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Vapor−Liquid−Liquid Locus of the System Pentane + Water

Fang-Yuan Jou and Alan E. Mather*

Department of Chemical and Materials Engineering, University of Alberta,
Edmonton, Alberta T6G 2G6, Canada

The three-phase (vapor−aqueous liquid−hydrocarbon liquid) equilibria in the system pentane + water have been measured over the range of temperature from 273 to 453 K. The locus is in good agreement with previous measurements. The concentration of pentane in the aqueous phase was measured, and Henry's constants were calculated.

Introduction

Equilibria between water and hydrocarbons are important in production of oil and gas and in studies of environmental contamination. The present work was undertaken as part of a project to determine the solubility of higher hydrocarbons in aqueous alkanolamine solutions.

Experimental Work

The measurements were made in an apparatus which has been used in this laboratory[1] for phase equilibria, and hence only a brief description follows. The main component of the apparatus was a visual cell. The large windows ensured that the presence and nature of the phases could be observed. The contents of the cell were mixed using a magnetically driven piston pump. A portion of the vapor was drawn from the top of the cell and pumped into the bottom of the cell. The cell and pump were housed in a large temperature-controlled air bath. The bath was equipped with refrigeration, to enable measurements at temperatures below ambient, and with heaters for higher temperatures.

The temperature of the contents of the cell was measured using a type J (iron/constantan) thermocouple. The thermocouple was calibrated against a platinum resistance thermometer and was determined to be accurate within ±0.1 K over the range of temperatures investigated. The pressure in the cell was measured with digital Heise (Stratford, CT) gauges (range 0−500 kPa and 0−10000 kPa). The gauges had an accuracy of 0.1% of full scale according to a calibration against a dead weight gauge.

The pentane (99+%) was supplied by Aldrich Chemical (Milwaukee, WI). Methylcyclohexane (used in the analysis) was also supplied by Aldrich and was 99% pure. The impurity in both chemicals is non-hydrocarbon. Double-distilled water was used.

To perform the experiments, water was fed into the system and a vacuum drawn to remove dissolved air. The amount of pentane needed to ensure three phases were present was found by experiment. The temperature controller was set, and the mixing pump was started. The system was allowed to circulate for 24 h to ensure equilibrium was reached. The pump was then stopped, and the pressure and temperature were recorded. A sample of the aqueous phase was drawn into an evacuated bomb containing a known amount (∼3 g) of methylcyclohexane and a magnetic stirrer bar. After mixing well, the aqueous portion was decanted to a capped vial and the hydrocarbon portion to a 2 mL vial closed with a septum. A syringe was used to inject 2 μL of the methylcyclohexane phase into an HP 5890 gas chromatograph equipped with a thermal conductivity detector. A 2 m × 3.18 mm stainless steel column packed with 100/120 mesh Chromosorb 104 was used to determine the concentrations of water, pentane, and methylcyclohexane. It was operated at 180 °C, and the retention times were 0.97, 1.50, and 1.70 min for pentane, water, and methylcyclohexane, respectively. The area of the water peak was <0.01%. Injection of the aqueous sample, which had been extracted with the methylcyclohexane, found an area for pentane and methylcyclohexane of <0.01%, confirming that the pentane had been completely extracted. Calibrations were made with mixtures of pentane and methylcyclohexane with mole ratios from 10^{-5} to 10^{-3}. The response factor was found to be 1:1 with a variation of 0.4%. From the analysis of the methylcyclohexane sample, the mass of pentane was calculated and then the mole fraction of pentane was calculated from this mass and the mass of the aqueous sample withdrawn from the cell.

Table 1. Three-Phase Locus of Pentane + Water, Composition of the Aqueous Phase x_2, Fugacity Coefficient $\hat{\varphi}_2$, and Henry's Constant $H_{2,1}$

T/K	P/kPa	10^5x_2	$\hat{\varphi}_2$	$H_{2,1}$/GPa
273.2	24.3	1.27	0.987	1.8
283.2	38.0	1.02	0.982	3.5
298.2	70.0	1.06	0.971	6.1
311.5[a]	118.2	1.15	0.957	9.3
313.2	122.4	1.24	0.956	8.9
343.2	300	1.66	0.917	14.9
367.5[a]	617	2.35	0.861	19.6
373.2	712	2.68	0.847	19.3
393.2	1150	4.20	0.791	17.9
413.2	1770	7.13	0.727	14.4
423.3[a]	2124	6.99	0.700	16.5
453.2	3633	18.9	0.605	8.4

[a] Gillespie and Wilson.[2]

Results

Data for the three-phase locus were obtained over the range of temperatures from 273 to 453 K. The results are presented in Table 1. A comparison of these data with published values of the three-phase locus is given in Figure

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* To whom correspondence should be addressed. E-mail: alan.mather@ualberta.ca.

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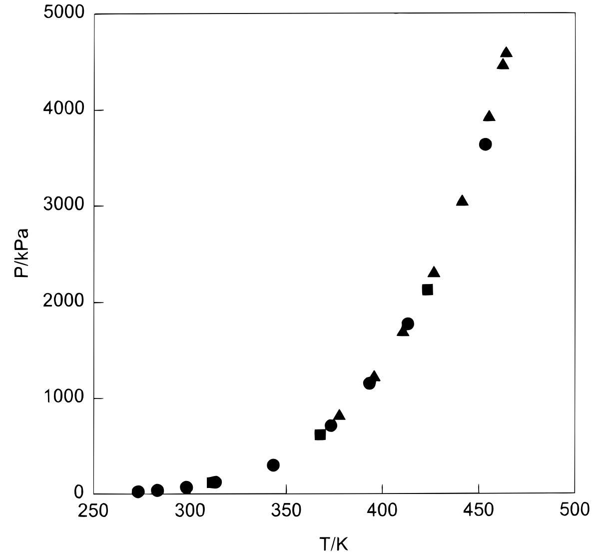

Figure 1. Three-phase locus of pentane + water: ●, this work; ■, Gillespie and Wilson;[2] ▲, Brunner.[3]

1, where the data of Gillespie and Wilson[2] and Brunner[3] are plotted. The highest point (463.8 K, 4577 kPa) is the upper critical end point (K point), which is the termination of the three-phase locus. The three sets of data can be seen to be in good agreement. All the three-phase data were correlated with a Clausius−Clapeyron-type equation. A least-squares fit of all three sets of data yielded the following equation:

$$\ln(P/\mathrm{kPa}) = 15.871 - 3466.9/(T/\mathrm{K}) \tag{1}$$

The average absolute deviation between the data and this equation is 9.3 kPa, and the maximum deviation is 148 kPa, which occurs at the K point.

Henry's constants for pentane in water were obtained from the solubility data. The equation

$$y_2 P \hat{\varphi}_2^{v} = H_{2,1} x_2 \gamma_2^{*} \tag{2}$$

denotes the equality of the fugacity of pentane (2) in the vapor and aqueous phases. Here the unsymmetrical activity coefficient is unity at the very low concentrations of pentane in the aqueous phase. To determine the Henry's constant, the composition of the vapor phase is needed. It was estimated from

$$y_2 = \frac{P - p_1^{s}}{P} \tag{3}$$

The Peng−Robinson equation of state[4] was used to calculate the fugacity coefficients of pentane. A value of 0.35 for the binary interaction parameter was obtained from Eubank et al.[5] A new value of y_2 was calculated using eq 2, and the fugacity coefficients were recalculated. Convergence occurred in a couple of iterations. The fugacity coefficients and the Henry's constants are given in Table 1. Gillespie and Wilson[2] reported Henry's constants as P/x. Their three points were treated in the same fashion, and the Henry's constants are plotted in Figure 2. Agreement is good at the lower temperatures, and a maximum in the Henry's constant occurs around 375 K.

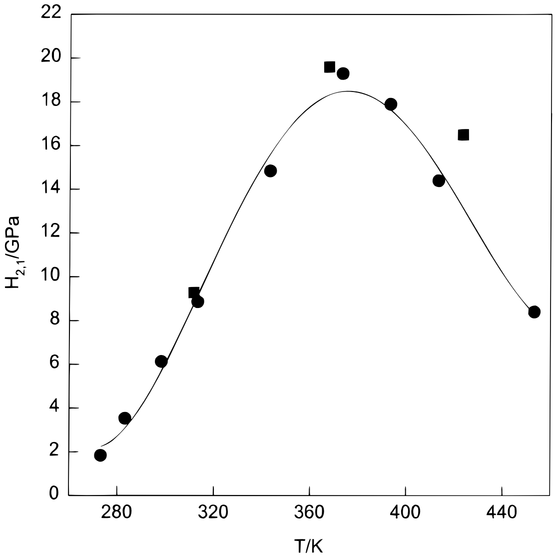

Figure 2. Henry's constant of pentane in water as a function of temperature: ●, this work; ■, Gillespie and Wilson.[2]

Conclusions

New experimental data for the three-phase locus of the system pentane + water have been obtained. They are in good agreement with published data. Henry's constants have been calculated from measurements of the concentration of pentane in the aqueous phase.

Nomenclature

Roman Symbols

H = Henry's constant
p^{s} = vapor pressure
P = total pressure
T = absolute temperature
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Greek Symbols

γ^{*} = activity coefficient (unsymmetrical convention)
$\hat{\varphi}$ = fugacity coefficient (mixture)

Subscripts

1 = solvent (water)
2 = solute (pentane)

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