GENERAL RESEARCH

Measurement of Limiting Activity Coefficients Using Non-Steady-State Gas Chromatography

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Non-steady-state gas chromatography (NSGC) is a novel method for the determination of limiting activity coefficients of volatile solutes in volatile solvents. Both uncoated wide-bore fused-silica open tubular columns and columns packed only with deactivated solid support can be used. Solvent is injected and allowed to coat the walls or the solid support packing; while it evaporates and elutes from the column, small samples of solute are repetitively injected. Limiting activity coefficients are simply related to the decrease in solute retention time over the lifetime of the column and to the solvent and solute vapor pressures. Results are given for 10 alcohols and ketones in water solvent at 25 °C; benzene, *n*-pentane, ethyl acetate, and 3 chloromethanes in methanol and ethanol solvents at 25 °C; 17 polar and nonpolar compounds in 1-butanol and 1-pentanol solvents in the range 35–55 °C; 8 polar and nonpolar solutes in toluene at 30 and 40 °C; and *n*-pentane, dichloromethane, and methanol in $CHCl_3$ solvent at 25 °C. The average relative standard deviation is 6.4%. Agreement with activity coefficient data reported in the literature is satisfactory.

Activity coefficients of organic compounds in solutions are of theoretical and practical interest in chemical engineering and solution thermodynamics. For example, they are used in the design of separation schemes based on phase equilibria such as distillation and solvent extraction. In aqueous solutions, the limiting (infinite dilution) activity coefficient, γ_1^∞, is related directly to the solubilities, Henry's Law constants, and partition coefficients of organic solutes, all of which are useful in modeling the fate of these compounds in natural water systems and in the design of water pollution control processes.

A number of methods have been devised for the experimental determination of activity coefficients. A standard procedure is differential ebulliometry, in which the boiling point difference between a solution and the solvent is measured as a function of composition. It is a reliable but time-consuming technique. Eckert et al. (1981), Thomas et al. (1982), and Trampe and Eckert (1990) have improved the apparatus and used it to study a wide variety of systems. Limiting activity coefficients cannot be obtained directly but are found by extrapolation of data for dilute solutions to infinite dilution. Because these infinite dilution values are often of the greatest utility in modeling (e.g., UNIFAC) and in theories of solution, measurement methods that provide them directly are of interest.

Conventional gas–liquid chromatography (GC) has often been used to measure the infinite dilution values of volatile solutes in a stationary phase (Conder and Young, 1979), but the low volatility of the solvent restricts application to systems primarily of theoretical interest. Volatile solvents have been studied by GC by presaturating the carrier gas with solvent vapors (Mash and Pemberton, 1980; Eckert et al., 1981; Thomas et al., 1982; Thomas and Eckert, 1984; Palmer, 1984; Terasawa et al., 1986; Itsuki et al., 1987). However, the weight of solvent phase present in the column is never known accurately; either the column has to be removed and weighed after a series of measurements, or the solvent weight has to be calculated based on the retention volume of a solute of independently known activity coefficient. This is the major source of error in the GC measurement using volatile solvents (Knoop et al., 1989).

Head-space GC has been used to advantage as a sensitive analytical tool to measure the composition of the vapor phase in equilibrium with a solution; infinite dilution activity coefficient values can be derived from these data (Hussam and Carr, 1985; Weidlich and Gmehling, 1985; Weidlich et al., 1986; Park et al., 1987). Systems in which solubilities are small can be studied by a related technique, gas-stripping or dynamic head-space GC (Leroi et al., 1977; Yin and Hassett, 1986).

We illustrate here the application of a novel GC technique, non-steady-state GC (NSGC) (Belfer and Locke, 1984; Belfer et al., 1990) to the determination of limiting activity coefficients of volatile solutes in volatile solvents. In NSGC, the column is initially packed with bare GC solid support material or is an uncoated wide-bore fused-silica open tubular column. Liquid solvent is injected into the heated injection port of a conventional GC. The vapors are transported into the column by the carrier gas, and if the column temperature is lower than the solvent boiling point, liquid solvent condenses in a more-or-less uniform film on the packing material or onto the walls of the capillary tube. Once the solvent has equilibrated in the column and the excess vapors have eluted, the GC detector
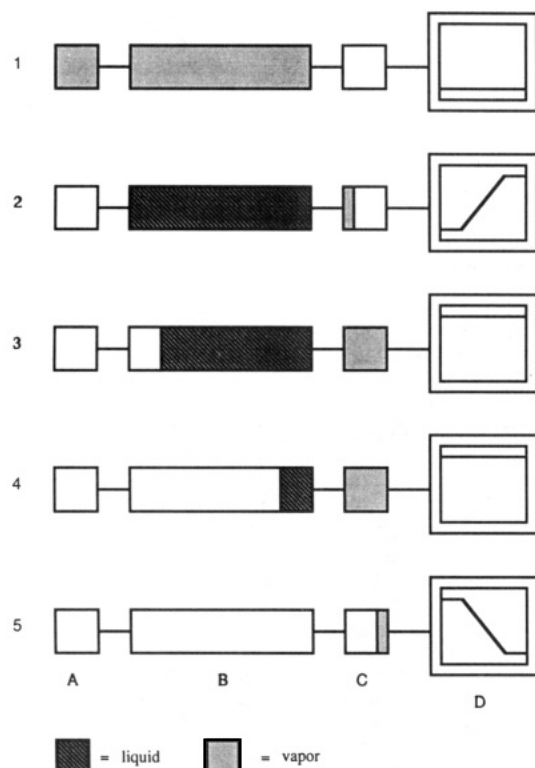

Figure 1. Schematic representation of non-steady-state gas chromatography. A is the injection port, B the gas chromatographic column, C the thermal conductivity detector, and D a recorder. In 1, solvent is injected into the heated injection port and evaporates, and solvent vapor fills the column; only helium is in the detector, and the baseline is low. In 2, solvent vapors condense to liquid and coat the walls of the open tubular column or the solid support and begin to elute. In 3 and 4, the high, steady baseline follows the continued elution of the solvent from the column as it saturates the carrier gas and passes into the detector; this signal can be zeroed to a low level to enable detection of solutes injected into the column. In 5, the column has lost all solvent, and the baseline drops back to the steady low reading of the carrier gas.

stabilizes and gives a high, flat baseline, recording the plateau of the eluting solvent vapors. The baseline can be zeroed to a low value. As carrier gas enters the column, it becomes saturated with solvent vapor. Solvent is thus steadily depleted from the wetted packing or walls of the capillary, starting at the inlet end of the column. The solvent-saturated carrier gas elutes from the column, passes through the heated detector, and escapes or is diverted through a trap for recovery of the solvent. A schematic diagram of the NSGC model is shown in Figure 1.

Once a steady baseline has been achieved, small amounts of a solute more volatile than the solvent are injected repetitively. Because the total weight of solvent in the column decreases with time, the retention volume of an injected solute is reduced over the lifetime of the column. This is depicted in Figure 2. The basic criterion for feasibility of study of a solute is that it must be of higher volatility than the solvent (volatility is the product of vapor pressure and activity coefficient). This allows study of binary mixtures at both ends of the composition diagram in some cases. Solutes of volatility lower than the solvent will elute at the tail of the solvent band, precluding study of their solution properties by NSGC.

A straightforward analysis of the system (Belfer and Locke, 1984) leads to a simple equation relating the limiting activity coefficient of the solute (=1) in the solvent (=2) to the ratio of their vapor pressures, $p_2°/p_1°$, and the rate at which retention time decreases with time of injection, $\Delta t_R/\Delta t$. The relationship can be derived as follows:
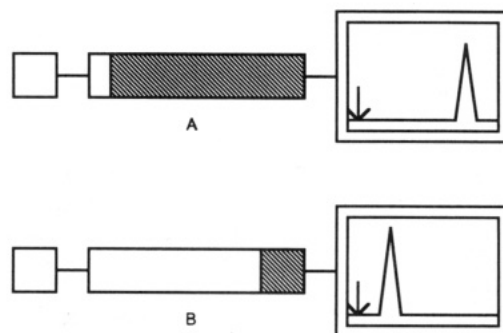
Figure 2. Representation of the change in retention time over time in non-steady-state gas chromatography. In A, early in the life of the column, the column contains a large amount of solvent. In B, most of the solvent has eluted, and the retention time of the solute is reduced. The change is linear with time.

In conventional (steady state) GC, the solute net retention volume, V_N, is the retention volume less that of air, corrected for the column pressure drop by using the Martin and James correction factor, j (Conder and Young, 1979). V_N is related to $\gamma_1°$ by

$$V_N = K_1 V_2 = RTw_2/p_1°M_2\gamma_1^\infty = RTn_2/p_1°\gamma_1^\infty \quad (1)$$

where K_1 and $p_1°$ are the distribution coefficient and vapor pressure of the solute, and V_2, w_2, M_2, and n_2 are respectively the volume, weight, molecular weight, and number of moles of solvent in the column. This equation is derived by assuming the vapor phase is ideal and that the solutions are sufficiently dilute to be in the Henry's law region.

In NSGC, the decrease in retention volume is proportional to the decrease in the amount of solvent:

$$\Delta V_N = K_1 \Delta V_2 = (RT/p_1°\gamma_1^\infty)\Delta n_2 \quad (2)$$

At constant carrier gas flow rate, F, and constant column temperature, T, the loss of solvent is directly proportional to time. Over a time interval $\Delta t = t_1 - t_2$, where t_1 and t_2 are two different times of injections of solute, the loss of solvent is

$$-(\Delta n_2/\Delta t) = n_v F = p_2° F/RT \quad (3)$$

where n_v is the number of moles of volatilized solvent per unit volume of gas phase. Combining equations

$$\gamma_1^\infty = -(p_2°/p_1°)/(\Delta V_N/F\Delta t) \quad (4)$$

Noting for constant F that $\Delta V_N/F = \Delta t_R$

$$\gamma_1^\infty = -(p_2°/p_1°)/(\Delta t_R/\Delta t) \quad (5)$$

Thus all one needs to determine limiting activity coefficients are the vapor pressures and the solute retention times measured at different injection times. Although in principle only two injections are needed, the larger the number of solute injections made, the better the precision of the measurement. One need not wait until a solute peak has eluted before making a subsequent injection, so long as one can distinguish among peaks. One could also inject mixtures of solutes if they are separable. It is unnecessary to wait for a column to become dry; new solvent can be injected at any time to renew the column.

As the rear of the solvent band moves through the column, the carrier gas/solvent vapor mixture is replaced by pure carrier gas. If the viscosity of the former is not appreciably different from that of the carrier gas, the net flow rate will be constant, and only the retention time change need be measured. If the viscosity changes substantially over the lifetime of the column, flow rate will

also change. In this case flow rate should be measured at the injection time and at the elution time for each injection, and the F in eq 4 would refer to the arithmetic averages of the two.

Experimental Part

Packed Column NSGC. A dual column, dual thermal conductivity detector GC was assembled from components. The $^1/_8$-in. injection ports were taken from a discarded Perkin-Elmer Model 600 GC and were heated with 150-W cartridge heaters (Industrial Heaters, Bronx, NY) powered by a Variac. The detector was a Gow-Mac dual hot-wire cell with W filaments, powered by a Gow-Mac power supply bridge control unit Model 40-200 (Gow-Mac Instruments, Bridgewater, NJ). The detector, also heated with a cartridge heater, and the injection ports were mounted onto an insulated aluminum lid covering a Lauda Refrigerating Circulator Model RMS-20 (Brinkmann Instruments, Westbury, NY). The circulator, which has temperature control accuracy of ±0.01 °C, was filled with water and served as the thermostatic oven for the dual 4 ft or 6 ft × $^1/_8$-in. o.d. stainless steel columns. The circulator also monitors temperature and presents it digitally. The bath temperature was generally set to 25.00 °C. The temperatures of the injectors and detector, generally set to 150 °C, were monitored with Fe–constantan thermocouples attached to a Varian pyrometer. Helium carrier gas flow was controlled by two Nupro precision needle valves (R. S. Crum & Co., Mountainside, NJ), one for each column, and measured by using a soap-bubble flow meter. Flow rates were typically 20 mL/min. Inlet pressure was measured with a Heise bourdon tube-type precision pressure gauge (Heise Gauge, Newton, CT). Atmospheric pressure was measured with a wall-mounted mercury barometer. Signals from the detector were recorded either on a Shimadzu Model R-111 strip chart recorder or a Shimadzu Model CR6A recording integrator (Shimadzu Scientific Instruments, Silver Spring, MD). The columns were packed with either 80/100 mesh Supelcoport or silanized 80/100 mesh glass beads (Supelco, Bellefonte, PA), and coiled to be completely immersed in the water bath.

Although a single column GC should produce equivalent results, the two-column arrangement facilitates stabilization of the baseline. One column is attached to the sample side of the detector and the other to the reference side. Identical volumes of solvent, in the range 0.05–4 mL depending on the column and the solvent, are injected into each, sample column first and reference column immediately following. Initially, a major disruption of the baseline occurs, and solvent can sometimes be seen bubbling out of the end of the detector if an excessive quantity was injected. In 10–45 min the baseline stabilizes, and the recorder can be brought to zero by using an attenuation of 16–128×, usually 32×. Injection of 0.1 μL or less of neat solutes produces half-scale peaks.

Open Tubular Column NSGC. The apparatus and procedures used here have been fully described recently (Belfer et al., 1990). Briefly, a Hewlett-Packard 5890A GC equipped with a Hewlett-Packard modulated thermal conductivity detector and splitless injector was used with a 30 m × 0.53-mm i.d. uncoated Hewlett-Packard fused silica capillary column. The stability of this detector enables the use of only one column. Helium flow rates were in the range 2–10 mL/min. Solvent volumes injected were 25–50 μL. Solutes were injected as vapor or solutions in the solvent, at concentrations such that injection of 0.1 μL introduces 1–10 μg of solute.

Materials. Water was glass-distilled; the organic solvents used, methanol, ethanol, 1-pentanol, toluene, and

Table I. Vapor Pressures of Solvents, Torr[a]

solvent	25	30	35	40	45	55
water	23.8[b]					
methanol	125[c]					
ethanol	59.8[c]					
1-butanol			13.9		25.8	46.0
1-pentanol			5.19		10.3	19.2
toluene		36.6		59.0		
chloroform	199[b]					

[a] Vapor pressures at 25 °C from references cited; those at higher temperatures from American Institute of Chemical Engineers (1983). [b] National Academy of Sciences (1923). [c] Wilhoit et al. (1973).

Table II. Vapor Pressures of Solutes, Torr[a]

solute	25	30	35	40	45	55
methanol	125[b]	163	209	266	334	517
ethanol	59.8[b]	79.0	104	135	174	281
1-propanol	20.9[b]					
2-propanol	45.2[b]					
1-butanol	6.18[b]					
2-butanol	18.3[b]					
acetone	231[c]	285	349	424	512	731
2-butanone	90.6[c]		145		221	327
2-pentanone	35.4[c]					
3-pentanone	35.4[c]					
ethyl acetate	94.2[d]		149		230	344
diethyl ether		645	772	917	1082	1481
n-pentane	509[e]	616	735	871	1025	1397
n-hexane		189	231	281	339	483
n-heptane			73.7		115	173
n-octane			24.1		39.8	63.3
cyclohexane			152		227	329
1-hexane		229	279	338	406	576
benzene	94.4[e]		148		223	326
toluene			46.7		74.0	113
CH_2Cl_2	435[f]	533	642	769	915	1269
$CHCl_3$	199[e]		297		435	620
CCl_4	113[e]					
CCl_2FCClF_2			476[g]		672[g]	930[g]

[a] Vapor pressures at 25 °C from references cited; vapor pressures at other temperatures from American Institute of Chemical Engineers (1983). [b] Wilhoit et al. (1973). [c] Ambrose et al. (1975). [d] Rossini et al. (1953). [e] National Academy of Sciences (1923). [f] Philippe et al. (1973). [g] Calculated from Knoop et al. (1989).

chloroform, were Baker HPLC grade (J.T. Baker Chemical Co., Phillipsburg, NJ) or equivalent. Solutes were generally reagent grade or HPLC grade, or obtained from Aldrich (Aldrich Chemical Co., Milwaukee, WI). All were used without further purification. Neither solvent nor solute purity is as important in GC methods as in ebulliometric procedures. Minor impurities in the solute either are separated from that solute or, if not, have an insignificant effect on its retention time. A minor solvent impurity will interfere only if it interacts strongly with the solvent or a solute. Vapor pressures of all solvents and solutes at the temperatures used are given in Tables I and II, respectively.

Results and Discussion

Test of the Model. According to the model described above, for a solvent that wets the solid support material or the capillary walls, a uniform film of solvent should result after the solvent vapors have condensed in the column. The solvent band should then elute starting from the inlet end of the column, leaving behind bare column packing or bare capillary walls. Thus the vapor phase mole fraction of solvent should remain essentially constant over the life of the column, and the liquid film thickness should

Table III. Activity Coefficients in Water, 25.00 °C

compound	NSGC	sd[a]	lit. values
methanol	1.74	0.17	1.64,[b] 1.51,[c] 1.53[d]
ethanol	4.03	0.52	3.92,[b] 3.74,[e] 3.76[f]
1-propanol	15.0	1.3	13.8,[b] 11.7[d]
2-propanol	7.75	0.69	8.13,[b] 6.54[d]
1-butanol	53.7	7.1	51.6,[b] 53.5,[c] 55.7[g]
2-butanol	22.4	2.1	26.2,[b] 27.4[d]
acetone	7.31	0.79	7.56,[b] 7.17,[f] 7.80[d]
2-butanone	27.6	3.5	27.8,[b] 26.2,[d] 25.98[f]
2-pentanone	102	15	98.9,[b] 104[d]
3-pentanone	113	16	113,[b] 104[d]

[a] sd is the standard deviation in the NSGC value, $n = 5$. [b] Mash and Pemberton (1980). [c] Butler et al. (1935). [d] Pierotti et al. (1959). [e] Hansen and Miller (1957). [f] Park et al. (1987). [g] Buttery et al. (1969).

be approximately the same wherever there is liquid in the column.

To test the former, a column packed with 80/100 mesh silanized glass beads was used at 25 °C, into which was injected 1.5 mL of *n*-octane solvent. After equilibration of the solvent in the column, effluent was passed through a heated line into the 1.4-mL gas-sampling valve of a Perkin-Elmer Model 154 GC equipped with a squalane column at 100 °C and a thermal conductivity detector. Injections of the effluent vapor sample were made every 10 min. Areas of the resulting octane peaks, monitored by using a Shimadzu CR6A recording integrator, were essentially constant over the lifetime of the column. Thus we conclude that solvent is eluting from the column at a constant rate.

Liquid film thickness can be estimated by comparing measurements of chromatographic efficiency, i.e., plate height, H, over the life of the column. Consider a packed column operated at a carrier gas velocity, v, greater than the optimum, i.e., one in which stationary-phase non-equilibrium (mass-transfer resistance) is controlling efficiency. Here, the van Deemter equation (Giddings, 1965) reduces to

$$H = ck'd_f^2v/(1 + k')^2D_s \qquad (6)$$

where c is a constant, k' the solute partition ratio, D_s the solute diffusion coefficient in the stationary phase, and d_f the average thickness of the solvent film. If plate heights are measured at different times (t_1 and t_2) during the column lifetime, the ratio of the liquid film thickness at the two times is given by

$$d_{f2}/d_{f1} = [H_2k_1'F_1(1 + k_1')^2/H_1k_2'F_2(1 + k_2')^2] \qquad (7)$$

since F is proportional to v. For 8 injections of acetone solute in octane solvent over the life of the column, the ratio d_{f2}/d_{f1} averaged 0.98 (standard deviation, 0.15), with no apparent trend over time. Thus the liquid film thickness over the life of the column is approximately constant, which we take to be further verification of the solvent plateau model.

The best test of the model, of course, is whether NSGC provides limiting activity coefficients in agreement with those obtained by other methods. This is illustrated below for a variety of solute–solvent systems.

Water Solvent. In Table III are given the measured activity coefficients of several alcohols and ketones in water at 25.00 °C. To obtain these data, 0.5 mL of H_2O was injected into both of the 4 ft × $^1/_8$-in. o.d. columns, each packed with 1.30 g of 80/100 mesh Supelcoport, with a He flow rate of 20 mL/min. The system required about 45 min to equilibrate, and the column lifetime was approximately 9 h. It was necessary to average the flow rate

Table IV. Limiting Activity Coefficients by NSGC in Ethanol, 25.00 °C

compound	this work	sd[b]	Yang et al. (1988)
benzene	5.21	0.14	5.21
n-pentane	9.49	0.26	
ethyl acetate	3.61	0.08	
CH_2Cl_2	2.50	0.14	
$CHCl_3$	1.71	0.05	1.65
CCl_4	5.14	0.09	5.27

[a] Standard deviation in the experimental value, $n = 5$.

between injections (eq 4) because there was a significant change in mobile-phase viscosity as the water eluted from the column. Also included in Table III are activity coefficient values reported in the literature. The agreement of the activity coefficient sets is quite good, given that the average relative standard deviation of the NSGC data is 11.5% and that Mash and Pemberton (1980) cite differences in literature data of up to 40% for some aqueous systems.

Systems of highly disparate polarity such as aqueous solutions of organic compounds present a particularly severe test of any experimental method, especially chromatographic methods, including NSGC. Solubilities of many organic compounds in water solvent are small, i.e., their activity coefficient values are large. Solutions may not be at infinite dilution even at the lowest detectable sample size injected. Low solubility can promote gas–liquid interfacial adsorption at finite solute concentrations, which obfuscates interpretation of retention data (Conder and Young, 1979). In our packed column NSGC, we are already near the limit of thermal conductivity detectability, so we could not reduce the sample size injected significantly to assess the effect on the derived activity coefficient values. In addition, the change in retention time with injection time is small, which increases experimental error. Also, although water would not be expected to wet the silanized solid support material, forming globules and droplets of solvent rather than a smooth, uniform film, the model does not require a uniform liquid film but requires only that the net rate of evaporation of solvent from the column is constant. Experimental work is in progress to study the effects of these problems in NSGC. However, adsorption of even polar solutes on the silanized solid support appears not to be a problem; injection of solutes into the dry column produced symmetrical peaks with retention times identical with that of air. In any case, the experimental activity coefficients reported here and quite possibly many of those in the literature should not be considered true limiting values. The solutions are probably insufficiently dilute to prevent solute–solute interactions from occurring.

Ethanol and Methanol Solvents. In Table IV are listed NSGC activity coefficient values in ethanol solvent at 25.00 °C obtained by us, and values reported by Yang et al. (1988), who also used NSGC, with a 4 ft × 6-mm i.d. column packed with a 80/100 mesh diatomaceous earth solid support material, at 25 °C. The agreement is remarkably good and provides an excellent test of the universality of the method. We used both silanized glass bead columns and columns packed with Supelcoport. As long as the columns were completely saturated at the start of a run, the data obtained on the two different columns agreed within experimental error. The Supelcoport column required injection of 1.75 mL of ethanol and lasted about 7 h. The glass bead column was saturated with 0.5 mL of ethanol and had a lifetime of about 2 h. Data obtained for the glass bead column were slightly more precise (2% vs 5% average standard deviation).

Table V. Limiting Activity Coefficients in Methanol, 25 °C

compound	NSGC	sd[a]	lit. value
benzene	7.17	0.16	7.5[b]
n-pentane	19.5	1.0	27.0[c]
acetone	2.16	0.07	
CH$_2$Cl$_2$	2.81	0.06	
CHCl$_3$	2.34	0.05	
CCl$_4$	7.58	0.19	

[a] Standard deviation in the experimental value, $n = 5$. [b] Deal and Derr (1964). [c] Gerster et al. (1960).

Table VI. Limiting Activity Coefficients in 1-Butanol

compound	temp, °C			lit. value[a]
	35.0	45.0	55.0	
n-pentane	4.12	3.83	3.85	4.06[a]
n-hexane	4.83	4.66	4.67	5.00[b]
n-heptane	5.55	5.39	5.21	5.14[a]
n-octane	6.26	6.01	6.64	6.39[c]
1-hexene	4.41	4.03	3.89	
cyclohexane	4.05	3.82	3.82	3.74,[a] 4.01[b]
benzene	2.96	2.94	2.81	2.84[a]
toluene	3.19	3.30	3.21	3.42[c]
CH$_2$Cl$_2$	1.97	1.94	1.92	1.86[b]
CHCl$_3$	1.32	1.40	1.38	1.20[b]
CCl$_2$FCClF$_2$	4.61	4.25	4.65	
methanol	1.12	1.08	1.05	
ethanol	1.02	1.01	1.00	0.934[c]
acetone	2.14	2.00	1.83	2.4[c]
2-butanone	2.15	1.95	1.74	2.06[c]
diethyl ether	1.88	1.81	1.68	
ethyl acetate	2.43	2.30	2.09	

[a] Vernier et al. (1969), 25 °C. [b] Thomas et al. (1982), 20 °C. [c] Park et al. (1987), 25 °C.

The results for methanol solvent at 25.00 °C are given in Table V. Again, glass bead and Supelcoport packings gave equivalent results; injection of 1.5 mL of methanol was required for the former and 2.50 mL for the Supelcoport column. For neither the ethanol nor the methanol solvents was there observed a substantial change in carrier gas flow rate, so that activity coefficients were determined from the slope of a plot of solute retention time, t_R, vs injection time, t, taken over the usable life of the column (eq 5). There are few data in the literature for methanol solvent available for comparison. For slightly soluble solutes, e.g., hydrocarbons, methanol may present some of the same problems as water.

1-Butanol and 1-Pentanol Solvents. An open tubular column was used to measure limiting activity coefficients in 1-butanol and 1-pentanol. In both cases, equilibration as noted by a flat baseline was achieved in about 5–6 min after injection of 25 μL of solvent. Measurements in 1-butanol were made at 35.0, 45.0, and 55.0 °C and are presented in Table VI. A few values measured at 25 °C by Park et al. (1987), who used a head-space GC method, are included for comparison, along with other literature data. Activity coefficients in 1-pentanol were measured at 35.0, 45.0, and 55.0 °C and are presented in Table VII along with the normal (steady state) GC results of Knoop et al. (1989), who presaturated the carrier gas with 1-pentanol vapors. The estimated error in both sets of data is ±10%.

The gas chromatograph used with the wide-bore capillary column could not be operated reliably and reproducibly at temperatures much less than 30 °C because of heat produced by the injector and detector; this is common to most GCs with forced-air ovens but without cryocooling capabilities. This type of oven, while capable of less accurate and precise control of temperature than the liquid circulator, has the distinct advantage that rapid temper-

Table VII. Limiting Activity Coefficients in 1-Pentanol

compound	temp, °C					
	35.0		45.0		55.0	
	NSGC	lit.[a]	NSGC	lit.[a]	NSGC	lit.[a]
n-pentane	4.31	3.81	3.69	3.73	3.53	3.66
n-hexane	4.26	4.09	4.17	4.02	3.68	3.94
n-heptane	4.70	4.64	4.61	4.55	4.70	4.45
n-octane	5.80		5.42	3.94	5.30	
cyclohexane	3.42	3.27	3.51	3.23	3.28	3.20
1-hexene	3.43	3.32	3.23	3.50	3.48	3.49
benzene	2.93	2.58	2.66	2.54	2.62	2.50
toluene	3.02	2.99	3.05	2.89	3.07	2.80
methanol	1.24	1.14	1.35	1.13	1.20	1.12
ethanol	1.09		1.17	1.12	1.14	1.12
acetone	2.43	2.25	2.07	2.07	2.10	1.91
2-butanone	2.19	2.06	2.16	1.96	1.84	1.86
diethyl ether	1.75	1.67	1.95	1.66	1.59	1.67
CH$_2$Cl$_2$	2.09	1.80	1.84	1.78	1.80	1.76
CHCl$_3$	1.46		1.29		1.32	
CCl$_2$FCClF$_2$	4.07	3.91	3.68	3.78	3.58	3.65

[a] Data extrapolated from measurements at 30, 40, and 50 °C (Knoop et al., 1989).

Table VIII. Limiting Activity Coefficients in Toluene

compound	temp, °C					
	20.0		30.0		40.0	
	NSGC[a]	lit.[b]	NSGC	lit.[b]	NSGC	lit.[b]
n-pentane	1.64	1.85	1.61	1.78	1.58	1.94
n-hexane	2.10	1.87	1.85	1.77	1.62	1.93
1-hexene	1.36	1.44	1.33	1.43	1.30	1.55
methanol	20.5	21.4	19.0	18.5	17.6	17.4
ethanol	18.9	17.3	14.7	15.2	10.8	14.9
CH$_2$Cl$_2$	0.91	0.83	0.87	0.83	0.83	1.00
acetone	2.19	1.97	1.96	1.93	1.75	2.08
diethyl ether	1.01	1.12	1.01	1.12	1.02	1.24

[a] NSGC values extrapolated to 20 °C from data measured at 30 and 40 °C. [b] Knoop et al. (1989).

Table IX. Limiting Activity Coefficients in Chloroform, 25 °C

compound	γ_1^∞	sd[a]
n-pentane	2.13	0.06
CH$_2$Cl$_2$	1.26	0.02
methanol	9.55	0.62

[a] Standard deviation, $n = 5$.

ature changes can be made. For our purposes, this ability facilitates the far more rapid equilibration of the solvent in the open tubular column. Liquid solvent is injected while the column is set at a temperature slightly greater than the solvent boiling point. Once the initial pressure surge has relaxed, the oven door is opened and the column temperature set back to the operating value. The resulting rapid cooling produces a uniform, thick liquid film that stabilizes in 5–6 min. This could not be done with a liquid bath.

Toluene Solvent. Measurements were made at 30.0 and 40.0 °C in the open tubular column. The results are presented in Table VIII, along with conventional GC-derived data of Knoop et al. (1989). To complete the comparison, NSGC data were extrapolated to 20.0 °C. On the whole, the agreement of the two data sets is again satisfactory.

Chloroform Solvent. A few determinations were made with the packed column apparatus using CHCl$_3$ as solvent. These are listed in Table IX. It was necessary here to use the Supelcoport column at 25.00 °C. Injection of 4.0 mL of solvent required 1 h to stabilize, and the column lasted another 45 min, sufficient for five injections of solutes. One

of the limitations of the NSGC method is evident here, since solutes of potential interest such as CCl_4, ethanol, benzene, and acetone all have lower volatilities than chloroform and elute after the solvent tail.

Dichloromethane similarly is too volatile a compound to be studied by using NSGC. Some initial work was done with CCl_4 as solvent, but shortly after the start of these experiments, the filaments in the thermal conductivity detector failed, possibly because of attack by the high concentrations of chlorocarbons on the tungsten filaments. It was decided not to continue this line of investigation.

Vapor-Phase Interactions. Corrections for vapor-phase nonideality were calculated for representative systems from the truncated virial equation of state using second virial coefficients computed according to Reid et al. (1987). In all cases the correction amounted to a few percent in the activity coefficient, well below the estimated experimental error, $\pm 10\%$. For example, for the polar solute–polar solvent system methanol (1)/H_2O (2)/He (3), the vapor-phase mole fraction of water vapor $y_2 = 0.0198$, and the relevant second virial coefficients (cm^3 mol^{-1}) at 25 °C are $B_{22} = -4622$, $B_{33} = 37.98$, and $B_{23} = 15.80$, from which the mixture second virial coefficient, $B_m = 35.28$, and the fugacity coefficient, $\phi_1 = 0.985$. For a nonpolar solute–nonpolar solvent system [studied earlier (Belfer and Locke, 1984)] n-pentane (1)/n-octane (2)/He (3), $y_2 = 0.0117$, $B_{22} = -4316$, $B_{23} = 57.8$, $B_m = -220.2$, and $\phi_1 = 0.998$. The vapor-phase mole fraction of the solute was negligible. Although this method of calculating virial coefficients is crude, the fugacity coefficient is not very sensitive to the precise values. Consequently we feel justified to ignore these corrections, as was also done for example by Thomas et al. (1982) and Eckert et al. (1981), who used conventional GC for their measurements.

Conclusions

NSGC has the advantages of experimental simplicity, speed, and ability to provide infinite dilution activity coefficients directly. On the basis of the variability of published limiting activity coefficients obtained by the more conventional techniques, the accuracy and precision of NSGC seem neither substantially worse nor better. There are, of course, limitations to this technique. It is applicable only to systems in which the solute is of greater volatility than the solvent. As is true with most methods, NSGC may be of limited utility in cases where limiting activity coefficients are rather large. Accuracy may be compromised in systems where the possibility of interfacial adsorption exists and where the lack of detector sensitivity precludes use of the extremely small samples required to ensure infinite dilution. With NSGC, problems of precision arise when retention times are short and when the change in retention time over time is either rather small or large. It would not be possible to study mixed volatile solvents by NSGC, in which cases the head-space GC method has clear superiority. We are continuing to study the technique and its range of applications.

Acknowledgment

Registry No. $CHCl_3$, 67-66-3; methanol, 67-56-1; ethanol, 64-17-5; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; toluene, 108-88-3.

Literature Cited

Ambrose, D.; Ellender, J. H.; Lees, E. B.; Sprake, C. H. S.; Townsend, R. J. Thermodynamic Properties of Organic Oxygen Compounds. XXXVIII. Vapor Pressures of Some Aliphatic Ketones. *J. Chem. Thermodyn.* **1975**, *7*, 453–472.

American Institute of Chemical Engineers, Design Institute for Physical Property Data. *Project 801, DCAP II Users Guide*; The Pennsylvania State University: University Park, PA, 1983.

Belfer, A. J.; Locke, D. C. Non-Steady State Gas Chromatography for Measurement of Activity Coefficients. *Anal. Chem.* **1984**, *56*, 2485–2489.

Belfer, A. J.; Locke, D. C.; Landau, I. Non-Steady State Gas Chromatography Using Capillary Columns. *Anal. Chem.* **1990**, *62*, 347–349.

Butler, J. A. V.; Ramchandani, C. N.; Thomson, D. W. The Solubility of Nonelectrolytes. I. Free Energy of Hydration of Some Aliphatic Alcohols. *J. Chem. Soc.* **1935**, 280–285.

Buttery, R. G.; Ling, L.; Guadagni, D. G. Food Volatiles. Volatilities of Aldehydes, Ketones, and Esters in Dilute Water Solution. *J. Agric. Food Chem.* **1969**, *17*, 385–389.

Conder, J. R.; Young, C. L. Physicochemical Applications of Gas Chromatography. Wiley-Interscience: New York, 1979.

Deal, C. H.; Derr, E. L. Selectivity and Solvency in Aromatics Recovery. *Ind. Eng. Chem. Process Des. Dev.* **1964**, *3*, 394–399.

Eckert, C. A.; Newman, B. A.; Nicolaides, G. L.; Long, T. C. Measurement and Application of Limiting Activity Coefficients. *AIChE J.* **1981**, *27*, 33–40.

Giddings, J. C. *Dynamics of Chromatography*; Marcel Dekker: New York, 1965; p 40.

Gerster, J.; Gorton, J.; Eklund, R. Selective Solvents for Separation of n-Pentane from 1-Pentene by Extractive Distillation. *J. Chem. Eng. Data* **1960**, *5*, 423–429.

Hansen, R. S.; Miller, F. A. A New Method for Determination of Activities of Binary Solutions of Volatile Liquids. *J. Phys. Chem.* **1954**, *58*, 193–196.

Hussam, A.; Carr, P. W. Rapid and Precise Method for the Measurement of Vapor/Liquid Equilibria by Headspace Gas Chromatography. *Anal. Chem.* **1985**, *57*, 793–801.

Itsuki, H.; Terasawa, S.; Yamana, N., Ohotaka, S. Gas–Liquid Chromatographic Determination of Partial Molar Free Energies at Infinite Dilution of 18 Organic Solutes in n-Hexane Solvent at 25.0 °C. *Anal. Chem.* **1987**, *59*, 2918–2921.

Knoop, C.; Tiegs, D.; Gmehling, J. Measurement of γ^∞ Using Gas-Liquid Chromatography. 3. Results for the Stationary Phases 10-Nonadecanone, N-Formylmorpholine, 1-Pentanol, m-Xylene, and Toluene. *J. Chem. Eng. Data* **1989**, *34*, 240–247.

Leroi, J. C.; Masson, J. C.; Renon, H.; Fabries, J. F.; Sannier, H. Accurate Measurement of Activity Coefficients at Infinite Dilution by Inert Gas Stripping and Gas Chromatography. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 139–144.

Mash, C. J.; Pemberton, R. C. Activity Coefficients at Very Low Concentrations for Organic Solutes in Water Determined by an Automatic Chromatographic Method. *NPL Report Chem. 111*; National Physical Laboratory: Teddington, Middlesex, U.K., July 1980; 24 pp.

National Academy of Sciences. *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*; McGraw-Hill: New York, 1923; Vol. III.

Palmer, D. A. A Practical Synthesis of Experimental and Correlation Techniques for Modeling Highly Nonideal Systems with Many Components. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 259–266.

Park, J. H.; Hussam, A.; Couasnon, P.; Fritz, D.; Carr, P. W. Experimental Reexamination of Selected Partition Coefficients from Rohrschneider's Data Set. *Anal. Chem.* **1987**, *59*, 1970–1976.

Philippe, R.; Jambon, C.; Clechet, P. Thermodynamic Properties of Dimethylsulfoxide and Halomethane Mixtures. II. Vapor Pressures and Excess Functions. *J. Chem. Thermodyn.* **1973**, *5*, 431–444.

Pierotti, G. J.; Deal, C. H.; Derr, E. L. Activity Coefficients and Molecular Structure. *Ind. Eng. Chem.* **1959**, *51*, 95–102.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; American Petroleum Institute; The Carnegie Press: Pittsburgh, 1953.

Terasawa, S.; Itsuki, H.; Yamaki, H. Gas Liquid Chromatographic Method for Determination of Partial Molar Free Energy at Infinite Dilution in Volatile Solvents and Its Application to Acetonitrile/Benzene Systems. *Anal. Chem.* **1986**, *58*, 3021–3027.

Thomas, E. R.; Eckert, C. A. Prediction of Limiting Activity Coefficients by a Modified Separation of Cohesive Energy Density

Model and UNIFAC. *Ind. Eng. Chem. Process Des. Dev.* **1984,** *23,* 194-209.

Thomas, E. R.; Newman, B. A.; Long, T. C.; Wood, D. A.; Eckert, C. A. Limiting Activity Coefficients of Nonpolar and Polar Solutes in Both Volatile and Nonvolatile Solvents. *J. Chem. Eng. Data* **1982,** *27,* 399-405.

Trampe, D. M.; Eckert, C. A. Limiting Activity Coefficients from an Improved Differential Boiling Point Technique. *J. Chem. Eng. Data* **1990,** *35,* 156-162.

Vernier, P.; Raimbault, C.; Renon, H. Proprietes Thermodynamique des Solutins Infinitiment Diluees D'Hydrocarbares dans les Solvants Polaires. *J. Chim. Phys. Physicochim. Biol.* **1969,** *66,* 429-436.

Weidlich, U.; Gmehling, J. Extension of UNIFAC by Headspace Gas Chromatography. *J. Chem. Eng. Data* **1985,** *30,* 95-101.

Weidlich, U.; Berg, J.; Gmehling, J. Extension of UNIFAC by Headspace Gas Chromatography. 2. *J. Chem. Eng. Data* **1986,** *31,* 313-317.

Wilhoit, R. C.; Zwolinski, B. J. Physical and Chemical Properties of Aliphatic Alcohols. *J. Phys. Chem. Ref. Data* **1973,** *2,* Suppl. 1.

Yang, Y.; Xiao, S.; Li, H.; Fu, Y. Measurement of Infinite Dilution Activity Coefficients by Nonsteady State Gas Chromatography. *Chengdu Keji Daxne Xuebao (J. Chengdu Univ. Sci. Technol.)* **1988,** *No. 1,* 35.

Yin, C.; Hassett, J. P. Gas Partitioning Approach for Laboratory and Field Studies of Mirex Fugacity in Water. *Environ. Sci. Technol.* **1986,** *20,* 1213-1217.

Reactivity of Technical Phosphorus Pentasulfide

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The reactivity of technical P_4S_{10} with alcohols or water, in either heterogeneous or homogeneous processes, is a direct function of its solidification rate, which determines to what extent the dissociated state prevailing in the molten sulfide is retained in the solid. ^{31}P NMR analysis reveals that quenched melts of P_4S_{10} contain more redox products P_4S_9, P_4S_7, and phosphorus polysulfides P_mS_y ($y/m >$ 2.5) but seemingly less elemental sulfur than slowly cooled (unquenched) or annealed specimens.

It has long been recognized that the reactivity of technical phosphorus pentasulfide with alcohols or water grows with the rate of its solidification (Robota, 1959; Moedritzer and Van Wazer, 1963; Cremer, 1965; Vincent, 1969; Cueilleron and Vincent, 1970; Childs, 1971) and is depleted by annealing (Robota, 1959; Roth and Taylor, 1960; Knapsack, 1965; Vincent, 1969; Niermann et al., 1979). Quenched grades of P_4S_{10} are commonly produced by cooling the molten sulfide from 310–350 °C to room temperature on a revolving drum, so as to obtain flakes with a thickness under 1 mm, which may ultimately be ground to powder; chilling devices giving thicker flakes (e.g., 3–5 mm) afford much less reactive grades, hereafter referred to as "unquenched".

Moedritzer and Van Wazer (1963) have shown that the reaction rate of a number of phosphorus sulfides—including P_4S_{10}, either pure recrystallized or quenched from the melt—with *n*-butanol is proportional to their surface area; patent data confirm these observations (Knapsack, 1965). The fact that the heterogeneous alcoholysis of P_4S_{10} is sensitive to soluble nucleophilic catalysts (Démarcq, 1972; see also supplementary material (see the paragraph at the end of the paper)) suggests that the above kinetics is not simply determined by the slow dissolution rate of the unreacted solid but is largely controlled by surface attack by the alcohol (or by the catalyst, affording soluble reactive intermediates). An alternative mechanism (Bencze, 1970), involving rapid dissolution of the phosphorus sulfide, followed by rate-limiting homogeneous alcoholysis, is not supported by our own experiments (unpublished).

The enhanced reactivity of quenched P_4S_{10} has been ascribed to its containing an amorphous phase (Cremer, 1965; Förthmann and Schneider, 1966; Childs, 1971). However, given the chemical inhomogeneity of technical P_4S_{10}—presence of redox dissociation products, especially P_4S_9 (Démarcq, 1981)—the question arose as to what ex-

tent its reactivity was dependent on its physical state (crystallinity, particle size, friability) or on its chemical composition. This prompted us to investigate the kinetics of the homogeneous alcoholysis and hydrolysis of this sulfide in relation to its NMR analysis.

Experimental Section

Materials. Technical phosphorus pentasulfide was obtained from Atochem and other commercial sources. Pure P_4S_{10} and P_4S_9 were prepared as previously described (Démarcq, 1990a). Pure P_4S_7 was a commercial product, further recrystallized from carbon disulfide. CS_2 was purified and dried as in prior work (Démarcq, 1987).

Procedures. The homogeneous alcoholysis of phosphorus sulfides was performed in carbon disulfide, using Bu^nOH as the alcohol; the concentration of the latter was monitored by measuring the IR absorptivity of the free OH vibration at 3640 cm^{-1} (accuracy ±ca. 3%). The results are shown in Figure 1.

For studying the homogeneous hydrolysis we used a two-phase procedure previously described (Démarcq, 1990a), in which a CS_2 solution of phosphorus sulfide is stirred with water and the extent of reaction determined by acidimetry of (water-soluble) hydrolysis products. Taking the solubility of phosphorus sulfides in water as negligible and the solubility of water in the organic phase as practically constant and equal to that in neat CS_2—i.e., 142 ppm at 25 °C—the process may be regarded as pseudo-one-phase and pseudo-first-order. The accuracy is about ±0.5%. The results are shown in Figure 2.

^{31}P NMR spectra were obtained at 121.5 MHz (Bruker AC 300 spectrometer) or at 80.76 MHz (Jeol FX 200) by using 2.5–3 g/L solutions (no insoluble residue) of phosphorus pentasulfide in carbon disulfide. The pulse angle was generally set to 30 or 70°, with the relaxation delay varying from 2 to 20 s and the acquisition time from 0.4 to 3.3 s. Chemical shifts are referenced to external 85%