MUTUAL SOLUBILITIES OF CUMENE + WATER

By

BROOKS DAVID BENNETT

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Oklahoma State University
Stillwater, Oklahoma
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Thesis Approved:

Jan Wagner

Thesis Advisor

Mart S. Hyt

KAMGasem

Wayne B. Powell

Dean of the Graduate College

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NOMENCLATURE

A_R = Chromatographic area ratio

ΔC_p = Specific Heat of solution

E = Ethanol

CM = Cumene

ΔG = Free energy of solution

ΔH = Enthalpy of solution

ΔS = Entropy of solution

R = Gas constant

T = System temperature

T_c = Critical temperature

T_R = Reduced temperature of the system

TP = 2,2,4-trimethylpentane

W = Water

W_R = Gravimetric weight ratio

x_i = Mole fraction of component *i*.

CHAPTER I

INTRODUCTION

Cumene (isopropylbenzene) is one of the top 50 chemicals manufactured in the United States with an estimated annual production rate of 4.5 billion pounds per year (15). Approximately 90% of all cumene is used as an intermediate in the manufacture of phenol, acetone, and α-methyl styrene (8). Cumene is also found in detergents and surfactants, solvents, paint thinners, and aviation fuel. Cumene has been detected in surface water and sediments at concentrations from 0.1 to 59 μg/liter and 0.02 to 19 μg/g, respectively (21).

Most industrial processes use liquid-phase alkylation with sulfuric or hydrofluoric acid or vapor-phase alkylation with phosphoric acid and employ water in some phase of the process. With increasingly stringent controls placed on the levels of aromatic emissions by the U.S. Environmental Protection Agency, removal of these becomes increasingly important.

Solvent extraction has been recognized as one of the best developed technologies for chemical and petrochemical wastewater treatment of low concentration substances. For the technology to be implemented successfully, reliable liquid-liquid equilibrium data are needed for the modeling and design of these process units. Currently, these data are not plentiful, are inaccurate, or conflict with other experimental data.

CHAPTER II

RELEVANT WORK

A continuous flow apparatus was used by Glew and Robertson (7) to study the cumene + water system. The other solubility data reported in the literature have been determined by closed-system analysis with mechanical agitation or time as the promoter for mass transport. For the agitated systems, sample times of 2 to 4 days were reported by Stearns (18), McAuliffe (11), and Price (14), while Elgin (5) reports 5 hours and Andrews (1) 20 hours. Price reports 2 to 4 hours, while Krzyzanowska and Szeliga (9) report 3 weeks. For mechanically agitated systems, emulsions are likely and it is necessary to allow the mixture to stabilize for an extended period of time This leads to the lengthy sample times reported by these investigators.

Of the available literature data, only two researchers reported multiple points for the cumene solubility in water: 12 points by Glew and Robertson (7) and 4 points by Sanemasa and Araki (16). Temperature ranges were 298-353 K and 288-318 K, respectively. Only Englin (5) reports solubility values of water in cumene, and these data are limited to 4 points for the temperature range of 273-323 K.

Liquid-liquid mutual solubilities for several hydrocarbon + water systems have been reported by Chen and Wagner (2-4). These include water + benzene and water and the following alkylbenzenes: ethylbenzene, p-xylene, 1,3,5-trimethylbenzene, and butylbenzene. The work presented here is an extension of their work to include the cumene + water system.

CHAPTER III

EXPERIMENTAL SECTION

CONSISTENCY OF THE APPARATUS

An apparatus designed and constructed by Chen and Wagner (2) was used to carry out the solubility measurements. The accuracy of the apparatus has been demonstrated thermodynamically, and experimental methods and analytical techniques were verified using the toluene system subsequent to the cumene analysis. The solubility measurements for the water phase system are well within the experimental error of the procedure and agree with the results of other investigators (3).

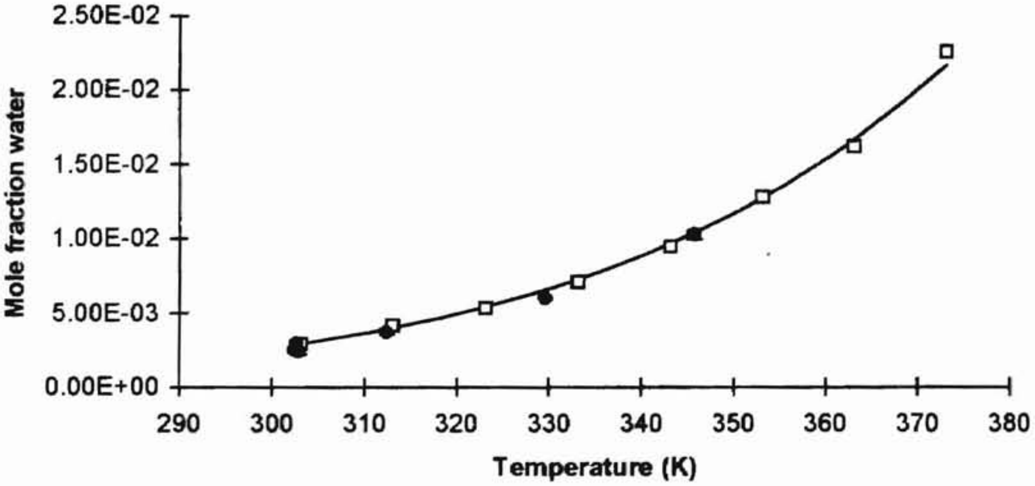

Figure 1. Solubility of water in toluene (□ Chen and Wagner, • this work; — Data Fit)

Figure 1 shows the reproducibility of the experimental procedure and the apparatus. The good agreement in the lower and mid-temperature regions was deemed to be sufficient to establish the consistency of the apparatus and methods, and no attempts were made to reproduce measurements at the higher temperatures.

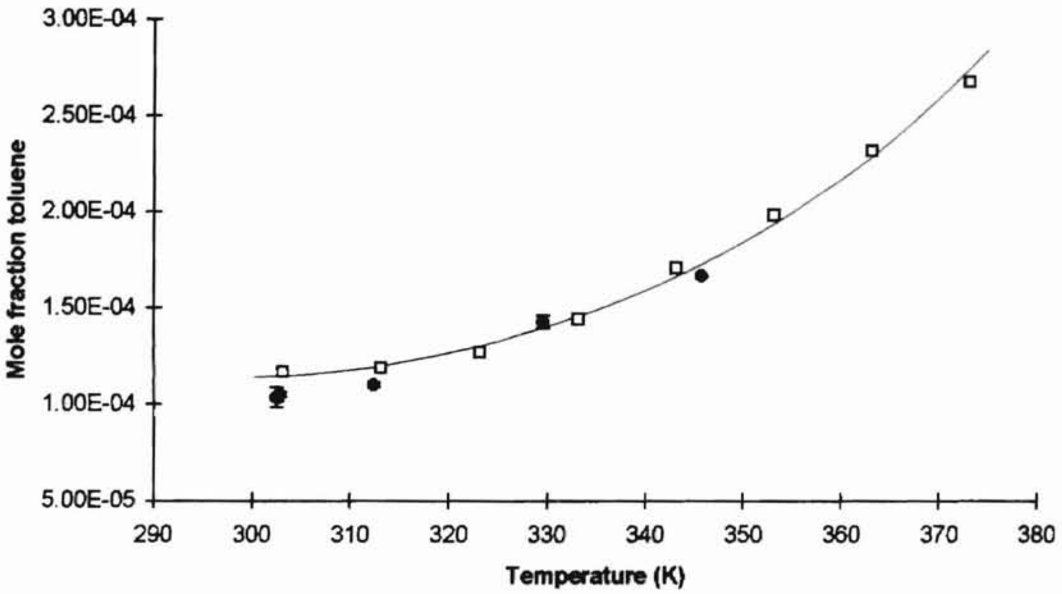

Figure 2: Solubility of toluene in water (□ Chen and Wagner; • This Work; — Data Fit)

Figure 2 shows disagreement in the lower temperature range for the solubility of toluene in water. The results differ from reported literature values (3). Gill (7) reports an enthalpy of solution of 1.73 kJ/mol based on calorimetric measurements, while Chen and Wagner (3) reports a value of 0.37 kJ/mol. Other solubility-based enthalpies found in the literature for toluene range from 1.7 to 4.7 kJ/mol, and the remaining alkylbenzenes studied by Chen and Wagner (4) show good consistency with literature values. It must be noted, however, that data reduction techniques employed are first and second derivative analysis and are highly sensitive, especially close to the minimum solubility temperature, to individual data points.

Table 1: Chen and Wagner's alkylbenzene data.

Compound	ΔH(kJ/mol) Chen and Wagner	ΔH(kJ/mol) Literature (6)	ΔC_p(J/mol) Chen and Wagner	ΔC_p(J/mol) Literature (6)
Benzene	3.69	2.08	207	225
Toluene	0.37	1.73	351	263
Ethylbenzene	4.38	2.02	338	318
p-Xylene	3.48	N/A	347	N/A
1,3,5-Trimethylbenzene	4.49	N/A	352	N/A
Propylbenzene	N/A	2.3	N/A	391
Butylbenzene	1.27	N/A	645	N/A

Table 1 shows that the enthalpy of solution is consistent for most of the alkylbenzenes for both the literature data (1.73-2.3 kJ/mol) and Chen and Wagner's data (3.69-4.49 kJ/mol), with the exception of toluene. Table 1 also shows an increase in the heat capacity of solution with molecular weight for the literature and Wagner's data, (3) while toluene is inconsistent with these results.

APPARATUS

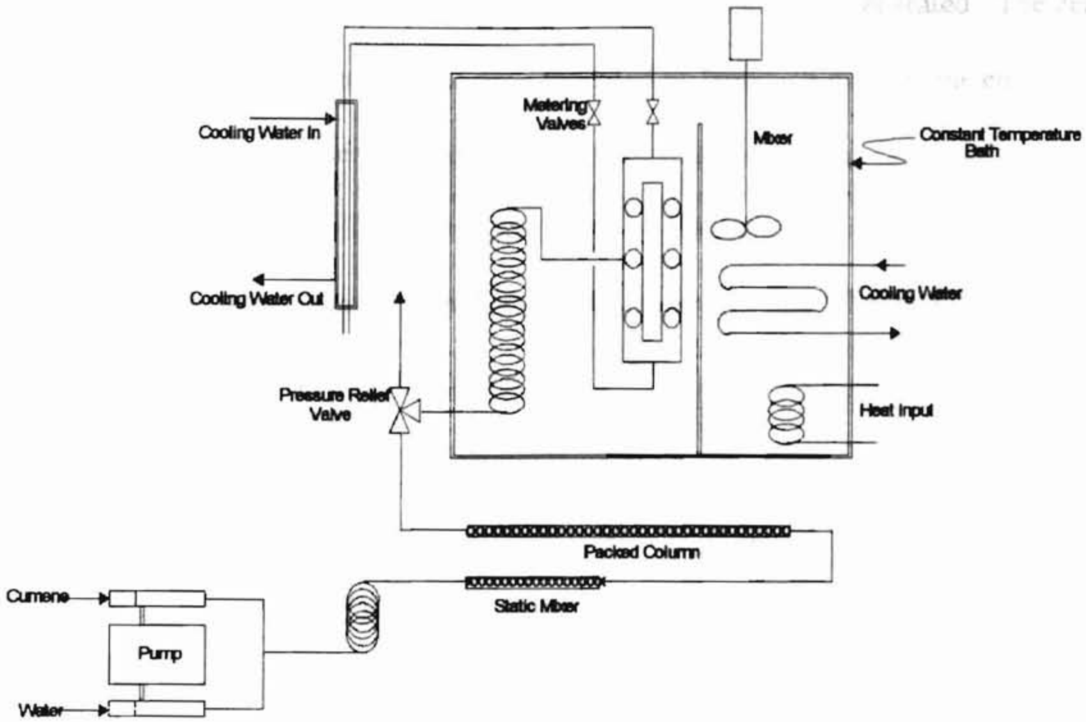

Figure 3. Diagram of Continuous Flow Mutual Solubility Apparatus

To provide for the continuous sampling of the system, an LCD Analytical Type NSI-33R minipump is used, and flow rates are maintained at approximately 2.0-3.2 ml/min (total flow). A flow system is used to facilitate intimate contact between the cumene and water phases to provide the necessary mass transfer between the phases. The mixture enters approximately 1.2 m of 0.635 cm (O.D.) tubing containing a static mixer consisting of notched and twisted stainless steel. Following the static mixer is a 3.6 m long section of 0.635 cm (O.D.) tubing containing 1.5 mm diameter glass beads. A final 1.2 m section of tubing of 0.635 cm (O.D.) is used to convey the components to the constant-temperature bath, where they enter a 10 m × 0.32 cm (O.D.) section of coiled tubing to bring the mixture to equilibrium at the desired temperature. The cumene and water mixture enter the equilibrium cell where the two liquid phases are separated. The cell is a Jerguson JT-40 sight gauge that has been modified by tapping a port for the entering feed and installing spring washers to compensate for thermal expansion.

The equilibrium cell and 10 m section of coiled tubing are immersed in a Neslab TEV-70 constant-temperature bath that contains Dow-Corning Silicon 200 heat transfer fluid. The uniformity of the bath temperature is within 0.1 K, and the temperature of the bath is maintained to within ±0.2 K of the temperature set point. The thermocouple is calibrated with a Minco platinum resistance thermometer that is NIST traceable. The pressure at the feed port of the sight gauge is monitored using a Sensotec STJE-AP112 pressure transducer with a 450D readout device.

Flow control of the streams exiting the equilibrium cell is accomplished using two Whitey Series SS-22RS2 micrometering valves. Tight interface control is necessary to prevent entrainment in both the organic and liquid phases. The interface level is controlled to within ±0.5 cm of the feed port location by either varying the flow rate of cumene or water from the equilibrium cell. In addition to flow control, the valves can be used to adjust the pressure of the system. The valves are immersed in the temperature bath to minimize phase separation in the valve bodies.

MATERIALS

The sampling bottles with open-hole caps and Teflon-lined silicon septa were obtained from Alltech. For the calibration of the gas cromatograph, 2 ml, 25 ml, and 118 ml bottles were used. For the cumene and water phase sampling, 58 ml and 118 ml bottles were used. The 99.9 %+ purity 2,2,4-trimethylpentane and cumene (99%) were obtained from Aldrich Chemical Company. The ethanol (USP Absolute-200 Proof) was from AAPER Alcohol and Chemical Company and was dehydrated over 4A molecular sieves from Fisher Chemical Company for 1 month. Nanopure water was obtained from the Microbiology Department at Oklahoma State University. Impurities were checked using an Dionex Series 4500I Ion Chromatograph and was less than one part per billion (ppb) for all contaminants. Table 2 lists the materials and chemicals used in the experiment.

Table 2: Materials and Chemicals

Material/Chemical	Catalog Number	Company
2,2,4-Trimethylpentane	25,877-6	Aldrich
Cumene	18,579-5	Aldrich
Nanopure Water	N/A	N/A
Ethanol	N/A	Aldrich
GasChrom 254 GC Column	2486	Alltech
4A Molecular Sieves	05256	Alltech
2 ml Crimp Top Vials	95221	Alltech
2 oz Amber Bottles	9537	Alltech
4 oz Amber Bottles	9538	Alltech

Compositions were measured with a Hewlett-Packard 5880A gas chromatograph using a thermal conductivity detector. Integration was accomplished with a Hewlett-Packard Level-4 integrator. The GasChrom 254 (Packed, 80-100 mesh, 1.8 m, 0.32 cm stainless steel coil) was obtained from Alltech.

All gravimetric measurements were made with a Mettler gravimetric balance with a precision of ±0.05 mg.

CHAPTER IV

EXPERIMENTAL PROCEDURE

GC CALIBRATION

The Hewlett-Packard 5880A gas chromatograph was calibrated using serial dilution techniques for ethanol with water and for cumene with 2,2,4-trimethylpentane. Volume ratios of 10:1 ethanol/water and 2,2,4-trimethylpentane/cumene were used in the initial dilutions, followed by a series of 2:1 dilutions until the lower detection limits were reached. The lower detection limit can be established by carrying out the dilutions until the GC response is no longer linear on a log-log graph of the mass ratio as a function of area ratio. Standards were prepared gravimetrically in 25 ml vials, cooled to 4 °C to reduce the effects of head space in the vial, stabilized for 30 min then immediately transferred into 11 ml crimp-top vials. All samples and standards were analyzed at the GC conditions listed in Table 3. Hamilton syringes are used to inject the samples in the GC.

Table 3. Gas Chromatograph Operating Conditions

Operating Conditions	Cumene Phase	Water Phase
Injector Temperature, °C	270	270
Detector Temperature, °C	300	300
Column Temperature, °C	270	150-270*
Carrier Gas Flow, ml/min	36	36

*Column temperature was ramped 30 °C/min to obtain proper chromatogram separation

The calibration curves are prepared by regressing the log(mass ratio) to the log(area ratio). Since the dehydrated ethanol contains small amounts of water (~.04-.10 %) that can significantly alter results, a procedure established by Chen and Wagner (3) is used. A single-point blanking method can not be used (3) because the calibration curves indicate a nonlinear response between the mass and area ratios and the concentration of the analyte from the dilution can at times be on the same order of magnitude as the water in the ethanol. A constant is introduced into the calibration equation that represents the effect of the trace water in the dehydrated ethanol, and is based on a multiple-point calibration.

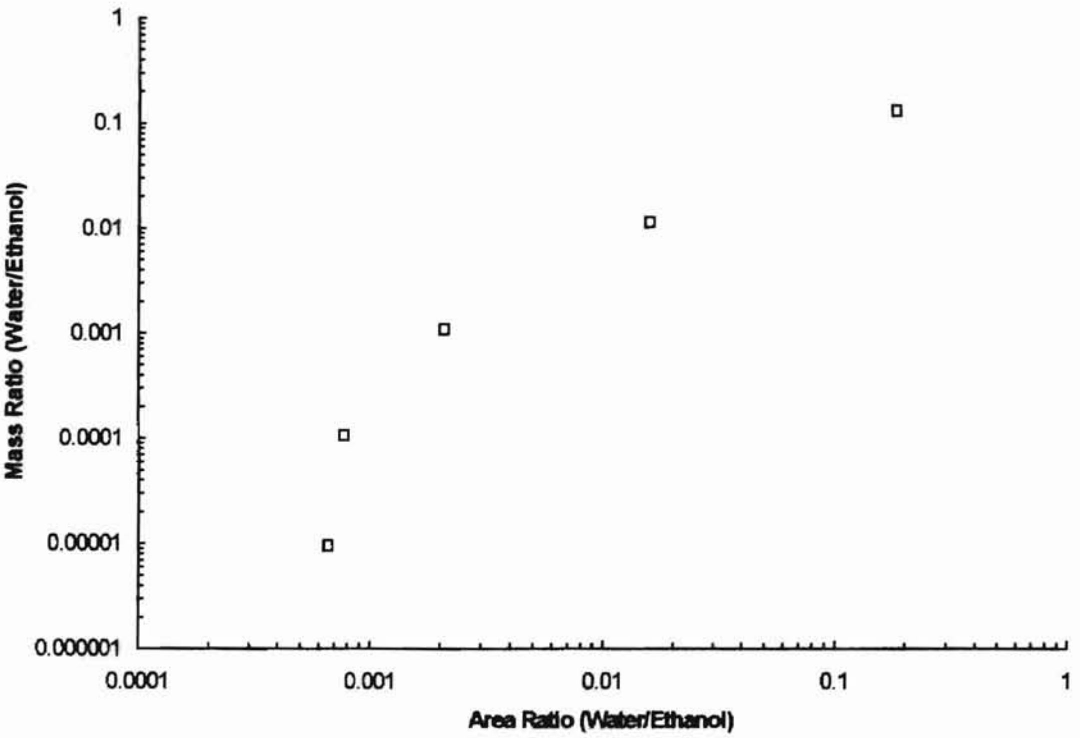

Figure 4. Calibration curve for water in ethanol (□, data)

Figure 4 shows that the lower detection limit is approximately 2.0×10^{-4}. Once the lower detection limit is established, the data in the linear region can be regressed to obtain the value for the constant for the blanking procedure. The general equation is of the form

$$W_R\left(\frac{W}{E}\right) = C_1 \times A_R\left(\frac{W}{E}\right)^{E_1} - C_2 \times A_{R,Blank}\left(\frac{W}{E}\right)^{E_2} \qquad (1)$$

where the second term is the value of the constant used in the regression, and can be calculated by extrapolating the data in the linear region to the x-intercept. Values of the constant are dependent upon the water concentration in the ethanol and can vary by batch.

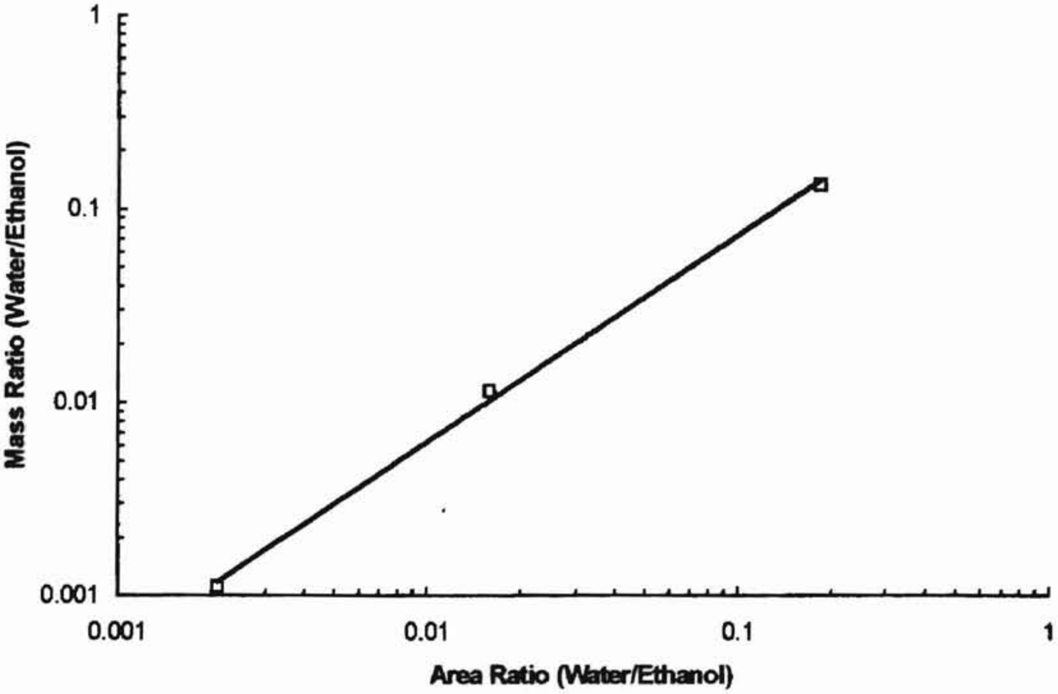

Figure 5. Calibration curve for water in ethanol (□, data: —, Eq. 2)

Figure 5 represents the data in the linear region and the regression results. The regression is used to determine the blanking constant, where the value of the blank is simply the weight ratio term in the following equation, using the area ratio of the ethanol blank:

$$W_R\left(\frac{W}{E}\right) = 0.8875 \times A_R\left(\frac{W}{E}\right)^{1.0719} \tag{2}$$

where W_R is the weight ratio of water (W) to ethanol (E) and A_R is the area ratio of water to ethanol. From this, we get the blanking equation:

$$C_b = 0.8875 \times A_{R,blank}\left(\frac{W}{E}\right)^{1.0719} \tag{3}$$

The constant is then added to each point (mass ratio of water/ethanol) when plotted for the final calibration curve, as shown in Figure 6.

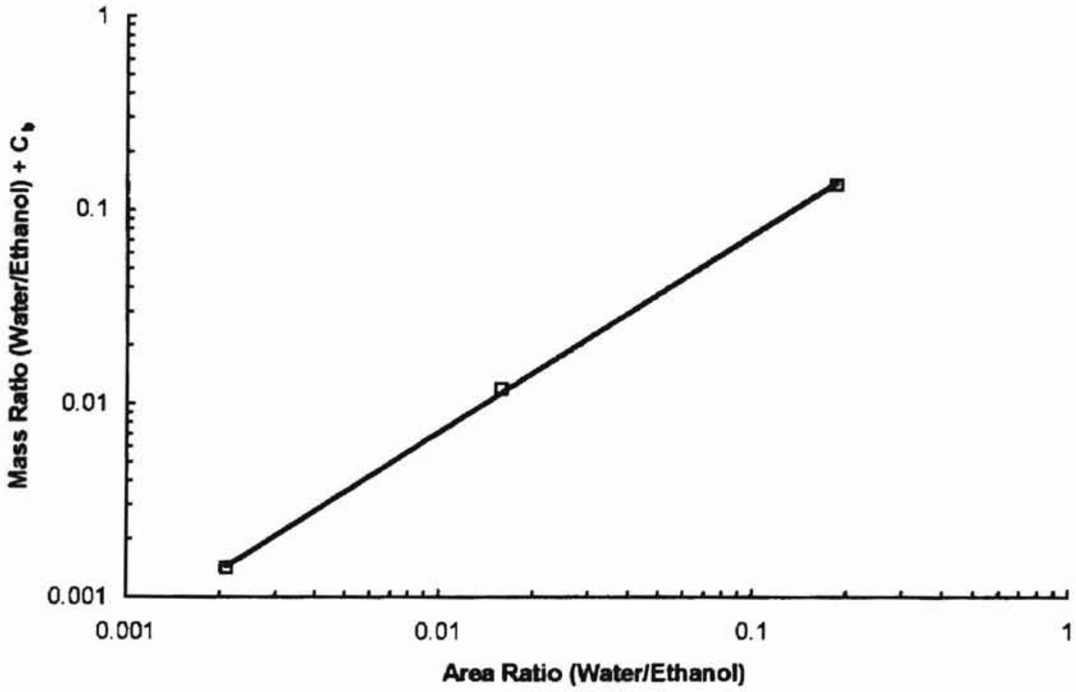

Figure 6. Calibration curves for water in ethanol (□, data:—, Eq. 4)

After the final blanking procedure, we have the equation

$$W_R\left(\frac{W}{E}\right) = 0.9098 \times A_R\left(\frac{W}{E}\right)^{1.1132} - 0.9098 \times A_{R,Blank}\left(\frac{W}{E}\right)^{1.1132} \qquad (4)$$

where $A_{R,Blank}$ is the area ratio of the ethanol blank. Figure 6 shows the final calibration curve with the constant included. The procedure as described above conveniently allows for multiple batches of ethanol to be used without having to recalibrate the chromatograph.

For the calibration of 2,2,4-trimethylpentane and cumene the same procedure is used, although no corrections are necessary due to the low solubility of trimethylpentane in water at room temperature (0.35 ppm at 298 K) (2).

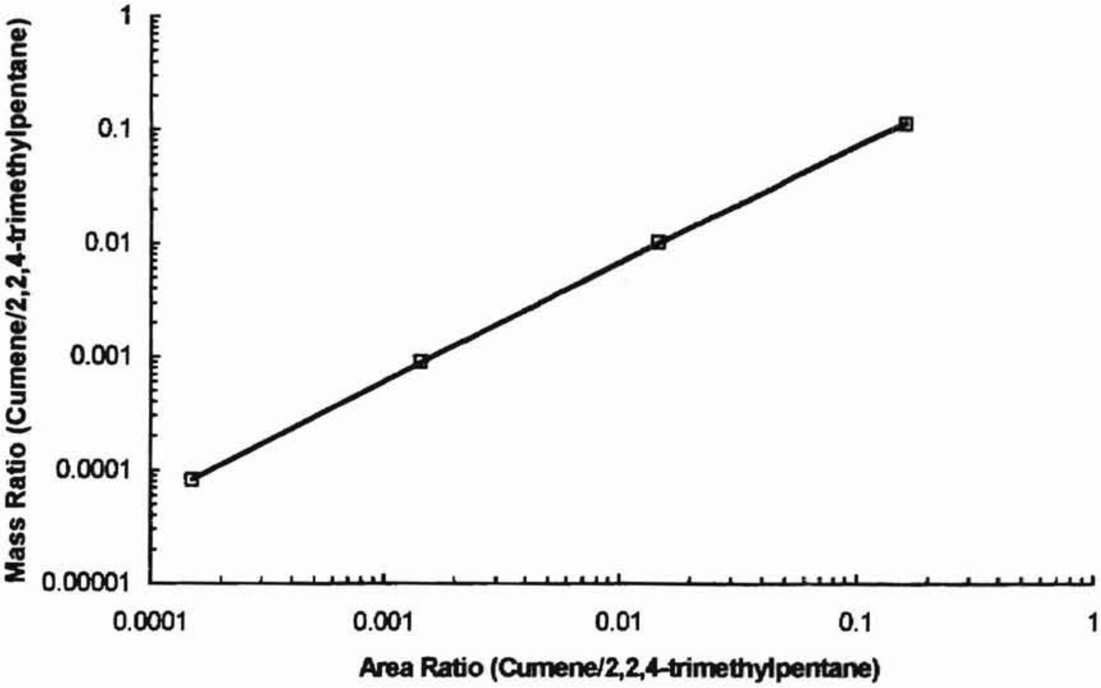

Figure 7. Calibration curve for cumene in 2,2,4-trimethylpentane (□, data: —, Eq. 5)

Figure 7 shows the data and curve fit for cumene/2,2,4-trimethylpentane. The following equation represents the calibration regression

$$W_R\left(\frac{CM}{TP}\right) = 0.8428 \times A_R\left(\frac{CM}{TP}\right)^{1.0479} \tag{5}$$

where (CM) is cumene and (TP) is 2,2,4-trimethylpentane.

SAMPLE ANALYSIS PROCEDURE

A new 2 oz. bottle is weighed on a balance to ±0.05 mg. It is then filled with 2,2,4-trimethylpentane or dehydrated ethanol and weighed again. The difference in the masses yields the amount of extractant or cosolvent added. Amounts of trimethylpentane and ethanol can vary, depending on the temperature. Trimethylpentane amounts varied from 2.0 - 3.2 ml and where increased with temperature in an attempt to remain at the same point on the calibration curve, as much as possible. To minimize the amount of ethanol, 3.0 - 6.0 ml were used and increased linearly with temperature from 303 to 373 K. After the masses are determined, the bottles are then cooled to 4 °C before the sampling procedure. The 2,2,4-trimethylpentane added to the sample bottle serves as an extractant for the cumene and also as an internal standard for GC analysis. The dehydrated ethanol serves as an internal standard and a homogenizing cosolvent.

The water and cumene feed are pumped through the apparatus for a period equal to the residence time of the system. The system flow rate should be in the range 2-3.2 ml/min. No significant variations in the solubilities at these flow rates were noticed by Chen and Wagner (1) and were verified by this study. At very low flow rates proper mixing is not accomplished and equilibrium is not achieved; at higher flow rates fluid entrainment is possible. Determining the residence time can be done by flushing the system with water and measuring the time it takes for the cumene to fill the sight gage to the inlet tap with the cumene flow controller closed. Typical residence times range from 50 to 75 min.

Once the system has equilibrated, the sample is passed through a Teflon lined septa and into the sample bottle. The sample bottles are filled to within 3 ml of the top to reduce the head space and to prevent a significant amount of mass transfer to the vapor phase.

The water phase sample is repeatedly and vigorously shaken to extract the cumene from the water immediately after sampling. This will also prevent the sample from freezing due to the elevated freezing point of the water by the cumene. The sample is then cooled to 4 °C and allowed to stabilize for at least 4 hrs before GC analysis. The operating conditions for the GC are listed in Table 3. The cumene phase is shaken after sampling and analyzed immediately.

CHAPTER V

RESULTS AND DISCUSSION

CUMENE SOLUBILITY IN WATER

The cumene solubility measurements were correlated using a non-linear regression program. Equation (6) gives the mole fraction of cumene in water and is correlated using the reduced temperature (the system temperature divided by the critical temperature of cumene).

$$\ln X_c = 15.457 - \frac{24.869}{T_R} + \frac{5.755}{T_R^2} \tag{6}$$

Figure 8 shows the data from this work corresponds well with Glew's measurements (7), yet is somewhat higher than the values of Sanemasa and Araki (16). Sanemasa and Araki (16) reported values for benzene that were "in serious disagreement of benzene with the literature; some 10 % lower than most literature values" (16). The same experimental procedure was used by Sanemasa and Araki for cumene solubility data, and the resulting values are 12 % lower than the values reported in this study. This is probably due to loss of solute in vapor above the aqueous solution as opposed to dissolution into the liquid phase (13). The escaping tendency of the solute vapor is reduced in this study by the ethanol blanket.

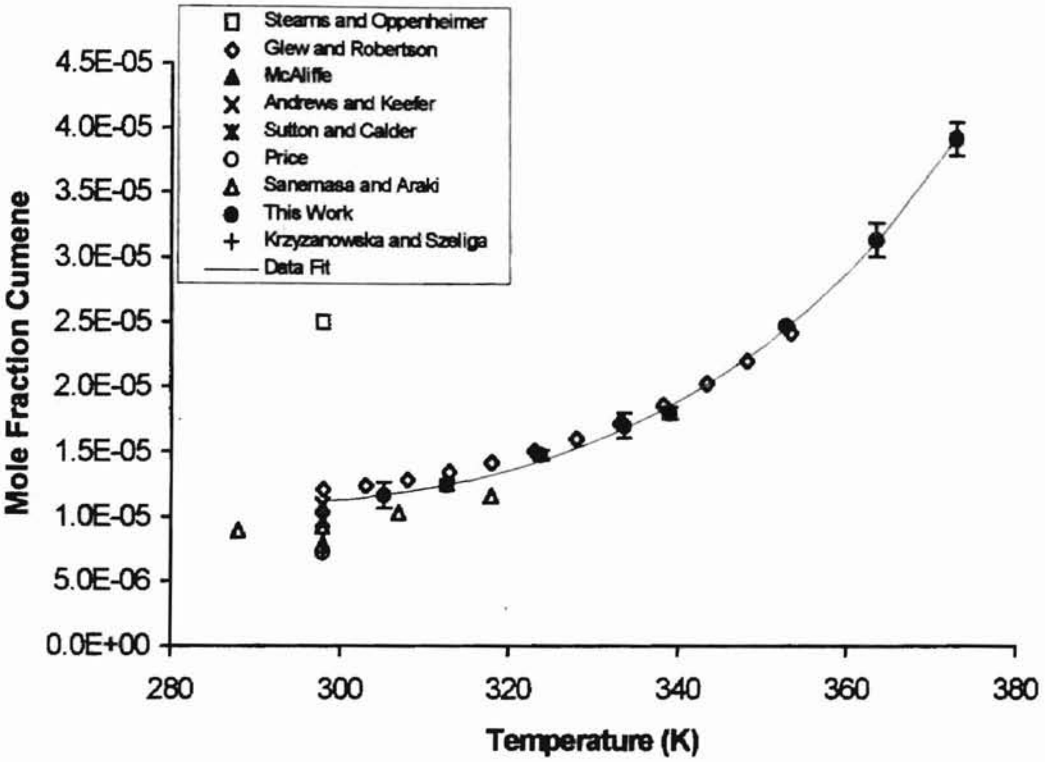

Figure 8. Solubility of Cumene in Water

From the Gibbs-Duhem equation

$$-\left(\frac{\partial \ln x_i}{\partial T}\right)_P = \frac{\Delta \overline{H_i}}{RT^2} \tag{7}$$

where ΔH_i is the difference between the partial molar enthalpy of component *i* in solution and the molar enthalpy of pure *i*. From Equations (6) and (7), the enthalpy of solution can be estimated. By assuming a very dilute system, the solvent activity coefficient (γ_i) is equal to one and the solute activity coefficient equivalent to

$$\gamma_i = \frac{1}{x_i}$$

hence, the enthalpy of solution is given by

$$\Delta H = -RT\left(\frac{24.869}{T_{R,i}} + \frac{11.510}{T_{R,i}^2}\right) \tag{8}$$

The enthalpy of solution obtained from Equation (8) is 2.63 ± 1.56 kJ/mol and compares well with the value of 3.56 kJ/mol reported by Glew et al. (7).

From the definition of the specific heat capacity, C_p, the specific heat of solution can be approximated as

$$\Delta C_P = \left(\frac{\partial \Delta H}{\partial T}\right) \tag{9}$$

and from Equations (6) and (9)

$$\Delta C_{P_i} = R\left(\frac{24.869}{T_R} + \frac{23.020}{T_R^2}\right) \tag{10}$$

The specific heat of the solution at 298 K was 0.419 ± 0.119 kJ/mol compared to 0.338 kJ/mol as reported by Wauchope and Hague (22). The enthalpy and specific heat of solution are first and second derivative results of solubility data, respectively. Derivative analysis, especially second derivative, is extremely sensitive to the solubility measurements and typically conflicts with other values found in the literature that use solubility data. It is good practice then to compare solubility-derived solution properties with calorimetric ones. For cumene none was available, but the fact that two independent solubility-derived studies yielded results that are consistent lends considerable support that the solubility measurements are correct.

The minimum solubility of the hydrocarbon in water occurs when

$$\frac{\partial \ln x}{\partial T} = 0 \tag{11}$$

Hence, the minimum solubility temperature can be approximated as

$$T_{\min} = -T_c\left(\frac{2C}{B}\right) \tag{12}$$

The calculated minimum solubility of 292.0 K compares well with a value of 285.8 reported by Glew (7), and is consistent with the other C_6-C_{10} alkybenznes, as reported by Chen and Wagner (4).

The excess Gibbs energy is given by

$$\Delta G_c^o = -RT\ln x_c \tag{13}$$

and yields a value of 28.2 ± 0.082 kJ/mol compared to 28.1 kJ/mol reported by Glew (7).

From fundamental property relations

$$\Delta H = \Delta G + T\Delta S \tag{14}$$

the entropy of mixing is -0.087 ± 0.0064 kJ/mol, Glew (7) reports a value of -0.082 kJ/mol. Table 4 summarizes the thermodynamic solution properties for cumene in water at 298 K.

Table 4: Thermodynamic functions for cumene in water at 298 K

	ΔH_c	ΔC_{pc}	ΔS_c	ΔG_c	$T_{\min,c}$
This Work	2.63 kJ/mol	0.419 kJ/mol	-0.087 kJ/mol	28.2 kJ/mol	292.0 K
Literature	3.56 kJ/mol	0.338 kJ/mol	-0.082 kJ/mol	28.1 kJ/mol	285.8 K
Reference	(7)	(22)	(7)	(7)	(7)

The cumene solubility measurements reported in this study, combined with previously published data by Chen and Wagner (2-4), are plotted as a function of molecular weight and temperature. A non-linear regression was used to fit the data and is intended only to show a trend and is not for the prediction of solubilities. Figure 9 indicates a decrease is solubility with increasing molecular weight and decreasing temperature. The fact that cumene falls in line with the other alkylbenzenes lends further support to the accuracy of the measurements.

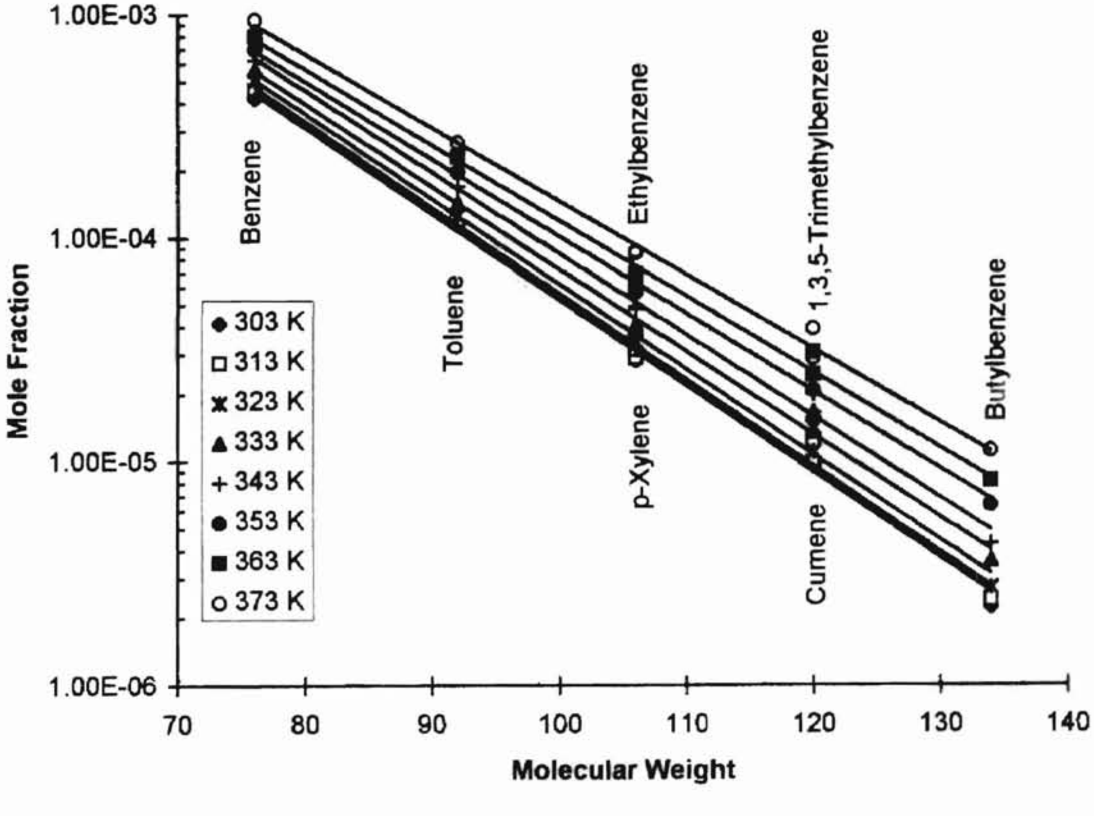

Figure 9: Effects of hydrocarbon molecular weight on solubility of alkylbenzenes

WATER SOLUBILITY IN CUMENE

For environmental wastewater concerns, the primary objective is to predict the hydrocarbon solubility in water so emission control devices can be designed and properly operated. Water solubility in cumene is not as valued, and as such, very limited data is available for water in cumene. The only literature data available are from Englin (5), and the temperature range is only slightly overlapping with this work. For the temperatures covered by both studies, the agreement is good between data, and the data curves seem to "fit" to one another, as can be seen from Figure 10

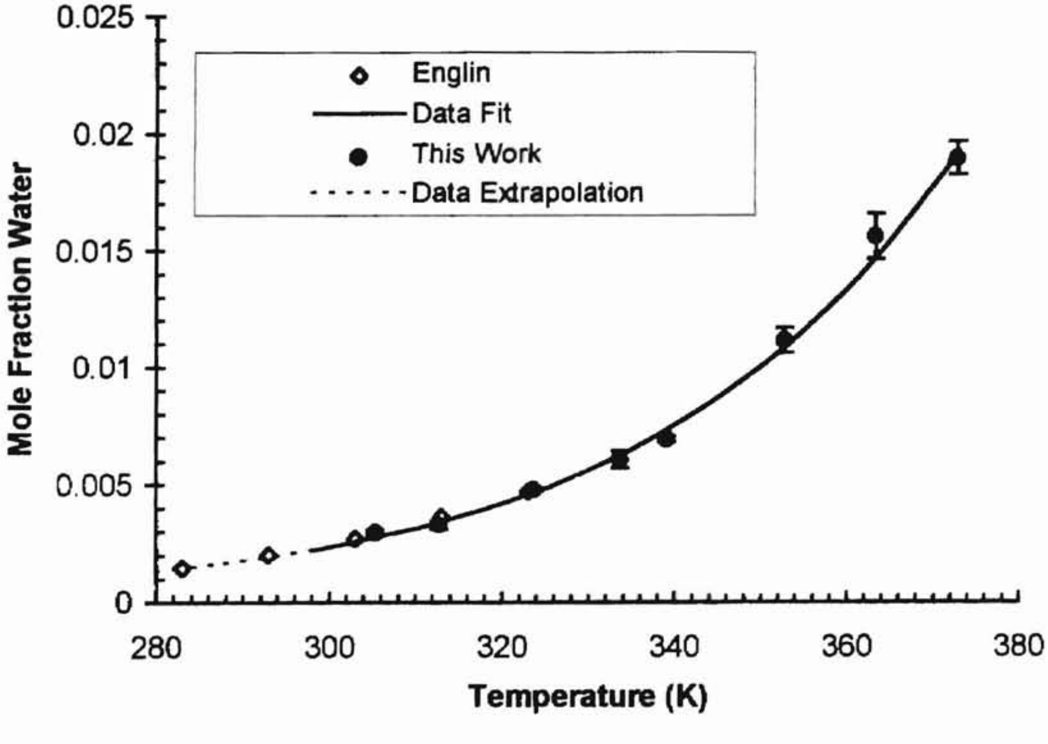

Figure 10. Solubility of Water in Cumene

A nonlinear regression performed on the data from this work yielded the following equation.

$$\ln X_w = 13.268 - \frac{13.935}{T_R} + \frac{2.309}{T_R^2} \tag{15}$$

From the following two relationships

$$\Delta G_w = -RT \ln x_w \tag{16}$$

$$\Delta S_w = -\frac{\partial \Delta G_w}{\partial T} \tag{17}$$

the entropy of mixing can be approximated as

$$\left(\frac{\partial \ln x_w}{\partial T}\right) = \frac{\Delta S_w}{RT} \tag{18}$$

where ΔS_w is the difference between the partial molar entropy of component *i* in solution and the molar entropy of pure *i*. Assuming the entropy of mixing for water dissolving in the cumene is essentially constant, Equation (17) can be integrated. Results by Chen and Wagner (4) showed that the slope ($\partial \ln x_i / \partial T$) for the water phase is essentially constant for most alkylbenzenes, and indicated that liquid water dissolving into a liquid hydrocarbon phase is a process of breaking hydrogen bonds. Table 5 lists the values for the entropy and enthalpy of mixing for cumene and the hydrocarbons studied by Chen and Wagner (2,3,4). Results are consistent with the existing theory as discussed above, with the enthalpy and entropy of solution being essentially constant for all the alkylbenzenes. The enthalpy of mixing (21.1 ± 1.97 kJ/mol) is consistent with the approximate hydrogen bond energy of 21-29 kJ/mol (20). Values reported by Chen and Wagner (4) ranged from 23.3-25.7 kJ/mol. The entropy of mixing for water in cumene (0.706 ± 0.0055 kJ/mol) is consistent with the other alkylbenzenes (2-4).

Table 5. Entropy and Enthalpy of Solution for Water in Cumene at 298 K

Hydrocarbon	ΔH_w(kJ/mol)	ΔS_w(kJ/mol)
Benzene	23.3	0.0782
Toluene	23.9	0.0802
Ethylbenzene	24.1	0.0808
p-Xylene	24.4	0.0818
1,3,5-Trimethylbenzene	23.7	0.0794
Cumene	21.1	0.0706
Butylbenzene	25.7	0.0862

Based on the given assumptions, all values for the enthalpy of solution should be constant; however, cumene has a significantly higher dipole moment than the other alkylbenzenes studied. This higher dipole moment allows the water to assimilate into the cumene phase more readily, hence the lower enthalpy of solution. Table 6 list the dipole moments for the compounds studied.

Table 6: Comparison of dipole moments of selected alkylbenzenes

Component	Dipole Moment
Benzene	0.03
Butylbenzene	0.36
Cumene	0.4-0.65
Ethylbenzene	0.37-0.39
Toluene	0.3-0.387
1,3,5-Trimethylbenzene	0.13
p-Xylene	0.1

SUMMARY

Mutual solubilities of cumene + water mixtures have been measured for a temperature range of 303 to 373 K using a method and apparatus described by Chen and Wagner (2). Heat capacity, enthalpy, and entropy of solution have been calculated and compare well with the literature data available for cumene. Fundamental thermodynamic relationships, such as the definition of heat capacity and the Gibbs-Duhem equation, were used to calculate the mixture physical properties using derivative-solubility data analysis. The enthalpy of solution for water is approximately equal to the molar hydrogen bonding energy of water. The result is consistent with existing theory of solution thermodynamics and tends to support the accuracy of the measurements. Enthalpy of solution for cumene is also consistent with literature values derived from solubility data.

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Appendix A

Solubility and Thermodynamic Data for Cumene + Water

Table A1. Solubility of Cumene in Water

Temperature (K)	Pressure (psia)	Mole Fraction Cumene	Standard Deviation	Number of Samples
305.3	15.6	1.16E-05	9.53E-07	6
312.7	16.0	1.24E-05	5.66E-07	3
323.8	15.6	1.48E-05	1.22E-06	6
333.6	16.1	1.70E-05	1.45E-06	4
339.1	15.5	1.80E-05	5.38E-07	6
352.8	15.5	2.47E-05	1.83E-07	3
363.5	24.1	3.14E-05	1.90E-06	3
373.1	25.3	3.93E-05	1.67E-06	6

Table A2. Solubility of Cumene in Water (all measurements)

Temperature (K)	Pressure (psia)	Mole Fraction Cumene
305.3	15.6	9.324E-06
305.3	15.6	1.189E-05
305.3	15.6	1.263E-05
305.3	15.6	1.111E-05
305.3	15.6	1.261E-05
305.3	15.6	1.123E-05
312.7	16.0	1.190E-05
312.7	16.0	1.237E-05
312.7	16.0	1.303E-05
323.8	15.6	1.518E-05
323.8	15.6	1.490E-05
323.8	15.6	1.429E-05
323.8	15.6	1.486E-05
323.8	15.6	1.433E-05
323.8	15.6	1.542E-05
333.6	16.1	1.887E-05
333.6	16.1	1.597E-05
333.6	16.1	1.642E-05
333.6	16.1	1.731E-05
339.1	15.5	1.743E-05
339.1	15.5	1.796E-05
339.1	15.5	1.883E-05

Table A2 cont.

Temperature (K)	Pressure (psia)	Mole Fraction Cumene
339.1	15.5	1.776E-05
339.1	15.5	1.845E-05
339.1	15.5	1.759E-05
352.8	15.5	2.470E-05
352.8	15.5	2.455E-05
352.8	15.5	2.489E-05
363.5	24.1	2.942E-05
363.5	24.1	3.111E-05
363.5	24.1	3.321E-05
373.1	25.3	4.079E-05
373.1	25.3	4.007E-05
373.1	25.3	3.619E-05
373.1	25.3	3.918E-05
373.1	25.3	3.949E-05
373.1	25.3	4.052E-05

Table A3. Solubility of Water in Cumene

Temperature (K)	Pressure (psia)	Mole Fraction Water	Standard Deviation	Number of Samples
305.3	15.6	2.98E-03	2.04E-04	5
312.7	16.0	3.40E-03	2.51E-04	2
323.8	15.6	4.81E-03	1.05E-04	3
333.6	16.1	6.10E-03	4.32E-04	3
339.1	15.5	6.97E-03	1.31E-04	6
352.8	15.5	1.17E-02	8.38E-04	3
363.5	24.1	1.62E-02	1.39E-03	3
373.1	25.3	1.90E-02	1.10E-03	6

Table A4. Solubility of Water in Cumene (all measurements)

Temperature (K)	Pressure (psia)	Mole Fraction Water
305.3	15.6	3.21E-03
305.3	15.6	2.87E-03
305.3	15.6	2.96E-03
312.7	16.0	3.48E-03
312.7	16.0	3.12E-03
323.8	15.6	4.91E-03
323.8	15.6	4.71E-03
323.8	15.6	4.82E-03
333.6	16.1	5.56E-03
333.6	16.1	6.29E-03
333.6	16.1	6.47E-03
339.1	15.5	7.03E-03
339.1	15.5	6.88E-03
339.1	15.5	6.88E-03
339.1	15.5	7.17E-03
339.1	15.5	7.00E-03
339.1	15.5	6.81E-03
352.8	15.5	1.04E-02
352.8	15.5	1.20E-02
352.8	15.5	1.12E-02
363.5	24.1	1.69E-02

Table A4 cont.

Temperature (K)	Pressure (psia)	Mole Fraction Water
363.5	24.1	1.51E-02
363.5	24.1	1.43E-02
373.1	25.3	1.86E-02
373.1	25.3	1.80E-02
373.1	25.3	1.93E-02
373.1	25.3	1.83E-02
373.1	25.3	1.86E-02
373.1	25.3	2.10E-02

Table A5. Enthalpy of Solution for Cumene

Temperature	ΔH(kJ/mol)	ΔH(Cal/mol)
298	2.63	629
303	4.74	1133
313	8.76	2092
323	12.53	2992
333	16.07	3838
343	19.40	4634
353	22.55	5386
363	25.52	6095
373	28.33	6767

Table A6. Heat Capacity of Solution for Cumene

Temperature	ΔC_p(J/mol)	ΔC_p(cal/mol)
298	419	100
303	398	95
313	359	86
323	325	78
333	294	70
343	266	64
353	241	58
363	218	52
373	197	47

Table A7. Entropy and Enthalpy of Solution for Water in Cumene

Temperature	ΔH(kJ/mol)	ΔS(kJ/mol)
298	21.1	0.0706
303	21.9	0.0723
313	23.6	0.0754
323	25.2	0.0780
333	26.7	0.0802
343	28.1	0.0819
353	29.4	0.0834
363	30.7	0.0845
373	31.9	0.0854

Appendix B

Solubility Data for Toluene + Water

Table B1. Solubility of Toluene in Water

Temperature (K)	Pressure (psia)	Mole fraction Toluene	Standard Deviation	Number of Measurements
302.6	17.0	1.03E-04	1.79E-06	3
302.5	15.9	1.04E-04	7.29E-06	3
302.9	16.1	1.05E-04	2.22E-06	2
312.4	16.1	1.10E-04	1.40E-06	3
329.6	15.7	1.43E-04	1.43E-05	2
345.8	15.5	1.67E-04	5.79E-07	2

Table B2. Solubility of Toluene in Water (all measurements)

Temperature (K)	Pressure (psia)	Mole Fraction Toluene
302.6	17.0	1.01E-04
302.6	17.0	1.04E-04
302.6	17.0	1.04E-04
302.5	15.9	9.58E-05
302.5	15.9	1.10E-04
302.5	15.9	1.05E-04
302.9	16.1	1.04E-04
302.9	16.1	1.07E-04
312.4	16.1	1.09E-04
312.4	16.1	1.11E-04
312.4	16.1	1.11E-04
329.6	15.7	1.39E-04
329.6	15.7	1.46E-04
345.8	15.5	1.66E-04
345.8	15.5	1.67E-04

Table B3. Solubility of Water in Toluene

Temperature (K)	Pressure (psia)	Mole Fraction Water	Standard Deviation	Number of Measurements
302.6	17.0	2.94E-03	2.20E-04	3
302.5	15.9	2.54E-03	8.24E-05	3
302.9	16.1	2.43E-03	3.21E-04	3
312.4	16.1	3.73E-03	2.28E-04	3
329.6	15.7	6.00E-03	3.63E-05	2
345.8	15.5	1.03E-02	----	1

Table B4. Solubility of Water in Toluene (all measurements)

Temperature (K)	Pressure (psia)	Mole Fraction Water
302.6	17.0	3.17E-03
302.6	17.0	2.74E-03
302.6	17.0	2.90E-03
302.5	15.9	2.64E-03
302.5	15.9	2.50E-03
302.5	15.9	2.49E-03
302.9	16.1	2.77E-03
302.9	16.1	2.39E-03
302.9	16.1	2.13E-03
312.4	16.1	3.81E-03
312.4	16.1	3.92E-03
312.4	16.1	3.48E-03
329.6	15.7	5.98E-03
329.6	15.7	6.03E-03
345.8	15.5	1.03E-02

Appendix C

Error Analysis

ERROR PROPAGATION

To determine the propagation of errors in the results, we take Eq (7) which is of the form

$$\partial H = f(x_i, T) \tag{19}$$

where x_i and T are directly measured quantities. Errors in Δx_i and ΔT will cause an error in ΔH, so that

$$\partial H + \Delta \partial H = f(x_i + \Delta x_i, T + \Delta T) \tag{20}$$

Expanding the right-hand member using a Taylor's theorem for a function of several variables we have

$$\Delta(\Delta H) = \frac{\partial \Delta H}{\partial x_i} \Delta x_i + \frac{\partial \Delta H}{\partial T} \Delta T \tag{21}$$

which is the total differential of the function ΔH.

With further simplification and substitution, we arrive at the law of propagation of errors for the enthalpy of solution

$$R = \sqrt{\left(\left(\frac{\partial \Delta H}{\partial x_i} \right)^2 \Delta x_i^2 + \left(\frac{\partial \Delta H}{\partial T} \right)^2 \Delta T^2 \right)} \tag{22}$$

From Equation (7)

$$\left(\frac{\partial \ln x_i}{\partial T} \right)_P = \frac{\Delta \overline{H_i}}{RT^2}$$

we can approximate the left-hand term as

$$\frac{\ln x_2 - \ln x_1}{T_2 - T_1} \tag{24}$$

and this will allow us to evaluate the function. This approximation is excellent for the water-in-cumene analysis. For the cumene solubility analysis we must evaluate the function at points close to the temperature at which the variable is measured, and in a region that is linear in x_i and T.

The following equation was derived and used to calculate the error propagation:

$$R(\Delta H) = \sqrt{\left(\left(\frac{-RT^2}{x_1(T_2 - T_1)}\right)^2 \Delta x_i^{\,2} + \left(\frac{RT^2(\ln x_2 - \ln x_1)}{(T_2 - T_1)^2}\right)^2 \Delta T^2\right)} \qquad (25)$$

The propagated errors for the other thermodynamic functions were derived in a similar manner. Below are the forms of the remaining error propagation equations.

$$\Delta(\Delta G) = \frac{-RT}{x}\Delta x \qquad (26)$$

$$\Delta(\Delta S) = \sqrt{\left(\frac{-RT}{x_1(T_2 - T_1)} + \frac{R}{x_1}\right)^2 \Delta x^2 + \left(\frac{RT(\ln x_2 - \ln x_1)}{(T_2 - T_1)^2}\right)^2 \Delta T^2} \qquad (27)$$

$$\Delta(\Delta C_p) = \sqrt{\left(\frac{RT^2}{x_1(T_2 - T_1)^2}\right)^2 \Delta x^2 + \left(\frac{2RT^2(\ln x_2 - \ln x_1)}{(T_2 - T_1)^3}\right)^2 \Delta T^2} \qquad (28)$$

SAMPLE CALCULATION

Given the following conditions:

$T_1 = 305$ K

$T_2 = 373$ K

$x_1 = 1.16E\text{-}05$

$x_2 = 3.93E\text{-}05$

R= 0.008314 kj/mol K

$\Delta T = 0.1$ K

$\Delta x_i = 1.67E\text{-}06$

and substituting into Equation (25),

$$R(\Delta H) = \sqrt{\left(\left(\frac{-0.008314 \times 298^2}{1.16E-05(373-305)}\right)^2 \Delta x_i^{\,2} + \left(\frac{0.009314 \times 298^2\left(\ln(3.93E-05) - \ln(1.16E-05)\right)}{(373-305)^2}\right)^2 \Delta T^2\right)}$$

we arrive at the error propagation (± 1.56 kj/mol) for the enthalpy of mixing for cumene + water. The remaining results are summarized in Table C1.

Table C1: Propagated error for cumene

	ΔH_c	ΔC_{pc}	ΔS_c	ΔG_c
Error	±1.56 kJ/mol	±0.119 kJ/mol	±0.0064 kJ/mol	±0.082 kJ/mol

Table C2: Propagated error for water

	ΔH_c	ΔS_c
Error	±1.97 kJ/mol	±0.0055 kJ/mol

Appendix D

Thermocouple and Pump Calibrations

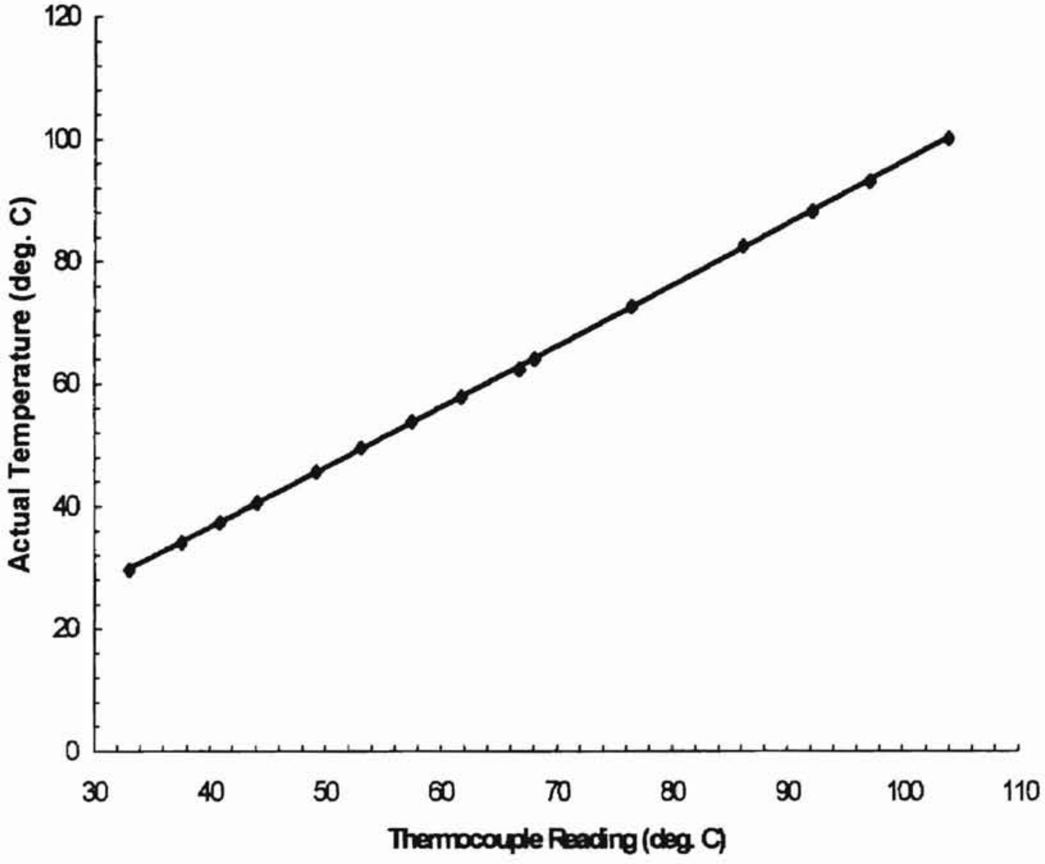

Figure D1. Thermocouple calibration for cumene/water apparatus

Table D1: Thermocouple calibration data

Thermocouple Reading (°C)	Measured Resistance (Ω)	Actual Temperature (°C)
33.0	111.89	29.7
37.6	113.65	34.21
40.9	114.96	37.5
44.1	116.18	40.6
49.2	118.19	45.7
53.1	119.74	49.64
57.5	121.40	53.87
61.8	122.97	57.87
66.8	124.75	62.41
68.1	125.38	64.02
76.5	128.77	72.7
86.2	132.65	82.65
92.2	134.84	88.3
97.2	136.75	93.2
104.0	139.43	100.15

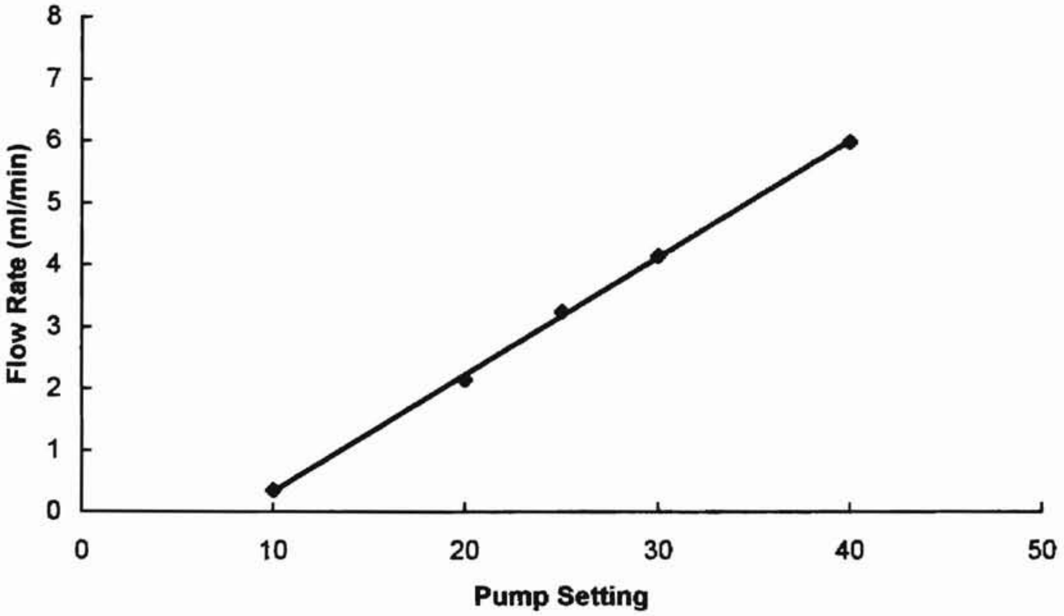

Figure D2. Calibration curve to determine residence time

Data was regressed linearly to obtain a calibration curve for the mini-pump, which was in turn used to calculate the residence time for a particular flow rate. The following equation was used to determine the residence time of the system

$$RT = \frac{170}{\left(0.1894 \times \left(\mathit{pump\ setting}\right) - 1.5607\right)} \tag{28}$$

Table D2: Pump Calibration Data

Pump Setting	Flow Rate (ml/min)
10	0.353
20	2.14
25	4.14
30	3.24
40	6.00

VITA

Brooks David Bennett

Candidate for the Degree of

Master of Science

Thesis: Mutual Solubilities of Cumene + Water

Major Field: Chemical Engineering

Personal Data: Born in Redondo Beach, California on 06 September 1970 and left as fast as possible. Son of Reginald and Sandra Bennett.

Education: Received a Bachelor of Science from Oklahoma State University in Stillwater, Oklahoma in May 1995. Began the requirements for a Master of Science in Chemical Engineering at Oklahoma State University in January 1996. Completed the Requirements for the Master of Science degree at Oklahoma State University in December, 1997

Experience: Served as a Teaching Assistant for Thermodynamics January 1996 to August 1997