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An Efficient and Reliable Gas Chromatographic Method for Measuring Liquid–Liquid Mutual Solubilities in Alkylbenzene + Water Mixtures: Toluene + Water from 303 to 373 K

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An efficient and reliable gas chromatography (GC) method has been developed for measuring mutual solubilities of alkylbenzenes and water. The reliability and precision of the method are demonstrated for toluene and water in the temperature range 303–373 K at pressures within 1 bar of the three-phase curve. The reproducibility of the GC analysis of a given sample is excellent; the absolute average percentage deviation of the analysis is consistently less than 1.0%. The method has also been used to determine the solubility of other alkylbenzenes in water at concentrations as low as 10 ppm (mass), and water solubility in alkylbenzenes as low as 300 ppm (mass). The average percentage deviation of these measurements is less than 6.0%, due largely to the high precision of the GC analysis. The method developed here minimizes the use of sophisticated analytical instrumentation, which makes it suitable for routine analysis. The method employs a GC equipped with a standard thermal conductivity detector, and a single column is used for analysis of samples of both the organic and the water phases. The overall time required for a single analysis is less than 15 min.

Many alkylbenzenes are considered toxic or hazardous to human health and must be removed from waste water streams before the effluent can be discharged into the environment. The design of appropriate processing units requires information on alkylbenzene solubilities in water. Accurate and reliable mutual solubility data for water and hydrocarbons are vital to a better understanding of the liquid water structure and its solution behavior. Although many measurements have been reported in the literature since the beginning of the century, agreement among different investigators is poor. This lack of consistency in measurements can be attributed to many factors. However, the main difficulty appears to be measuring solubilities in the low concentration range, from 1000 to 1 ppm. With the introduction of the GC, the analytical technique has realized a quantum improvement, and the difficulty of analysis at low analyte concentrations has been largely resolved, though not completely eliminated. The remaining key factors are sample treatment prior to the analysis and appropriate GC columns.

Many recommendations concerning sample treatment and proper instrumentation for the analysis of trace organic compounds in water have appeared in the literature. Poole et al. (*1*), Namiesnik et al. (*2*), and Jennings and Rapp (*3*) present good reviews. Some of their recommendations have been used in the routine analysis of trace organics in water (*4*). There are also many suggestions for the GC analysis of trace water in an organic solvent (*5–22*). However, none of these has been widely accepted in practice, presumably for the following reasons: (1) the Karl Fischer titration method has become a *de facto* standard method for water content determination, and highly specialized and automated commercial units are readily available, (2) the reliability and accuracy of GC methods have not been well demonstrated for routine applications, (3) some GC methods are complicated and require both specialized personnel and analytical equipment which may not be readily available, and (4) some GC methods are tedious and inefficient and do not have general applicability.

In this study, we present a detailed GC method for the determination of mutual solubilities of alkylbenzenes and water in the very low concentration range. The precision and reliability of the method are demonstrated by applying it to the determination of toluene + water mutual solubilities. A single column is used for both the toluene and the water analyses, and the time required for a single run is less than 15 min. The method is reliable and accurate down to the 10 ppm level of the analyte concentration for both the organic and the water phases, provided appropriate sample preconcentration and solvent purification techniques are adopted.

Experimental Section

In the discussion which follows, we demonstrate the GC method by applying it to the determination of the liquid–liquid mutual solubilities of water and toluene. The equilibrium measurement unit and sampling technique have been described elsewhere (*23*).

Materials and Apparatus. The 25-mL sampling vials and the 60- and 125-mL sampling bottles with open-hole caps and Teflon-lined silicon septa are from Alltech. The 99.9%+ grade 2,2,4-trimethylpentane, toluene, and methylene chloride were obtained from Aldrich Chemical Co. and used without further purification. Ethanol, USP Absolute-200 Proof from AAPER Alcohol and Chemical Co., was dehydrated and stored over 4A molecular sieves from Fisher Chemical Co.

A Hewlett-Packard 5880A gas chromatograph equipped with a thermal conductivity detector (TCD) and a Hewlett-Packard Level-4 integrator were used. A Porapak Q GC column (packed, 80–100 mesh, 1.8 m, 0.32-cm stainless steel coil) from Alltech Chemical Co. was used for preliminary analyses. This was replaced with a GasChrom 254 column (Packed, 80–100 mesh, 1.8 m, 0.32-cm stainless steel coil) to achieve better resolution for organic components. The drying oven was a VWR Scientific Model 1410. Chromatographic helium was obtained from Sooner Gas Supply, Inc.

Glassware for Sample Transfer or Storage. The sampling vials and bottles were meticulously cleaned using the following procedure: (1) soaked in Micro Clean solution for 24 h, (2) rinsed with tap water, (3) rinsed with methylene chloride, (4) rinsed with methanol, (5) rinsed with distilled water, and (6) dried at 100 °C under vacuum overnight. The cleaned vials or bottles were removed from the oven, and when cool enough to handle, loosely capped and stored in a desiccator.

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The septa for vials and bottles were cleaned by soaking in ethanol for 24 h and, subsequently, soaking in distilled water for 2 h. After a final rinse with distilled water, the septa were oven dried at 50 °C under vacuum.

The cleanness of the sampling vials and bottles is extremely important for reproducibility in sample analysis; extreme care should be exercised for this part of the overall analytical procedure.

Standard Preparation and Calibration. Serial dilution techniques were used to prepare the standard solutions for toluene diluted in 2,2,4-trimethylpentane (methylene chloride can also be used) and for water diluted in dehydrated ethanol. The standard solutions were prepared gravimetrically over the range in which the actual analysis would be conducted, with an approximately constant solution concentration ratio maintained between consecutive dilutions. All standards were analyzed immediately to establish calibration curves.

A "monitoring solution" containing the mixed analytes in the concentration range of the standards was also prepared during the course of calibration. This solution was then analyzed, and the area ratios of the analytes to the respective standards were recorded. These area ratios were then used to monitor the stability of the GC system on a daily basis.

Sample Analysis Procedure. A dry, clean sample bottle is removed from the desiccator and the cap tightened. The sampling bottle is weighted to ±0.1 mg before and after 2,2,4-trimethylpentane or dehydrated ethanol is added. The difference in mass gives the amount of solvent added. The bottle is then cooled to 4 °C in a refrigerator before it is used to collect the sample. After the sample is collected, the sampling bottle is weighed again. The difference in mass before and after sample collection gives the actual amount of the sample collected.

The known amount of 2,2,4-trimethylpentane added to the sample bottle before the water phase is sampled serves as both an internal standard and an extractant. Similarly, the known amount of dehydrated ethanol added before the organic phase is sampled serves as an internal standard and as the homogenizing cosolvent.

The water-phase samples are shaken vigorously to extract the dissolved organics from the water into the 2,2,4-trimethylpentane phase. The sample is then stabilized for at least 4 h before any of the 2,2,4-trimethylpentane phase is injected into the GC.

After a water-phase sample is extracted with 2,2,4-trimethylpentane and the 2,2,4-trimethylpentane phase is analyzed, 2 μL of water in contact with the 2,2,4-trimethylpentane phase is injected at the lowest GC attenuation to check for any response from the analyte being analyzed. This step serves to monitor the actual recovery of the extraction process used to concentrate the analyte. If the recovery of the analyte is less than 100%, a second extraction may be necessary. However, recovery was always greater than 99.9 mass % throughout this study, when the mass ratio of 2,2,4-trimethylpentane to water phase is 0.20 to 0.30. Therefore, a second extraction was not required to correct for possible analyte losses during the sample concentration step.

The organic-phase samples are also vigorously shaken to homogenize the mixture and are analyzed immediately. The dehydrated ethanol is also analyzed to obtain the area ratio of the water to ethanol. This ratio is used to correct for the small amount of water introduced into the organic-phase sample by the dehydrated ethanol.

Operating conditions for the GC are given in Table 1. The injection sample size for both phase samples is 2 μL, and contact with the atmosphere is avoided. For routine analysis, a 2-μL monitoring sample (usually prepared while standard solutions are being made) is injected prior to the sample analysis at the beginning of each working day to monitor the GC stability. If the resulting chromatogram indicates a significant (more than 1%) change in the area ratios of analytes to respective standards, the whole system is recalibrated. Sample analysis begins only after system stability is confirmed. Recalibration is required after approximately 60 sample injections.

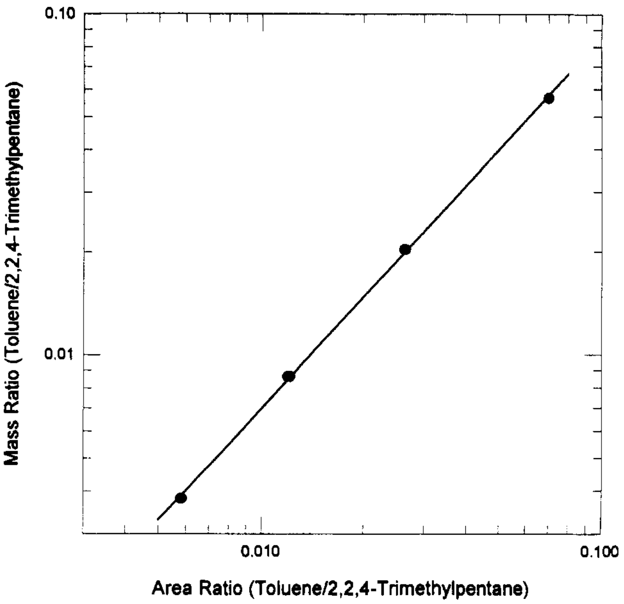


Figure 1. Calibration curve for toluene in 2,2,4-trimethylpentane (●, data; —, eq 1).

Table 1. Gas Chromatograph Operating Conditions

operating condition	hydrocarbon-phase analysis	water-phase analysis
Porapak Q Column		
injector temperature, °C	240	200
column temperature, °C	240	200
detector temperature, °C	240	220
carrier/reference gas flow, mL/min	30	30
auxiliary gas flow, mL/min	40	40
GasChrom 254 Column		
injector temperature, °C	270	270
column temperature, °C	250–270	150–270
detector temperature, °C	300	300
carrier/reference gas flow, mL/min	30	30
auxiliary gas flow, mL/min	40	40

Results and Discussion

Calibration. All of the analyses reported here are obtained with a GasChrom 254 column. The calibration curves for toluene + 2,2,4-trimethylpentane and water + ethanol are shown in Figures 1 and 2, respectively. The reproducibility of all points on the calibration curves is within 1.0%. The following calibration curves were obtained by linear regression: For toluene (A) + 2,2,4-trimethylpentane (B)

$$\log W_R(A/B) = 1.08389 \log A_R(A/B) - 0.01200 \quad (1)$$

and for water (D) and ethanol (E)

$$\log (W_R(D/E) + C) = 1.01518 \log A_R(D/E) - 0.05573 \quad (2)$$

where W_R and A_R are the mass and area ratios, respectively, of analyte to solvent and C is a constant.

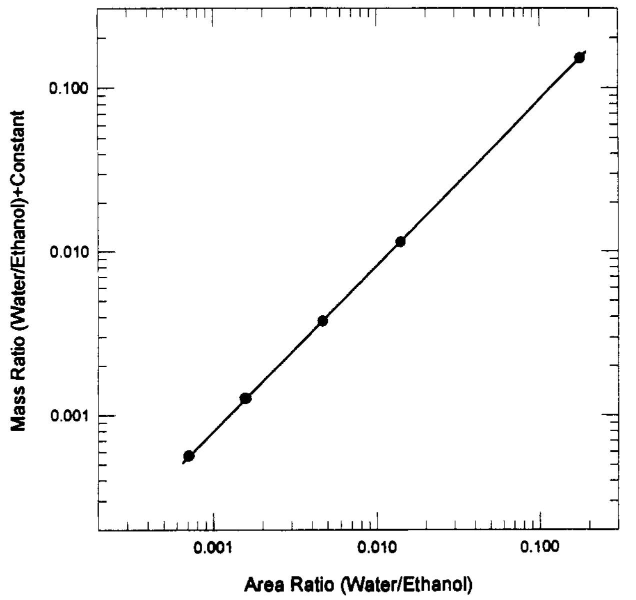


Figure 2. Calibration curve for water in ethanol (●, data; —, eq 2).

The constant C in the water and ethanol calibration curve represents the combined effects of trace water in the dehydrated ethanol and the limit of the GC response. Because the calibration results indicate a nonlinear relation between W_R and A_R on log–log coordinates, the conventional blanking method cannot be used, especially at the low analyte concentrations. Also, the thermal conductivity detector gives no response below the detection limits of the analyte. The effects from the blank and the detection limit can be represented better by introducing a constant into the regression based on multiple-point (as compared to single-point blanking) calibration. The value of the constant is approximately 2.5×10^{-4} and can change whenever a new batch of dehydrated ethanol is used in the analysis. There is little variation when the analyses use the same batch of dehydrated ethanol solvent. Since the GC detection limit for water under the conditions listed in Table 1 appears to be around 1.0×10^{-5} mass ratio of water to ethanol, or approximately 4.0% of the value of the constant C, a new value can be easily estimated by running a dehydrated ethanol blank.

The calculated value of W_R is sensitive to the value of C at low values of W_R ($<1.0 \times 10^{-4}$). Therefore, the injected sample should have a water concentration at least 1 order of magnitude higher than the constant C. This can be accomplished in three ways. The first is to further dehydrate the ethanol solvent, which can be very difficult in practice. The second is to concentrate the water in the sample before it is homogenized by ethanol. Brady et al. (*24*) used ethylene glycol to concentrate the water before the sample was analyzed using Karl Fischer titration. A similar procedure can be used with GC analysis. The third is to minimize the amount of ethanol, and thus maximize the water to ethanol mass ratio. Certainly, the third method may not be feasible all the time, especially when there is a thermodynamic miscibility limit imposed on such ratio tuning. Since the ethanol used here serves as both the reference compound and the cosolvent to homogenize the sample, the quantity used can be minimized to the limit at which the sample can be homogenized. This point is further illustrated in the following section.

Example Calculation. The example given here is from the measurement of the mutual solubility of toluene and water at 303 K near the three-phase liquid–liquid–vapor equilibrium curve. For the organic-phase sample there are six replicates as shown in Table 2.

Table 2. Chromatographic Analysis of Toluene-Phase Samples Collected at 303 K

replicate	W_R[a] (ethanol + toluene)	A_R[b] (water + ethanol)	W_R[c] (water + ethanol)	W_R[d] (water + toluene)	mole fraction of water[e]
1	0.010 4	0.007 753	0.006 064	0.000 613	0.000 312
2	0.104 44	0.006 600	0.005 109	0.000 534	0.000 272
3	0.094 07	0.007 123	0.005 542	0.000 521	0.000 266
4	0.101 09	0.007 796	0.006 100	0.000 617	0.000 314
5	0.099 83	0.007 099	0.005 522	0.000 551	0.000 281
6	0.099 66	0.007 585	0.005 868	0.000 585	0.000 298
dehydrated ethanol		0.000 270			

[a] From gravimetric analysis. [b] From chromatographic analysis. [c] Calculated using eq 3. [d] Calculated using eq 4. [e] $x_{H_2O} = 1/[1 + (18/92)(1/W_R)]$.

Since $A_R = 2.700 \times 10^{-4}$ for the dehydrated ethanol, we obtain $C = 2.10 \times 10^{-4}$ from the calibration curve for water and ethanol by nonlinear regression. For each of the samples 1–6, A_R(D/E) can be used to calculate W_R(D/E) from eq 2 rewritten as

$$W_R(\mathrm{D/E}) = 10^{(1.015\log[A_R(\mathrm{D/E})]-0.05573)} - C \qquad (3)$$

The actual amount of water in toluene is then calculated from

$$W_R(\mathrm{D/A}) = W_R(\mathrm{D/E})\, W_R(\mathrm{E/A}) \qquad (4)$$

Note that the mass of the organic-phase sample is approximated as the mass of toluene. This is a reasonable approximation considering the low water solubility in the sample. Also note that the correction, C, amounts to about 5.0% of the value of W_R for water and ethanol. The magnitude of this correction can be decreased, if less ethanol solvent is used to homogenize the sample. However, since good reproducibility is clearly achieved, no further efforts were made in this direction.

For the solubility of toluene in water, the calculation is similar to that shown above, but no correction is required. A correction may be required for the loss of isooctane into the water phase during the extraction procedure. Because the solubility of isooctane in water is small at room temperature (0.35 ppm at 298 K), and the isooctane to sample weight ratio is controlled, a correction was not required in this work. Therefore, we do not present the calculation procedure here.

Efficiency of Analysis. Typical chromatograms are shown in Figures 5 and 6 for the analysis of toluene in water and water in toluene, respectively. The required time for a single run is less than 7 min for water and less than 2 min for toluene. This is significantly less than the time required by other methods (*10*). The peak shape is symmetrical for both toluene and water and does not exhibit the tailing reported by Oguchi et al. (*19*). This good separation efficiency is achieved on a standard 1.8-m × 0.32-cm packed stainless steel coiled column which is available commercially (GasChrom from Alltech). Previous methods using large customer packed columns and injection of large-volume samples (*13*) are avoided.

Comparison of Measured Mutual Solubility Data of Toluene and Water with Literature Data. We presented the liquid–liquid mutual solubility of benzene and water previously (*23*) using essentially the same analytical technique presented above. Here, we present the mutual solubility data of toluene and water from 303 to 373 K to demonstrate the reliability of the proposed GC method. Results are summarized in Table 3. All measurements are made within 1 bar

Table 3. Mutual Solubilities of Toluene and Water[a]

		toluene solubility in water			water solubility in toluene		
T, K	P, bar	10^3x	$10^3\sigma$	N	10^3x	$10^3\sigma$	N
303.15	1.0	0.117	0.002 61	6	2.91	0.189	6
313.15	1.0	0.119	0.003 57	6	4.16	0.065	6
323.15	1.0	0.127	0.001 44	6	5.30	0.394	6
333.15	1.5	0.144	0.003 65	6	7.11	0.204	6
343.15	2.5	0.171	0.005 47	6	9.46	0.261	6
353.15	2.5	0.198	0.005 61	13	12.8	0.646	13
363.15	3.5	0.232	0.002 39	6	16.2	0.495	6
373.15	3.5	0.268	0.005 95	6	22.6	1.02	6

[a] x = mole fraction, $\sigma(x)$ = standard deviation, and N = number of measurements.

of the three-phase curve, and the effect of pressure on liquid–liquid equilibrium can be neglected.

Toluene Solubility in Water. The new toluene solubility in water results are shown in Figure 3 together with data from the literature (*25–31*). The solubilities reported by Bohon and Claussen (*27*) and Pierotti and Liabastre (*29*) appear too high. Hefter (*32*) reached the same conclusion. Sanemasa et al. (*30, 31*) reported two sets of measurements obtained in 1981 and 1982. The 1982 solubilities were approximately 8% lower than the 1981 values. Our data are in excellent agreement with the Sanemasa et al. (*30*) 1981 measurements and the value reported by Gross and Saylor (*28*) at 298 K.

The new toluene solubility measurements were correlated with temperature by the following equation:

$$\ln\frac{1}{x_t} = -12.21 + 21.39\frac{1}{T_{rt}} - 5.372\frac{1}{T_{rt}^{2}} \qquad (5)$$

where x_t is the mole fraction of toluene and T_{rt} is the system temperature divided by the critical temperature of toluene, 591.8 K. The constants in eq 5 are obtained by least-squares regression techniques. This relationship can be used to estimate the heat of solution by assuming the activity coefficients for water in the water phase and for toluene in the toluene phase are unity. From the Gibbs–Duhem equation

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P \cong \frac{\Delta H_i}{RT^2} \qquad (6)$$

where ΔH_i is the difference between the partial molar enthalpy of component i in solution, H_i, and the pure molar enthalpy, H_i°, at temperature T. The partial molar heat capacity at constant pressure, ΔC_{P_i} in defined as

$$\Delta C_{P_i} = (\partial(\Delta H_i)/\partial T)_P \qquad (7)$$

From equations 5–7, the specific heat of solution at 298 K is estimated as 351 J·mol^{-1}·K^{-1}. Gill et al. (*33*) report a value of 363 J·mol^{-1}·K^{-1} based on calorimetric measurements. Also, the minimum solubility temperature obtained by extrapolation of eq 5 is 297.3 K. This is in excellent agreement with the value of 291.6 K from calorimetric measurement (*33*).

Water Solubility in Toluene. The solubility of water in toluene results together with those reported in the literature (*25, 34–37*) are plotted as a function of temperature in Figure 4. Tarassenkow and Poloshinzewa (*37*) covered the same temperature range, and there is some disagreement between the two sets of measurements, particularly in the temperature dependence of the water solubility. We correlated our data using least-squares regression with the following equation:

$$\ln(1/x_w) = -1.483 - 9.647 \ln T_{rw} \qquad (8)$$

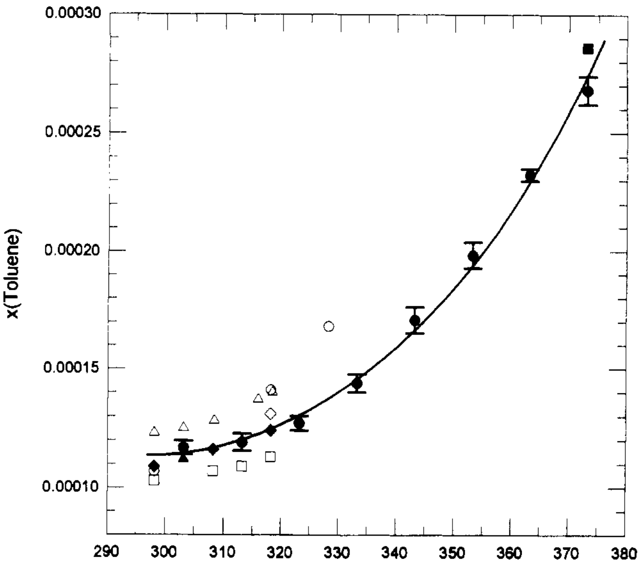


Figure 3. Toluene solubility in water: (●) this work, (■) Anderson and Prausnitz (*25*), (◇) Bradley et al. (*26*), (△) Bohon and Claussen (*27*), (▲) Gross and Saylor (*28*), (○) Pierotti and Liabastre (*29*), (◆) Sanemasa et al. (*30*), (□) Sanemasa et al. (*31*).

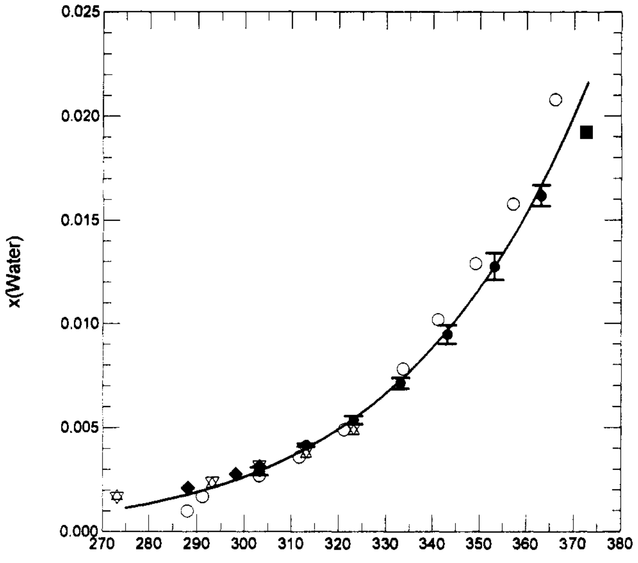
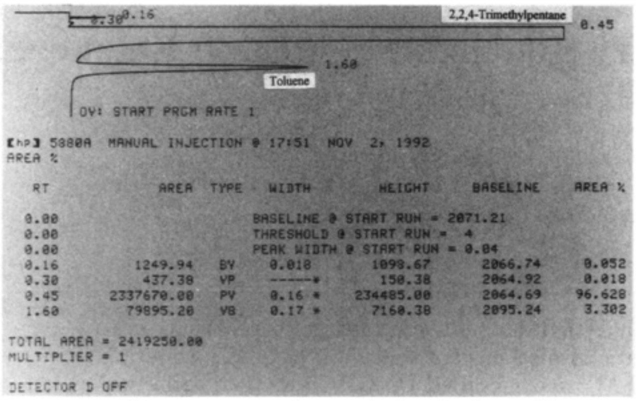


Figure 4. Water solubility in toluene: (●) this work, (■) Anderson and Prausnitz (*25*), (△) Englin et al. (*34*), (▽) Glasoe and Schultz (*35*), (◆) Rosenbaum and Walton (*36*), (○) Tarassenkow and Poloshinzewa (*37*).

where x_w is the mole fraction of water and T_{rw} is the system temperature divided by the critical temperature of water, 647.3 K. From this relationship, the estimated partial molar excess enthalpy is 23.9 kJ·mol^{-1} at 298 K. This is close to the value of 23.3 kJ·mol^{-1} for benzene (*23*) and close to the hydrogen-bonding energy of water (21–29 kJ·mol^{-1}). Current theory and experimental evidence (*38*) indicate that liquid water dissolving into a liquid hydrocarbon phase is essentially a process of breaking hydrogen bonds. Since the Tarassenkow and Poloshinzewa (*37*) data are lower than most of our measurements when temperature is lower than 313 K, and the calculated heat of solution using their data (correlated with eq 8) is 97.9 kJ·mol^{-1}, Tarassenkow and Poloshinzewa's data may not be reliable. Our results appear very consistent with the majority of values at temperatures below 323 K. The datum given by Anderson and Prausnitz (*25*) near 373 K is



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  0.30           437.38  VP   ------*      150.38     2064.92     0.018
  0.45       2337670.00  PV   0.16 *    234485.00     2064.69    96.628
  1.60         79895.20  VB   0.17 *      7160.38     2095.24     3.302

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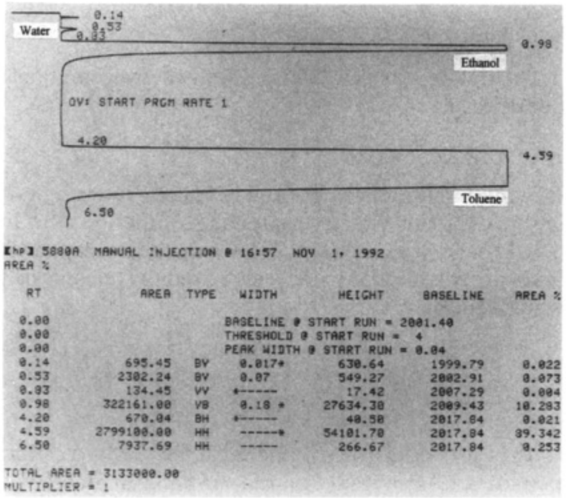
Figure 5. Chromatogram for analysis of toluene in water.



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  0.83         134.45  VV   *-----       17.42     2007.29     0.004
  0.98      322161.00  VB   0.18 *    27634.30     2009.43    10.283
  4.20         670.04  BH   *-----       40.50     2017.84     0.021
  4.59     2799100.00  HH   -----*    54101.70     2017.84    89.342
  6.50        7937.69  HH   -----       266.67     2017.84     0.253

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Figure 6. Chromatogram for analysis of water in toluene.

somewhat lower than ours.

Limits of the Method. In addition to the toluene + water system data reported here, we have used the GC method for water and benzene (*23*), *p*-xylene, 1,3,5-trimethylbenzene, ethylbenzene, and butylbenzene (*39*). For these organic compounds dissolved in water, the method appears reliable and accurate down to 10 ppm (mass) for butylbenzene in water (*39*). The combined precision (equilibrium measurement and GC analysis) is always better than 6.0% for hydrocarbon solubility in water. For water solubility in the alkylbenzenes, the method is used down to about 300 ppm (mass). Further sample treatment methods are needed to extend the range of application, as pointed out in the section on calibration. Nevertheless, water solubility in liquid organic solvents is always above 100 ppm (mass) when the equilibrium temperature is above 273.15 K, and the method proposed here can be applied to determine the water solubility in various liquid organic solvents.

The method does not have an apparent upper limit on the water concentration. The dilution method can easily be used to bring the high water concentration of the sample to the concentration range best suited for the GC analysis. From our experience, the method can be used directly with confidence to determine the water content in an organic sample when concentrations are above 300 ppm.

Summary

An efficient and reliable GC method was developed for measuring liquid–liquid mutual solubilities in alkylbenzene + water. The reliability, precision, and efficiency were demonstrated by applying the method in the determination of the liquid–liquid mutual solubility of toluene + water. The required instrumentation is a GC equipped with a thermal conductivity detector and an integrator. A standard commercially available column is used for both water and organic solute analyses. The GC method presented here can be useful for routine analysis of the water content in organic solvents.

Acknowledgment

Comments and suggestions by Robert L. Robinson, Jr., are acknowledged.

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