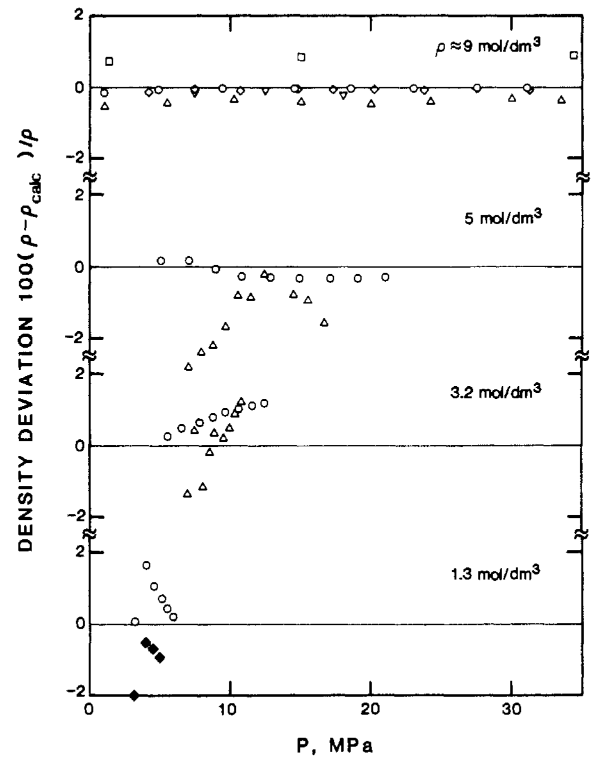

Figure 2. Comparison of *PVT* data for benzene from various sources: ▽, ref *1*; □, ref *2*; ◆, ref *3*; △, ref *4*; ◇, ref *5*; ○, this work. In order to compare data at slightly different densities, we use an equation of state as a base. Absolute deviations from the base line indicate only the ability of the equation to reproduce the data. The relative deviations between data sets indicate the quality of the agreement.

surements. In addition, some samples were held at temperatures of 623 and 723 K for periods in excess of 50 h each while monitoring the pressure. Again, the pressure remained constant within the precision of the measurements. Since no observable effect on the obtained pressures was detected, even above 650 K where decomposition was confirmed, the last measurements were routinely made to the maximum temperature of 723 K.

The data from the present work are tabulated in Table I. In order to allow a convenient comparison with data from other sources at slightly different temperatures and pressures we use an equation of state for benzene, due to Goodwin (*7*), as a base line. Comparisons with various data sets which overlap with the present work are shown in Figure 2. The data of Gehrig and Lentz (*4*) along isochores cover the widest range; however, comparison with these data over the complete range is complicated by the fact that their densities for adjacent isochores appear to be irregular (*7*). The data of Teichmann (*5*) along isochores and of Glanville and Sage (*2*) and Connolly and Kandalic (*1*) along isotherms are confined primarily to the higher density region below the critical temperature. Comparison with these data sets at approximately 9 mol/dm^3 is shown at the top of Figure 2. Agreement with the results of ref *1*, *4*, and *5* is excellent; however, the data of ref *2* appear to be somewhat high. At lower densities and higher temperatures the differences between our data and those of ref *4* often exceed 3-4% and the isochores exhibit dissimilar trends as indicated in the second and third plots of Figure 2. This discrepancy is well outside of our estimated experimental uncertainty of 0.5% in density and is inconsistent with the accuracy we have reported for other fluids (*6*, *8*). Comparison with the data of Gornowski et al. (*3*) is confined to low pressures and lower densities because of the limited range of their data. A comparison with the data of ref *3* at approximately 1.3 mol/dm^3 is shown in the lower plot in Figure 2. Absolute density deviations from the base line shown in Figure 2 reflect only the ability of the equation of state to reproduce the data; it is the relative difference between the data sets that indicates the quality of the agreement.

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Solubilities of Synthesis Gas Components in a Paraffinic Oil under Methanol Synthesis Conditions

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The solubilities of synthesis gas components hydrogen, carbon monoxide, carbon dioxide, and nitrogen in a paraffinic oil were measured at the operating conditions of methanol synthesis in the slurry phase. Gas solubilities were expressed by Henry's constants. The effect of temperature on gas solubilities was correlated with the molar heats of absorption. The results are useful for analysis of reaction kinetics and for modeling of methanol synthesis and other processes of syngas conversion in the slurry phase.

Introduction

An increasing activity in research and development of methanol synthesis in the liquid phase (*1-6*) has been recently observed. The novel feature of this technology is that methanol is derived from the conversion of synthesis gas over a catalyst dispersed in an inert liquid. Usually a paraffinic base mineral oil, e.g., Freezene-100 oil (*2*, *3*), or molten paraffin wax (Vestowax SH 105) (*5*, *6*) are used as the nonvolatile liquid medium. The selection of suitable liquid being simultaneously a catalyst carrier and heat-transfer medium is of great importance.

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Table I. Experimental Solubilities of Synthesis Gas Components in a Paraffinic Oil (*n*-Alkanes C_{15}–C_{36}) at Different Temperatures

gas	T, K	p, MPa	c, mol/dm^3	He, MPa dm^3/mol
H_2	471	2.95	0.087	33.0
	475	1.74	0.052	33.5
	474	1.55	0.046	33.3
	476	1.29	0.038	33.7
	473	0.82	0.025	33.5
	495	3.13	0.094	33.3
	495	2.36	0.071	33.4
	492	1.75	0.053	32.8
	493	1.48	0.047	31.9
	496	0.86	0.027	32.0
	513	2.87	0.089	32.3
	513	2.40	0.074	32.5
	513	1.74	0.054	32.2
	515	1.49	0.047	31.8
	514	0.80	0.026	31.4
	531	2.84	0.090	31.6
	534	2.46	0.079	31.2
	534	2.13	0.067	31.6
	533	1.65	0.054	30.9
	537	1.24	0.039	31.8
	532	0.73	0.024	30.9
N_2	477	3.35	0.112	30.0
	474	2.87	0.096	29.7
	473	2.48	0.085	29.4
	474	1.97	0.067	29.6
	475	1.64	0.057	29.0
	473	1.30	0.045	28.8
	474	1.08	0.036	29.1
	475	0.84	0.030	28.3
	495	3.07	0.100	30.7
	492	2.48	0.084	29.6
	497	1.67	0.057	29.1
	492	1.24	0.044	28.3
	494	0.95	0.033	28.7
	513	2.61	0.089	29.4
	514	2.42	0.083	29.0
	513	1.97	0.068	28.9
	513	1.56	0.055	28.5
	513	1.17	0.042	28.1
	513	0.95	0.034	27.9
	535	2.45	0.084	29.2
	534	1.88	0.067	28.3
	534	1.57	0.055	28.4
	534	1.13	0.041	27.5
	536	0.83	0.030	27.6
CO	471	0.43	0.024	17.9
	470	0.34	0.020	17.0
	471	0.28	0.016	17.5
	470	0.26	0.015	17.3
	471	0.20	0.012	16.7
	472	0.18	0.010	18.0
	471	0.16	0.009	17.8
	492	0.42	0.025	16.8
	491	0.30	0.018	16.7
	492	0.19	0.011	17.3
	491	0.15	0.009	16.7
	492	0.10	0.006	16.7
	514	0.42	0.026	16.2
	513	0.32	0.019	16.8
	512	0.17	0.012	14.2
	512	0.15	0.009	16.7
	513	0.10	0.006	16.7
	532	0.52	0.031	16.8
	531	0.38	0.021	18.1
	534	0.23	0.015	15.3
	532	0.17	0.011	15.5
	531	0.14	0.008	17.5
CO_2	474	2.27	0.193	11.8
	471	1.85	0.170	10.9
	472	1.45	0.138	10.6
	473	1.08	0.105	10.3
	470	0.90	0.090	10.0
	493	2.13	0.175	12.3
	490	1.43	0.125	11.5
	492	1.06	0.096	11.1
	493	0.93	0.084	11.0
	495	0.75	0.069	10.8
	513	2.01	0.154	13.1
	514	1.69	0.134	12.6
	513	1.22	0.102	12.0
	513	0.99	0.084	11.8
	512	0.73	0.063	11.5
	534	1.86	0.135	13.8
	530	1.41	0.109	12.9
	532	1.12	0.089	12.6
	532	0.98	0.079	12.5
	533	0.74	0.061	12.2

In order to determine the kinetics of methanol synthesis in a slurry phase and for engineering design purposes the solubilities of components of the reaction mixture in the liquid phase must first be known. There have been few measurements of hydrogen and carbon monoxide solubilities in molten paraffins under Fischer-Tropsch synthesis conditions (*7–11*).

Except for Peter and Weinert's data (*7*) there is a complete lack of information on solubility data for carbon dioxide which is required in the feed gas mixture to maintain methanol catalyst activity. Nitrogen is also frequently present in the synthesis gas, so its solubility data in the liquid medium could be useful.

The work presented here was undertaken to provide data on solubilities of the synthesis gas components in a mixture of liquid paraffins which can be used as a liquid medium for the methanol synthesis in a slurry phase.

Experimental Section

A paraffinic mineral oil with an average molecular weight 366 was used in this study to simulate the liquid phase present during the methanol synthesis in a slurry reactor. Gas chromatogram of the liquid presents a wide spectrum of *n*-alkanes of carbon number ranging from C_{15} to C_{36} with a maximum of C_{21}–C_{26}. Its density and vapor pressure at the experimental temperatures may be reasonably well correlated by the following expressions

$$\rho = 0.8577 - 5.65 \times 10^{-4}(T - 273)\ \mathrm{g/cm^3} \qquad (1)$$

$$\ln p = 1.1510 - 2327.4/T\ \mathrm{MPa} \qquad (2)$$

with T in K. The measurements are based on a batch gas absorption by surface aeration in an initially degassed or saturated liquid (at atmospheric pressure). The experimental technique was described in detail by Ledakowicz et al. (*8*). The main advantage of this method is that a laborious quantitative analysis of gas and liquid phases can be avoided. A knowledge of the total gas pressure change due to absorption, volume of the gas and liquid phases, and temperature of the system is necessary to determine the solubility of the gas in the liquid. The method requires an exact temperature control and pressure recording. Estimated errors in pressure, volume, and temperature in the present measurement were ±0.1%, ±0.2% and ±0.4%, respectively. The equilibrium cell used in this study was a commercial stainless steel magnedrive autoclave (Haage Co., Type 1220) with a volume of 1 L. The autoclave was additionally equipped with a highly resolving pressure sensor (Setra System Inc., Type 205/Z) coupled with a sensitive recorder. The autoclave was well insulated and a special device was constructed for heating the cover of the autoclave to compensate the heat losses. Thus the temperature differences between the gas and liquid phases were minimized to 1 K. Although the experimental technique is mainly aimed at determination of mass-transfer coefficients k_La gas solubilities in any liquid or slurry phase can be also measured exactly enough. The validity of our experimental procedure for determination of gas solubility was tested with the standard system CO_2–H_2O.

The measured values at ambient temperatures agree within a few percent with the previously reported values of Henry's constants (*12*, *13*) determined by different methods.

Results

Experimental data for the solubilities of synthesis gas components in the paraffinic oil were obtained at temperatures ranging from 471 to 536 K and at partial pressures ranging from 0.15 to 3.5 MPa. The solubility of various gases in the liquid phase as a molar concentration of H_2, N_2, CO, and CO_2 in the paraffin oil at the partial pressure and temperatures is presented in Table I.

It was assumed that the solubilities followed Henry's law

$$p = \mathrm{He}\,C \qquad (3)$$

where p is the partial pressure of the solute gas, He is the Henry constant, and C is the molar concentration of gas in liquid. Henry's law constants, as calculated from eq 3, are also shown in Table I. These constants were reproducible to within ±5%. From our data the assumption appears to hold for the whole range of partial pressure measured only for H_2 and CO. However, the carbon dioxide and nitrogen solubilities obey Henry's law only to the pressure of about 1.2 MPa and 2.0 MPa, respectively. At higher pressures the solubilities of CO_2 and N_2 are lower than those predicted with Henry's constant.

Observation of the gas solubilities at various temperatures studied shows that the solubilities of H_2, N_2, and CO increase with increasing temperature, while the solubility of CO_2 decreases.

The temperature dependence of the solubilities may be correlated reasonably well by expressing the logarithm of Henry's constants as a linear function of the reciprocal of the absolute temperature. Least-squares analysis of the raw data yields the relation

$$\mathrm{He}_i = a_i \exp(-b_i/RT) \qquad (4)$$

where the dimension of coefficient a_i is MPa dm^3/mol and b_i may be interpreted as the heat of absorption, J/mol. The values of the coefficients a_i and b_i for various gases are presented in Table II. It is significant to note that the solubility of CO_2 is much more sensitive to temperature than the solubility of CO, H_2, and N_2.

Table II. Coefficients for the Calculation of Henry's Constants according to Eq 4 for the Temperature Range of 471–536 K

gas	a_i, MPa dm^3/mol	b_i, J/mol	p_i, MPa
H_2	18.17	-2440.6	0–3.1
N_2	21.51	-1199.8	0–2.0
CO	9.92	-2152.9	0–0.5
CO_2	59.43	6920.9	0–1.2

Equation 4 is in agreement with the relation expected from thermodynamic principles and provides a convenient method for interpolating in order to determine the hydrogen, nitrogen, carbon monoxide, and carbon dioxide solubilities at intermediate temperatures. Henry's constants for the paraffin oil obtained in this study are in fair agreement with the other solubility data reported in the literature (*7–11*).

The results could be useful for the analysis of reaction kinetics and for modeling of methanol synthesis and other processes of syngas conversion in a slurry phase.

Registry No. CO, 630-08-0; CO_2, 124-38-9; H_2, 1333-74-0; N_2, 7727-37-9; methanol, 67-56-1.

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