Table II. $\Delta G°$, $\Delta H°$, and $\Delta S°$ for Solutions of H_2O and D_2O in Carbon Tetrachloride, Toluene, and Cyclohexane

(T = 298°K)

	$\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/deg mol
H_2O in CCl_4	-1.27 ± 0.01	5.4 ± 0.4	23 ± 1
D_2O in CCl_4	-1.19 ± 0.02	4.8 ± 0.4	20 ± 1
H_2O in toluene	-1.92 ± 0.01	4.4 ± 0.1	21.2 ± 0.3
D_2O in toluene	-1.81 ± 0.01	4.5 ± 0.1	21.3 ± 0.3
H_2O in cyclohexane	-0.67 ± 0.04	4.0 ± 0.6	15 ± 2
D_2O in cyclohexane	-0.62 ± 0.03	4.0 ± 0.8	15 ± 2

literature. There is a marked discrepancy between our values for H_2O in cyclohexane and those in ref. *8* at 25° and 30°C. However, our value at 25°C checks well with the most recent value of 0.00345 mol/l. given in ref. *5*.

Values for the log of the solubility and the corresponding value of $1/T$ were analyzed with a least-squares program on an IBM 1130 computer to determine the best slope for the straight line. From the relation $\log K_s = \Delta H°/2.3\,RT +$ constant, where K_s is the solubility in mol/l., the slope of the $\log K_s$ vs. $1/T$ plot is equal to $\Delta H°/2.3\,R$. Values for $\Delta H°$ were calculated using the value $\Delta H° = 2.303 \times 1.987 \times$ slope. Values for $\Delta G°$ were calculated from the relation $\Delta G° = -2.303RT \log K_s$. Values for $\Delta S°$ were calculated from the relation $\Delta S° = (\Delta G° - \Delta H°)/T$. These values are given in Table II. By use of the root-mean-square deviations of the values for $\log K_s$, the maximum and minimum values for the slopes of $\log K_s$ vs. $1/T$ were determined, and from these the limits of the $\Delta H°$ values were set. The limits of $\Delta G°$ were based on the root-mean-square deviations of the values of K_s and the limits of $\Delta S°$ were determined from the variation of $\Delta G°$ and $\Delta H°$.

Differences in the values of $\Delta H°$ are of the same order as the precision in $\Delta H°$ and there appears to be no significant difference in the values for H_2O and D_2O. There is a significantly lower value for $\Delta S°$ for cyclohexane which seems to be the result of a low value for $\Delta G°$ rather than an effect due to $\Delta H°$.

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Solubility of Carbon Dioxide in Mixed Paraffinic Hydrocarbon Solvents at Cryogenic Temperatures

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The solubility of carbon dioxide in mixed paraffinic hydrocarbon solvents of methane, ethane, propane, and *n*-butane below the carbon dioxide triple point is reported for several temperatures of industrial interest. The solubility of carbon dioxide in ethane–propane mixtures can be computed as the molal average of the two constituent binary solubility limits. On the other hand, all ternary and quaternary systems containing methane show significant deviations from this molal average solubility, having a larger solubility in a mixture than that in one or in both pure hydrocarbons separately. With parameters determined from binary-system equilibrium data alone, the solubility of solid carbon dioxide in multicomponent systems can be predicted by the Wilson equation to an overall accuracy of ±4.0 mol % over the entire range of the solubility curve, or to an accuracy of ±1.0 mol % up to 10 mol % carbon dioxide solubility. The predictive accuracy of the Wilson equation is primarily dependent on the accuracy with which each binary parameter pair describes the carbon dioxide solubility relationship in pure hydrocarbons.

Cryogenic processes for separation of hydrocarbons from natural gas or for removal of carbon dioxide from other process streams require accurate knowledge of the solubility of solid carbon dioxide in hydrocarbons, particularly in multicomponent systems. However, the experimental data for the solubility of carbon dioxide below its triple point in hydrocarbons have been very limited.

Clark and Din (*5*) measured the solubility of carbon dioxide in ethane–ethylene mixtures and Cheung and Zander (*4*) reported limited data on the solubility of carbon dioxide in methane–ethane mixtures. By far the most complete and thorough study of the solubility of solid carbon dioxide in methane–ethane mixtures was made by Jensen (*13*), who also deter-

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mined the solubility in single hydrocarbons of methane, ethane, propane, and *n*-butane. The solubility of carbon dioxide in methane was reported by Davis et al. (*6*), Brewer and Kurata (*3*), and others (*4, 8*). The solubility of solid carbon dioxide in pure heavy hydrocarbons was reported by Im (*12*).

The principal purpose of the work reported here was to determine experimentally the solubility of carbon dioxide below its triple point at several temperatures and pressures of industrial interest in the following solvent systems:

Solvent system	Temp. range, °K	Pressure range, atm
Methane–propane	150–208	4.5–23.5
Methane–*n*-butane	185–210	12.5–32.9
Ethane–propane	190–208	1.2– 4.0
Methane–ethane–propane	190–208	13.6–27.2

Experimental data so obtained were analyzed in terms of existing correlations to find a means of predicting the solubility of solid carbon dioxide in multicomponent hydrocarbon systems in general.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental equipment and procedure are described in detail elsewhere (*12*). Briefly, the solubility was determined by analyzing liquid samples withdrawn from a glass equilibrium cell maintained at a given temperature and pressure. Constant temperature was provided in an air bath using liquid nitrogen as the refrigerant. The bath temperature was measured by means of a calibrated platinum resistance thermometer. Although the calibration accuracy of the thermometer was better than ±0.1°K, the maximum uncertainty for temperature measurement is given as ±0.2°K because of a small thermal gradient present in the bath. Pressure measured by a Heise gauge was accurate to ±0.03 atm. The Heise gauge itself was calibrated against a Seager laboratory transfer standard gauge.

Liquid samples were analyzed on a F&M Model 720 gas chromatograph calibrated daily using 13 standard mixtures of accurately known compositions. The maximum relative uncertainty for composition was 3.2%, as estimated from statistical analysis of calibration data. The hydrocarbons used were of research grades furnished by Phillips Petroleum Co.; the carbon dioxide was Coleman grade, obtained from Matheson Gas Products. Each fluid used had a stated purity of 99.9+ mol % and subsequent analysis by the gas chromatograph did not disclose any evidence contrary to the claimed purity.

The system fluids were charged into the glass equilibrium cell from a manifold consisting of two stainless steel reservoirs for mixture preparation, two Heise gauges, a manual pump for precision metering and a vacuum system. Normally, a hydrocarbon mixture of predetermined composition was metered in first, followed by carbon dioxide. The amount of each fluid mixture charged was so determined as to create only a small vapor space when the system comes to equilibrium. After the cell was charged and the temperature control was established at the desired setting, the feed line was closed off from all parts of the charging manifold except the Heise gauge. After 1 or 2 hr during which the cell content was frequently agitated manually by means of a agitator coil located inside the equilibrium cell, in turn actuated by an externally located magnet, stabilization of the cell pressure indicated that equilibrium was attained. In the quaternary system, the desired pressure was established by addition of methane in small increments.

An average of 3 to 5 samples was analyzed for each equilibrium condition, and the reproducibility of replicated sample analyses was better than 1.0% relative deviation.

EXPERIMENTAL RESULTS

Unsmoothed experimental data are presented in Tables I through IV by system. According to the phase rule, the solid-

Table I. Solubility of Carbon Dioxide in Methane–Propane Mixtures along Solid-Liquid-Vapor Locus

T, °K	P, atm	Liquid composition, mole fraction		
		CO_2	CH_4	C_3H_8
208.2	21.81	0.6201	0.2120	0.1679
208.2	13.98	0.5975	0.1396	0.2628
205.2	23.34	0.4595	0.2919	0.2486
205.2	13.58	0.4320	0.1630	0.4050
200.2	23.07	0.2613	0.3713	0.3674
200.2	10.11	0.2633	0.2181	0.5185
185.2	20.86	0.1051	0.5277	0.3672
185.2	11.36	0.1094	0.2635	0.6271
165.2	13.07	0.0292	0.6334	0.3374
165.2	7.49	0.0332	0.3157	0.6511
150.2	7.49	0.0103	0.6418	0.3479
150.2	4.51	0.0108	0.3178	0.6614

Table II. Solubility of Carbon Dioxide in Methane–n-Butane Mixtures along Solid-Liquid-Vapor Locus

T, °K	P, atm	Liquid composition, mole fraction		
		CO_2	CH_4	n-C_4H_{10}
210.2	30.69	0.7812	0.1934	0.0254
210.2	23.14	0.7486	0.1622	0.0892
210.2	13.07	0.6797	0.0927	0.2277
208.2	32.87	0.6351	0.2813	0.0836
208.2	25.45	0.6325	0.2322	0.1353
208.2	14.19	0.5461	0.1430	0.3109
205.2	31.74	0.4448	0.4165	0.1387
205.2	25.11	0.4560	0.3113	0.2327
205.2	15.38	0.3916	0.1776	0.4308
200.2	32.87	0.3204	0.4842	0.1954
200.2	25.32	0.2953	0.3867	0.3180
200.2	15.48	0.2504	0.2109	0.5387
185.2	24.36	0.1048	0.5601	0.3351
185.2	12.59	0.1137	0.2508	0.6355

Table III. Solubility of Carbon Dioxide in Ethane–Propane Mixtures along Solid-Liquid-Vapor Locus

T, °K	P atm	Liquid composition, mole fraction		
		CO_2	C_2H_6	C_3H_8
208.2	4.56	0.6320	0.2637	0.1043
208.2	3.85	0.5774	0.1455	0.2772
205.2	3.98	0.4655	0.3981	0.1364
205.2	3.27	0.4141	0.2070	0.3789
200.2	2.99	0.2823	0.5150	0.2027
200.2	2.38	0.2593	0.2782	0.4626
190.2	1.63	0.1320	0.6372	0.2309
190.2	1.19	0.1183	0.3364	0.5453

Table IV. Solubility of Carbon Dioxide in Methane–Ethane–Propane Mixtures along Solid-Liquid-Vapor Locus

T, °K	P, atm	Liquid composition, mole fraction			
		CO_2	CH_4	C_2H_6	C_3H_8
208.2	27.22	0.6455	0.2408	0.0289	0.0848
208.2	27.22	0.6741	0.2242	0.0686	0.0331
208.2	20.41	0.6566	0.1761	0.0424	0.1249
208.2	20.41	0.6430	0.1755	0.1224	0.0591
205.2	27.22	0.4969	0.3240	0.0452	0.1339
205.2	27.22	0.4976	0.3200	0.1225	0.0599
205.2	20.41	0.4888	0.2381	0.0676	0.2055
205.2	20.41	0.5047	0.2315	0.1768	0.0870
205.2	13.61	0.4584	0.1541	0.0876	0.2999
205.2	13.61	0.4829	0.1438	0.2520	0.1203
200.2	27.22	0.3097	0.4278	0.0625	0.2000
200.2	27.22	0.3151	0.4147	0.1774	0.0828
200.2	20.414	0.3095	0.3102	0.0958	0.2845
200.2	20.41	0.3136	0.3188	0.2533	0.1143
200.2	13.61	0.3025	0.1964	0.1291	0.3720
200.2	13.61	0.3202	0.1874	0.3350	0.1573
190.2	20.41	0.1673	0.4301	0.1102	0.2924
190.2	20.41	0.1530	0.4447	0.2749	0.1274
190.2	13.61	0.1477	0.2734	0.1636	0.4153
190.2	13.61	0.1530	0.4447	0.2749	0.1274

liquid-vapor equilibrium of a ternary and a quaternary system has 2 and 3 degrees of freedom, respectively. For ternary systems, the variables chosen to define the equilibrium state were temperature and the component ratio in the solvent mixture. For the quaternary system, pressure was chosen as the third variable to satisfy the phase rule. In the present work, the solid phase was assumed to be pure carbon dioxide, and carbon dioxide was designated as the solute so that the solubility in the liquid phase refers to mole percent composition of carbon dioxide.

Several interesting observations can be made on the solubility of carbon dioxide in mixed hydrocarbon solvents. A ternary system containing methane differs in its solubility behavior from systems which contain components whose critical temperatures are above the triple point of carbon dioxide—i.e., condensable components. In the carbon dioxide–ethane–propane system, solubility isotherms are linear so that the solubility in this system can be expressed as the molal average of two binary system solubility limits as given by

$$\chi = \theta x_{12} + (1 - \theta)x_{13}$$

where χ is the ternary system solubility, θ is the mole fraction of component 2 (one of hydrocarbon components) in the solvent mixture, and x_{12} and x_{13} are binary system solubility limits of carbon dioxide in components 2 and 3, respectively. This linear relationship may be termed as the "ideal mixed-solvent behavior." On the other hand, all other multicomponent systems studied in this work which contained methane showed approximately quadratic deviations from this linear solubility for temperatures above the methane critical temperature as shown in Figures 1 and 2 for two ternary systems. This deviation usually results in a solubility greater than that in either pure hydrocarbon. Furthermore, the deviation tends to become greater the higher the temperature is above the methane critical temperature.

CORRELATION

In view of the excellent results obtained by Jensen (*13*) and Im (*12*) in correlating experimental solubilities of solid carbon dioxide in pure hydrocarbons with the Wilson equation (*21*), the experimental solubility data obtained in this work were correlated with the Wilson equation alone. To make maximum use of information obtained from the binary system solubility studies (*12*), the Wilson constants representing binary solute-solvent interactions were given by solubility relationships in carbon dioxide–hydrocarbon binary systems. The Wilson constants representing the solvent-solvent interaction were determined from experimental vapor-liquid equilibrium data of the solvent binary systems. The overall accuracy for all systems studied is 4.0 mol % over the entire solubility range. It is 1.0 mol % up to 10 mol % solubility, which is the range of practical concern. A more detailed presentation of the correlation is deposited with the ACS Microfilm Depository Service.

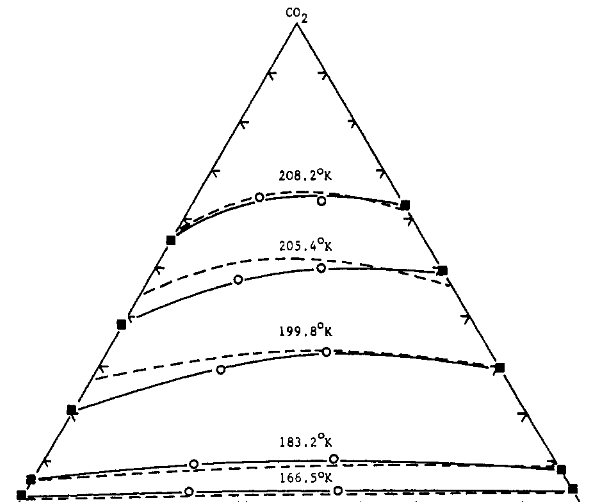

Figure 1. Solubility of carbon dioxide in methane–ethane mixtures along solid-liquid-vapor locus. Composition coordinates are in mole fraction

○ Ternary system data of Jensen (13)
■ Binary system data of Jensen (13) and Davis et al. (6)
—— Experimental
– – – Predicted by Wilson equation with solvent-pair parameters determined from vapor-liquid equilibrium data

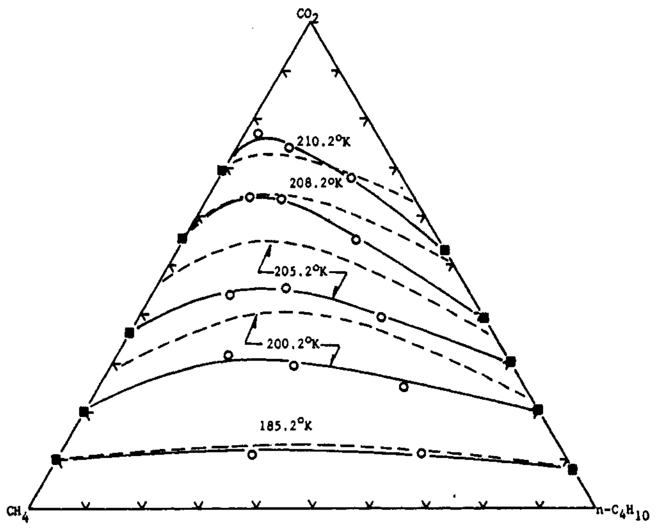

Figure 2. Solubility of carbon dioxide in methane-*n*-butane mixtures along solid-liquid-vapor locus. Composition coordinates are in mole fraction

○ Ternary system data of this work
■ Binary system data of Jensen (13) and Davis et al. (6)
—— Experimental
– – – Predicted by Wilson equation with solvent-pair parameters determined from vapor-liquid equilibrium data

CONCLUSION

The presence of methane in carbon dioxide–hydrocarbon multicomponent systems has a marked influence on the solubility behavior of solid carbon dioxide. For a system containing only condensable hydrocarbons, the solubility can be computed as the molal average of binary solubility limits, but all systems containing methane show approximately quadratic deviations from this linear relationship.

The solubility of solid carbon dioxide in mixed hydrocarbon solvents can be satisfactorily predicted with a two-parameter-model Wilson equation with solvent-pair parameters estimated from vapor-liquid equilibrium data of binary hydrocarbon systems, without direct recourse to multicomponent system data. The overall predictive accuracy obtained was ±4.0 mol % over the entire solubility range, and ±1.0 mol % up to 10 mol % carbon dioxide solubility.

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Thermodynamic Excess Property Measurements for Acetonitrile–Benzene–*n*-Heptane System at 45°C

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Vapor-liquid equilibrium, excess enthalpy, and excess volume data for the acetonitrile–benzene–*n*-heptane system at 45°C are reported. The vapor-liquid equilibrium measurements cover the three binaries, the ternary solubility envelope, and the miscible ternary region. A static equilibrium cell was used, and the phase compositions were obtained by gas-liquid chromatography. The excess enthalpy and excess volume measurements cover only the binaries. A Tronac isothermal titration calorimeter was used for the enthalpy measurements. Glass dilatometers were used to measure the excess volume directly.

The development of suitable equations for correlating the thermodynamic properties of partially miscible multicomponent systems has been hampered by a lack of experimental data. Consequently, a long-range program is under way to supply the needed data for a number of partially miscible ternary systems. To date, binary and ternary vapor-liquid equilibrium data have been reported for the sulfur dioxide–pentane–benzene system at −17.8°C (*1*).

Data have now been measured for the partially miscible acetonitrile–benzene–*n*-heptane system at 45°C. Included are vapor-liquid equilibrium (G^E) data for the three binary mixtures and for 51 points in the ternary region. Eighteen of the ternary points are vapor-liquid-liquid equilibria that produce nine tie lines. Excess enthalpy (H^E) and excess volume (V^E) data are also presented for the three binary mixtures. The new binary data compare favorably with literature data on the same systems, and the binary and ternary vapor-liquid equilibrium data are thermodynamically consistent. Mutual thermodynamic consistency of G^E and H^E data has also been tested with the Gibbs-Helmholtz equation.

EXPERIMENTAL

The acetonitrile and benzene were obtained from Fisher Scientific Co. and the *n*-heptane from Phillips Petroleum Co. Analysis by gas-liquid chromatography showed the following ratios of impurity areas to total summed areas of the chromatograms: acetonitrile, 0.1%, benzene, 0.04%; *n*-heptane, 0.11%. Hence, all three compounds were used as received without further purification.

Vapor-Liquid Equilibrium. Figure 1 shows the equipment for the vapor-liquid and the vapor-liquid-liquid equilibrium measurements. The static equilibrium cell has been described previously (*1*). The water bath was maintained at 45°C by a Haake Unitherm Controller, Model A, sensitive to 0.01°C. Absolute bath temperature was measured with a NBS calibrated thermometer having 1/10°C divisions. Tempera-

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