Table X. Data Used for SWAP Predictions

				fractions			
	T, °C	P, torr	T_{760},[a] °C	aromaticity	naphthenicity	branching	heteroatomicity
thianthrene	173.83	3.28	327	1.0	0	0	0.143
thionaphthene	71.01	3.88	162	1.0	0	0	0.111
dibenzothiophene	131.75	1.55	287	1.0	0	0	0.0769
2-propylthiophene	28.67	4.13	136	0.625	0	0	0.125

[a] These are for the structural homomorph.

Table XI. Comparison of Measured and Calculated Normal Boiling Points for Coal-Related Liquids Using SWAP

	T_{760}, °C	
compd	measured	calcd
thianthrene	364–366	340
thionaphthene	221–222	220
dibenzothiophene	332–333	323
2-propylthiophene	157–160	158

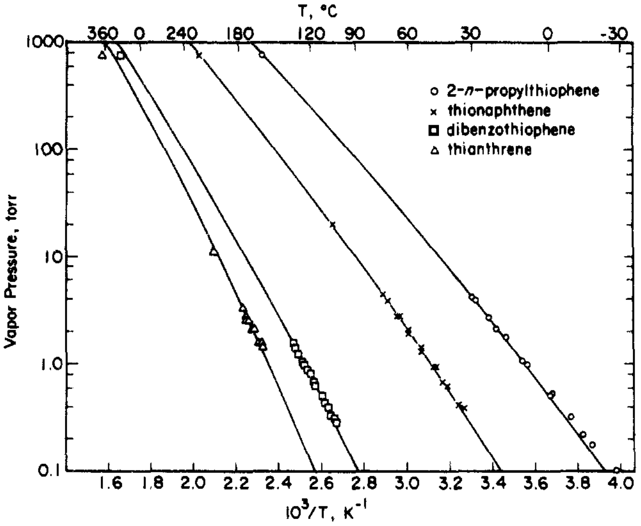

Figure 3. Experimental (points) and calculated vapor pressures using SWAP (lines). Calculations based on one (low) vapor-pressure datum.

achieved through easily measured fractions of aromaticity, naphthenicity, branching, and heteroatomicity instead of precise structural information. Therefore, the SWAP method is readily extended to complex mixtures (cuts or fractions) for which precise structural information cannot be determined. We are interested here in assessing the reliability of SWAP in extrapolating from the relatively low vapor pressures and temperatures reported in this work to the higher vapor pressures and temperatures found in most industrial processing equipment. Reliable vapor-pressure data at higher temperatures, however, are often difficult to obtain because of chemical decomposition.

The data used to determine the SWAP parameters for each of the four compounds studied in this work are presented in Table X. Calculated extrapolations are shown in Figure 3. SWAP is used to extrapolate the low-temperature data by ~3 orders of magnitude to 1000 torr.

For comparison, we also show normal boiling points and other available data in Figure 3 and Table XI for each of the compounds studied. These data were obtained from ref *6*. For both of the relatively low-boiling compounds (thionaphthene and 2-propylthiophene), SWAP predictions of normal boiling point are good while those for the relatively high-boiling compounds (thianthrene and dibenzothiophene) show considerably more error. However, we do not know the reliability of the published boiling points. It is possible that, because of the high temperatures at which these compounds boil, they may have fused or condensed during boiling-point determination, causing the measured boiling temperature to be too high.

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Ternary Phase Equilibria. Dichlorobenzene–*n*-Heptane–Solvent Systems

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Phase equilibrium and tie-line data for the ternary systems comprising *o*- and *p*-dichlorobenzene–*n*-heptane and the solvents nitromethane and aqueous methanol (95 vol %) determined at 20.5 °C are presented. The tie-line data are also correlated by Hand's method.

Introduction

Ternary phase equilibrium and tie-line data are essential for the understanding of solvent extraction and salting-out operations. The study of the phase equilibrium and tie-line data of *o*- and *p*-dichlorobenzene was undertaken with a view to

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Table I. Mutual Solubility and Tie-Line Data for *o*-Dichlorobenzene–Nitromethane–*n*-Heptane

mutual solubility data, wt %

ortho isomer	nitromethane	*n*-heptane
0	95.7	4.3
5.5	90.0	4.5
9.5	85.5	5.0
18.8	75.0	6.2
23.5	69.0	7.5
37.0	50.0	13.0
45.1	34.8	20.1
46.2	22.9	30.9
44.1	16.4	39.5
38.6	9.9	51.5
25.4	6.1	68.5
14.6	5.6	79.8
5.0	6.0	89.0
0	6.2	93.8

tie-line data, wt %

n-heptane phase			nitromethane phase		
ortho isomer	nitromethane	*n*-heptane	ortho isomer	nitromethane	*n*-heptane
4.1	5.9	90.0	2.5	93.2	4.3
9.2	5.9	84.9	5.5	90.0	4.5
17.5	5.5	77.0	10.2	83.8	6.0
29.5	7.5	63.0	17.5	75.5	7.0
37.8	9.1	53.1	23.1	69.0	7.9
43.0	15.0	42.0	30.1	60.5	9.4

evaluate the possibility of employing distribution of two isomers between two solvents as a means for separating them. The isomers are important intermediates in the organic chemical industry and are usually separated by the fractional distillation and crystallization from the product mixture obtained by the chlorination reaction of benzene.

Experimental Section

All chemicals used in this study were of normal laboratory reagent grade.

Various methods (*1*) have been described in the literature for the determination of ternary liquid equilibria and tie-line data. The most widely employed is probably the synthetic method of Othmer et al. (*2*). This method, which was used by the author previously for the separation study of chloronitrobenzene and chlorotoluene isomers (*3*, *4*), was adopted for the study. The binodal solubility curves were determined for the individual isomers distributed between *n*-heptane and a polar solvent. Two solvents chosen for investigation were nitromethane and aqueous methanol (95 vol %). To add tie-line data, we prepared various mixtures of known composition within the heterogeneous region and brought them to equilibrium. The conjugate phases were analyzed by measurement of the refractive index in conjunction with calibration curves prepared with systems of known composition on the solubility curve. The values of composition determined were checked by material-balance calculation. All determinations were carried out at a temperature of 20.5 ± 0.5 °C. Titer values were measured to ±0.05 mL. Weighings were made to 0.1 mg with a Mettler balance. The accuracy of the experimental data is within ±1%.

Results and Discussion

The mutual solubility and tie-line data for the four systems studied are presented in Tables I–IV. The corresponding equilibrium distribution and selectivity diagrams for both isomers are given in Figures 1 and 2. The tie-line data for all systems are correlated satisfactorily by Hand's method (*5*) as shown in Figure 3, in which good straight lines are obtained.

Table II. Mutual Solubility and Tie-Line Data for *p*-Dichlorobenzene–Nitromethane–*n*-Heptane

mutual solubility data, wt %

para isomer	nitromethane	*n*-heptane
1.5	94.0	4.5
7.7	87.6	4.7
14.3	80.0	5.7
21.1	71.0	7.9
29.4	59.4	11.2
33.8	50.0	16.2
38.0	37.0	25.0
40.8	20.1	39.1
37.0	11.0	52.0
29.5	8.5	62.0
20.8	7.6	71.6
11.4	7.6	81.0
3.5	7.6	88.9

tie-line data, wt %

n-heptane			nitromethane phase		
para isomer	nitromethane	*n*-heptane	para isomer	nitromethane	*n*-heptane
3.2	7.9	88.9	1.7	93.3	5.0
13.5	7.8	78.7	7.0	87.4	5.6
19.5	7.6	72.9	10.0	84.2	5.8
24.5	7.6	67.9	13.7	81.3	6.0
29.5	8.5	62.0	15.5	78.0	6.5
37.0	11.0	52.0	21.0	71.0	8.0

Table III. Mutual Solubility and Tie-Line Data for *o*-Dichlorobenzene–Aqueous Methanol–*n*-Heptane

mutual solubility data, wt %

ortho isomer	aqueous methanol (95 vol %)	*n*-heptane
	2.0	98.0
9.8	2.0	88.2
15.4	1.9	82.7
26.1	1.8	72.1
43.5	1.8	54.7
51.8	1.8	46.4
60.5	1.8	37.7
65.1	1.8	33.1
35.4	47.1	17.5
29.5	53.8	16.7
20.5	64.5	15.0
11.0	76.6	12.4
5.3	84.4	10.3
	8.5	91.5

tie-line data, in wt %

n-heptane phase			aqueous methanol phase		
ortho isomer	aqueous methanol	*n*-heptane	ortho isomer	aqueous methanol	*n*-heptane
9.5	2.0	88.5	5.3	83.7	11.0
18.1	1.9	80.0	11.3	75.7	13.0
31.7	1.9	66.4	18.5	67.4	14.1
43.4	1.8	54.8	24.5	60.5	15.0
52.0	1.8	46.2	29.5	55.0	15.5
60.7	1.8	37.5	33.5	50.0	16.5

Pure methanol and *n*-heptane have an appreciable mutual solubility, which reduces their potential value as a solvent pair. This can be minimized by the addition of small quantities of water. However, the addition of water also reduces the solubility of the isomers in the methanol phase and hence reduces the solvent loading which can be achieved. Methanol/water (95% v/v) was found to be the best compromise, giving an increase in the separation factor for the least reduction in solvent loading.

It is clear from the distribution and selectivity diagrams in Figures 1 and 2 that the difference in the distribution coefficients of the two isomers for the aqueous methanol system is small

Table IV. Mutual Solubility and Tie-Line Data for *p*-Dichlorobenzene–Aqueous Methanol–*n*-Heptane

mutual solubility data, wt %		
para isomer	aqueous methanol (95 vol %)	*n*-heptane
8.5	1.7	89.8
12.2	1.7	86.1
21.6	1.5	76.9
32.6	1.5	65.9
41.0	1.5	57.5
44.8	1.2	54.0
51.0	1.2	47.8
30.1	55.9	14.0
22.5	63.5	14.0
17.5	69.0	13.5
7.0	81.0	12.0

tie-line data, wt %					
para isomer	aqueous methanol	*n*-heptane	para isomer	aqueous methanol	*n*-heptane
8.8	1.7	89.5	4.7	83.8	11.5
16.5	1.6	81.9	8.7	79.3	12.0
27.3	1.5	71.2	15.3	71.2	13.5
32.6	1.5	65.9	18.2	67.8	14.0
40.5	1.5	58.0	21.0	65.0	14.0
50.0	1.3	48.7	25.0	61.0	14.0

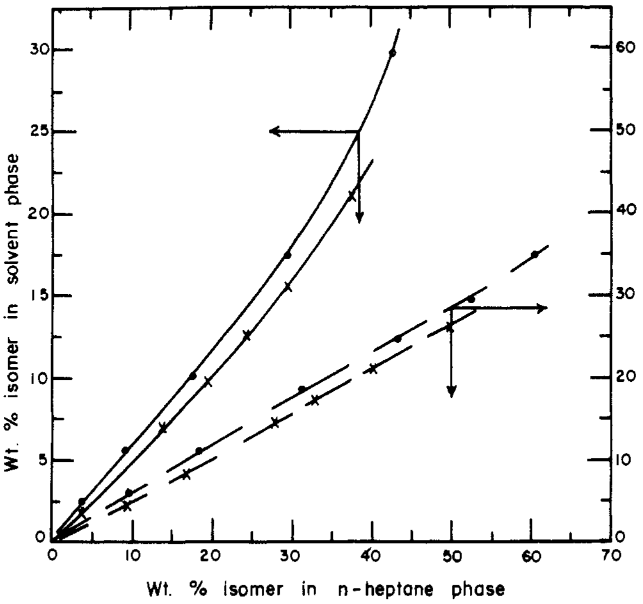

Figure 1. Equilibrium distribution diagrams for ortho and para isomers: (—) *n*-heptane and nitromethane; (- - -) *n*-heptane and aqueous methanol; (●) ortho isomer; (X) para isomer.

compared to that for the nitromethane system. The nitromethane system appears to be promising for a possible separation of the isomers. However, the increased miscibility limits the concentration range of mixtures to be separated.

Also the values of the separation factor, which is a ratio of distribution coefficients of ortho isomer to para isomer and a measure of the ability of a solvent pair to separate the two isomers, are low and vary from 1.2 to 1.1 with an increase in the isomer concentrations in the heptane phase. The values of the separation factor are easily calculated from the equilibrium distribution diagrams in Figure 3. As the separation factor is low, there will be consequent need for a large number of contacting stages.

Glossary

X	liquid-phase composition in wt %
X_{IS}	wt % isomer in solvent phase
X_{IH}	wt % isomer in *n*-heptane phase

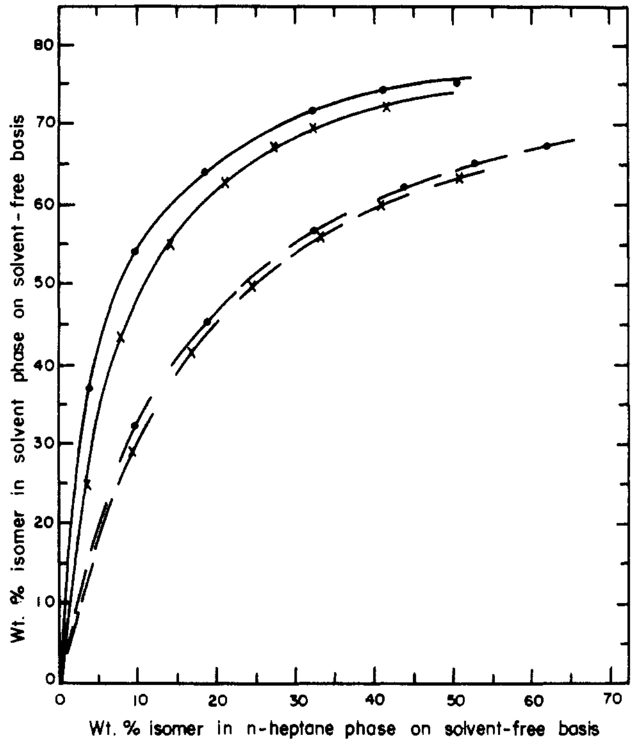

Figure 2. Selectivity diagrams for ortho and para isomers (legend as in Figure 1).

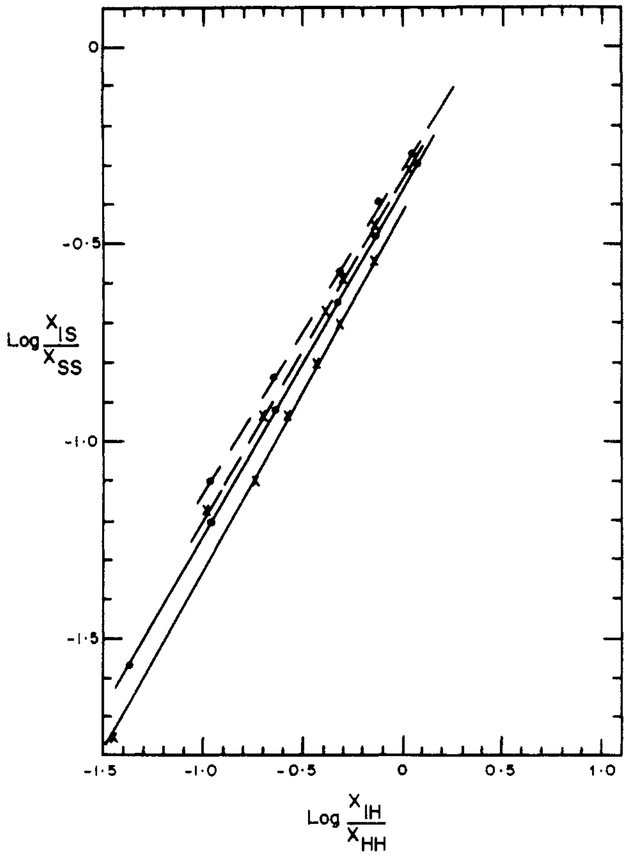

Figure 3. Hand's plot of tie-line correlation (legend as in Figures 1 and 2).

X_{SS}	wt % solvent in solvent phase
X_{HH}	wt % *n*-heptane in *n*-heptane phase

Subscripts

I	isomer
S	solvent

H *n*-heptane

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Vapor–Liquid Equilibrium Study of the H_2–CH_4 System at Low Temperatures and Elevated Pressures

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The *K* values for the H_2–CH_4 system were measured at 10 different temperatures and up to the respective critical pressures for five of those temperatures, −90, −100, −110, −120, and −130 °C. For the other lower temperatures, −140, −150, −155, −160, and −165 °C, *K* values were measured up to 20.684 or 27.579 MPa. Henry's constants for hydrogen in methane at each of the above temperatures were evaluated and reported.

Introduction

In view of the increasing interest in the recovery of hydrogen from coal liquefaction processes, the data on vapor–liquid equilibria (VLE) of the H_2–CH_4 system reported in the literature (*1*, *4*, *5*, *10*, *12*, *13*, *18*, *22–24*) must be critically examined and augmented. The data points were found to be scarce and show considerable inconsistencies so that reasonable interpolation, extrapolation, and parametric extraction lead to inaccuracies. The purpose of this work is to obtain self-consistent, extensive VLE data on the H_2–CH_4 system for the temperature and pressure ranges of interest in synthetic natural gas (SNG) processes.

Experimental Section

The apparatus and the experimental procedure used in this investigation are essentially the same as those discussed by Mraw et al. (*16*) in the methane–carbon dioxide studies. The equilibrium cell, the magnetic circulating pump, and sampling valves were immersed in a cryostat with commercial-grade isopentane and a eutectic mixture of isopentane and isohexane as the bath fluids. The bath temperature was controlled to better than 0.01 °C of the reported value. Liquid nitrogen was used as the coolant. The fine temperature control was achieved by using a small (50 W) heater which injected heat into the system through a Thermotrol proportional controller. The temperature was measured with a Leeds and Northrup certified platinum resistance thermometer (serial no. 1331413) calibrated against a National Bureau of Standards reference.

Before the experiments were started, the entire system was evacuated and then flushed with methane. After thermal equilibrium had been achieved, methane was charged into the cell up to the desired liquid level. Hydrogen was then added to obtain the desired pressure. Further pressure adjustments were needed during early stages of the equilibration process to compensate for the hydrogen dissolution in the methane-rich liquid.

The equilibrium composition of liquid and vapor samples were measured chromatographically. A thermal conductivity detector manufactured by Tracor Instruments, Inc., was used. A 6-ft long, $^1/_8$-in. o.d., stainless-steel tubing packed with 120-mesh molecular sieve 5A was used to achieve the base-line separation of H_2 and methane. The gas-chromatographic conditions were as follows: oven temperature, ambient temperature (22 °C); carrier gas, gas mixture of 8.5% H_2 and 91.5% He; flow rate, 59.2 cm^3/min; detector, 240 Ma at 67 °C. The signal from the detector was integrated by a Spectra Physics Autolab Minigrator and recorded on a Hewlett Packard 7100B strip chart recorder.

The selection of carrier gas for chromatographic analysis of both hydrocarbon and hydrogen posed some difficulties. The anomalous behavior of hydrogen when helium is used as the carrier gas has long been known (*14*). Pietsch (*19*) discovered that a helium–hydrogen mixture has a minimum thermal conductivity at ~8 mol % hydrogen. Purcell and Ettre (*20*) demonstrated that, when a H_2–He gas mixture containing more than 8 mol % hydrogen can be used as the carrier gas, the hydrogen response becomes totally negative with respect to other compounds, thus changing the polarity of the detector giving a positive response for the quantitative analysis of hydrogen. Commercially available H_2–He gas mixtures with 8.5% H_2 and the balance helium were thus chosen as a carrier gas. However, the similarity in thermal conductivity between H_2 and its carrier gas makes the detection of hydrogen at low concentration very difficult (if not impossible).

Mixtures with known concentrations of H_2 and CH_4 were prepared by using two precision positive displacement pumps. These mixtures were used to calibrate the thermal conductivity detector (TCD) response for various concentrations of both components. The procedure for preparation and analysis of these calibration mixtures was described by Mraw et al. (*15*). The calibration curve of the TCD response, registered as peak area, vs. mole fraction of each component was prepared. Four commercially prepared calibration mixtures containing 20, 40, 60, and 80 mol % methane were found to be consistent with the calibration curve.

With the proper arrangement of the gear systems of the two precision displacement pumps, the calibration gas mixtures with the hydrogen concentration as low as 0.0051 mole fraction could be made. The calibration curve of methane is linear for the whole range with a maximum accuracy of 0.1%. In order to effectively use our existing analytical setup, we prepared an

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