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# Gas–Liquid Equilibrium in Binary Mixtures of Methane with *n*-Decane, Benzene, and Toluene

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**Compositions of saturated equilibrium liquid and vapor phases are determined in a flow apparatus for mixtures of methane and *n*-decane at 150, 240, 270, 290, and 310 °C, for methane and benzene at 150, 190, and 230 °C, and for methane and toluene at 150, 190, 230, and 270 °C. Pressures extend to near the criticals of the mixtures starting from 20 atm or from somewhat above the vapor pressure of the solvent whichever is higher.**

## Introduction

Gas–liquid equilibrium data on binary mixtures of a light gas and a heavy solvent are of interest for a number of industrial processes. The saturated liquid composition represents solubility data of the light gas and the saturated vapor gives dew point information. Both types of information are needed for process design and analysis.

In this work we determine the compositions of saturated equilibrium liquid and vapor phases of three binary mixture systems of methane at temperatures above those of previous investigations of these systems. Pressures extend to near the criticals of the mixtures starting from 20 atm or from somewhat above the vapor pressure of the solvent whichever is higher.

Mixtures of methane and *n*-decane were studied by Reamer et al. (*10*) at temperatures from 37.8 to 237.8 °C and pressures up to 357 atm and by Beaudoin and Kohn (*1*) at -25 to +150 °C and 10–100 atm.

Mixtures of methane and benzene have been studied in a number of laboratories. The temperatures and pressures of the investigations are as follows: Savvina (*12*) at 40–150 °C and up to 369 atm; Elbishlawi and Spencer (*6*) at 65.6 °C and 7–327 atm; Stepanova and co-workers (*15*) at 0–60 °C and up to 348 atm; Ipatieff and Monroe (*8*) at 100–250 °C and up to 152 atm; Sage et al. (*11*) at 38–104 °C and 27–204 atm; Schoch et al. (*13*) at 38 °C and 92–408 atm. The last three studies reported only the liquid-phase compositions.

Mixtures of methane and toluene have been studied at the following conditions: Savvina at 40–150 °C and up to 420 atm; Elbishlawi and Spencer at 65.6 °C and 7–360 atm; Kobayashi and co-workers (*2*, *9*) at -84 to +4 °C and up to near the critical pressure of the mixture at each temperature.

## Experimental Section

The experimental apparatus and procedure of this work have been described (*14*).

Methane gas was purchased from Matheson with a certified purity of 99+%. *n*-Decane was supplied by Aldrich Chemical Co. with a minimum purity of 99+%. Benzene and toluene obtained from Mallinckrodt Co. are analytical reagent grade with a reported boiling point range of 0.5 and 1.0 °C, respectively. Gas chromatographic analyses indicate the actual purities to be higher than claimed. Samples were collected from the condensates of cell effluents on both the gas and liquid sides for all experiments and analyzed by gas chromatography. No decomposition products were observed at any of the conditions studied.

## Results and Discussion

Results of this work are presented in Tables I–IV and Figures 1–6. Each phase composition in the tables represents the mean of two or three samples. The mole fractions of methane of the multiple samples agree to within 2%. The individual sample compositions are shown in Figures 1, 3, and 5 as separate points when they can be distinguished.

The equilibrium cell temperature did not fluctuate by more than 0.2 °C during the determination of all the points on an isotherm for the methane + *n*-decane mixtures, 0.6 °C for methane + benzene, and 0.7 °C for methane + toluene.

Table I presents gas–liquid equilibrium data on methane + *n*-decane mixtures at the two lower temperatures of this work, i.e., at 150.0 and 237.8 °C. The former temperature was the

Table I. Methane + *n*-Decane at Lower Temperatures. Compositions of Saturated Gas and Liquid Phases of This Work and Two Previous Studies

| *t*, °C | *p*, atm | $x_M$ |  |  | $y_M$ |  |  |
|---|---|---|---|---|---|---|---|
|  |  | this work | Reamer (*10*) | Beaudoin (*1*) | this work | Reamer (*10*) | Beaudoin (*1*) |
| 150.0 | 30 | 0.1075 | 0.1040$^a$ | 0.0990 | 0.9738 | 0.9739$^a$ | 0.973 |
|  | 40 | 0.1375 | 0.1378$^a$ | 0.1311 | 0.9780 | 0.9782$^a$ | 0.978 |
|  | 50 | 0.1722 | 0.1688$^a$ | 0.1631 | 0.9801 | 0.9801$^a$ | 0.980 |
|  | 60 | 0.2035 | 0.2000$^a$ | 0.1935 | 0.9811 | 0.9812$^a$ | 0.982 |
|  | 70 | 0.2309 | 0.2296$^a$ | 0.2214 | 0.9819 | 0.9820$^a$ | 0.983 |
| 237.8 | 27.2 | 0.0914 | 0.0937 |  | 0.8029 | 0.7928 |  |
|  | 54.4 | 0.1866 | 0.1933 |  | 0.8725 | 0.8700 |  |
|  | 85.1 | 0.2853 | 0.2895 |  | 0.8912 | 0.8858 |  |
|  | 119.1 | 0.3855 | 0.3837 |  | 0.8911 | 0.8861 |  |
|  | 153.1 | 0.4840 | 0.4763 |  | 0.8737 | 0.8713 |  |
|  | 170.1 | 0.5430 | 0.5379 |  | 0.8563 | 0.8533 |  |
|  | 184.4 | 0.5946 | 0.5980$^a$ |  | 0.8318 | 0.8290$^a$ |  |

$^a$ Interpolated values.

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Table II. Methane + *n*-Decane at Higher Temperatures

| $p$, atm | $x_M$ | $y_M$ | $K_M$ | $K_D$ |
|---|---|---|---|---|
| | | 269.6 °C | | |
| 30.10 | 0.0946 | 0.6795 | 7.18 | 0.3540 |
| 50.31 | 0.1706 | 0.7638 | 4.48 | 0.2848 |
| 100.05 | 0.3508 | 0.8051 | 2.30 | 0.3002 |
| 125.02 | 0.4440 | 0.7901 | 1.78 | 0.3775 |
| 149.45 | 0.6682 | 0.7116 | 1.07 | 0.8692 |
| | | 290.1 °C | | |
| 29.97 | 0.0911 | 0.5528 | 6.07 | 0.4920 |
| 50.04 | 0.1744 | 0.6690 | 3.84 | 0.4009 |
| 74.88 | 0.2744 | 0.7118 | 2.59 | 0.3972 |
| 99.65 | 0.3817 | 0.7055 | 1.85 | 0.4763 |
| 109.99 | 0.4399 | 0.6835 | 1.55 | 0.5650 |
| 114.62 | 0.4652 | 0.6604 | 1.42 | 0.6350 |
| | | 309.9 °C | | |
| 30.24 | 0.0857 | 0.4133 | 4.82 | 0.6417 |
| 50.05 | 0.1794 | 0.5476 | 3.05 | 0.5513 |
| 70.25 | 0.2834 | 0.5749 | 2.03 | 0.5932 |
| 79.78 | 0.3481 | 0.5646 | 1.62 | 0.6679 |
| 85.23 | 0.4032 | 0.5177 | 1.28 | 0.8081 |

Table III. Methane + Benzene Gas-Liquid Equilibrium Data

| $p$, atm | $x_M$ | $y_M$ | $K_M$ | $K_B$ |
|---|---|---|---|---|
| | | 147.9 °C | | |
| 19.61 | 0.0252 | 0.6516 | 25.86 | 0.3574 |
| 33.01 | 0.0502 | 0.7630 | 15.20 | 0.2495 |
| 46.69 | 0.0823 | 0.7994 | 9.71 | 0.2186 |
| 99.50 | 0.1739 | 0.8208 | 4.72 | 0.2169 |
| 148.29 | 0.2651 | 0.8140 | 3.07 | 0.2531 |
| 200.68 | 0.3754 | 0.7809 | 2.08 | 0.3508 |
| 239.46 | 0.4947 | 0.7222 | 1.46 | 0.5498 |
| | | 188.7 °C | | |
| 29.82 | 0.0346 | 0.5285 | 15.27 | 0.4884 |
| 50.50 | 0.0762 | 0.6439 | 8.45 | 0.3855 |
| 99.63 | 0.1801 | 0.7120 | 3.95 | 0.3513 |
| 136.79 | 0.2609 | 0.7250 | 2.78 | 0.3721 |
| 160.87 | 0.3179 | 0.7163 | 2.25 | 0.4159 |
| | | 228.0 °C | | |
| 50.57 | 0.0648 | 0.4485 | 6.92 | 0.5897 |
| 72.01 | 0.1145 | 0.5326 | 4.65 | 0.5278 |
| 100.24 | 0.1806 | 0.5715 | 3.16 | 0.5229 |
| 125.36 | 0.2464 | 0.5564 | 2.26 | 0.5886 |
| 134.89 | 0.2842 | 0.5418 | 1.91 | 0.6401 |
| 143.67 | 0.3243 | 0.5153 | 1.59 | 0.7173 |

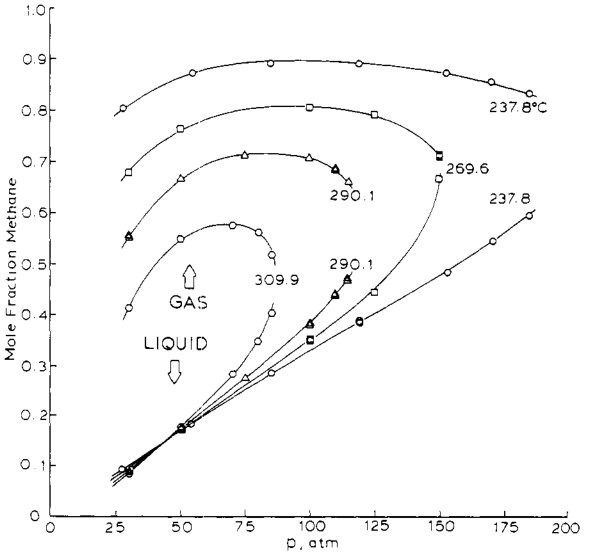

**Figure 1.** Isothermal pressure-composition diagram for methane + *n*-decane.

Table IV. Methane + Toluene Gas-Liquid Equilibrium Data

| $p$, atm | $x_M$ | $y_M$ | $K_M$ | $K_T$ |
|---|---|---|---|---|
| | | 149.3 °C | | |
| 19.95 | 0.0353 | 0.8426 | 23.87 | 0.1632 |
| 29.88 | 0.0545 | 0.8808 | 16.16 | 0.1261 |
| 50.77 | 0.0954 | 0.9100 | 9.54 | 0.0995 |
| 99.08 | 0.1949 | 0.9231 | 4.74 | 0.0955 |
| 150.66 | 0.2879 | 0.9148 | 3.18 | 0.1196 |
| 200.00 | 0.3858 | 0.8981 | 2.33 | 0.1659 |
| 246.95 | 0.4897 | 0.8493 | 1.73 | 0.2953 |
| | | 188.9 °C | | |
| 20.03 | 0.0280 | 0.6724 | 24.01 | 0.3370 |
| 30.10 | 0.0486 | 0.7499 | 15.43 | 0.2629 |
| 49.70 | 0.0884 | 0.8144 | 9.21 | 0.2036 |
| 98.83 | 0.1897 | 0.8606 | 4.54 | 0.1720 |
| 150.00 | 0.2850 | 0.8593 | 3.02 | 0.1968 |
| 199.61 | 0.4106 | 0.8257 | 2.01 | 0.2957 |
| 227.37 | 0.4925 | 0.7848 | 1.59 | 0.4240 |
| 249.40 | 0.6332 | 0.6780 | 1.07 | 0.8779 |
| | | 227.6 °C | | |
| 19.90 | 0.0179 | 0.3668 | 20.49 | 0.6447 |
| 29.56 | 0.0379 | 0.5283 | 13.94 | 0.4903 |
| 49.91 | 0.0841 | 0.6712 | 7.98 | 0.3590 |
| 99.79 | 0.1964 | 0.7479 | 3.81 | 0.3137 |
| 147.28 | 0.3098 | 0.7439 | 2.40 | 0.3711 |
| 166.47 | 0.3807 | 0.7120 | 1.87 | 0.4650 |
| | | 270.0 °C | | |
| 30.37 | 0.0219 | 0.2476 | 11.31 | 0.7692 |
| 49.90 | 0.0718 | 0.4222 | 5.88 | 0.6225 |
| 69.57 | 0.1246 | 0.5039 | 4.04 | 0.5667 |
| 99.44 | 0.2155 | 0.5493 | 2.55 | 0.5745 |
| 113.60 | 0.2736 | 0.5416 | 1.98 | 0.6311 |

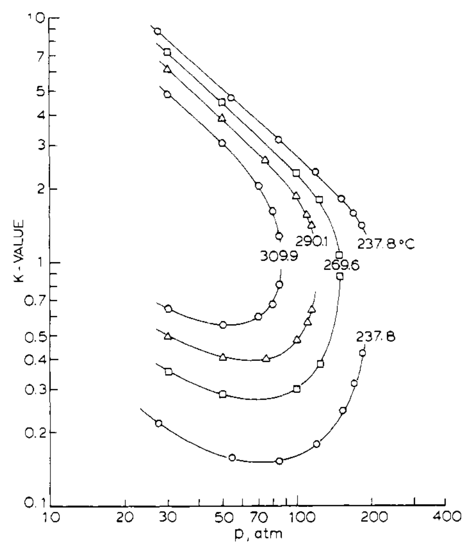

**Figure 2.** Isothermal $K$ values for methane + *n*-decane.

highest reported by Beaudoin and Kohn (*1*) and the latter was the highest reported by Reamer et al. (*10*). We interpolated the data of Reamer et al. to obtain values at 150 °C for a comparison with the data of this work. The comparisons shown in Table I illustrate that the three studies are in generally good agreement. The gas compositions all agree to within 1% in mole fractions of methane. The liquid compositions of this work do not differ by more than 4% in mole fractions of methane from those of Reamer et al., while the data of Beaudoin and Kohn also agree with those of Reamer et al. to within 5%. DeVaney and co-workers (*5*) recently reported data at 204.4 °C and 68 atm. The agreement between their data and the interpolated

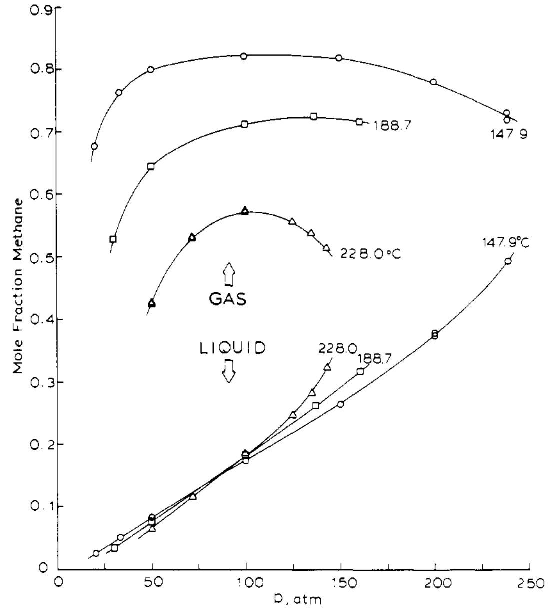

**Figure 3.** Isothermal pressure-composition diagram for methane + benzene.

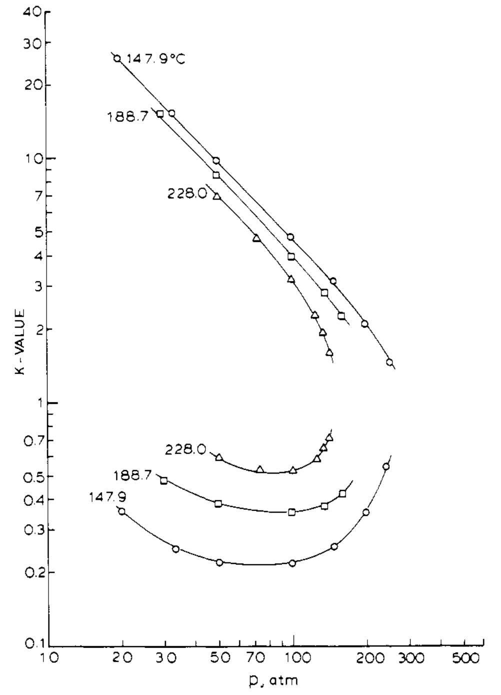

**Figure 4.** Isothermal $K$ values for methane + benzene.

values from this study is better than 1% in both $x_M$ and $y_M$.

Table II presents gas-liquid equilibrium data on methane + $n$-decane mixtures at the three higher temperatures of this work, i.e., at 269.6, 290.1, and 309.9 °C. No data are available from other sources at these temperatures.

Figure 1 presents the saturated phase compositions of methane + $n$-decane mixtures at various isotherms as a function of pressure. Figure 2 presents the $K$ values. These figures indicate the close approach of our data to the critical states. It is clear from the figures why experiments are not carried out at higher temperatures and pressures.

Table III presents gas-liquid equilibrium data on methane + benzene mixtures. Figure 3 shows the saturated phase compositions and Figure 4 shows the $K$ values.

Table IV presents gas-liquid equilibrium data on methane + toluene mixtures. Figure 5 shows the saturated phase compositions and Figure 6 shows the $K$ values.

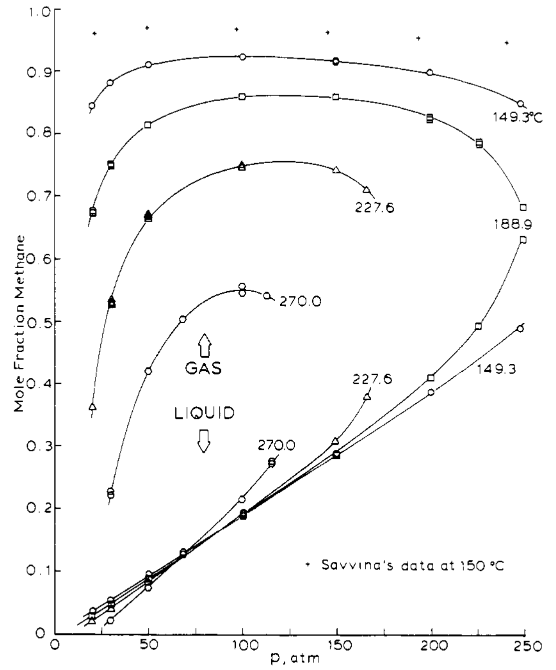

**Figure 5.** Isothermal pressure-composition diagram for methane + toluene.

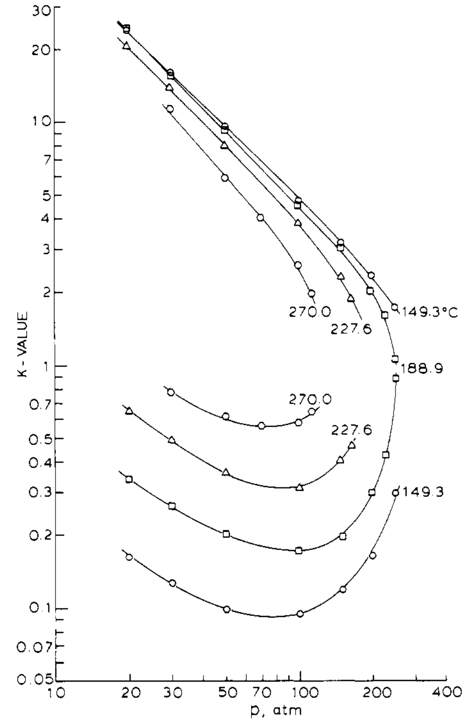

**Figure 6.** Isothermal $K$ values for methane + toluene.

The temperature range of our methane + benzene and methane + toluene data overlaps with that of Savvina at 150 °C, but the phase compositions are in wide disagreement. To illustrate the difference, we reproduce in Figure 5 the gas composition isotherm at 150 °C reported by Savvina for methane + toluene mixtures. It is substantially above our isotherm of 149.3 °C. The difference is even larger in terms of mole fraction of toluene. Discrimination of the two sets of data can therefore be made on the basis of the latter difference, since a reliable calculation can be readily made of the concentration of toluene in the saturated gas from its vapor pressure and the imperfection of the gas mixture (*3*). The calculation shows that the $y_T$ values of Savvina are too low by about 1 order of magnitude.

One use of this type of data is to check correlations. The present data have been used to check the Chao–Seader (*4*) and Grayson–Streed (*7*) correlations. The Chao–Seader correlation represents the $K$ values of methane in methane + $n$-decane with an absolute average deviation of 14%. The deviation is the largest at the highest temperature. The average error of $K_M$ for the three lower isotherms is less than 8%. The $K$ values of $n$-decane are correlated to within 11%. For methane + benzene mixtures Chao–Seader represents the $K$ values of both components with an average deviation of 8%. For methane + toluene mixtures we find an average error of 8% for methane and 15% for toluene. The Grayson–Streed correlation gives much larger deviations for methane but slightly smaller deviations for the solvents.

## Glossary

| | |
|---|---|
| $K$ | vaporization equilibrium ratio $\equiv y/x$ |
| $p$ | pressure, atm |
| $t$ | temperature, °C |
| $x$ | mole fraction in liquid phase |
| $y$ | mole fraction in vapor phase |

*Subscripts*

| | |
|---|---|
| B | benzene |
| M | methane |
| D | $n$-decane |
| T | toluene |

## Literature Cited

(1) Beaudoin, J. M., Kohn, J. P., *J. Chem. Eng. Data*, **12**, 189 (1967).
(2) Chang, H. L., Kobayashi, R., *J. Chem. Eng. Data*, **12**, 517 (1967).
(3) Chao, K. C., Greenkorn, R. A., "Thermodynamics of Fluids", Marcel Dekker, New York, 1975, p 291.
(4) Chao, K. C., Seader, J. D., *AIChE J.*, **7**, 598 (1961).
(5) DeVaney, W., Berryman, J. M., Kao, P. L., Eakin, B., "High Temperature V-L-E Measurements for Substitute Gas Components", GPA Research Report RR-30, 1978.
(6) Elbishlawi, M., Spencer, J. R., *Ind. Eng. Chem.*, **43**, 1811 (1951).
(7) Grayson, H. G., Streed, C. W., "Sixth World Petroleum Congress in Frankfort/Main", Section VII, paper 20, June 19th–26th, 1963.
(8) Ipatieff, V. N., Monroe, G. S., *Ind. Eng. Chem.*, **14**, 166 (1942).
(9) Lin, Y. N., Hwang, S. C., Kobayashi, R., *J. Chem. Eng. Data*, **23**, 231 (1978).
(10) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **34**, 1526 (1942).
(11) Sage, B. H., Webster, D. C., Lacey, W. N., *Ind. Eng. Chem.*, **28**, 1045 (1936).
(12) Savvina, Ya. D., *Tr., Vses. Nauchno-Issled. Inst. Prir. Gazov*, **17**, 189 (methane + benzene), 190 (methane + toluene) (1962).
(13) Schoch, E. P., Hoffmann, A. E., Kasperik A. S., Lightfoot, J H., Mayfield, F. D., *Ind. Eng. Chem.*, **32**, 788 (1940).
(14) Simnick, J. J., Lawson, C. C., Lin, H. M., Chao, K. C., *AIChE J.*, **23**, 469 (1977).
(15) Stepanova, G. S., Vybornova, Ya. I., Velikovskii, A. S., *Gaz. Delo. Nauchno-Tekhniche. Sbornik*, **9**, 3 (1965).

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# Gas–Liquid Equilibrium in Binary Mixtures of Methane with Tetralin, Diphenylmethane, and 1-Methylnaphthalene

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**Compositions of saturated equilibrium liquid and vapor phases are determined in a flow apparatus for mixtures of methane + tetralin at 190, 270, 350, and 390 °C and for methane + diphenylmethane and methane + 1-methylnaphthalene at 190, 270, 350, and 430 °C. The pressure extends to 250 atm or near the criticals of the mixtures, starting from 20 atm or from above the vapor pressure of the solvent.**

## Introduction

There is a scarcity of experimental information on the equilibrium phase behavior of mixtures of methane + heavy aromatic hydrocarbons at conditions of elevated temperatures and pressures. Such information on the saturated liquid represents solubility data of methane in the heavy solvents, and the data on the saturated vapor give dew point information. Both types of information are needed for process design and analysis.

In this work we determine the compositions of saturated equilibrium liquid and vapor phases of binary mixtures of methane with tetralin, diphenylmethane, and 1-methylnaphthalene, respectively. No previous data on mixtures of methane + tetralin have been reported. Henry constants for methane in diphenylmethane and in 1-methylnaphthalene were measured by Chappelow and Prausnitz (*1*) at 25–200 °C. The dew points of the same two systems were recently studied by Kaul and Prausnitz (*2*) at 50–170 °C and 9–80 atm. Stepanova (*6*) reported the solubility of methane in 1-methylnaphthalene at 0–60 °C at low pressures.

## Experimental Section

The experimental apparatus and procedure of this study have been described (*4*).

The equilibrium temperature is measured by a chromel–alumel thermocouple that has been calibrated against a National Bureau of Standards certified platinum resistance thermometer. The temperatures are accurate to ±0.1 °C. Pressures above 30 atm are measured by a Heise gauge that reads pressures up to 340 atm. Lower pressures are measured by a Heise gauge that reads pressures up to 34 atm. Both gauges are accurate to ±0.1% of full scale.

Since our apparatus is of the flow type we have paid attention to the attainment of equilibrium in the apparatus. We have made several tests and all gave positive results to within the uncertainty of the experiments (*3–5*, *7*).

Methane gas was obtained from Matheson with a minimum purity of 99%. The hydrocarbon solvents were all purchased

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