Table II. Measured Equilibrium Compositions and Flow Rates at 602.8 K and 21.80 bar

	mole fracn toluene in	
tot flow rate, mL/h	liquid	vapor
100	0.423	0.659
150	0.421	0.655
200	0.421	0.655
250	0.423	0.656
300	0.425	0.658
350	0.421	0.659
400	0.423	0.655

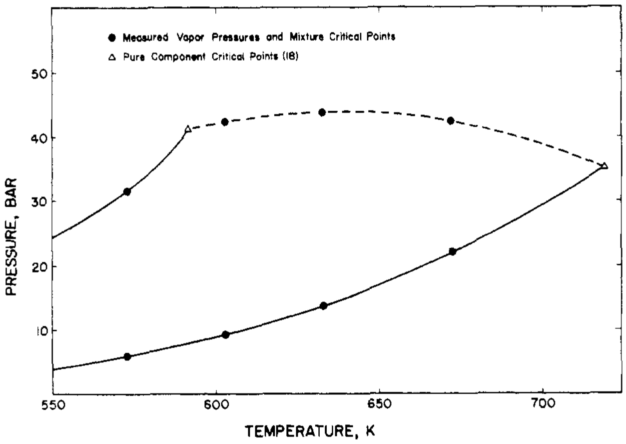

Figure 3. Pressure-temperature projection of gas-liquid critical curves for the tetralin/toluene system.

measure VLE at elevated temperatures for systems containing tetralin (*16*) clearly indicate the need for a flow technique for this type of study.

The measured vapor pressures and critical pressures can be used to construct the complete gas-liquid critical curve for this system (see Figure 3). The gas-liquid critical curve is continuous and exhibits a shallow pressure maximum (*17*). For the methanol/tetralin system which was previously studied, the critical curve exhibits a more pronounced pressure maximum (*3*).

Registry No. Tetralin, 119-64-2; toluene, 108-88-3.

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Solubility of Cycloparaffins in Distilled Water and Salt Water

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Solubilities of cyclopentane, cyclohexane, methylcyclohexane, and cycloheptane were measured in distilled water and salt water (34.5 parts of NaCl per thousand parts of water). The salt water solubilities were correlated by the polar solubility parameter method. A method for predicting salt water solubility from known distilled water solubility was developed.

Introduction

The transport and fate of organic chemicals released into the environment is a major concern today for environmental protection. Leakage of gasoline from underground storage tanks is a good example of current interest. Solubility of the leaked materials is one of the physical chemical properties that determines the transport rate of the pollutants in the environment.

This paper describes experimental measurements of solubility of cycloparaffins of the molecular weight range found in gasoline. Most of the measurements were at 25 °C. Solubility was determined in distilled water for comparison with the literature values and in sodium chloride solutions having salinity in the range of sea water.

Experimental Section

The experimental approach was an adaptation of the method used by Polak and Liu (*1*). Hydrocarbon was equilibrated with water in 40-mL vials fitted with Teflon-lined septa. Water (~20 mL) was placed into the vial first. The vial was inverted and hydrocarbon was injected by means of a hypodermic needle into the space above the water. A second needle in the air space allowed air to escape as hydrocarbon was injected.

The vials were placed in inverted position in a constant temperature bath controlled to within ±0.1 °C. Except for occasional gentle swirling no agitation was done. After about 2 weeks the water and hydrocarbon layers had equilibrated, and the water layer was analyzed to determine hydrocarbon solubility.

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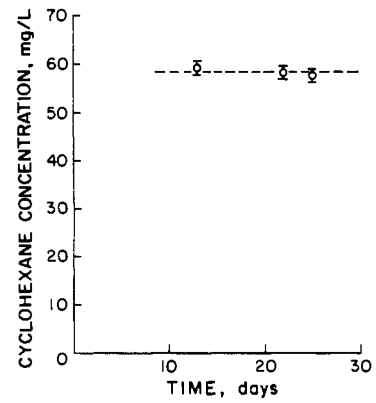

Figure 1. Approach to equilibrium.

Table I. Experimental Results

	solubility, mg/L (at 25 °C except as noted)		
	distilled water		salt water[a] (this work)
hydrocarbon	this work	lit.	
cyclopentane	164 ± 3.6	160,[b] 156[c]	128 ± 1.0
cyclohexane	58.4 ± 1.0	55,[c] 57.5[d]	40.1 ± 0.4
cycloheptane	27.1 ± 1.4 (30 °C)	30[c] (25 °C)	17.0 ± 0.2 (30 °C)
methylcyclohexane	16.7 ± 0.6	16[b]	11.5 ± 0.1

[a] 34.5 parts NaCl per 1000 parts water. [b] Price (*5*). [c] McAuliffe (*6*). [d] Mackay and Shiu (*7*).

The vials were sampled with the aid of a microliter syringe. Two-microliter samples were injected into a gas chromatographic column. The column used was $^1/_8$-in.-diameter stainless steel, 10 ft long; 3% SP-1500 on CARBOPACK B at 150 °C; helium carrier gas at 30 mL/min; flame ionization detector. This column permits direct injection of aqueous samples.

Figure 1 shows the approach of a typical vial to equilibrium over a period of several weeks. After 2 weeks, the slope of the least-squares line through the three determinations was zero within experimental error. Solubility determinations were done for distilled water and for salt water (34.5 parts of sodium chloride by weight per 1000 parts of water). All cycloparaffins were obtained from Aldrich Chemical Co.: cyclopentane (97%), cyclohexane (99.9%), cycloheptane (98%), and methylcyclohexane (99%). They were used without further purification. The gas chromatograms showed that the very small amounts of impurities remained in the hydrocarbon phase and thus had negligible cosolvent effect on the aqueous solubility.

Results

Table I shows the resulting distilled water and salt water solubilities. Literature values of distilled water solubility are given for comparison. All results are averages of four replicate determinations. Precision is shown by the standard deviation of this average. Relative precision is better than ±5.2% for all results. The satisfactory agreement with literature values is an indication of the validity of the method used in this work and the accuracy of the results.

Discussion

The results were correlated by means of the polar solubility parameter theory (*2*). For sparingly soluble materials, like the cycloparaffins, the solubility (mole fraction) can be shown to be equal to the reciprocal of the activity coefficient of the solute in the dilute solution:

$$x_{is} = 1.0/\gamma_i^{\infty} \tag{1}$$

Table II. Solubility Parameter Correlation Results

	ψ_{12}, cal			solubility in salt water,[a] mg/L	
component	dist water	salt water[a]	$\Delta\psi_{12}$	exptl	pred
cyclopentane	198.0	197.3	0.7	128	124
methylcyclopentane[b]	198.0	197.1	0.9	29.2	30.5
cyclohexane	198.1	197.2	0.9	40.1	44.3
methylcyclohexane	198.6	197.8	0.8	11.5	11.4
cycloheptane	197.8	196.8	1.0	17.9	19.6

[a] 34.5 parts of NaCl per 1000 parts of water. [b] Data from Price (*5*).

Thus the prediction of the solubility reduces to the prediction of this activity coefficient. Helpinstill and Van Winkle used a modification of the regular solution theory of Hildebrand (*3*) to calculate activity coefficients.

$$RT \ln \gamma_2^{\infty} = V_2[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}] + RT\left[\ln\left(\frac{V_2}{V_1}\right) + \left(1 - \frac{V_2}{V_1}\right)\right] \tag{2}$$

The key to this approach is the use of a polar solubility parameter, τ_1, to characterize the solvent power of the polar solvent, water.

The solubility parameters (λ_i), polar solubility parameters (τ_i), and molar volumes, V_i, are all pure-component parameters, which are normally known. The only mixture parameter in the equation is the interaction energy, ψ_{12}, which must be determined from experimental solubility data. Helpinstill and Van Winkle found that, for nonpolar solutes in a single solvent, e.g., water, ψ_{12} is approximately constant for a given homologous series (paraffins, olefins, aromatics).

Table II (first column) shows that this is true for the cycloparaffins in distilled water based on the solubility data reported earlier. The second column of Table II was calculated by using the same polar solubility parameter as for pure water. These new values of interaction energy characterize the solvent power of salt water (34.5 parts of NaCl per thousand) for the cycloparaffins. The salt water interaction energies are also approximately the same.

The approximate constancy of ψ_{12} provides a method for predicting approximately the solubility (in distilled water or salt water) of an unknown compound of the same class. Thus using ψ_{12} for a compound of known solubility and similar structure one could calculate an approximate solubility for a compound whose solubility has not been determined. The calculated solubility is quite sensitive to the value used for ψ_{12} and so the resulting prediction will only be approximate. Errors of ±50% in predictions would be common.

For example, using ψ_{12} for methylcyclohexane the distilled water solubility of ethylcyclohexane was predicted to be 5.5 mg/L. An estimate from a nomograph given by Kabadi and Danner (*4*) gives 3.3 mg/L.

The third column of Table II shows that the difference in ψ_{12} from distilled water to salt water is approximately constant and of the order of 0.8. This provides a way of predicting salt water solubility if distilled water solubility is known. One deducts 0.8 from ψ_{12} for distilled water to get an estimate for ψ_{12} for salt water. Using this estimate one computes an approximate salt water solubility. Column four of Table II shows that the solubilities predicted in this way for the cycloparaffins are quite satisfactory.

Acknowledgment

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Registry No. NaCl, 7647-14-5; cyclopentane, 287-92-3; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; cycloheptane, 291-64-5.

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Vapor–Liquid Equilibria for *m*-Cresol/Quinoline at Temperatures between 523 and 598 K

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Binary vapor–liquid equilibria are reported for the binary systems of *m*-cresol and quinoline at 250, 275, 300, and 325 °C as well as pure-component vapor pressures. These compounds are of interest because they form highly nonideal mixtures and are also models for coal liquids. Due to hydrogen-bonding capabilities, both *m*-cresol and quinoline are quite hygroscopic. Water was found to be a major impurity and had very large effects on the vapor pressures and the VLE measurements, even at extremely low concentrations. The *m*-cresol/quinoline data indicated a high-boiling azeotrope at very low *m*-cresol concentrations that disappeared at higher temperatures.

Introduction

As part of a continuing effort to study the phase behavior of coal-derived liquid model compounds, an equilibrium flash vaporization flow system has been developed (*1*). This system can be used to measure vapor–liquid equilibria (VLE) data at temperatures up to 350 °C and pressures up to 10 MPa and was initially used to study the ethanol/water and the methanol/ethanol systems (*1*).

This equipment has recently been used to generate phase behavior data at 250, 275, 300, and 325 °C for the binary systems of quinoline and *m*-cresol as well as pure-component vapor pressures. These compounds have been selected for two major reasons. Firstly, the compounds are polar and exhibit hydrogen bonding. Thermodynamic research for highly nonideal compounds has been left virtually untouched especially at high temperatures and pressures. Without actual data, proposed equations of state and mixing rules for nonideal systems cannot be tested. Therefore, results of this research will provide basic thermodynamic data for the evaluation and development of models. Secondly, it has been found that the modeling of coal liquids with traditional Kesler–Lee type petroleum correlations (*2*) gives unpredictable results. It has been proposed that the failure of the petroleum correlations for the coal liquids is due to the presence of polar associating compounds in the coal liquids (*3*). *m*-Cresol is considered to be typical of the acidic compounds in coal liquids and quinoline a typical base; consequently, the interactions between *m*-cresol and quinoline may be indicative of the interactions occurring in coal liquids.

A major problem has been encountered in obtaining the VLE data. Since both *m*-cresol and quinoline are capable of hydrogen bonding, they are both quite hygroscopic. Water has been found to be the major impurity and has surprisingly significant effects even at extremely low concentrations. Estimations of the effects of water on our measurements are included in this paper.

Experimental Section

The VLE data were generated on an equilibrium flash vaporization flow system which can operate at temperatures up to 350 °C and pressures up to 10 MPa. A detailed description of the equipment has been previously presented (*1*). The temperature measurements have an estimated accuracy of ±0.1 °C and the pressure measurements are estimated to have an accuracy of ±0.7 kPa below 689.5 kPa and ±3.5 kPa between 689.5 and 3500 kPa. The flow system was particularly advantageous for compounds which decompose at elevated temperatures, since decomposition products tend to be flushed from the equilibrium cell.

The sample analyses were performed on an Hewlett-Packard Model 5710A gas chromatograph with a flame ionization detector (FID). The column chosen was a Hewlett-Packard Series 530 19095S #100 which has a 2.65-μm coating of methylsilicone. The column performed well because it is slightly polar and therefore separates quinoline and *m*-cresol. Each sample was bracketed by two standards so that a relative response factor could be calculated for the sample. With good technique, the accuracy of the analyses was shown to be ±0.001 mole fraction. This accuracy was determined by analyzing samples whose concentrations were known by weight.

The *m*-cresol was purchased from Sigma Chemical Co. with a stated purity of 99%; by gas chromatograph analysis it was typically found to be 99.8%. However, the water content was difficult to determine below 0.1 wt %. All of the *m*-cresol was distilled in a Perkin Elmer spinning band distillation column to remove the water to the lowest possible level. Vapor pressure measurements agreed with literature values, indicating successful removal of the contaminants.

Synthetic quinoline was purchased from J.T. Baker and Alfa Products at a purity level of 99%. Synthetic quinoline was required since other sources of quinoline had significant quantities of isoquinoline as a contaminant. The quinoline was distilled to raise the purity to 99.9%, as determined by gas chromatography, and to eliminate water.

Even though the samples were initially purified to 99.9%, the integrity of the samples was monitored while the physical measurements were being made. If decomposition products