/T)^{4.5}\Big] \qquad (16)$$

TABLE 2

Antoine Constants for Listed Solutes Applicable over the Indicated Temperature Ranges

Solute	A	B	C	T/K
Propionaldehyde	16.2315	2659.02	-44.15	235-350 [a]
Butyraldehyde	16.1668	2839.09	-50.15	255-380 [a]
Valeraldehyde	16.1623	3030.20	-58.15	277-412 [a]
2-Propanone	16.6513	2940.46	-35.93	241-350 [a]
2-Butanone	16.5986	3150.42	-36.65	257-376 [a]
2-Pentanone	16.0031	2934.87	-62.25	275-410 [a]
2-Hexanone	8.1852	2117.2		280-400 [b]
2-Heptanone	7.36537	1650.47	-54.48	273-348 [c]
Methyl acetate	16.1295	2601.92	-56.15	245-360 [a]
Methyl propionate	16.1693	2804.06	-58.9	260-385 [a]
Methyl butyrate [d]				
Methyl valerate [d]				
Methyl caproate [d]				
n-Propanol	17.5439	3166.38	-80.15	285-400 [a]
n-Butanol	17.2160	3137.02	-94.43	288-404 [a]
n-Pentanol	7.17758	1314.56	168.11 [e]	
n-Hexanol	7.86045	1761.26	196.66 [e]	
n-Heptanol [d]				

[a] Ref. 29: $\ln p_A^o = A - B/(T + C)$. [b] Ref. 31: $\log p_A^o = A - B/T$. [c] Ref. 31: $\log p_A^o = A - B/(T + C)$. [d] From graphical interpolation of data reported in ref. 31. [e] Ref. 32: $\log p_A^o = A - B(t/^oC + C)$.

where V_A^c and T_A^c are the solute critical volume and temperature, respectively, and where n_A is the number of its carbon atoms. Eqn. 16 appears to be obeyed strictly by normal hydrocarbons. For other solutes, a "pseudo" carbon number derived from vapor pressure data and the correlations discussed by Guggenheim and Wormald (34) must be employed. In this work, values of n_A for oxygenated compounds were calculated by assuming that each O atom contributed 1.0 unit toward the total effective carbon number.

The solute specific retention volumes V_g^o for all solutes at four temperatures, Table 5, were calculated from the expression:

TABLE 3

Vapor Pressures of Listed Solutes at 293-308 K

	p_A^o /torr			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	257.9	318.3	389.6	473.2
Butyraldehyde	88.53	112.0	140.5	174.6
Valeraldehyde	26.25	34.35	44.44	56.91
2-Propanone	184.9	229.9	283.6	347.1
2-Butanone	74.91	94.74	118.8	147.6
2-Pentanone	26.91	35.23	45.61	58.43
2-Hexanone	9.18	12.14	15.89	20.63
2-Heptanone	2.82	3.91	5.35	7.23
Methyl acetate	172.6	216.5	269.2	331.8
Methyl propionate	66.55	85.47	108.6	136.8
Methyl butyrate	24.55	32.23	41.95	54.10
Methyl valerate	14.5	19.07	25.10	32.37
Methyl caproate	2.84	3.85	5.16	6.86
n-Propanol	14.56	20.48	28.36	38.72
n-Butanol	4.178	6.155	8.901	12.65
n-Pentanol	1.55	2.35	3.48	5.08
n-Hexanol	0.539	0.822	1.23	1.81
n-Heptanol	0.150	0.235	0.363	0.551

$$V_g^o = \frac{3}{2} F_{fm}\left(\frac{t'_R}{w_S}\right)\left(\frac{273}{T_{fm}}\right)\left(\frac{p_o - p_w}{p_w}\right)\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right] \tag{17}$$

where t'_R is the "corrected" solute retention time; F_{fm} is the flow rate (measured with a soap-bubble flowmeter) at the column outlet; w_S is the column weight of stationary phase; T_{fm} is the temperature of the flowmeter; p_i and p_o are the column inlet and outlet pressures (the latter was taken as barometric) and p_w is the vapor pressure of water at T_{fm}. Because of their long retentions, the elution volumes of n-hexanol and n-heptanol were measured at 333, 338, 343, and 348 K, and then extrapolated to the (lower) temperatures of interest. A comparison of the retentions with those published elsewhere (23) was made for the V_g^o of n-pentane, n-

TABLE 4

Second-Interaction Virial Coefficients $-B_{AA}/dm^3\ mol^{-1}$ of Listed Solutes at 293-308 K

	$-B_{AA}/dm^3\ mol^{-1}$			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	0.949	0.909	0.872	0.837
Butyraldehyde	1.51	1.44	1.37	1.31
Valeraldehyde	2.34	2.22	2.11	2.01
2-Propanone	0.946	0.906	0.868	0.833
2-Butanone	1.54	1.47	1.40	1.34
2-Pentanone	2.23	2.12	2.01	1.92
2-Hexanone	3.48	3.29	3.12	2.96
2-Heptanone	4.93	4.65	4.40	4.16
Methyl acetate	1.13	1.08	1.03	0.983
Methyl propionate	1.74	1.65	1.57	1.50
Methyl butyrate	2.61	2.48	2.35	2.24
Methyl valerate	4.09	3.86	3.65	3.46
Methyl caproate	5.55	5.23	4.93	4.66
n-Propanol	1.14	1.09	1.05	1.00
n-Butanol	1.82	1.74	1.65	1.58
n-Pentanol	2.72	2.58	2.45	2.33
n-Hexanol	4.00	3.78	3.58	3.39
n-Heptanol	5.70	5.37	5.07	4.79

hexane, n-heptane, and n-octane. The results at 273-333 K are provided in Table 6, and are everywhere in agreement to within ca. ± 2%. The solute fugacity-corrected molal-based activity coefficients calculated with eqns. 7 and 9 are then listed in Table 7.

The data show that, first, with increasing temperature, the activity coefficients decrease for all solutes except 2-hexanone, methyl valerate, and methyl caproate, the activity coefficients of which increase with increasing temperature. Secondly, the activity coefficients of the aldehyde solutes increase with increasing carbon number; while minima were

TABLE 5

Gas-Liquid Chromatographic Specific Retention Volumes $V_g^o/cm^3\ g^{-1}$ for Listed Solutes with OV-1 Stationary Phase at 293-308 K and 333-348 K

A. 293-308 K

	$V_g^o/cm^3\ g^{-1}$			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	81.40	66.82	55.21	45.90
Butyraldehyde	227.8	183.5	148.9	121.6
Valeraldehyde	637.6	504.1	401.6	322.4
2-Propanone	79.60	65.76	54.67	45.73
2-Butanone	226.5	180.5	144.9	117.2
2-Pentanone	644.3	495.4	384.2	300.4
2-Hexanone	1833.	1359.	1018.	769.7
2-Heptanone	5215.	3731.	2699.	1973.
Methyl acetate	124.0	101.1	82.93	68.48
Methyl propionate	347.6	274.3	218.1	174.7
Methyl butyrate	974.3	744.3	573.7	445.9
Methyl valerate	2731.	2020.	1509.	1138.
Methyl caproate	7654.	5481.	3968.	2903.
n-Propanol	218.9	166.2	127.3	98.40
n-Butanol	611.0	458.5	347.4	265.5
n-Pentanol	1705.	1265.	947.7	716.7
n-Hexanol	4759.	3490.	2586.	1934.
n-Heptanol	13240.	9628.	7053.	5220.

B. 333-348 K

Solute	333.2 K	348.2 K	353.2 K	358.2 K
n-Hexanol	4759.	3490.	2586.	1934.
n-Heptanol	13240.	9628.	7053.	5220.

TABLE 6

Comparison of Gas-Liquid Chromatographic Specific Retention Volumes V_g^o/cm^3 g^{-1} of Listed Solutes with OV-1 Stationary Phase at 293-333 K

Solute	V_g^o/cm^3 g^{-1}				
	293.2 K	303.2 K	313.2 K	323.2 K	333.2 K
n-Pentane					
This	92.27	67.77	48.87	35.87	27.06
Ref. 23		70.00	50.29	36.87	27.55
n-Hexane					
This	279.9	186.2	126.5	88.07	62.95
Ref. 23		184.8	126.4	88.47	63.28
n-Heptane					
This	799.6	502.8	322.4	213.3	143.6
Ref. 23		489.0	317.3	211.4	144.4
n-Octane					
This	2292.	1341.	806.5	510.0	324.3
Ref. 23		1296.	796.4	504.5	328.5

observed in the activity-coefficient data for the ketone and ester solutes. The latter behavior, while unusual, is not entirely unprecedented. Two factors govern the data, namely, the solute vapor pressures and their retentions, each of which can change independent of the other. For example, when the number of carbon atoms is increased, solute vapor pressures decrease while the retention volumes increase. The retention behavior of the alcohol solutes was very complex, and no regularities could be discerned in the respective activity coefficient data.

Liquid-Liquid Chromatography

The solute specific retention volumes V_g^T at four temperatures with pure methanol and with 90:10 v/v methanol:water are provided in Tables 8 and 9. The specific retention volumes at 298 K were determined with seven mobile-phase combinations, 100, 90, 70, 50, 30, 10, and 0% methanol; these results are given in Table 10.

TABLE 7

Fugacity-Corrected Molal-Based Infinite-Dilution Activity Coefficients for Listed Solutes with OV-1 Stationary Phase at 293-308 K

	${}^{m}\gamma_{A}^{S,\infty}$			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	0.766	0.745	0.726	0.709
Butyraldehyde	0.792	0.765	0.741	0.719
Valeraldehyde	0.951	0.904	0.864	0.827
2-Propanone	1.088	1.043	1.002	0.965
2-Butanone	0.941	0.919	0.899	0.881
2-Pentanone	0.918	0.897	0.880	0.865
2-Hexanone	0.944	0.948	0.951	0.953
2-Heptanone	1.079	1.070	1.064	1.059
Methyl acetate	0.749	0.721	0.697	0.676
Methyl propionate	0.690	0.670	0.653	0.638
Methyl butyrate	0.665	0.653	0.641	0.630
Methyl valerate	0.402	0.406	0.407	0.412
Methyl caproate	0.729	0.740	0.750	0.760
n-Propanol	4.982	4.588	4.255	3.969
n-Butanol	6.217	5.529	4.964	4.498
n-Pentanol	6.003	5.247	4.652	4.147
n-Hexanol	6.185	5.438	4.823	4.312
n-Heptanol	7.973	6.888	5.996	5.244

The retention data were first examined for any effects due to sample size, flow rate, and liquid phase loading, i.e., the extent to which the retentions were independent of the system conditions. Runs carried out at different carrier velocities and with various sample sizes confirmed that the retention volumes were indeed independent of flow rate and the amount injected. Next, the V_g^T of four solutes at 298 K were obtained with four columns to assess whether the liquid-phase loading affected the retention measurements. The specific retention volumes, together with the averaged values for each solute, are presented in Table 11. The deviations, as shown, are somewhat higher than is generally expected for the column-to-column reproducibility of V_g^T data, although not inordinately so. More importantly, the retentions vary randomly about the mean, that is, appear to be

TABLE 8

Liquid-Liquid Chromatographic Specific Retention Volumes $V_g^T/\mathrm{cm}^3\ \mathrm{g}^{-1}$ for Listed Solutes with Methanol Mobile Phase at 293-308 K

	$V_g^T/\mathrm{cm}^3\ \mathrm{g}^{-1}$			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	0.270	0.128	0.223	0.137
Butyraldehyde	0.261	0.081	0.317	0.270
Valeraldehyde	0.445	0.161	0.436	0.332
2-Propanone	0.085	0.133	0.294	0.180
2-Butanone	0.137	0.166	0.393	0.332
2-Pentanone	0.171	0.218	0.488	0.398
2-Hexanone	0.199	0.242	0.592	0.441
2-Heptanone	0.218	0.284	0.701	0.502
Methyl acetate	0.114	0.142	0.171	0.279
Methyl propionate	0.171	0.194	0.227	0.355
Methyl butyrate	0.199	0.251	0.289	0.426
Methyl valerate	0.232	0.240	0.346	0.521
Methyl caproate	0.284	0.341	0.403	0.654
1-Propanol	0.142	0.133	0.123	0.100
1-Butanol	0.213	0.199	0.180	0.147
1-Pentanol	0.289	0.261	0.237	0.194
1-Hexanol	0.355	0.332	0.294	0.237
1-Heptanol	0.431	0.393	0.355	0.289

insensitive to the liquid loading. Thus, although it is difficult to assess the absolute accuracy of the data, the precision of the V_g^T presented in Table 11 suggest that what interfacial effects there might be do not, on average, exceed ca. ± 5% of the absolute retentions.

In order to check for any potential loss of stationary phase, the retention volumes of 2-pentanone, methyl butyrate, and n-pentanol with 50% as well as 100% methanol were remeasured following the completion of a full series of retention runs, i.e., on having passed from pure methanol to pure water carrier at all temperatures. The agreement between the two

TABLE 9

Liquid-Liquid Chromatographic Specific Retention Volumes $V_g^T/\mathrm{cm}^3\ \mathrm{g}^{-1}$ for Listed Solutes with 90:10 v/v Methanol:Water Mobile Phase at 293-308 K

	$V_g^T/\mathrm{cm}^3\ \mathrm{g}^{-1}$			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	0.384	0.531	0.512	0.497
Butyraldehyde	0.171	0.475	0.436	0.422
Valeraldehyde	0.327	0.507	0.261	0.507
2-Propanone	0.047	0.166	0.365	0.327
2-Butanone	0.081	0.190	0.464	0.441
2-Pentanone	0.114	0.265	0.478	0.497
2-Hexanone	0.137	0.289	0.507	0.507
2-Heptanone	0.166	0.341	0.521	0.587
Methyl acetate	0.194	0.213	0.317	0.554
Methyl propionate	0.213	0.322	0.497	0.583
Methyl butyrate	0.261	0.521	0.564	0.602
Methyl valerate	0.455	0.663	0.758	0.805
Methyl caproate	0.597	0.857	0.924	0.848
1-Propanol	0.175	0.204	0.199	0.190
1-Butanol	0.232	0.256	0.237	0.218
1-Pentanol	0.284	0.313	0.265	0.246
1-Hexanol	0.346	0.370	0.298	0.275
1-Heptanol	0.403	0.426	0.332	0.303

sets of measurements for all three solutes and with both mobile-phase compositions invariably fell to within at worst ± 2%.

Having established that the retentions were reasonably precise, we proceeded at this point to calculate the relevant excess thermodynamic data of solution, where the results that follow were derived with the column containing a liquid loading of 11.13% (the highest employed in this study) so as to minimize any residual contributions to the retentions from interfacial effects. Also, the solute infinite-dilution mole-fraction based activity coefficients were calculated in all cases from the GLC-derived ${}^{m}\gamma_A^{S,\infty}$, Table 7, via eqn. 15. The results obtained with pure methanol mobile phase

TABLE 10

Liquid-Liquid Chromatographic Specific Retention Volumes $V_g^T/\mathrm{cm}^3\ \mathrm{g}^{-1}$ for Listed Solutes with OV-1 Stationary Phase and Mobile Phases Comprised of Indicated Decreasing Percentages (v/v) of Aqueous Methanol at 298 K

	$V_g^T/\mathrm{cm}^3\ \mathrm{g}^{-1}$						
Solute	100%	90%	70%	50%	30%	10%	0%
Propionaldehyde	0.128	0.531	0.586	0.352	0.375	0.693	0.869
Butyraldehyde	0.0805	0.475	0.331	0.179	0.383	0.422	0.688
Valeraldehyde	0.161	0.507	0.868	0.420	1.513	2.648	1.094
2-Propanone	0.133	0.166	0.208	0.242	0.279	0.327	0.365
2-Butanone	0.166	0.190	0.332	0.407	0.445	0.587	0.810
2-Pentanone	0.218	0.265	0.360	0.843	1.143	1.506	2.065
2-Hexanone	0.242	0.289	0.483	1.430	2.829	5.485	6.278
2-Heptanone	0.284	0.341	0.621	2.510	7.177	14.70	17.80
Methyl acetate	0.142	0.213	0.308	0.535	0.602	0.625	0.824
Methyl propionate	0.194	0.322	0.360	0.853	1.629	2.117	2.652
Methyl butyrate	0.251	0.521	0.568	2.169	4.485	6.887	8.365
Methyl valerate	0.294	0.663	1.198	3.988	11.43	20.13	22.51
Methyl caproate	0.341	0.857	1.900	7.995	30.76	66.86	79.32
n-Propanol	0.133	0.204	0.232	0.242	0.365	0.422	0.526
n-Butanol	0.199	0.256	0.317	0.355	0.512	0.602	0.673
n-Pentanol	0.261	0.313	0.384	0.521	0.805	0.952	1.165
n-Hexanol	0.332	0.370	0.469	0.706	1.630	2.605	3.353
n-Heptanol	0.393	0.426	0.554	0.895	3.344	7.361	11.45

TABLE 11

Liquid-Liquid Chromatographic Specific Retention Volumes $V_g^T/cm^3\ g^{-1}$ of Listed Solutes with Water Mobile Phase and Indicated Replicate Columns Containing OV-1 Stationary Phase at 298 K

					$V_g^T/cm^3\ g^{-1}$			
Column	% w/w OV-1	Wt. Packing/g	w_S/g	V_M/cm^3	Valeral-dehyde	Methyl butyrate	2-Pentanone	n-Pentanol
I	7.25	18.7595	1.3600	17.0	0.949	1.105	2.288	8.171
II	8.10	18.9943	1.5385	17.3	0.939	1.032	2.173	8.498
III	9.15	19.4440	1.7791	17.0	1.030	1.224	2.294	8.327
IV	11.13	18.9636	2.1113	16.9	1.094	1.165	2.065	8.365
				Ave.	1.003	1.144	2.205	8.304

TABLE 12

Mole-Fraction Based Infinite-Dilution Activity Coefficients for Listed Solutes in Methanol at 293-308 K

	$^{x}\gamma_A^{M,\infty}$			
Solute	293.2 K	298.2 K	303.2 K	308.2 K
Propionaldehyde	7.250	2.338	9.046	8.535
Butyraldehyde	3.337	1.513	7.873	7.308
Valeraldehyde	7.667	3.576	5.530	10.19
2-Propanone	2.330	3.397	7.170	4.256
2-Butanone	3.215	3.740	8.602	7.085
2-Pentanone	3.813	4.799	10.42	8.371
2-Hexanone	4.609	5.620	13.69	10.21
2-Heptanone	5.848	7.467	18.17	12.94
Methyl acetate	2.095	2.517	2.933	4.577
Methyl propionate	2.866	3.197	3.647	5.467
Methyl butyrate	3.277	4.025	4.480	6.470
Methyl valerate	2.290	2.931	3.428	5.233
Methyl caproate	5.121	6.195	7.391	12.04
n-Propanol	17.49	14.94	12.78	9.571
n-Butanol	32.74	27.00	21.80	16.01
n-Pentanol	42.85	33.56	26.88	19.53
n-Hexanol	54.29	44.26	34.56	24.76
n-Heptanol	84.90	66.48	51.97	36.74

at four temperatures are presented in Table 12, and with seven mobile-phase compositions at 298 K in Table 13.

To estimate the degree of accuracy of the activity coefficients, a comparison was carried out of the data for the solutes employed in this work with those in common with independent studies reported elsewhere; the results are presented in Table 14. The first set of values, reported by Wasik, Tewari, Miller, and Martire (36,37), were determined by a method developed by May, Wasik, and Freeman (38), which has been claimed to be capable of unsurpassed accuracy for measurements of this type. (In making

TABLE 13

Mole-Fraction Based Infinite-Dilution Activity Coefficients for Listed Solutes in Aqueous Solutions of Indicated Decreasing Concentrations (% v/v) of Methanol at 298 K

	$\gamma_A^{x\,M,\infty}$						
Solute	100%	90%	70%	50%	30%	10%	0%
Propionaldehyde	2.338	10.34	13.14	9.214	11.60	25.80	35.80
Butyraldehyde	1.513	9.518	7.629	4.818	12.20	16.12	29.14
Valeraldehyde	3.576	11.99	23.63	13.36	56.91	119.6	54.74
2-Propanone	3.397	4.527	6.545	8.860	12.12	17.03	21.06
2-Butanone	3.740	4.557	9.172	13.16	17.01	26.96	41.19
2-Pentanone	4.799	6.229	9.723	26.59	42.58	67.50	102.5
2-Hexanone	5.620	7.166	13.78	47.66	111.4	259.6	329.1
2-Heptanone	7.467	9.553	19.99	94.46	319.3	786.0	1055.
Methyl acetate	2.517	4.023	6.685	13.57	18.04	22.52	32.90
Methyl propionate	3.197	5.651	7.264	20.09	45.41	66.70	98.40
Methyl butyrate	4.025	8.904	11.17	49.80	121.8	224.6	302.3
Methyl valerate	2.931	7.054	14.26	56.98	193.2	408.7	506.3
Methyl caproate	6.195	16.60	42.09	207.9	946.0	2470.	3247.
n-Propanol	14.94	24.46	32.06	38.96	75.89	96.61	133.5
n-Butanol	27.00	37.02	52.83	69.06	117.6	166.1	205.6
n-Pentanol	33.56	42.93	60.61	96.12	175.7	249.5	338.4
n-Hexanol	44.26	52.58	76.77	134.9	368.4	707.6	1012.
n-Heptanol	66.48	76.85	114.9	216.8	957.6	2532.	4364.

TABLE 14

Comparison of Mole-Fraction Based Infinite-Dilution Activity Coefficients for Listed Solutes with Water at 298 K

	$^{x}\gamma_{A}^{M,\infty}$					
Solute	This[a]	Ref. 36[b]	Ref. 24[a]	Ref. 39[c]	Ref. 40[d]	Ref. 41[e]
Propionaldehyde	35.80		48.67	63.-73.	24.6	62.10
Butyraldehyde	29.14		69.2			299.1
2-Propanone	21.06		61.86	24.-26.	7.96	7.55
2-Butanone	41.19	29.19				31.79
2-Pentanone	102.5		135.1			143.9
2-Hexanone	329.1					659.5
2-Heptanone	1055.	1554.	882.2			3031.
1-Propanol	133.5				17.2	13.04
1-Butanol	205.6	63.78				60.08
1-Pentanol	338.4	414.5				279.0
1-Hexanol	1012.	1324.				1299.
1-Heptanol	4364.	4939.				5941.

[a] GLC/LLC. [b] Calculated from volume-fraction based activity coefficients $^{\phi}\gamma_{A}^{M,\infty}$, where $^{x}\gamma_{A}^{M,\infty} = {}^{\phi}\gamma_{A}^{M,\infty}\ \rho_{W}\ M_{A}/(\rho_{A}\ M_{W})$; and where ϕ indicates a volume fraction, ρ_{A} and M_{A} are the density and molecular weight of the solute, and ρ_{W} and M_{W} are the density and molecular weight of water (cf. refs. 37,38). [c] GLC; 293-303 K. [d] GLC; 297 K. [e] Calculated.

the comparison the literature data were converted from volume-fraction to mole-fraction based activity coefficients.) The combined GLC/LLC technique has also been used by Janini and Qaddora (24). Their results for some solutes in common with those of this work are in the fourth column of Table 14. The fifth and sixth columns then provide the GLC activity coefficient data taken from refs. 39 and 40, these being the only data of these kinds of which we are aware. By way of complementing the experimental data, activity coefficients were estimated by the method devised by Pierotti, Deal, and Derr (41), which is based upon the molecular structures of the solute and solvent. The values calculated with pure water carrier are given in the last column of Table 14. The agreement for solutes with n of 5 or more is clearly substantially better than that for solutes with fewer than this number of carbon atoms, the largest discrepancy being for n-butanol.

In seeking to interpret the activity coefficient data, we note first that all were substantially greater than unity, as might be expected in any event on the basis of the generally poor solubility of most organic compounds in aqueous solvents. The data also verified that all solutes were much more soluble in methanol than in water. One consequence of this was that, for a given mobile phase, the greater the organic character of a solute, the larger was its activity coefficient.

van't Hoff plots of ln(retention volume) against reciprocal absolute temperature are generally linear in chromatography, thereby enabling the determination of molar enthalpies of solution $\Delta\bar{H}_S$. However, no such linearity was extant with the systems studied in this work. For example, plots of ln(activity coefficient) with inverse temperature were curved for the aldehyde solutes; the ketones gave maxima with mobile phases of 90% as well as 100% methanol; and the esters showed an increase with pure methanol as well as 90% methanol except for methyl acetate and methyl caproate solutes. These results clearly point to the existence of multiple retention mechanisms. In contrast, all of the alcohol solutes gave decreasing activity coefficients with both mobile-phase compositions as the temperature was increased, which indicates that only a single mechanism was responsible for their retentions. [Pecsar and Martin (36) reported maxima in the van't Hoff plots of their activity coefficient data for aldehyde and alcohol solutes with water over the temperature range 273-313 K.] Nevertheless, little else can be said at this time in speciating the interactions without further and considerable study and experimentation.

The activity coefficient data did not regress linearly with carbon number (n), as can be seen in the data provided in the foregoing tables. For example, except for the values found with 30% methanol at 298 K and with 90% methanol at 303 and 308 K, the activity coefficients of the aldehyde solutes passed through minima with increasing carbon number. In contrast, the activity coefficients of the ketone solutes increased with increasing carbon number at all mobile-phase compositions and temperatures. The activity coefficients of the esters generally increased with carbon number, although methyl valerate gave lower activity coefficients than expected. (These results could be due to inaccurate vapor pressure data.) The activity coefficients of the alcohols increased with increasing number of carbons as well as with increasing water in the mobile phase at 298 K.

Overall, the interactions governing all of the retentions reported in this work are without doubte quite complex. Nevertheless, it is hoped that the data resulting from this study will help contribute to an understanding of these phenomena, and that the work will serve in addition as a useful model for future studies of these kinds.

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