Headspace Gas Chromatographic Measurements of Limiting Activity Coefficients of Eleven Alkanes in Organic Solvents at 25 °C. 2. Accuracy and Precision

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The accuracy of the infinite dilution activity coefficients reported in Part 1 is examined here through two independent tests. First, the data are critically compared to values reported in the literature which were obtained by several different techniques, including headspace gas chromatography. Second, the data are validated by studying the consistency between our partition coefficient data for normal alkanes (*n*-pentane to *n*-nonane) and those obtained for the solutes methane to butane by completely different methods. A long-term study performed by using *n*-hexadecane as a solvent allowed us to control the consistency of this set of measurements and also established that the precision of the method is better than 5%.

Introduction

The determination of limiting activity coefficients (γ^∞) involves the measurement of mixtures in which one component is at very low concentration. Since the applicability of a measurement technique for γ^∞ of mixtures of nonelectrolytes depends primarily on the volatility of the solute and solvent, no experimental methods can be universal. Besides the traditional static techniques, the other most developed methods include dynamic gas chromatography (Laub and Pecsok, 1978; Conder and Young, 1979), gas stripping (Leroi et al., 1977; Richon et al., 1980; Li et al., 1993), non-steady-state gas chromatography (Belfer and Locke, 1984), liquid−liquid chromatography (Locke, 1968; Alessi and Kikic, 1974), differential ebulliometry (Thomas et al., 1982b; Trampe and Eckert, 1990), and headspace gas chromatography (Ioffe and Vitenberg, 1982; Hussam and Carr, 1985). Some comprehensive reviews can be found in (McGlashan (1979), Tiegs et al. (1986), and Hait et al. (1993)). In a comparison of the accuracy of γ^∞ values obtained by the most common methods, Kikic et al. (1983) assigned similar standard deviations (0.01−0.05) to ln γ^∞ values measured by dynamic GC, gas stripping, and ebulliometry. However, for dynamic GC only the uncertainties associated with measured quantities were taken into account and effects such as interfacial and solid support adsorption were omitted. Dynamic GC is fast and accurate (2%) for volatile solutes in nonvolatile solvents provided that the corrections for interfacial adsorption contributions to retention are adequately introduced. However, for volatile solvents, the error involved in the measurement of the amount of stationary phase significantly increases the uncertainty. Despite presaturation of the carrier gas with the volatile solvent, an estimated accuracy of about 15% has been reported (Thomas et al., 1982a).

An alternative method for the determination of γ^∞ of solutes in volatile solvents is headspace gas chromatography (HSGC). The main features of the method are accuracy, precision, number of γ^∞ values obtainable per day, applicability to relatively volatile solvents, and feasibility of automating the whole procedure. Several variants of this technique have been used in the determination of partition coefficients (Rohrschneider, 1973; Ioffe and Vitenberg, 1982; Hussam and Carr, 1985; Park et al., 1987; Guitart et al., 1989; Kolb et al., 1992; Ettre et al., 1993) and of activity coefficients for binary or tertiary mixtures over the whole range of compositions (Milanová and Cave, 1982; Shaw and Anderson, 1983).

In Part 1, we presented an extensive database of infinite dilution activity coefficients of five normal, four branched, and two cyclic alkanes in 67 organic solvents at 25 °C, all measured by equilibrium headspace gas chromatography. The quality of these data is discussed here in detail.

The accuracy of the γ^∞ values can be estimated, at least in principle, by direct comparison with literature data. A very complete compilation of activity coefficient data was established in the DECHEMA Data Bank (Tiegs et al., 1986), which gathers all the experimental γ^∞ values previously reported in the literature. Most data there were acquired by dynamic GC, which reflects the importance of this technique in the development of extensive databases. However, these limiting activity coefficients often differ greatly in accuracy and reliability, even those values obtained by the same experimental method. As an example, in the Data Bank there exist three γ^∞ values for cyclohexane in dimethylformamide at 25 °C, all collected by dynamic GC measurements, with differences as large as 100%. This extremely high uncertainty makes it very difficult to compare with certainty the agreement between our data and that previously reported. Linearity between the ln K and the number of carbon atoms of normal alkane solutes in a given solvent can be used to evaluate the self-consistency of the data. Although the linearity is only crude, it does provide a useful guide to help discern suspect data. Plots of this type were constructed with our data and with data collected from the literature, and the plots were

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Table 1. Precision Estimated for Each Measurement Step

procedure	estimated precision
sample preparation	0.05−0.1%
gas standard preparation	1%
automatic buret deliveries	1%
peak area or peak height determinations	1%

used as a method to test the quality of the data. An additional method to estimate the accuracy of the data is to examine the predicted γ^∞ for a solute in itself. Using the Raoult law standard state, the activity coefficient for a solute in itself must be exactly unity. Six of the 11 solutes were also used as solvents; thus, this information will be used to predict an "experimental γ^∞ value" for a solute in itself. Any difference from unity constitutes an estimate of the accuracy of the experimental data.

Finally, the consistency of the database is validated by comparison of the trends established by data obtained from other sources. From Ostwald solubility data for methane through *n*-butane, partition coefficients were calculated and compared to the values obtained by HSGC for *n*-pentane through *n*-nonane in the same solvents. Continuity of ln *K* versus solute carbon number within the two set of data is an indication of the consistency of the data.

The precision of the data was also critically evaluated. An estimation of the relative experimental uncertainty associated with each independent measurement is presented. To evaluate the effects of long-term variations associated with the experimental variables, especially those affecting the detector response, periodic measurements of activity coefficients of all the solutes in *n*-hexadecane were conducted. According to the results of this long-term study, the precision of the direct HSGC methodology was estimated at about 5%.

Results and Discussion

Precision of HSGC Measurements. The analytical determinations were carried out under constant instrumental conditions for the 11 solutes in a given solvent. The instrument was fully automated. Vapor-phase samples were transferred to the chromatograph under computer control by using a sampling loop. This methodology is much more precise than manual injection, and more important, it eliminates operator errors. In accord with the relative standard deviations, the within run repeatibility of the activity coefficient data is typically better than 2%, while the reproducibility of the data between runs is typically 3%. In Table 1 we show the relative standard deviation associated with each of the manual steps. Clearly, the major contributions to the error in the experimental procedure are the manual gas standard preparation necessary to calibrate the FID detector and the variability in the peak signal.

Indirect HSGC techniques have the advantage that no detector calibration is required (Ioffe and Vitenberg, 1982; Ettre et al., 1993; Chai and Zhu, 1998). The determination of the partition coefficient is based on the independent measurements (at least two) of the headspace solute concentration from two sealed vials containing different masses of solute or different volume ratios. The partition coefficient is obtained from the differences in the signals produced by the vapor-phase solute concentration in these vials. However, the method is not accurate when those differences are small, that is, when large partition coefficients (K > 100) are measured (Ettre et al., 1993). In a recent study, Chai et al. (1998) found that the measurement precision was highly dependent both on the partition coefficient magnitude and on the volume ratios. They also suggested that a very large volume ratio between vials is essential in order to obtain acceptable precision when K is >200. However, this strategy becomes very impractical for simultaneously measuring the headspace concentration of several infinitely dilute solutes having very different partition coefficients.

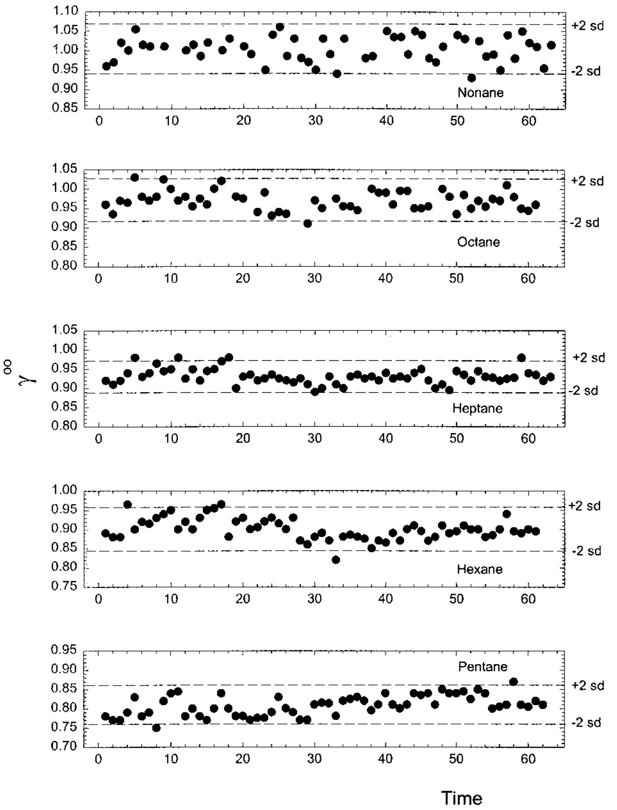

Figure 1. Long-term stability of γ^∞ values of *n*-alkanes in *n*-hexadecane.

We also performed a long-term study, which consisted of periodically measuring the partition coefficient of the solutes in *n*-hexadecane, with two objectives in mind. First, we wanted to check the integrity and consistency of the measurements and track possible problems with the instrument and the analytical procedures throughout this lengthy set of experiments. Second, we wanted to estimate the precision of the direct HSGC methodology proposed in Part 1 over a long period of time. To do this, the whole HSGC analysis was performed by running the solvent *n*-hexadecane after every third or fourth solvent. *n*-Hexadecane was chosen as a reference solvent because there exist several reliable sources for dilute activity coefficients of alkanes in this solvent measured by different techniques (Dallas and Carr, 1994). The results of this performance study are shown in Figures 1 and 2. The activity coefficient values for all the mixtures are well within ±5% of the mean over a time of 6 months. Considering that the partition coefficients of these alkanes in *n*-hexadecane spanned a range from 150 up to 15 000, the similarity of the relative standard deviations indicates that the measurement precision in this approach is completely independent of the magnitude of K.

Comparison to Literature Data. The accuracy of the equilibration instrument and measurement procedures was assessed by comparing the data with literature values. Table 2 compares the γ^∞ values of several alkanes in *n*-hexadecane at 25 °C as measured by HSGC with those surveyed from literature studies, including previous HSGC

Table 2. Comparison of γ^∞ Values of Alkanes in *n*-Hexadecane with Literature Reported Values

solute	γ^∞(this work)	γ^∞(HS-GC)[a]	γ^∞(capil)[b]	γ^∞(GC)[c]	γ^∞(GC)[d]	γ^∞(gas stripping)[e]
n-pentane	0.83_8	0.874 (−4.1)[f]	0.852 (−1.6)	0.854 (−1.9)		0.825 (1.6)
n-hexane	0.89_5	0.898 (−0.3)	0.902 (−0.8)	0.902 (−0.8)	0.903 (−0.9)	0.888 (0.7)
n-heptane	0.91_7	0.924 (−0.8)	0.930 (−1.4)	0.930 (−1.4)	0.922 (−0.5)	0.931 (−1.5)
n-octane	0.95_6	0.980 (−2.4)	0.951 (0.5)	0.951 (0.5)		0.986 (−3.0)
n-nonane	0.98_7	1.021 (−3.3)	0.984 (0.3)	0.971 (1.6)		
2-methylpentane	0.91_3	0.893 (2.2)	0.933 (−2.1)	0.847 (7.8)		0.91 (0.3)
2,4-dimethylpentane	0.98_6	0.977 (0.9)	0.995 (−0.9)	0.931 (5.9)		
2,5-dimethylhexane	1.02_4	1.017 (0.7)	1.024			
2,3,4-trimethylpentane	0.93_7	0.923 (1.5)	0.934 (0.3)			
cyclohexane	0.80_4	0.817 (−1.6)	0.808 (−0.5)	0.794 (1.3)	0.813 (−1.1)	
ethylcyclohexane	0.85_0	0.840 (1.2)	0.848 (0.2)			

[a] Dallas and Carr, 1994. [b] Zhang et al., 1993. [c] Abraham et al., 1987. [d] Castells et al., 1990. [e] Richon et al., 1980.

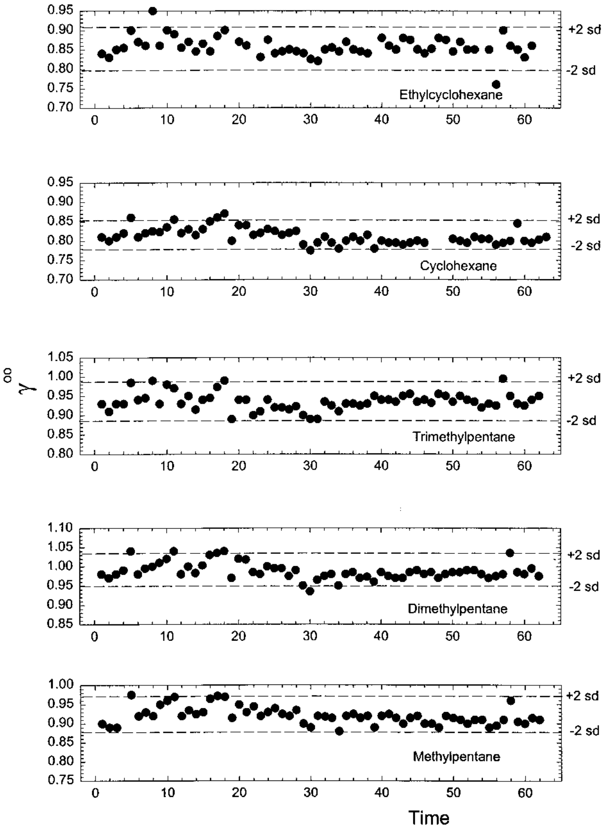

Figure 2. Long-term stability of γ^∞ values of branched and cyclic alkanes in *n*-hexadecane.

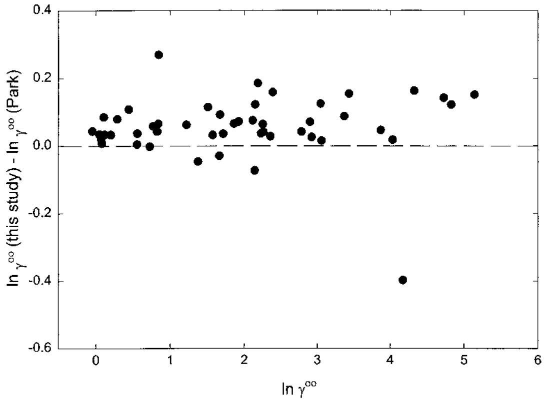

Figure 3. Comparison of limiting activity coefficients obtained in this study with those reported in Park et al. (1987).

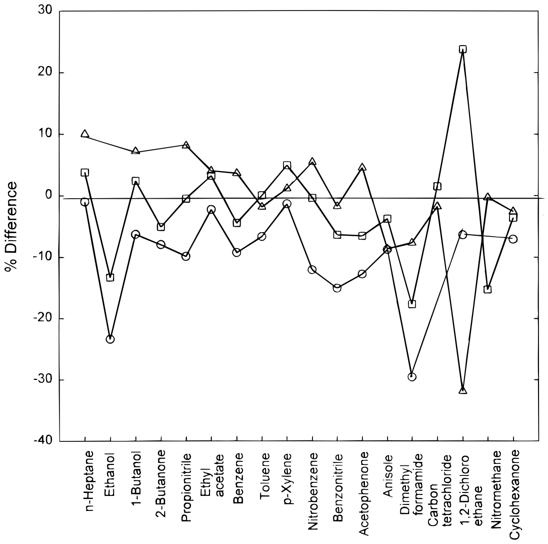

Figure 4. Percentage difference of γ^∞ for *n*-pentane (○), *n*-hexane (□), and cyclohexane (△) in several solvents between this study and those from Thomas et al. (1982a).

measurements conducted in this laboratory. On the whole, agreement between our γ^∞ values, which are the average of more than 60 independent measurements with a precision better than 5% (see Figures 1 and 2), and those from the literature is quite good.

Park (1988) used HSGC to measure gas−liquid partition coefficients at 25 °C of several solutes in a group of solvents which included those previously studied by Rohrschneider (Rohrschneider, 1973). *n*-Octane was a test solute, whose value could be compared to the present set of data. As a whole, the absolute average percent difference between the γ^∞ values of *n*-octane in 48 common solvents measured by Park and our set of data is 8%. Figure 3 shows the residuals between both direct HSGC studies. The bias observed in this plot does not depend on the absolute γ^∞ value, suggesting similar systematic errors in all the solvents. The adsorption of octane vapors to the transfer lines would be a possible explanation for the smaller partition coefficients observed in Park's measurements.

A comparison of the HSGC data with those obtained by other techniques was performed by using a comprehensive database from DECHEMA Data Bank and other more recent publications. A table including the complete compilation is available upon request. The experimental values contained in the Data Bank were obtained by using several techniques, but practically all the available data correspond to γ^∞ values of normal alkanes and cyclohexane. We noted, however, that the quality of these data is very diverse. To deal with these uncertainties, we limited the comparison of our γ^∞ values to the more complete and consistent databases acquired by a single laboratory. The results are plotted in the following figures. Figures 4 and 5 show the percent differences of γ^∞ values of three and four solutes, respectively, in several solvents measured in this study

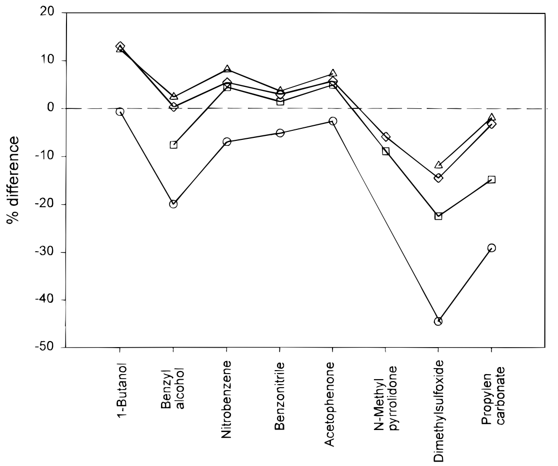

Figure 5. Percentage difference of γ^∞ for *n*-pentane (○), *n*-hexane (□), *n*-heptane (△), and cyclohexane (?) in several solvents between this study and those from Vernier et al. (1969).

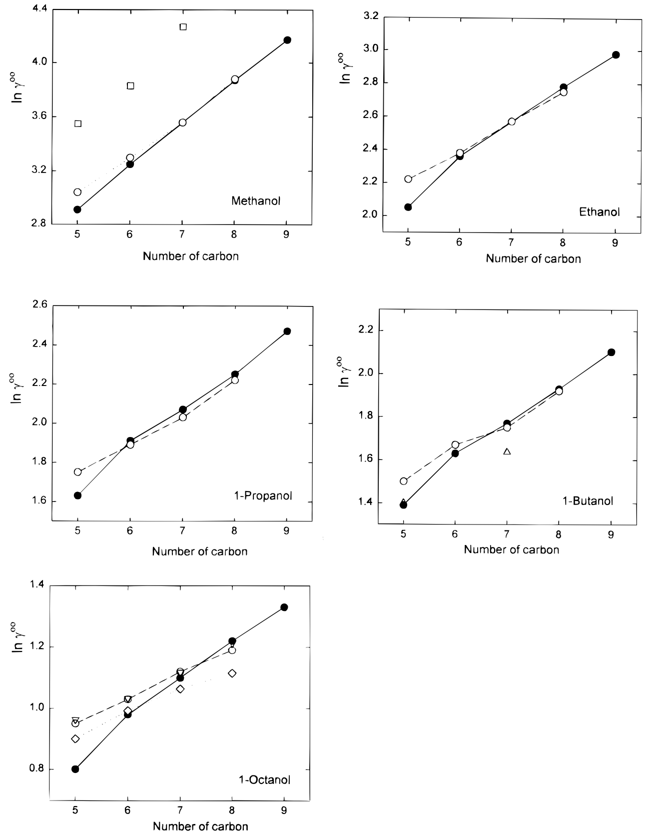

Figure 6. Plots of ln γ^∞ versus solute carbon number for normal alkanes in 1-alkanols: ●, this study; ○, taken from Vrbka et al. (1997); △, from Tewari et al. (1982); ◇, from Gruber et al. (1997); □, from Vega and Coca (1990).

compared to those reported previously. Both sets of data were acquired by dynamic GC, although the data in Figure 4 were obtained at 20 °C instead of 25 °C. Given the usually small excess partial molar enthalpies of alkanes, only a minor difference in γ^∞ is expected due to the 5 °C difference in temperature. From the figures, it is clear that our γ^∞ values for *n*-pentane are systematically low. This observation is consistent with difficulties in measuring partition coefficients for highly volatile solutes with our HSGC methodology for two principal reasons. First, we believe that loss of *n*-pentane by volatilization during the preparation of sample by weight difference is a possible source of error that would be manifested as a higher partition coefficient than the true value. Second, and more important, in all cases we assumed that equilibrium is not disturbed by the sample removal and that the amount of solute which is lost to the vapor phase is negligible. Though a correction was introduced to account for this loss in mixtures having lower partition coefficients, it is clear that the accuracy of such data is not similar to the others. This is an indication of the limits of applicability of the present methodology. Those systems for which partition coefficients are less than 100 could be measured with an improved accuracy by considering the solute mass conservation in the calculations. On the other hand, this comparison shows no bias for the other less volatile alkanes.

Further evidence of the reliability of our data can be observed in plots of homologue trends. Figure 6 shows a comparison of γ^∞ values of *n*-alkanes in 1-alkanols with literature values. Open circles correspond to data compiled at 25 °C by Dohnal et al. (Dohnal and Vrbka, 1997). This data set is a very reliable one, since the authors have evaluated the accuracy of γ^∞ data for mixtures of *n*-alkanes and 1-alkanols from several literature sources in the context of a IUPAC Project of Compilation of Limiting Activity Coefficients. Again, close agreement for all the mixtures except those involving *n*-pentane is observed. Several other data taken from Tiegs et al. (1986) were also included. The plots for methanol show that γ^∞ data measured by liquid−liquid chromatography are decidedly larger than those obtained by using any other technique. Locke (1968) also found that the γ^∞ values of *n*-pentane, *n*-hexane, and *n*-heptane in acetonitrile measured by LLC were systematically larger (up to 40%) than those obtained statically. Alessi and Kikic (1974) later ascribed this discrepancy to the mutual solubilities of the two solvents used as stationary and mobile phases. Similar comparisons were performed with other systems for which data for *n*-alkanes were available (data not shown here), and the observations are similar to those of Figures 4−6: data collected from liquid−liquid chromatography were inconsistent with those obtained with other methods, but no other trend was detected between the HSGC data when compared with those from other techniques. These results confirm the accuracy of the present HSGC methodology. Finally, a further proof of consistency among our data is the quality of the linear correlation between ln *K* and carbon number for the normal alkanes, as indicated in Table 3 in Part 1 of this study. Although the linearity of this relationship is not strictly thermodynamically required, the experimental uncertainty prevents detection of any curvature.

Accuracy of γ^∞ for a Solute in Itself. Another way to estimate the accuracy of these data is from the error in predicting γ^∞ for a solute “infinitely dilute in itself”. By definition, under these conditions the activity coefficient must be unity, regardless of the standard state convention. Since six *n*-alkanes and cyclohexane were used as both solutes and solvents, these systems were tested here. In Part 1, we showed that the relationship between ln *K* and the number of carbons in the *n*-alkane was linear within the experimental error. The slope and intercept from the regression were used to estimate the partition coefficient of an *n*-alkane in itself by interpolation. Then, the relationship between γ^∞ and *K* can be used to determine the “experimental” value of the activity coefficient of a solute in itself,

$$\gamma^\infty = RT/(P^{\text{sat}}KV_1)$$

Table 3. Comparison of Theoretical and Extrapolated Values of ln *K* and γ^∞

system	ln *K*(theory)[a]	ln *K*(expl)[b]	$\gamma^{\infty\ c}$
n-pentane	5.744	5.696 (0.036)	1.05
n-hexane	6.839	6.823 (0.065)	1.02
n-heptane	7.922	7.875 (0.016)	1.05
n-octane	9.004	8.937 (0.008)	1.07
n-nonane	10.096	10.034 (0.014)	1.06
cyclohexane	7.514	7.394 (0.053)	1.08

[a] Calculated from the definition $\gamma^\infty = 1$ and the saturated vapor pressure at 25 °C. [b] Estimated values for *n*-alkanes from regression of ln *K* against the solute carbon number. The cyclohexane experimental value was estimated from the regression of ln *K*(cyclohexane) versus ln *K*(ethylcyclohexane) in all solvents. [c] Estimated from $\gamma^\infty = RT/[P_2^{\mathrm{sat}} V_1 K(\mathrm{interpolated})]$.

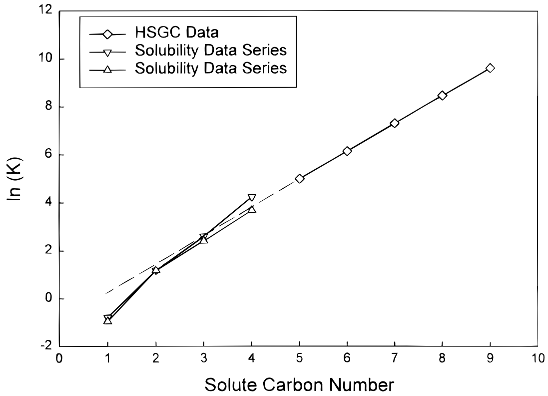

Figure 7. Plot of ln *K* as a function of the solute carbon number for the *n*-alkanes from methane through *n*-nonane in the solvent *n*-hexadecane

where P^{sat} and V_1 are the saturated vapor pressure and the molar volume of the solute at 25 °C, respectively. Table 3 gives the interpolated values of the partition coefficients and the "experimental" activity coefficients for a solute in the pure state. When the standard error of the prediction is taken into account, the estimated γ^∞ values are statistically unity.

Consistency of the Methodology. The Solubility Data Series (1982; 1986; 1987) provides Henry's law constants and Ostwald solubilities for methane, ethane, propane, and butane in a number of the solvents studied here. We expect that the empirical linear relationship between ln *K* and the number of carbons in the solute should extend to methane. Figure 7 illustrates the agreement between the values estimated from the measured solubilities of methane to *n*-butane in *n*-hexadecane and our data from *n*-pentane to *n*-nonane. Figure 7 is typical for all the solvents with both Ostwald coefficient and Henry's law constant data. As an example, Figure 8 shows the data for a variety of other solvents. No break occurs between the literature data for the gases methane to *n*-butane and the experimental HS-GC data for the longer linear alkanes. This continuity in the behavior from butane through pentane indicates that the partition coefficients for the gaseous alkanes are relatively consistent with those measured in this study by HSGC.

Conclusions

Headspace analysis provides an easy, fast, and accurate way to determine partition coefficients (and, as a consequence, infinite dilution activity coefficients) for relatively volatile solutes in a wide variety of solvents. The method can be applied to the simultaneous determination of several solutes provided that all the solutes are infinitely dilute. The limits of the applicability of the present methodology are determined by the limits of quantitation of the components in the vapor phase. On the other hand, the accuracy of the determination decreases when the amount of solute in the vapor space of the equilibrium cell is large compared to the amount dissolved in the liquid (partition coefficients less than 100). Agreement with published data, even with those not determined by chromatographic techniques, is quite reasonable. With the exception of *n*-pentane, the data presented in this study are estimated to be accurate to ±5%. From replicate measurements most solute/solvent pairs show a precision better than 3% over a short-term study and one better than 5% over a longer period of study.

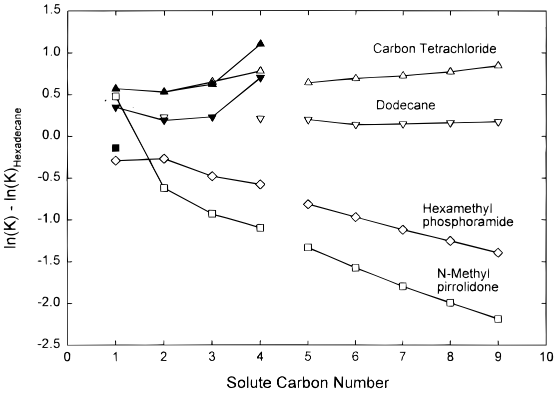

Figure 8. Difference in ln *K* for four solvents from ln *K* in *n*-hexadecane as a function of solute carbon number.

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