Headspace Gas Chromatographic Measurements of Limiting Activity Coefficients of Eleven Alkanes in Organic Solvents at 25 °C. 1

Cecilia B. Castells,[†,‡] David I. Eikens,[†] and Peter W. Carr*[,†]

Department of Chemistry, Kolthoff and Smith Hall, University of Minnesota, 207 Pleasant Street, SE, Minneapolis, Minnesota 55455

In the present study we report the infinite dilution activity coefficients (γ^∞) of 11 alkanes in 67 organic liquids at 25 °C measured by fully automated headspace gas chromatography. This study is part of a more comprehensive one whose main objective is to compare the predictive ability of several semitheoretical models to estimate alkane γ^∞ values. To do this it is obviously necessary to collect reliable experimental data spanning a wide range of chemical properties. The solutes include five linear (pentane to nonane), four branched (2-methylpentane, 2,4-dimethylpentane, 2,5-dimethylhexane, 2,3,4-trimethylpentane), and two cyclic (cyclohexane and ethylcyclohexane) alkanes. The solvents include several homologous series: *n*-alkanes, 1-alkenes, *n*-alcohols, 2-ketones, nitriles, acetates, and 34 other common volatile and nonvolatile solvents. Several modifications introduced to the previously reported instrumentation and to the quantitation method are discussed. The data presented are the average of at least two independent measurements with a precision better than 5%.

Introduction

The classical method of measuring both liquid and vapor compositions in equilibrium is the most difficult but also the most accurate when the range of compositions studied is essentially close to the region of infinite dilution. However, since limiting activity coefficients are commonly obtained by extrapolating data taken at finite concentrations, it can take hours to obtain a single γ^∞ value. On the other hand, with highly improved techniques, such as chromatographic methods, accurate measurements at very low concentrations can be made directly with much less effort and time. Among the chromatographic methods, dynamic GC is now well established for determining various thermodynamic properties including activity coefficients, Henry's constants, and second virial coefficients (Conder and Young, 1979; Laub and Pecsok, 1978). This approach is a very precise (Wicarova et al., 1970) and relatively fast method, but, in principle, it is limited to volatile solutes and nonvolatile solvents. Another drawback of dynamic GC measurements with packed columns is the possibility of adsorption of the solute on the support or to the gas−liquid interface. If adsorption occurs, the activity coefficients must be corrected, since retention involves both solute/solvent interactions and adsorption (Martin, 1961; Locke, 1976; Berezkin, 1978; Zhang et al., 1993).

Headspace gas chromatography (HSGC) analysis is based on a method originally proposed by Witcherle and Hála (1963). Using this method, activity coefficients are determined by accurately sampling the vapor phase over the solution in equilibrium at constant temperature (Hachenberg and Schmidt, 1977; Ioffe and Vitenberg, 1982; Hussam and Carr, 1985). This is a very fast and reliable technique that has the advantage of being applicable to a wide range of solvent and solute volatilities (Park et al., 1987; Park, 1988). The only limitation in the number of data that can be collected in a single run is the number of solutes that can be separated on the GC column under optimized conditions. Also with HSGC the contribution of interfacial adsorption and of adsorption to the support is avoided. On the other hand, the main disadvantage of this technique, as compared to dynamic GC, is the fact that the detector must be accurately calibrated.

The goal of this research was to measure the γ^∞ values of alkane solutes in a variety of solvents by automated HSGC and verify the quality of the measurements. We chose a HSGC methodology based on the possibility of studying a range of solvents which differ greatly in their volatilities with a single, fast technique. The solutes include 11 linear, branched, and cyclic hydrocarbons. The solvents include several homologous series and several other chemically and industrially common solvents. The compilation of infinite dilution activity coefficients of Tiegs et al. (1986) includes hydrocarbons in various solvents obtained by many different techniques. However, thus far we have not found any experimental studies in which a large number of alkane γ^∞ values in an extensive group of solvents were measured by a single self-consistent methodology. Given the vast array of errors and technical problems which can be encountered in these very different methods, we felt that a database in which errors are controlled and self-similar could be uniquely valuable.

In part 1, the data collection is presented and discussed. Since several modifications of the instrument and measuring method were introduced, a verification of the quality of the measurements is also presented. In Part 2, we focus on the accuracy and precision of the data.

* To whom correspondence should be addressed. E-mail: carr@chem.umn.edu. Fax: 612-626-7541.
[†] University of Minnesota.
[‡] Permanent address: CIDEPINT and División Química Analítica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115 (1900) La Plata, Argentina.

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Table 1. Virial Corrections for Nonideal Gas Phases[a]

	virial correction for the solvent			
solute[b]	pentane	hexane	nonane	benzene
PN		1.026	1.028	1.024
HX	1.011	1.018	1.019	1.018
HP	1.004		1.006	1.006
OC	0.998	0.999	0.999	0.999
NN	0.995	0.995		0.995
MP	1.015	1.025	1.025	1.023
DP	1.012	1.016	1.017	1.016
CH	1.006	1.01	1.011	1.010

[a] Temperature is 298.15 K, and total pressure is 1 atm. [b] Solute denomination: PN, *n*-pentane; HX, *n*-hexane; HP, *n*-heptane; OC, *n*-octane; NN, *n*-nonane; MP, 2-methylpentane; DP, 2,4-dimethylpentane; CH, cyclohexane.

Theory

The equality of the fugacities of the components in phases in contact is the basic condition for phase equilibrium. For a solute i in liquid and vapor phases,

$$f_i^{\mathrm{v}} = f_i^{\mathrm{l}} \tag{1}$$

or

$$y_i\phi_i P = \gamma_i x_i f_i^{\circ} = \gamma_i x_i \phi_i^{\mathrm{sat}} P_i^{\mathrm{sat}} \exp[V^{\mathrm{l}}(P - P_i^{\mathrm{sat}})/RT] \tag{2}$$

where y_i and x_i are the solute molar fractions in the gas and liquid phases, respectively. ϕ_i and γ_i are the corresponding gas- and liquid-phase activity coefficients of solute i. P is the total pressure, f_i° is the fugacity of the solute as a pure liquid, ϕ_i^{sat} is the saturated vapor-phase fugacity coefficient, P_i^{sat} is the saturated vapor pressure at temperature T, V^{l} is the liquid-phase molar volume, and R is the gas constant. From eq 2,

$$\gamma_i = (\phi_i/\phi_i^{\mathrm{sat}})(P/P_i^{\mathrm{sat}})(y_i/x_i)(PF)_i \tag{3}$$

At pressures of only a few atmospheres, the Poynting factor (the exponential term in eq 2) is very close to unity and is usually ignored (Walas, 1985). The validity of this assumption was checked here for some combinations of solutes and solvents. Table 1 shows the magnitude of the corresponding corrections. For the calculations, the virial coefficients and the mixed virial coefficients were obtained from Laub and Pecsok (Laub and Pecsok, 1978). Nitrogen was used as the third component in order to approximate the air in the gas phase. Most corrections amounted to about 1−2% of the uncorrected values, which are negligible as compared to the precision of the measurements. Likewise, at moderate pressures the ratio of the fugacity coefficients is close to unity, so the expression for the activity coefficient reduces to

$$\gamma_i \approx (P/P_i^{\mathrm{sat}})(y_i/x_i) \tag{4}$$

At pressures affording ideal gas behavior, the partial pressure of the solute, y_iP, is

$$y_iP = C_i^{\mathrm{g}}RT \tag{5}$$

where C_i^{g} denotes the molar concentration of component i in the gas phase. By combining eqs 4 and 5, and working at $x_i \rightarrow 0$, the solute infinite dilution activity coefficient in the solution at temperature T is

$$\gamma_i^{\infty} = C_i^{\mathrm{g}}\, RT/(P_i^{\mathrm{sat}}x_i) \tag{6}$$

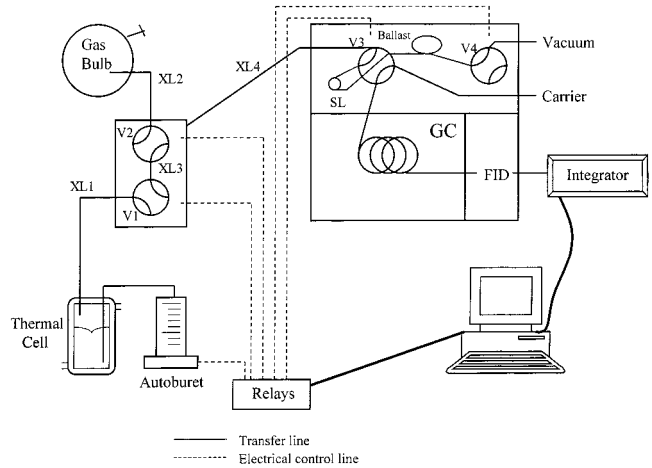

Figure 1. Headspace gas chromatograph. V denotes the valves (see the Experimental Section), XL show the transfer lines, and SL is the sample loop.

The partition coefficient K, defined as the ratio of molar concentrations of component i in liquid and vapor phases, $C_i^{\mathrm{l}}/C_i^{\mathrm{g}}$, is easily obtained as

$$K = RT/(P_i^{\mathrm{sat}}\,\gamma_i^{\infty}V^{\mathrm{l}}) \tag{7}$$

Experimental Section

Chemicals. All solutes and solvents used in this work were used as received from the supplier in the highest purity available. Solvent purity was verified either by injecting neat liquid onto a 15 m × 530 μm DB5 ID column (DB-5 J&W Scientific) or by analyzing samples drawn from the headspace over the pure solvent by HSGC.

Apparatus. The headspace chromatograph (HSGC) used in this study is similar to that described before which was used to measure vapor−liquid equilibria in several systems (Hussam and Carr, 1985; Park, 1988; Cheong, 1989; Li and Carr, 1993; Dallas, 1994). Several modifications are described here. A schematic of the instrument is shown in Figure 1. The main differences between previous and current HSGC equipment and procedures are as follows: the sampling valve (V1) was simplified, the method of altering the solute concentration in the equilibrium cell was improved (see below), and finally, all metal transfer lines were replaced with fused silica capillary tubing in order to minimize adsorption effects (Dallas and Carr, 1991). Briefly, the solute/solvent pairs under study are contained in the equilibrium cell (57 mL total volume) thermostated at (25.00 ± 0.02) °C by a large water bath (Model PTC-40 Temperature Controller, Tronac Inc.). The temperature was measured with a calibrated (±0.01 °C) calorimetric thermometer (Cat. No. 22630, Brooklyn Thermometer Company Inc.). The thermal cell is connected to a precalibrated automatic buret (Model ABU12, Radiometer) used to deliver aliquots of the solvent (5−10 mL). The autoburet was allowed to stay at room temperature except for solvents which boiled at <60 °C; when volatile solvents were used, the buret was wrapped in Tygon tubing and cooled by the flow of cold tap water. The headspace is sampled to the gas chromatograph (HP5790A, Hewlett-Packard) by a vacuum transfer system connected to the thermostated sample cell through a series of heated fused silica transfer lines. This sampling system consisted of two 4-port valves, V1 and V2 (Valco Instruments, Houston, TX) connected to the 6-port gas sampling valve, V3, and the 4-port gas sampling valve V4 of the gas analyzer. All valves

and transfer lines were heated at 170 ± 5 °C to avoid condensation and adsorption of vapors during the sampling process. The fused silica transfer lines were thread through 0.04 in. i.d. metal tubing, which was wrapped with heating tape. The loop volume was 100 μL. The solutes were separated in a (15 m × 530 μm i.d.) OV-1701 capillary column connected in series to a (15 m × 530 μm) DB-1701 column (DB-1701, J&W Scientific). The oven was programmed to hold at 40 °C for 2 min, then increase to 220 °C at 25 °C/min, and then hold at 220 °C for 1.6 min. For nonpolar solvents a 30 m × 530 μm i.d. DB-1 capillary column (DB-1, J&W Scientific) was used and the temperature program was as follows: hold at 40 °C for 0.5 min and then increase to 180 °C at 10 °C/min. For both temperature programs a 10-min cool down time is needed for the GC to return to 40 °C. Helium, previously passed through an oxygen and a moisture trap, was used as carrier gas. Detection was achieved with a flame ionization detector, and the signal recorded and integrated by a HP3390 or HP3396 integrator (Hewlett-Packard). A large glass gas bulb (12.408 L) maintained at (40 ± 1) °C was used to contain a known quantity of solute and used to calibrate the GC flame ionization detector (FID). The entire experiment was controlled by a Zenith Z-148 IBM-compatible microcomputer (Z149, Zenith Data Systems). A DT 2817 digital IO board is used to control the five relays, which control the autoburet, valves V1, V2, and V4, and the GC start. Valve V3 is controlled by the HP 5790 valve program. The integrator is interfaced to the computer via the RS232 serial port. Through serial communications the computer controls the start of the integrator and receives and stores the report after each run. The HSGC control program is written in Pascal (Borland Int., Turbo Pascal 4.0).

Sample Preparation. Stock liquid mixtures of the test solutes were prepared by weighting larger volumes of the less volatile solutes relative to the volume of the more volatile ones. This "unbalanced solute mixture" allowed us to measure similar peak sizes for all the solutes. 50.00 mL of solvent was placed in a volumetric flask, and 100−500 μL of the solute mixture was added by using a 10-mL gastight syringe (Precision Sampling Corp.). To keep the concentration of solute within the Henry's law region, the amount of solute mixture added depended on the expected partition coefficient in each solvent. All amounts were measured by weight differences.

Gas Standard Preparation. Stock solutions of the test solutes to be used in the FID calibration were prepared by weighing roughly equal volume amounts of each solute into a vial capped with a Teflon-faced silicone septum (Cat No. 2-3191, Supelco). For calculating the detector response, the gas bulb was placed under vacuum and then filled with 100 μL of the solute mixture by using a gastight syringe. The syringe weight difference was recorded to determine the amount of each solute added to the gas bulb. The sample is allowed to evaporate completely, so a known molar concentration of gas sample is generated.

Procedure. The method of varying the solute concentration in the thermal cell was modified significantly from that of previous work. A complete experimental run consisted of several steps. A prerun with a gas standard sample (three replicates) was done; from the average area and height counts of the gas standard replicates, the response factor (both area and height) for each solute was determined (Hussam et al., 1987). Next, a single sample of pure solvent headspace was taken to check its purity. We then pipetted 2−5 mL of the stock sample mixture into the equilibrium cell and allowed it to equilibrate for 30−60 min. Three replicate samples of the headspace vapor were taken. The concentration in the thermal cell was changed by addition of 5−10 mL of the pure solvent via the automatic buret and then vapor−liquid equilibrium was reestablished. Again three replicate headspace samples were injected. Each system was run at 4−7 different concentration levels. Finally, at the end of each run three replicates of the gas standard were taken and compared to the prerun gas standard to verify the integrity of the transfer lines common to the gas standard and the thermal cell. Typically agreement between the pre- and postrun gas standards was better than 1%.

Calculations. The average analytical measurements (areas or heights) for the triplicate samples of gas standard both before and after the run were used to obtain the response factor for each solute (RF_i). A correction due to the temperature difference between the gas bulb (40 °C) and the thermal cell (25 °C) was made (0.4%/°C for all species (Park, 1988)).

The raw analytical data at each concentration were analyzed according to the equation

$$S_k = (A_k - A_{ref})/(x_k - x_{ref}) \tag{8}$$

where S_k is the slope of either the area or the height (A_k) versus the solute mole fraction (x_k); the subscripts k and ref denote a concentration level k and a reference concentration ($x_{ref} \neq 0$), respectively. All calculations were done with both peak area and peak heights. For poorly resolved peaks, height measurements are clearly more accurate (Snyder and Kirkland, 1979). The calculation of the slopes based on a reference solute concentration (x_{ref}) is done for several reasons. First, a value of S_k independent of mole fraction indicates that the results were obtained under Henry's law conditions and that the detector response was linear. Those points not in the linear portion of the curve were removed. Second, the use of an $x_{ref} \neq 0$ should minimize errors due to small solvent impurities not detected in blank runs and eluting at the same time as the solute. It should be noted that the use of infinite dilution made the peak quite small (sometimes only a few hundred or thousand counts) and trace solvent impurities of only tens of counts could be problematic.

Finally, considering the decrease in the precision of the peak area or peak height at low concentrations, a weighted average of the slopes was used in the calculation of γ^∞. The slopes were weighted according to the standard deviation (sd_s) of the three replicate determinations at each concentration as follow:

$$S_{avg} = (1/W_T)\sum S_k(1/sd_s^2) \tag{9}$$

where $W_T = \sum(1/sd_s^2)$. The infinite dilution activity coefficients were calculated by combining eqs 6 and 8,

$$\gamma_i^\infty = RTS_{avg}/(P_i^{sat}RF_i) \tag{10}$$

Results and Discussion

One of the major difficulties in measuring accurate γ^∞ values is gathering data at concentrations where the solute is actually at infinite dilution. Due to analytical limitations, most classical methods involve working at a finite concentration range (usually $x > 0.05$), and various extrapolation techniques are then used to estimate the desired thermodynamic parameter in very dilute solution. However, infinite dilution activity coefficients so obtained are highly dependent on the equation used to fit the data and on the

Table 2. Recommended Values of the Infinite Dilution Activity Coefficients of Alkanes at 25 °C and 1 atm

solvent	coefficient[b] for the solute[a]										
	PN	HX	HP	OC	NN	MP	DP	DH	TP	CH	EC
1. pentane	1.05[m,c]	1.12[m]	1.14	1.22	1.21	0.98	1.12	1.16	1.22	1.30	1.40
2. hexane	0.99	1.02[m]	0.97	1.09	1.02	1.00	0.89	1.07	1.10	1.14	1.19
3. heptane	0.99	1.04	1.05[m]	1.07	1.05[m]	1.04	1.06	1.11	1.07	1.10	1.13
4. octane	0.98	1.03	1.05	1.07[m]	1.09	1.03	1.07	1.08[m]	1.06	1.05	1.01
5. nonane	0.95	1.01	1.03	1.12	1.14[m]	1.00	1.04	1.06	1.03	0.99	1.03
6. decane	0.88	0.99	0.98	1.05	1.18	1.00	1.04	1.06	1.01	0.95	1.02
7. dodecane	0.88	1.00	1.01	1.04	1.06	1.02	1.07	1.09	1.01	0.94	0.97
8. hexadecane	0.84	0.90	0.92	0.96	0.99	0.91	0.99	1.02	0.94	0.80	0.85
9. cyclohexane	1.22[m]	1.18	1.13	1.13	1.01	1.20	1.18	1.20	1.16	1.08[m]	1.05
10. squalane	0.58	0.65	0.70	0.71	0.68	0.65	0.72	0.77	0.68	0.53	0.59
11. 2,2,4-trimethylpentane	0.93	1.02	1.07[m]	1.11	1.16	1.01	1.05	1.06	1.08	1.06	1.20
12. methanol	18.42[m]	25.89	35.14	48.02	64.79	23.90	30.09	39.65	37.16	22.55	39.07
13. ethanol	7.78[c]	10.59	13.07	16.12	19.65	10.23[m]	11.85	14.31	13.35	9.24	13.43
14. propanol	5.11	6.73	7.91	9.52	11.83	6.47	7.47	8.61	8.05	5.74[m]	7.85
15. butanol	4.03	5.12	5.86	6.86	8.19	5.00	5.62	6.37	5.93	4.30	5.71
16. octanol	2.22	2.67	3.00	3.38	3.78	2.66	3.02	3.38	3.05	2.24	2.75
17. 2-propanol	5.39	6.53[m]	7.96	9.60	10.85	6.49	7.43	8.75	8.27	5.97	8.28
18. 1-hexene	1.03	1.10[m]	1.14	1.18	1.15	1.07	1.22[m]	1.15	1.17	1.21	1.28
19. 1-octene	0.97	1.02[m]	1.05	1.13[m]	1.19	1.04	1.07	1.09	1.07	1.04	1.12
20. 1-decene	0.93	0.86	1.00	1.03[m]	1.09	1.00	1.05	1.06	1.03	0.95	1.00
21. acetone	5.14	7.15[m]	8.45	10.58	12.86	6.89	7.67	9.38	8.71	6.52	9.35
22. 2-butanone	3.39	4.09	4.22	5.28	6.03	4.00	4.35	4.88	4.63	3.78	4.79
23. 2-pentanone	2.58	3.01	3.33	3.70	4.29	2.95	3.21	3.50	3.29	2.79	3.39
24. 2-heptanone	1.88	2.21	2.41	2.72	3.09	2.19	2.39	2.59	2.43	1.99	2.40
25. acetonitrile	17.04	27.97	39.55	56.51	78.75	25.22	33.61[m]	46.90	40.27	22.30	41.88
26. propionitrile	7.76[c]	10.94	13.86	17.73	22.47	10.35	12.54	15.19	14.37	9.08	14.03
27. butyronitrile	4.96	6.48	7.76	9.29	11.11	6.24	7.19	8.51	7.71	5.46	7.64
28. pentadecanenitrile	1.31	1.49	1.62	1.74[m]	1.88	1.50	1.69	1.85	1.61	1.24	1.39
29. methyl acetate	4.61	5.86	7.13	8.53	10.34	5.53	6.31	7.50	6.89	5.28	7.43
30. ethyl acetate	3.02	3.60	3.82	4.83	5.43	3.44	3.81	4.33	4.07	3.37[m]	4.30
31. butyl acetate	1.92	2.17	2.48[m]	2.78	3.09[m]	2.13	2.30	2.50	2.37	1.96	2.42
32. hexyl acetate	1.48	1.68	1.82	1.97	2.15	1.66	1.66	1.92	1.79	1.51	1.74
33. ethyl butyrate	1.73	1.97	1.99	2.40	2.66	1.93	2.08	2.25	2.17	1.86[m]	2.21
34. benzene	2.04	2.11[m]	2.06	2.31	2.37	2.25	2.42	2.19[m]	2.26	1.75	1.99
35. toluene	1.68	1.74	1.76	1.75	1.84	1.83	1.92	1.91	1.86	1.56	1.64
36. *p*-xylene	1.46	1.51	1.51	1.55	1.66	1.58	1.66	1.66	1.60	1.42	1.47
37. benzyl alcohol	9.83[c]	12.82	16.70	21.00	26.51	12.84	17.00	21.60	16.81[m]	7.96	12.88
38. nitrobenzene	6.56	8.17	9.47	10.91	12.48	8.30	10.02	11.90	9.99	6.12	8.08
39. anisole	3.32	3.79	4.16	4.52	4.88	3.87	4.38	4.77	4.27	2.83	3.45
40. benzonitrile	5.16	6.25	7.18	8.28	9.63	6.47	7.87	9.18	7.90	4.83	6.48
41. acetophenone	5.23	6.39	7.36	8.58	9.75	6.57	7.98	9.35	7.82	4.60	6.11
42. chlorobenzene	2.15	2.22	2.22	2.28	2.18	2.33	2.49	2.48	2.34	1.81	1.98
43. *N*-methylformamide	22.84	37.14	55.57	81.27	115.83	34.48	48.41	70.27	56.82	23.32	45.76
44. dimethylformamide	11.75	17.11	23.31	30.97	40.94	16.21	21.19	28.20	23.58	12.09	20.25
45. dimethylacetamide	8.46	11.31	14.59	18.53	23.44	10.96	13.78	17.32	14.68	8.26	12.89
46. *N*-methylpyrrolidone	9.60	13.13	16.77	21.26	26.69	12.70	16.11	20.21	16.54	8.31	12.93
47. dimethylsulfoxide	42.40[c]	68.68[c]	108.22	171.68	264.98	60.38	95.88	153.28	119.25	35.47	83.50
48. acetic acid	11.65	16.26[m]	22.52	29.01	37.62	16.16[m]	19.26	25.67	21.24	14.64	22.64
49. methylene chloride	3.22	3.42[m]	3.44	3.95	4.16	3.51	3.60	3.78	3.59	2.91	3.39
50. chloroform	1.96	2.03	2.06[m]	2.06	2.07	2.12[m]	2.12	2.07	2.00	1.66	1.87
51. carbon tetrachloride	1.33	1.35	1.34[m]	1.33	1.28	1.41	1.45	1.38	1.36	1.10	1.23
52. 1,2-dichloroethane	4.50[c]	5.17	5.80	6.43	7.16	5.11	5.64[m]	6.16	5.61	3.82	4.94
53. tetrahydrofuran	2.07	2.19	2.29[m]	2.33	2.45	2.17	2.16	2.20	2.18	1.87	2.14
54. *p*-dioxane	5.51	6.70	7.61	8.90	10.42	6.60	7.86	8.51	7.68	4.96	6.84
55. triethylamine	1.03	1.07	1.08[m]	1.09	1.10	1.08	1.08	1.14[m]	1.09	1.22	1.09
56. γ-butyrolactone	23.08[c]	35.06	51.45	75.85	106.95	32.20	45.67	66.79	53.11	20.91	41.95
57. hexamethylphosphoramide	3.15	3.94	4.69	5.57	6.62	3.86	4.56	5.43	4.78	2.80	3.96
58. trifluoroethanol	23.72	42.44	68.82	113.42	181.37	35.14	47.07	76.09	66.78	39.39[m]	87.76
59. hexafluoro-2-propanol	4.31[c]	24.07[c]	39.38	64.96	104.02	17.97	24.87	41.35	37.56	24.94	56.83
60. perfluorohexane	4.60	7.41	11.85	18.15	27.30	6.29	7.81	12.02	11.39	9.90	19.04
61. perfluorooctane	4.42	6.94	11.36	17.00	25.44	5.98	7.49	11.55	10.55	9.07	16.97
62. nitromethane	31.47[c]	50.32	80.04	125.57	190.86	43.66	61.59	96.23	79.17	36.68	78.93
63. nitropropane	5.35	7.08	8.58[m]	10.60	12.71	6.70	7.76	8.98	8.27	5.63	8.15
64. carbon disulfide	2.46	2.38	2.24	2.16	1.98	2.39[m]	2.73	2.51	2.46	1.63	1.73
65. cyclohexanone	3.69	4.30	4.83	5.33	5.96	4.21	4.62	5.09	4.66	3.00	3.96
66. propylene carbonate	25.80[c]	40.76	64.80	99.49	150.98	36.62	53.32	83.00	64.35	24.99	53.99
67. pyridine	5.40	6.52	7.43	8.52	9.69	6.67	7.88	8.28[m]	7.85	4.45	6.04

[a] Solute abbreviations: PN, *n*-pentane; HX, *n*-hexane; HP, *n*-heptane; OC, *n*-octane; NN, *n*-nonane; MP, 2-methylpentane; DP, 2,4-dimethylpentane; DH, 2,5-dimethylhexane; TP, 2,3,4-trimethylpentane; CH, cyclohexane; EC, ethylcyclohexane. [b] Modified values are marked with a superscript m (originally missed or outliers) or c (corrected for loss to the gas phase). See the text.

experimental concentration range studied. The extremely high sensitivity of the gas chromatograph with a flame ionization detector (FID) allows HSGC to be done at very low solute concentrations. The working range for all mixtures studied here was kept between 10^{-4} and 10^{-3} mole fraction. The main limitation in studying such dilute

Table 3. Regression Results of ln *K* versus *n*-Alkane Carbon Number at 25 °C and 1 atm Total Pressure

solvent	intercept	slope	s.e.[a]	R^b	N^c
pentane	−0.1 (0.2)[d]	1.16 (0.02)[d]	0.032	0.9998	3
hexane	−0.3 (0.1)	1.18 (0.02)	0.056	0.9997	4
heptane	−0.36 (0.01)	1.174 (0.002)	0.005	1.0000	3
octane	−0.43 (0.02)	1.171 (0.002)	0.007	1.0000	4
nonane	−0.37 (0.08)	1.15 (0.01)	0.026	0.9999	4
decane	−0.31 (0.09)	1.13 (0.01)	0.040	0.9998	5
dodecane	−0.60 (0.06)	1.153 (0.009)	0.028	0.9999	5
hexadecane	−0.78 (0.02)	1.156 (0.003)	0.008	1.0000	5
cyclohexane	−0.57 (0.09)	1.24 (0.01)	0.029	0.9999	4
squalane	−1.0 (0.1)	1.15 (0.02)	0.048	0.9997	5
2,2,4-trimethylpentane	−0.26 (0.02)	1.143 (0.002)	0.006	1.0000	4
methanol	−0.53 (0.02)	0.883 (0.003)	0.006	1.0000	4
ethanol	−0.49 (0.06)	0.968 (0.008)	0.026	0.9999	5
propanol	−0.43 (0.05)	0.993 (0.007)	0.024	0.9999	5
1-butanol	−0.56 (0.05)	1.025 (0.007)	0.021	0.9999	5
1-octanol	−0.71 (0.03)	1.066 (0.004)	0.014	1.0000	5
2-propanol	−0.63 (0.06)	1.019 (0.008)	0.024	0.9999	4
1-hexene	−0.21 (0.06)	1.168 (0.007)	0.022	1.0000	4
1-octene	−0.23 (0.09)	1.15 (0.01)	0.038	0.9999	3
1-decene	−0.4 (0.1)	1.15 (0.03)	0.074	0.9995	4
acetone	−0.28 (0.04)	0.966 (0.005)	0.014	1.0000	4
2-butanone	−0.5 (0.1)	1.06 (0.02)	0.054	0.9996	5
2-pentanone	−0.49 (0.04)	1.073 (0.006)	0.018	1.0000	5
2-heptanone	−0.46 (0.04)	1.076 (0.005)	0.016	1.0000	5
acetonitrile	−0.39 (0.08)	0.81 (0.01)	0.034	0.9998	4
propionitrile	−0.51 (0.06)	0.935 (0.008)	0.026	0.9999	5
butyronitrile	−0.59 (0.06)	0.998 (0.008)	0.024	0.9999	4
pentadecanenitrile	−0.92 (0.02)	1.108 (0.003)	0.010	1.0000	5
methyl acetate	−0.40 (0.02)	0.997 (0.002)	0.008	1.0000	5
ethyl acetate	−0.4 (0.1)	1.05 (0.02)	0.047	0.9997	5
butyl acetate	−0.41 (0.04)	1.076 (0.005)	0.016	1.0000	3
hexyl acetate	−0.54 (0.01)	1.105 (0.002)	0.006	1.0000	5
ethyl butyrate	−0.4 (0.1)	1.09 (0.02)	0.050	0.9997	5
benzene	−0.5 (0.1)	1.16 (0.02)	0.056	0.9997	4
toluene	−0.57 (0.04)	1.178 (0.006)	0.019	1.0000	5
p-xylene	−0.52 (0.06)	1.168 (0.008)	0.025	0.9999	5
benzyl alcohol	−1.17 (0.03)	0.948 (0.004)	0.008	1.0000	4
nitrobenzene	−1.22 (0.04)	1.038 (0.006)	0.017	1.0000	5
anisole	−0.91 (0.02)	1.101 (0.002)	0.007	1.0000	5
benzonitrile	−0.99 (0.02)	1.043 (0.002)	0.007	1.0000	5
acetophenone	−1.14 (0.03)	1.042 (0.004)	0.011	1.0000	5
chlorobenzene	−0.85 (0.05)	1.191 (0.006)	0.020	1.0000	5
N-methylformamide	−0.71 (0.07)	0.79 (0.01)	0.033	0.9997	5
dimethylformamide	−0.77 (0.05)	0.887 (0.007)	0.023	0.9999	5
dimethylacetamide	−0.89 (0.02)	0.943 (0.002)	0.007	1.0000	5
N-methylpyrrolidone	−1.07 (0.04)	0.943 (0.006)	0.017	0.9999	5
dimethylsulfoxide	−1.20 (0.07)	0.738 (0.008)	0.012	0.9999	3
acetic acid	−0.54 (0.07)	0.90 (0.01)	0.029	0.9999	4
methylene chloride	−0.5 (0.1)	1.13 (0.02)	0.055	0.9997	4
chloroform	−0.478 (0.004)	1.183 (0.001)	0.002	1.0000	4
carbon tetrachloride	−0.39 (0.03)	1.206 (0.004)	0.012	1.0000	4
1,2-dichloroethane	−0.783 (0.002)	1.081 (0.001)	0.000	1.0000	4
tetrahydrofuran	−0.40 (0.03)	1.156 (0.004)	0.011	1.0000	4
p-dioxane	−0.86 (0.03)	1.040 (0.004)	0.014	1.0000	5
triethylamine	−0.379 (0.006)	1.181 (0.001)	0.003	1.0000	4
γ-butyrolactone	−1.07 (0.05)	0.815 (0.006)	0.014	0.9999	4
hexamethylphosphoramide	−0.89 (0.02)	1.012 (0.002)	0.007	1.0000	5
trifluoroethanol	−0.43 (0.06)	0.691 (0.008)	0.024	0.9998	5
hexafluoro-2-propanol	−0.32 (0.07)	0.700 (0.009)	0.013	0.9999	3
perfluorohexane	−0.07 (0.04)	0.750 (0.005)	0.017	0.9999	5
perfluorooctane	−0.29 (0.06)	0.756 (0.008)	0.026	0.9998	5
nitromethane	−0.66 (0.05)	0.744 (0.006)	0.014	0.9999	4
nitropropane	−0.60 (0.06)	0.982 (0.008)	0.024	0.9999	4
carbon disulfide	−0.74 (0.03)	1.248 (0.004)	0.013	1.0000	5
cyclohexanone	−0.85 (0.01)	1.079 (0.002)	0.005	1.0000	5
propylene carbonate	−0.97 (0.04)	0.753 (0.006)	0.013	0.9999	4
pyridine	−0.85 (0.02)	1.052 (0.003)	0.009	1.0000	5

[a] Standard deviation of the fit. [b] Correlation coefficient. [c] Number of data. [d] The standard deviations for the coefficients are given in parentheses.

solutions was the accuracy in determining the weight of the sample for the more volatile liquids. Moreover, the linearity between concentration in the vapor phase and in the liquid phase was carefully checked for each solute/solvent pair.

Other primary concerns are the complete and reproducible transfer of the headspace sample from the equilibrium cell with minimal disturbance of the equilibrium and the measurement of accurate and reproducible detector response factors. The main features of the headspace device

Table 4. Regression Results for ln K of a Solute versus the Corresponding Value for a Reference Solute

solute[a]	reference solute	slope	intercept	s.e.[b]	correlation coefficient	N[c]
PN	HP	0.726 (0.008)[d]	−0.26 (0.06)	0.077	0.996	67
HX	HP	0.866 (0.005)	−0.16 (0.03)	0.045	0.999	67
OC	HP	1.117 (0.006)	0.24 (0.04)	0.051	0.999	67
NN	HP	1.24 (0.01)	0.46 (0.06)	0.087	0.998	67
MP	HP	0.825 (0.009)	−0.20 (0.06)	0.084	0.996	63
DP	HP	0.92 (0.01)	−0.17 (0.07)	0.093	0.996	64
DH	HP	1.043 (0.007)	0.02 (0.05)	0.061	0.999	63
TP	HP	0.991 (0.005)	0.57 (0.03)	0.041	0.999	66
CH	HP	0.78 (0.02)	1.0 (0.1)	0.137	0.987	62
EC	HP	1.00 (0.02)	1.3 (0.1)	0.153	0.991	67
CH	EC	0.792 (0.006)	−0.10 (0.05)	0.052	0.998	62

[a] Solute abbreviations as in Table 1. [b] Standard error of the fit. [c] Number of solvents in the correlation. [d] Standard deviations of the coefficients are given in parentheses.

used in this work have been previously discussed, and the entire procedure has been validated by means of several vapor/liquid equilibrium measurements (Hussam and Carr, 1985; Park et al., 1987; Cheong and Carr, 1990; Dallas and Carr, 1992; Li and Carr, 1993; Dallas and Carr, 1994). The major instrumental modification introduced in this study was to replace the nickel transfer lines by fused silica capillaries to reduce wall adsorption. Similarly, the Teflon minivalve for sample introduction in the gas bulb was isolated to avoid the adsorption of alkane vapors on its surface (Grob Jr. and Grob, 1978; Dallas and Carr, 1991).

One of the main differences in operation between this work and the previous reports lies in the procedure for varying the solute concentrations in the equilibrium cell. Previously, a fixed volume of solvent was weighed into the equilibrium cell and then increments of about 30−100 μL of the solute mixture were added via an automated 250 μL buret. However, the precision of the autoburet deliveries was found to be limited to about 5%. In this modified procedure, the initial solution containing the solute mixture is subsequently diluted with volumes of 5 to 10 mL of solvent added to the thermal cell through a calibrated automatic buret (50 mL) whose precision was better than 1%.

Recommended Infinite Dilution Activity Coefficient Values. Table 2 gives the γ^∞ values for the 11 alkanes in 67 solvents at 25 °C obtained in this study. The corresponding partition coefficients can be easily calculated from this set of data by using eq 7. The γ^∞ values are, in most cases, an average of at least two entirely separate replicate runs, and the percent relative standard deviation of this average never exceeded 3−4%. 1,1,1,3,3,3-Hexafluoro-2-propanol was the only solvent which was run only once due to its high cost. A more detailed study of the precision and accuracy of these data is presented in the following paper (Part 2). The identifying footnotes on some of the reported data indicate that the value presented was originally missed or modified in some way. *A modification of the raw analytical results was made for one of two reasons.* First, some γ^∞ values could not be measured or were obvious outliers. In most cases this was due to solvent overlap. To form a complete matrix for further data analysis, the missing values were estimated by two different techniques. For the *n*-alkanes the missing values were estimated by use of the well-known Martin equation, which predicts a linear relationship between ln K and the number of methylene groups in the solute. Table 3 shows the results of the regression analysis. The correlation between the ln K of normal alkanes and their respective carbon numbers is excellent. For all solvents the correlation coefficients were greater than 0.999. On the basis of this linear relationship the missing or outlying γ^∞ values of normal alkanes could be easily estimated. This equation could also be used to estimate γ^∞ values of somewhat shorter and longer alkanes if needed.

A linear relationship between ln K and the number of carbons does not exist for branched and cyclic alkanes. For these solutes the best predictor of their partition coefficients is the partition coefficient of another similar alkane in the same solvent. Table 4 shows the regression analysis of the ln K values of the branched and cyclic solutes versus the ln K of *n*-heptane in all the solvents. Regressions of branched alkanes have correlation coefficients better than 0.996. On the basis of these results, the missing γ^∞ values of branched solutes were replaced by estimates based on these regressions and the measured ln K of *n*-heptane in the same solvent. A similar regression analysis with cyclohexane and ethylcyclohexane gave poorer standard deviations (see Table 4). A plot of the data shows that the fluorinated solvents form a separate group clearly off the regression line. However, the ln K of ethylcyclohexane is a very good predictor of the ln K of cyclohexane: the correlation coefficient for 62 data points is 0.998. Missing and outlying γ^∞ values of cyclohexane were obtained from data for ethylcyclohexane in the corresponding solvent.

Second, in the data reported, the number of moles of the solute in the liquid phase was assumed to be constant throughout the experimental run and equal to the total number of moles added to the equilibrium cell. For solute/solvent combinations where the K is relatively large, this assumption is clearly correct. However, for highly nonideal mixtures (net low K) this approximation is not valid, since there is a non-negligible loss of solute to the gas phase and a correction becomes necessary. In fact, some correction is built into the calculation of the slope for the area versus liquid mole fraction relationship if the reference level is chosen at the lower concentration of the solute and only low concentration levels are used. Since the loss of solute to the gas phase is minimized with a low gas to liquid volume ratio, the low concentration levels are least influenced by this loss.

Most of the data reported here were not corrected for loss of solute to the gas phase. In all but six solvents, the partition coefficients for *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane are greater than 50. At this level the correction is very small (<2%). An estimate of the corrected partition coefficient for *n*-pentane can be determined by extrapolation from the ln K against solute carbon number regressions. In Table 5 we compare the corrected and uncorrected activity coefficient values for *n*-pentane and *n*-hexane in solvents where K is up to 100. The corrected values are identified as such in Table 2.

Table 5. Estimates of Corrected Activity Coefficients Due to Loss to the Gas Phase

solute/solvent no.[a]	uncorrected γ^∞	corrected γ^∞ [b]	$-\Delta\%$[c]
PN/13	7.55	7.78	3
PN/26	7.54	7.76	3
PN/37	8.79	9.83	11
PN/47	34.9	42.4	18
PN/56	21.1	23.1	9
PN/59	11.5	14.3	20
PN/62	27.5	31.5	13
PN/66	22.6	25.8	12
HX/46	13.1	13.3	0.2
HX/47	64.3	68.9	7
HX/59	22.6	24.1	7

[a] Solute abbreviation and solvent number as in Table 1. [b] Values obtained from extrapolations as indicated in the Results and Discussion section. [c] $\Delta\% = 100(\gamma^\infty_{\text{uncorrected}} - \gamma^\infty_{\text{corrected}})/\gamma^\infty_{\text{uncorrected}}$.

Conclusions

In this paper we present the infinite dilution activity coefficients of alkanes in an extensive group of organic liquids measured by automated headspace gas chromatography at 25 °C. The HSGC method measures the concentration of the solutes in the gas phase in equilibrium with the liquid phase. The solute losses to the gas phase from the liquid phase were less than 1% for systems whose partition coefficients are greater than 100. A correction was introduced in those systems where a significant amount of solute is transferred to the gas phase, that is, for partition coefficients less than 100. Finally, the data matrix was completed by estimating missing and outlying values on the basis of linear relationships between ln K and the number of carbon atoms of *n*-alkanes or with other partition coefficients.

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