ν	kinematic viscosity, cm^2/s
ρ	density, g/mL

Registry No. MDEA, 105-59-9; CO_2, 124-38-9.

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Received for review June 15, 1986. Revised February 28, 1989. Accepted May 26, 1989.

High-Pressure Binary Phase Equilibria of Aromatic Hydrocarbons with CO_2 and C_2H_6

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High-pressure vapor–liquid equilibria of several binary systems containing aromatic hydrocarbons as one component and supercritical carbon dioxide or ethane as the other component were measured by using a dynamic system in which both vapor and liquid phases were circulated. The aromatic hydrocarbons that were used in this study are anisole, benzaldehyde, tetralin, and 1-methylnaphthalene. The phase equilibria of binary systems containing carbon dioxide were measured at two different temperatures, 343 and 373 K, and pressures up to 22 MPa. For ethane binary systems, equilibrium measurements were made at 373 K and pressures up to 12 MPa. In addition to measuring temperature, pressure, and phase compositions, the vapor- and liquid-phase densities also were determined for both carbon dioxide and ethane binary systems.

Introduction

Although considerable phase equilibrium data are available for low molecular weight aliphatic hydrocarbons encountered in natural gas and oil industries, such data are scarce for high molecular weight hydrocarbons, especially aromatic hydrocarbons. High-pressure phase equilibrium data of systems containing aromatic hydrocarbons are necessary for design and operation of coal processing plants and for selective extraction of valuable chemicals from liquefied coal mixtures using a supercritical fluid solvent. In this study, we have measured binary phase equilibria of systems containing aromatic hydrocarbons (anisole, benzaldehyde, tetralin, and 1-methylnaphthalene) as one of the components and a supercritical fluid (carbon dioxide and ethane) as the other component.

The vapor–liquid equilibria of the system carbon dioxide–tetralin was measured since tetralin is present in significant amounts in many liquefied coal mixtures. Only limited data are available for this system. Experimental data for binaries of carbon dioxide with tetralin and 1-methylnaphthalene are available (*1*, *2*) at very high temperatures (462–704 K) and pressures only up to 5 MPa. Experimental data for the system carbon dioxide–1-methylnaphthalene are also reported by Morris and Donohue (*3*), who measured at two different temperatures, 353.15 and 413.15 K, and pressures up to 14.4 MPa. Limited experimental data are reported in literature for the carbon dioxide–benzaldehyde system (ambient pressure and temperatures ranging from 291 to 309 K) by Kunnerth (*4*). No literature data is available for the carbon dioxide–anisole system. Again, for ethane-anisole and ethane-benzaldehyde binary systems, phase equilibrium data are not available in literature. Only Henry's constant (*5*) and limited solubility data (*6*) are available for the ethane-1-methylnaphthalene system.

In order to measure the phase equilibria of systems containing high-pressure carbon dioxide or ethane as one of the components, we built an equilibrium apparatus that circulates both the vapor and liquid phases. This experimental system provides a rapid and reproducible means of obtaining phase equilibrium data. In addition to measuring the temperature, pressure, and vapor- and liquid-phase compositions, we also measured the vapor- and liquid-phase densities. Although density data are readily available for pure compounds, few density measurements for mixtures are reported in literature. For carbon dioxide systems, the equilibrium phase compositions and liquid and vapor densities of the mixtures were measured at two temperatures and various pressures ranging from 3 to 22 MPa. For binary systems containing ethane, the measurements were made at 373 K and pressures up to 12 MPa. The

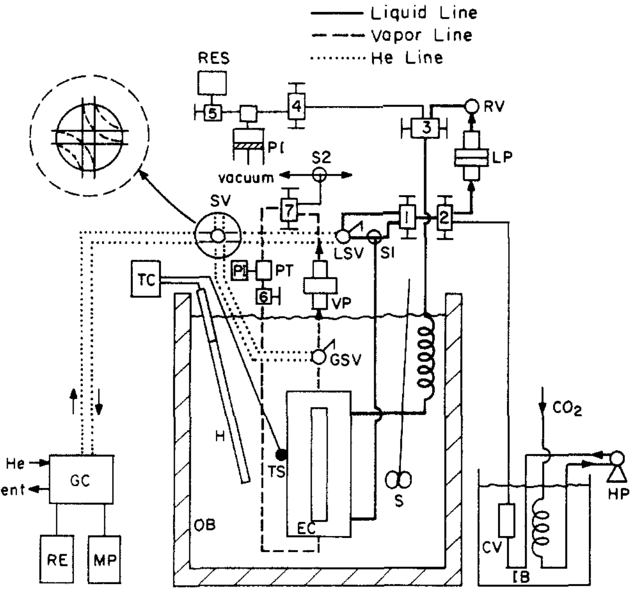

Figure 1. Schematic diagram of experimental apparatus: EC, equilibrium cell; GC, gas chromatograph; GSV, gas sampling valve; H, heater; HP, high-pressure pump; IB, ice bath; LP, liquid pump; LSV, liquid sampling valve; MP, microprocessor; OB, oil bath; PI, pressure indicator; PT, pressure transducer; RE, recorder; RES, reservoir; RV, relief valve; S, stirrer; S1, S2, switching valves; SV, eight-port switching valve; TC, temperature controller; TS, temperature sensor; VP, vapor pump.

density data along with phase compositions that are reported in this work can effectively be used to test equations of state and mixing rules for their applicability for designing coal processing plants.

Experimental System

Shown in Figure 1 is a schematic diagram of the experimental apparatus used for the determination of vapor–liquid equilibrium data from ambient conditions to 430 K and 25 MPa. The experimental system consists of a recirculation-type equilibrium cell which is made of 316 stainless steel. The cell is equipped with a glass window and has an internal volume of about 150 cm^3. The cell is immersed in a constant-temperture oil bath to ensure temperature uniformity. The contents of the cell are thoroughly mixed by countercurrent recirculation of the vapor and liquid phases. As shown in Figure 1, liquid enters the cell at the top left port and exits through the lower left port. The vapor phase is drawn from the top of the cell, and after entering through the bottom port, the vapor bubbles through the liquid phase. Equilibrium is usually attained in about 10 min.

The vapor and liquid phases are circulated with custom-built magnetic pumps. The body of the pumps and pistons are made of nonmagnetic 316 stainless steel, and the armature is made of magnetic steel. The vapor and liquid pumps are operated by an electromagnet and a permanent magnet, respectively. The electromagnet of the vapor pump generates a pulsating action, and the vapor flow rate is regulated by the frequency of the pulses. The vapor flow rate was about 60 cm^3/min during operation. The permanent magnet of the liquid pump moves up and down, and the motion is controlled by an eccentric and a motor. Since the motion of the permanent magnet is coupled with the motions of armature and piston inside the pump, the liquid is pumped through the liquid line. Because of small inside diameter of the sampling loop, the liquid phase is circulated at higher flow rates by bypassing the liquid sampling valve except at the time of sampling. The liquid flow rate was about 10 cm^3/min while bypassing the sampling valve and about 1 cm^3/min if the sampling valve was in operation.

The cell is coupled to a Varian gas chromatograph for direct analysis of the phases in equilibrium. The vapor sampling valve, which is a Rheodyne six-port valve with an external sampling loop of 100 μL, was immersed in the oil bath. The liquid sampling valve is another Rheodyne six-port valve, and an internal loop disk volume of 1 μL was used for analysis. Gas chromatograph analyses were made with a dual balanced thermal conductivity detector, and the mixture peaks were separated with a 24-ft-long $^1/_4$-in. outer diameter column filled with chromosorb W containing 6 wt % Carbowax 20M. The output analog signal was converted to a digital signal with a 12-bit analog to digital converter board, and the peak areas were subsequently evaluated by integrating the digital signal using a microprocessor.

The thermal conductivity detector of the gas chromatograph was calibrated at the experimental conditions by constructing a peak area versus number of moles graph for each component. This was done by injecting various known amounts of the pure components in a helium carrier gas and determining the corresponding peak areas. Injections were made using different new syringes, a gas sampling valve, and a liquid sampling valve. The calibration curves were fitted to a second-order polynomial in peak area. Also, by use of the calibration curves prepared with vapor sampling valve injection, the volume of the 1-μL internal sampling loop of the liquid sampling valve was accurately determined to be 1.031 μL. By use of these calibrations, the mole fractions of the vapor and liquid phases in equilibrium and the phase densities were determined. The liquid-phase compositions were slightly more reproducible than vapor-phase compositions. The liquid-phase compositions were usually reproducible to within a mole fraction of $\pm$0.0005, while the vapor-phase mole fractions were reproducible to a mole fraction of $\pm$0.0008. The overall estimated accuracy of our liquid-phase-composition measurements is about 1%. Since the vapor-phase compositions of heavy components are small (ranging from 0.06 to 0.001), the estimated accuracy of these measurements are in the range 1–10%.

The temperature of all the tubing and valves not submerged in the oil bath was maintained close to the equilibrium cell temperature with heavy-duty heating tape. Iron–constantan thermocouples were placed at various locations in the experimental apparatus to measure and control the system temperature. The temperature of the equilibrium cell was controlled to within $\pm$0.1 K from the desired set point. The pressure of the system was measured with a pressure transducer connected to the vapor-phase recirculating loop. The transducer has $\pm$0.5% accuracy at 34.5 MPa full scale range.

The carbon dioxide and ethane with a stated minimum purity of 99.99% were supplied by Matheson. The benzaldehyde with 99% minimum purity was obtained from Eastman Kodak Laboratories. The anisole and 1-methylnaphthalene both of 99% minimum purity were obtained from Aldrich Chemical. None of these chemicals were further purified since gas chromatographic analysis of the chemicals indicated no detectable impurities.

Results and Discussion

Phase equilibrium measurements were made on seven different binary systems. The vapor–liquid equilibria of the carbon dioxide–tetralin system were measured at 343.6 and 373.1 K and pressure ranging from 3.2 to 22.1 MPa. The vapor–liquid equilibrium data for carbon dioxide–anisole were obtained at 343.1 and 372.3 K and pressures ranging from 2.4 to 16.8 MPa. For the carbon dioxide–benzaldehyde system, measurements were carried out at 343.3 and 372.6 K and pressures ranging from 2.8 to 18.3 MPa. The vapor–liquid equilibrium data for carbon dioxide–1-methylnaphthalene system were measured at 372.6 K and pressures ranging from 3.7 to 20.7 MPa. Phase

Table I. Phase Equilibrium Data for Binary Systems Containing CO_2

press., MPa	mole fraction of CO_2 liquid	mole fraction of CO_2 vapor	K factor (y/x) K_1	K factor (y/x) K_2	density × 10^{-3}, kg/m^3 liquid	density × 10^{-3}, kg/m^3 vapor
Carbon Dioxide (1)–Anisole (2) System						
T = 343.1 K						
2.45	0.165	0.9901	6.001	0.012	0.945	0.041
5.17	0.326	0.9943	3.049	0.0085	0.957	0.098
8.20	0.513	0.9937	1.936	0.013	0.962	0.180
10.65	0.666	0.9893	1.486	0.032	0.958	0.273
12.82	0.864	0.9652	1.117	0.256	0.874	0.488
T = 372.3 K						
3.31	0.170	0.9875	5.795	0.015	0.975	0.053
7.37	0.357	0.9890	2.773	0.017	0.982	0.136
11.37	0.524	0.9841	1.877	0.033	0.958	0.231
15.20	0.699	0.9679	1.385	0.107	0.938	0.383
16.81	0.795	0.9456	1.190	0.265	0.893	0.502
Carbon Dioxide (1)–Benzaldehyde (2) System						
T = 343.0 K						
2.83	0.188	0.9943	5.283	0.0070	0.993	0.050
5.51	0.350	0.9958	2.844	0.0065	0.974	0.108
8.48	0.512	0.9963	1.947	0.0076	0.989	0.193
10.96	0.640	0.9936	1.553	0.018	0.988	0.301
13.58	0.792	0.9744	1.230	0.123	0.974	0.549
T = 372.6 K						
3.55	0.181	0.9926	5.499	0.0090	0.989	0.058
7.24	0.327	0.9938	3.036	0.0092	1.013	0.131
11.34	0.482	0.9882	2.052	0.023	1.016	0.235
15.23	0.614	0.9821	1.601	0.046	1.007	0.354
18.31	0.740	0.9635	1.302	0.141	0.982	0.564
Carbon Dioxide (1)–1-Methylnaphthalene (2) System						
T = 372.6 K						
3.72	0.130	0.9923	7.652	0.0087	0.857	0.050
7.31	0.268	0.9964	3.717	0.0049	0.847	0.116
11.96	0.398	0.9952	2.499	0.0080	0.875	0.217
16.02	0.491	0.9938	2.023	0.012	0.898	0.338
20.67	0.601	0.9847	1.639	0.038	0.884	0.488
Carbon Dioxide (1)–Tetralin (2) System						
T = 343.6 K						
3.24	0.187	0.9989	5.345	0.0014	0.882	0.055
6.10	0.315	0.9985	3.172	0.0022	0.950	0.117
10.51	0.496	0.9965	2.008	0.0072	0.890	0.250
15.30	0.663	0.9745	1.470	0.076	0.894	0.537
17.81	0.738	0.9591	1.300	0.156	0.880	0.651
19.16	0.932	0.9456	1.015	0.795	0.803	0.681
T = 373.1 K						
3.17	0.133	0.9969	7.479	0.0036	0.819	0.047
7.51	0.306	0.9971	3.261	0.0042	0.824	0.124
16.06	0.585	0.9877	1.689	0.030	0.826	0.359
20.26	0.694	0.9709	1.399	0.095	0.839	0.511
22.12	0.748	0.9589	1.283	0.163	0.868	0.566

equilibria for binary systems containing ethane as one of the components were measured at 372.5 K with pressures ranging from 2.41 to 9.65 MPa for the ethane–anisole system, from 2.41 to 11.58 MPa for the ethane–benzaldehyde system, and from 3.24 to 12.2 MPa for the ethane–1-methylnaphthalene system. Experimental measurements of carbon dioxide binaries and ethane binaries are tabulated in Tables I and II, respectively.

Table II. Phase Equilibrium Data for Binary Systems Containing Ethane (T = 372.5 K)

press., MPa	mole fraction of ethane liquid	mole fraction of ethane vapor	K factor (y/x) K_1	K factor (y/x) K_2	density × 10^{-3}, kg/m^3 liquid	density × 10^{-3}, kg/m^3 vapor
Ethane (1)–Anisole (2) System						
2.41	0.083	0.9832	11.86	0.018	0.796	0.024
3.52	0.151	0.9846	6.512	0.018	0.757	0.041
4.83	0.232	0.9863	4.261	0.018	0.737	0.060
6.01	0.313	0.9844	3.141	0.023	0.690	0.080
6.83	0.372	0.9830	2.640	0.027	0.676	0.095
9.65	0.539	0.9633	1.789	0.080	0.571	0.175
Ethane (1)–Benzaldehyde (2) System						
2.41	0.051	0.9920	19.41	0.0084	0.893	0.026
4.62	0.118	0.9917	8.404	0.0094	0.854	0.063
6.83	0.174	0.9917	5.699	0.010	0.845	0.098
8.00	0.206	0.9898	4.800	0.013	0.838	0.131
9.38	0.242	0.9858	4.080	0.019	0.835	0.165
Ethane (1)–1-Methylnaphthalene (2) System						
3.24	0.094	0.9687	10.36	0.035	0.800	0.043
5.02	0.149	0.9761	6.573	0.028	0.825	0.064
8.42	0.236	0.9825	4.168	0.023	0.900	0.109
10.10	0.270	0.9820	3.641	0.025	0.926	0.133
12.20	0.348	0.9841	2.828	0.024	0.976	0.212

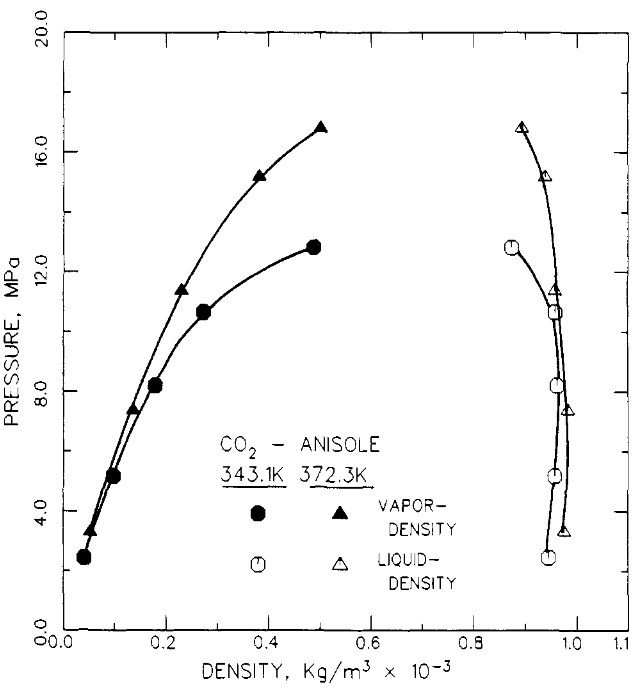

Figure 2. Equilibrium vapor and liquid densities as a function of pressure for the carbon dioxide–anisole system.

In addition to measuring the temperature, pressure, and vapor- and liquid-phase compositions, the vapor- and liquid-phase densities also were measured. For all seven binary systems investigated, the equilibrium phase density data are tabulated in Tables I and II. A typical plot of the vapor- and liquid-phase densities as a function of pressure is shown in Figure 2. In this figure, both the measured vapor- and liquid-phase densities for the system carbon dioxide–anisole are smooth functions of pressure. As the pressure is increased, both the vapor and liquid densities approach the mixture critical density. The vapor-phase density increases with increasing pressure and is a strong function of pressure. Even though the equilibrium liquid-phase composition is a strong function of pressure (Table I and Figure 3), the liquid-phase density is nearly constant except near the mixture critical point.

The liquid-phase mole fractions of carbon dioxide in anisole, benzaldehyde, and 1-methylnaphthalene at 373 K are compared in Figure 3. The comparison shows that carbon dioxide is least soluble in 1-methylnaphthalene and most soluble in anisole. This is due to the fact that the size difference between the carbon dioxide and 1-methylnaphthalene molecules is greater than that between carbon dioxide and anisole molecules. Even though both anisole and benzaldehyde have similar structure and molecular weight (108.14 and 106.12 respectively), carbon dioxide is more soluble in anisole than in benzaldehyde. This results because of strong dipole interactions between benzaldehyde molecules (the essential difference between benzaldehyde and anisole is the dipole moment value: 2.8 and 1.2

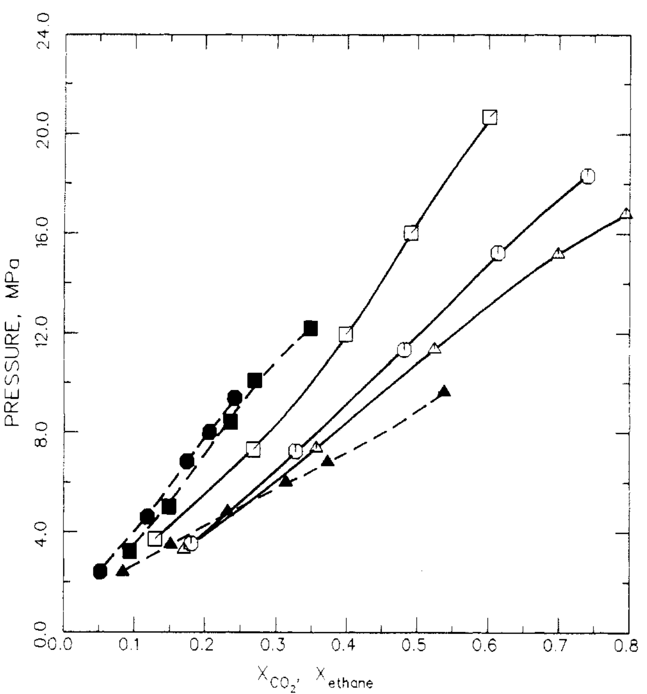

Figure 3. Comparison of liquid-phase mole fractions of both carbon dioxide (open symbols) and ethane (solid symbols) binary systems at 373 K. The other component in the binary systems is an aromatic hydrocarbon: △ and ▲, anisole; ○ and ●, benzaldehyde; □ and ■, 1-methylnaphthalene.

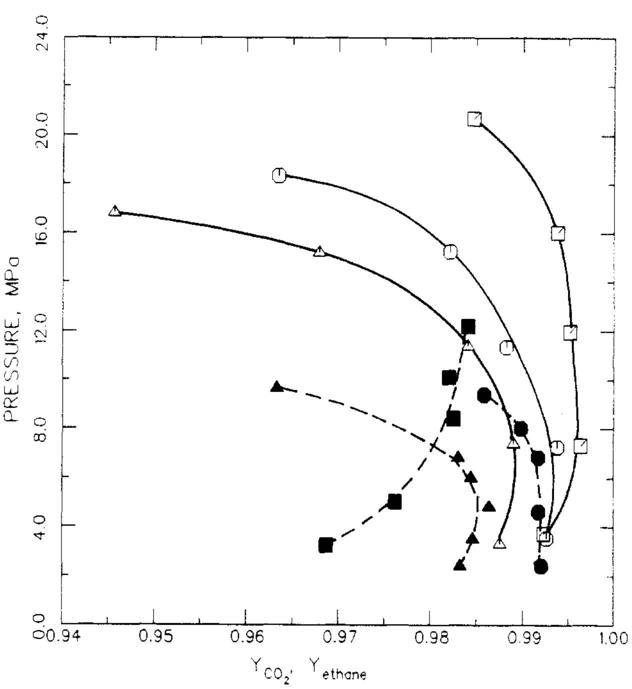

Figure 4. Comparison of vapor-phase mole fractions of both carbon dioxide and ethane binary systems. Key to symbols is same as that given in Figure 3.

D, respectively) which may result in specific orientation and more compact packing in benzaldehyde system than in anisole system. A comparison of molar volumes of pure benzaldehyde and anisole (for example, 101.5 and 109.0 cm^3/mol, respectively, at 295.2 K) also indicates strong specific interactions among benzaldehyde molecules. As a result, carbon dioxide is less soluble in liquid benzaldehyde than in anisole. The large dipole moment value of benzaldehyde may also result in considerable dipole–quadrupole interactions between benzaldehyde and carbon dioxide molecules. But, these interactions are not as strong as the dipole interactions between pure benzaldehyde molecules since the solubility of carbon dioxide is less in benzaldehyde than in anisole.

The liquid-phase mole fractions of ethane in anisole, benzaldehyde, and 1-methylnaphthalene at 373 K also are compared in Figure 3. This comparison of ethane binaries shows trends similar to that observed with carbon dioxide binary systems. Again, because of strong orientational forces in benzaldehyde molecules, ethane is less soluble in benzaldehyde than in anisole. In Figure 3, the solubility of ethane and carbon dioxide in an aromatic hydrocarbon can also be compared. Such comparison gives an indication of the differences in the nature of interactions between the light component and the aromatic hydrocarbon. For example, in binaries containing anisole, the liquid-phase mole fraction of ethane is greater than carbon dioxide. But, in binaries containing benzaldehyde and 1-methylnaphthalene, the liquid-phase mole fraction of ethane is less than carbon dioxide. Again, these shifts in solubility curves give an indication of the nature of interactions that are important in various systems: induction forces in the ethane–anisole system (average polarizability values for ethane and carbon dioxide are 43.3 × 10^{-25} and 26.5 × 10^{-25} cm^3, respectively); the quadrupole interactions between 1-methylnaphthalene molecules and between carbon dioxide and 1-methylnaphthalene; and the dipole interactions in benzaldehyde and dipole and quadrupole interactions between carbon dioxide and benzaldehyde molecules. As an example, in benzaldehyde, the large shift in the solubility of carbon dioxide compared to ethane gives an indication of the relative strengths of dipole–quadrupole interactions between carbon dioxide and benzaldehyde and induction forces between ethane and benzaldehyde (all other interactions in these two systems being nearly the same).

Figure 4 shows a comparison of vapor-phase compositions of both carbon dioxide and ethane binary systems. The solubility of aromatic hydrocarbons in high-pressure carbon dioxide and ethane mainly follows the order of saturation pressures of aromatic hydrocarbons at 373 K. Anisole, which has a higher vapor pressure, is most soluble, and 1-methylnaphthalene, with a lower vapor pressure, is least soluble. At pressures less than 6 MPa, the vapor-phase composition of 1-methylnaphthalene is greater than that of anisole and benzaldehyde. Since the vapor pressure of tetralin (at 373 K) is between benzaldehyde and 1-methylnaphthalene, the vapor-phase compositions of tetralin in the carbon dioxide–tetralin system lies between the benzaldehyde and 1-methylnaphthalene solubilities in carbon dioxide.

Conclusions

An experimental system, circulating both the vapor and liquid phases, has been used to determine the equilibrium phase compositions and densities of the mixture. The advantage of this apparatus is that it provides a rapid reproducible means of obtaining the equilibrium phase compositions as well as the phase densities. Phase equilibrium measurements were made on binary systems containing carbon dioxide or ethane as one of the components and anisole, benzaldehyde, tetralin, or 1-methylnaphthalene as the other component. The experimental measurements for the carbon dioxide binary systems indicate that the solubility of carbon dioxide in the liquid phase is in the order of anisole (most) > benzaldehyde > tetralin > 1-methylnaphthalene (least). Again, ethane is more soluble in anisole and, at low pressures, equally soluble in benzaldehyde and 1-methylnaphthalene. The vapor-phase solubility of hydrocarbons in dense carbon dioxide and ethane phase mainly follows the order of saturation vapor pressures of pure aromatic hydrocarbons. At high pressures, the vapor-phase compositions are in the order of anisole (most) > benzaldehyde > tetralin > 1-methylnaphthalene (least).

J. Chem. Eng. Data **1989**, *34*, 395-397

Acknowledgment

We thank Prof. W. B. Streett of Cornell University for providing the basic design of the magnetic pump used in this work.

Registry No. CO_2, 124-38-9; C_2H_6, 74-84-0; anisole, 100-66-3; benzaldehyde, 100-52-7; 1-methylnaphthalene, 90-12-0; tetralin, 119-64-2.

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Received for review August 3, 1988. Accepted June 15, 1989. Support of this research by the Division of Chemical Sciences of the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-FGO2-87ER13777 is gratefully acknowledged. A.B.C. also gratefully acknowledges a fellowship from GEM.

Excess Molar Enthalpies for Binary Liquid Mixtures of Furfural with Some Aliphatic Alcohols

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Excess molar enthalpies, H_m^E, for the binary liquid mixtures of furfural with some alphatic alcohols, viz., methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, have been determined at 308.15 K. The H_m^E values for all the binary mixtures studied are positive over the entire range of composition. At equimolar concentration, the H_m^E follows the order methanol < ethanol < 1-propanol < 2-propanol < 1-butanol < 2-butanol. Partial molar excess enthalpies have also been computed from the H_m^E data, and the results are discussed in the light of molecular interactions.

Introduction

The thermodynamic properties of binary liquid mixtures containing a self-associated component exhibit significant deviation from ideality arising not only from differences in molecular size but also from the changes related to the nature and extent of hydrogen bonding and molecular interactions between the like and unlike molecules. The ability of component molecules to form hydrogen bonding and interactions of dipolar origin have a marked effect on the enthalpies of mixing (*1*, *2*). In continuation of earlier investigations on thermodynamic properties of binary liquid mixtures containing a self-associated component (*3*-*5*), excess molar enthalpies for the binary mixtures of furfural with six aliphatic alcohols, namely, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, have been determined at 308.15 K over the entire composition range, and the results are reported in this paper. These studies are aimed at providing information on the binary mixtures with a view to understanding the nature of intermolecular interactions present.

Experimental Section

Laboratory reagent grade 1-propanol and 2-propanol supplied by BDH (India) and analytical reagent grade 1-butanol and 2-butanol supplied by E. Merck were purified as described below (*6*). The alcohols were refluxed over freshly ignited calcium oxide for about 8 h. The material was decanted and refluxed over magnesium turnings for about 4 h and then distilled by use of a 1-m-long column. Spectroscopic grade samples of methanol and ethanol supplied by Fluka were used as such without any further purification treatment. The sample of furfural was essentially the one used in earlier studies (*7*). The liquids were stored in brown glass bottles and fractionally distilled by use of a column of 15 theoretical plates immediately before use. The densities and refractive indexes of the purified liquids (Table I) agreed closely with accepted literature values (*6*, *8*-*10*).

Table I. Densities and Refractive Indexes of Liquids at 298.15 K

liquid	density/g cm^{-3} this work	density/g cm^{-3} lit.	refract. index this work	refract. index lit.
furfural	1.154 93	1.154 5 (8)	1.5239	1.5234 (*8*)
methanol	0.786 69	0.786 63 (*9*)	1.3261	1.3265 (*10*)
ethanol	0.785 18	0.785 17 (*9*)	1.3586	1.3594 (*10*)
1-propanol	0.799 62	0.799 87 (*9*)	1.3843	1.3837 (*10*)
2-propanol	0.781 19	0.781 26 (*6*)	1.3746	1.3752 (*10*)
1-butanol	0.806 26	0.806 03 (*9*)	1.3981	1.3973 (*10*)
2-butanol	0.802 72	0.802 60 (*6*)	1.3963	1.3950 (*10*)

Molar excess enthalpies were determined by use of an LKB microcalorimeter (Model 2107). Details of the calorimeter and the experimental method have been described elsewhere (*11*). The temperature of the calorimeter was kept constant to within ±0.005 K by circulating water from a thermostat maintained at 308.15 ± 0.002 K by using a Tronac precision temperature controller. The data points reported in this paper were obtained within ±0.005 K of the reported temperature, which was measured with a precalibrated platinum resistance thermometer coupled with a Leeds and Northrup Miller bridge. The technique and calibration were periodically checked by determining the excess molar enthalpies for the binary mixtures of *n*-hexane and cyclohexane. Our results were always within ±5 J mol^{-1} of the results reported by Ewing and Marsh (*12*).

Results and Discussion

The H_m^E values for the binary mixtures studied are summarized in Table II and are shown graphically as a function of the mole fraction of furfural, x, in Figure 1. Each set of experimental values were fitted to a smoothing equation of the type

$$H_m^E = x(1-x)[A_0 + A_1(1-2x) + A_2(1-2x)^2 + A_3(1-2x)^3] \tag{1}$$

where A_i's are adjustable parameters. Values of these parameters were determined by the least-squares methods and are presented in Table III, along with the standard deviation $\sigma(H_m^E)$. Since $\sigma(H_m^E)$ values for all the systems studied are less

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0021-9568/89/1734-0395$01.50/0